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ORGANOURANIUM CHEMISTRY WITH PHOSPHORUS YLIDES

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ORGANOURANIUM CHEMISTRY

WITH PHOSPHORUS YLIDES

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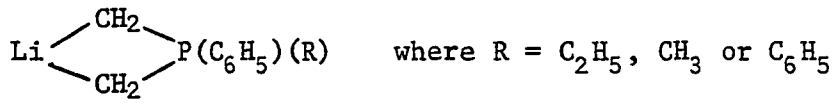
ABSTRACT

A new and novel class of organouranium complexes containing phosphorus ylides as ligands have been prepared and characterized. The phosphorus ylides used in this study were of the general formula:



where R = C_2H_5, CH_3 or C_6H_5

Although the preparation of several of these lithiated phosphoylides (R = CH_3 or C_6H_5) had previously been reported, no data on their characterization was available. Accordingly we have done so.

The addition of one equivalent of lithiated phosphoylide to one equivalent of $(C_5H_5)_3UCl$ results in dark green complexes of the formula: $(C_5H_5)_3UCHP(CH_3)(C_6H_5)(R)$, where R = C_2H_5, CH_3 or C_6H_5. These triscyclopentadienyluraniumphosphoylide complexes rapidly react with carbon monoxide at room temperature to give carbon monoxide insertion products of the formula: $(C_5H_5)_3U(CO)CHP(CH_3)(C_6H_5)(R)$, where R = C_2H_5, CH_3 or C_6H_5. On the basis of infrared data (ν_{CO} = 1660 cm^{-1}) a side-bonded or dihapto coordination of the acyl group is assigned for these complexes. This is only the second example of a triscyclopentadienyluranium complex expanding its coordination number from ten to eleven.

When two equivalents of lithiated phosphorus ylide are added to $(C_5H_5)_3UCl$, dark red dimeric complexes of the formula $(\mu\text{-}(CH)(CH_2)P(C_6H_5)(R)U(C_5H_5)_2)_2$ (where R = CH_3 or C_6H_5) result. Crystallization from diethyl ether produces deep red crystals of $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2\cdot(C_2H_5)_2O$ belonging to the monoclinc

space group $P2_1/c$ containing four molecules per unit cell of dimensions a = 12.675(8) Å, b = 16.462(8) Å, c = 25.837(25) Å and β = 124.43(5)°. Refinement converged for 3993 reflections with $I \geq 3$ (I) at $R_1 = 0.092$ and $R_w = 0.110$. Sohxlet extraction of this compound with pentane produces deep red crystals of $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2 \cdot C_5H_{12}$ belonging to the orthorhombic space group $P2_12_12_1$ with a = 16.026(12) Å, b = 23.453(13) Å, c = 12.679(3) Å and four molecules per unit cell. Refinement converged at $R_1 = 0.047$ and $R_w = 0.052$ for 1874 independent reflections with $I \geq 3(I)$. The complex is a biscyclopentadienyluranium dimer bridged by two phosphorus ylide ligands. In addition to being the first nine-coordinate organouranium compound it is the first example of a complex in which a phosphorus ylide both chelates a single metal atom and bridges two metal atoms through a methine bridge.

The ^1H nmr of $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2$ is temperature dependent. At ambient temperature enantiomerization and interchange of diastereotopic cyclopentadienyl groups occurs at a rapid rate on the nmr time scale. At low temperature these processes slow and an estimated $\Delta G^{\ddagger}_{253} = 10 \pm 1$ kcal/mole in toluene-d_8 and $\Delta G^{\ddagger}_{243} = 10 \pm 1$ kcal/mole in THF-d_8 are obtained. At lower temperatures another process begins to slow which is ascribed to the slowing of the rotation of one-half of the cyclopentadienyl groups.

The addition of three equivalents of lithiated phosphoylide to one equivalent of either $(C_5H_5)_3UCl$ or $(C_5H_5)UCl_3 \cdot 2THF$ produces gold colored complexes of formula $(C_5H_5)U((CH_2)_2P(C_6H_5)(R))_3$, where R = CH_3 or C_6H_5. These monomeric complexes consist of a uranium bound to one cyclopentadienyl group and three chelating phosphorus

ylides. These are the second example of nine-coordinated organouranium compounds. In addition, they contain six U-C σ bonds which is the most observed to date for any organouranium compound.

TABLE OF CONTENTS

List of Tables

Tables — Page

List of Illustrations

I. INTRODUCTION

The actinides are the elements following actinium in the sixth row of the periodic table, in which the 5f subshell is progressively filled with electrons. Although some of the actinides were first discovered almost 200 years ago,[1] their chemistry has only been investigated in depth in the 40 years since the discovery of the first synthetic transuranium elements. The initial impetus for studying f-electron systems was provided by the need to understand the products of nuclear fission. This led to the developement of separation techniques for actinides which provided an ample source of these materials for military and industrial applications, and for further chemical study.

The synthesis[2,3] of dicyclopentadienyl iron (ferrocene, $Fe(C_5H_5)_2$) in 1951 led to the opening of organometallic chemistry, a new and exciting field of coordination chemistry for d- and f-transition elements. The earliest attempts[4] at preparing organoactinide complexes occurred during the Manhattan Project when volatile uranium compounds were sought for gaseous isotope separation. These attempts to produce tetraalkyls such as tetramethyluranium were spectacularly unsuccessful. Unfortunately, these disappointing results led to the assumption that actinide-carbon σ-bonds were intrinsically unstable and efforts to prepare compounds containing a two-electron metal-carbon bond were abandoned.

The first successful synthesis of a 5f organometallic compound, triscyclopentadienyluranium chloride, was announced by Reynolds and Wilkinson[5] in 1956. During the decade following this discovery little

other work was reported except the preparation of some cyclopentadienyl and allyl complexes of the early actinides.[6-16] In 1968, Streitweiser and Müller-Westerhoff[17] announced the synthesis of "uranocene", dicyclooctatetraene uranium, which according to Hayes and Thomas "stimulated a renaissance of rare earth organometallic chemistry." For example, a variety of π-complexes[19] containing the cyclooctatetraene ligand and its derivatives, the indenyl ligand, the cyclopentadienyl ligand and its derivatives, and most recently[20] the carborane ligand, $C_2B_9H_{11}^{2-}$, have been prepared with the early actinides (Th, U, Np and Pu).

A simple molecular orbital calculation (Hückel type) for uranocene, showed that there were uranium f-orbitals of appropriate symmetry to overlap with cyclooctatetraene orbitals. This indicated that a portion of the bonding present in uranocene was possibly of a covalent nature. Although suggestions had been made of significant f-orbital involvement in actinide compounds,[21-23] until this time many workers involved in this area considered that the bonding in actinide compounds was almost exclusively ionic with limited f-orbital involvement.[24] The realization that covalency, to some degree, was present in organoactinide bonding led new workers into the area.

Although considerable success was achieved with π-complexes, the problem of preparing thermally stable actinide-carbon σ-bonds remained. This was overcome by several groups[25-29] in late 1972 and early 1973 with the assumption that the "proper choice of supporting ligands might stabilize such a two-electron linkage." Accordingly, with triscyclopentadienyluranium chloride and Grignard or lithium alkyls, a

large number of complexes containing a thermally stable σ-bond were prepared (eq. 1):

$$(C_5H_5)_3UCl \xrightarrow[\text{or RMgX}]{\text{RLi}} (C_5H_5)_3UR \qquad (1)$$

R = CH_3, n-C_3H_7, i-C_3H_7, n-C_4H_9, t-C_4H_9, neopentyl, allyl, 2-methylallyl, vinyl, C_6H_5, C_6F_5, ferrocenyl, $C_2C_6H_5$, p-tolyl, benzyl, 2-cis-2-butenyl, 2-trans-2-butenyl

It has proved possible to prepare[30] thorium-carbon σ-bonded organometallics in an analogous fashion (eq. 2):

$$(C_5H_5)_3ThCl \xrightarrow[\text{or RMgX}]{\text{RLi}} (C_5H_5)_3ThR \qquad (2)$$

R = n-C_3H_7, i-C_3H_7, n-C_4H_9, neopentyl, cyclohexyl, allyl, 2-cis-2-butenyl, 2-trans-2-butenyl

In addition to the cyclopentadienyl ligand as a stabilizing group, the indenyl ligand has also been used with success.[31,32]

The ^1H nmr of the uranium systems has produced some valuable insight into the bonding of these compounds. The U(IV) complexes are paramagnetic $5f^2$ systems containing two unpaired electrons. This paramagnetism produces large displacements in chemical shifts from their usual diamagnetic positions. These paramagnetic chemical shifts are comprised of contact and dipolar interactions. The contact interaction[33] arises from an electron-nucleus hyperfine interaction, in this case the delocalization of the unpaired 5f electron density onto the ligands, and the dipolar interaction[34] is a result of anisotropy in the magnetic susceptibility of the complex. It is possible to separate the observed chemical shifts into their dipolar and contact shift contributions. This has been done by Marks and co-workers for the triscyclopentadienyluranium alkyl complexes.[28]

They found that the contact shifts were rather large indicating significant 5f orbital covalent interaction involving polarization of the ligand orbitals or donation of ligand electron density into empty or partially filled uranium orbitals. No indication of back-donation of uranium electron density onto empty ligand orbitals was observed. Thus not only is it possible to prepare stable uranium-carbon σ-bonds, but the bonds also contain a significant amount of covalency.

Raymond and co-workers[35] have noted that the molecular structures observed for these and other actinide complexes seems to reflect a compromise between non-bonded ligand-ligand repulsions and the tendency to achieve a high coordination number, which for U(IV) generally appears to be ten.[36] This tendency toward ten coordination is vividly demonstrated in the unusual structure found for the ring-bridged biscyclopentadienyluranium halides which contain triply bridging chlorides.[37]

By using ligands with large steric requirements it is possible to design complexes with a coordination number less than ten. Such complexes which are coordinatively unsaturated often exhibit catalytic activity. Most recently, Marks and co-workers have used the pentamethylcyclopentadienyl ligand to prepare eight-coordinate uranium and thorium alkyl complexes (eq. 3).[38] The dimethyl

$$((CH_3)_5C_5)_2MCl_2 + 2RLi \longrightarrow ((CH_3)_5C_5)_2MR_2 + 2LiCl \qquad (3)$$

where R = CH_3 and M = U or Th

complexes react with hydrogen and carbon monoxide gas to produce the first organoactinide hydrides and novel O-bonded insertion products.[39,40]

While considerable success has been now achieved in the preparation

of organoactinides containing one or two σ-bonds, no neutral organoactinide complexes consisting solely of σ-bonding ligands has been prepared. The problem has been that the bonds formed by such ligands have not been of sufficient thermal stability to allow the isolation of their complexes at room temperature. One solution to this problem would be the use of phosphorus ylides, which form σ-bonds of high thermal stability, as ligands.

The term "ylide" was first used to describe a class of compounds studied by Staudinger and co-workers in the 1920's.[41] During the early 1950's Wittig and co-workers[42,43] developed these, principally ylides of phosphorus and sulfur, into an important class of reagents, for example, the Wittig olefin synthesis. The bonding in these compounds can be represented by these two resonance forms:

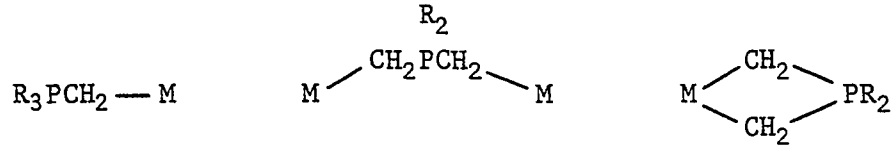
$$\underset{\text{ylene}}{CH_2{=}P(CH_3)_3} \longleftrightarrow \underset{\text{ylide}}{CH_2^{-}\text{-}P^{+}(CH_3)_3}$$

Of these two possible forms, modern techniques[44] and theoretical calculations[45-47] have shown that the ylide formulation predominates in the ground state of these molecules.

While these compounds have been used for almost 30 years as organic reagents, it was not until the mid 1960's that they attracted the attention of inorganic and organometallic chemists as possible ligand systems.[44] However since that time chemists have been highly successful in applying these compounds to transition organometallic chemistry.

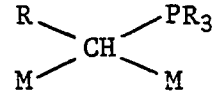
After some initial confusion, several ligand bonding modes of the

phosphorus ylides have emerged. They have been found principally as terminal ligands (as in A), bridging ligands (as in B) and chelating ligands (as in C).



A B C

More recently[48,49] a variation as a bridging ligand through only one



D

carbon atom has been observed (as in D).

Although these compounds exhibit several interesting bonding possibilities, their most remarkable feature is the unusual thermal stability of the ylide-metal bond. While most transition metal-carbon σ-bonds are of sufficient thermal stability to allow their isolation at room temperature, this is not the case for the group IB metals (Cu, Ag and Au). They form metal-carbon σ-bonds of only marginal stability at best. However, with phosphorus ylides, the organometallic complexes formed are of such high thermal stability that many of them may be purified by sublimation.[44]

Recently, there has appeared a short report[50] on a series of lanthanide phosphoylide complexes utilizing the $CH_2{=}P(CH_3)_3$ ligand. These trisphosphoylide complexes exhibit the chelating mode of bonding (type B) and are thermally stable above room temperature.

The use of phosphorus ylides as ligands with actinides has been ignored up until the present. It occurred to us that the σ-bonding stability afforded by phosphorus ylides toward transition and lanthanide metal centers should work with the actinides as well. It is the purpose of this dissertation to describe our preparation of organouranium phosphoylide complexes, their properties and structures, and the subsequent reactions of these complexes with Lewis bases.

II. DESCRIPTIVE CHEMISTRY AND SPECTRAL RESULTS

Triscyclopentadienyluranium chloride, $(C_5H_5)_3UCl$, was prepared by the method of Marks and co-workers.[51] This method has the advantage of using thallous cyclopentadienide which is much easier to handle than sodium cyclopentadienide used in previous preparations.[5] The $(C_5H_5)_3UCl$ we obtained gave an identical ^1H nmr and infrared spectrum to that reported by the above workers. We prepared the monocyclopentadienyl-uraniumtrichloride material, $(C_5H_5)UCl_3 \cdot 2THF$, via the method of Bagnall and Edwards.[52] The ^1H nmr and infrared were in agreement with that reported by the above workers. We found both of the above materials to be of sufficient purity for use in our synthetic work without recrystallization.

Several of the lithiated phosphorus ylides used in this study were prepared by the method of Manzer[53] shown in equation 4:

$$((CH_3)_2P(C_6H_5)(R))I + 2LiCH_3 \xrightarrow[(C_2H_5)_2O]{} Li\begin{matrix}CH_2\\ \diagup\quad\diagdown\\ CH_2\end{matrix}P(C_6H_5)(R)\downarrow + LiI + 2CH_4\uparrow \qquad (4)$$

where R = CH_3 or C_6H_5

This method works only for these two phosphonium salts. In order to prepare a lithiated phosphoylide where R = C_2H_5 it was necessary to use the route shown in equations 5 - 7:

$$((CH_3)_2P(C_2H_5)(C_6H_5))I + LiCH_3 \longrightarrow ((C_2H_5)(CH_3)(C_6H_5)PCH_2Li)I + CH_4\uparrow \qquad (5)$$

$$((C_2H_5)(CH_3)(C_6H_5)PCH_2Li)I \xrightarrow[\Delta]{} C_2H=P(C_2H_5)(CH_3)(C_6H_5) + LiI \qquad (6)$$

$$CH_2=P(C_2H_5)(CH_3)(C_6H_5) + LiCH_3 \longrightarrow Li\begin{matrix}CH_2\\ \diagup\quad\diagdown\\ CH_2\end{matrix}P(C_2H_5)(C_6H_5)\downarrow + CH_4\uparrow \qquad (7)$$

This is a general method[54] and should work well with any phosphonium salt.

The lithiated phosphorus ylides are insoluble in diethyl ether and $Li(CH_2)_2P(C_6H_5)_2$ and $Li(CH_2)_2P(CH_3)(C_6H_5)$ can be separated from the diethyl ether soluble LiI by washing with a large volume of this solvent. All of the lithiated phosphorus ylides are very soluble in THF or 1,2-dimethoxyethane.

Manzer reported no physical data for the lithiated phosphoylides and we have been unable to find any characterization data in the literature for these particular lithiated phosphoylides. Furthermore we were unable to find any report in the literature of the $CH_2=P(C_2H_5)(CH_3)(C_6H_5)$ phosphorane and its LiI salt. Accordingly we have obtained ^1H and ^{31}P nmr and infrared data for these compounds which are summarized in Tables 1 - 4.

The ^1H nmr spectrum of $CH_2=P(C_2H_5)(CH_3)(C_6H_5)$ obtained at 100 MHz in C_6D_6 is shown in Figure 1. The methylene protons show up as a doublet ($J(H_2CP)$ = 3 Hz) at -0.33 ppm. This coupling constant is about half that reported for other methylene phosphoranes.[55] The methyl doublet ($J(H_3CP)$ = 13 Hz) occurs at -1.69 ppm and the methyl of the ethyl group is seen as a doublet of triplets ($J(H_3CCH_2)$ = 7 Hz, $J(H_3CCP)$ = 17 Hz) centered at -1.08 ppm. The multiplet due to the methylene portion of the ethyl group is centered at -2.15 ppm and two multiplets due to the phenyl group occurs in the region -7.0 to -7.6 ppm.

The ^{31}P nmr of this compound obtained at 40.5 MHz in C_6D_6 consists of a broad multiplet at +13.37 ppm. No proton-phosphorus coupling

TABLE 1

Nuclear Magnetic Resonance Parameters for a
Methylene Phosphorane and its Lithium Iodide Adduct

Compound	Nucleus	Chemical Shift (ppm)
$(C_6H_5)(CH_3)(C_2H_5)P{=}CH_2$	^1H[a]	-7.75 (2H, multi) -7.35 (3H, multi) -2.15 (2H, multi) -1.69 (3H, d, $J(H_3CP)$ = 13 Hz) -1.08 (3H, dt, $J(H_3CCH_2)$ = 7 Hz), $J(H_3CCP)$ = 17 Hz) -0.33 (2H, d, $J(H_2CP)$ = 3 Hz)
	^{31}P[b]	+13.37 (multi)
$(C_6H_5)(CH_3)(C_2H_5)P{=}CH_2{\cdot}LiI$	^1H[a]	-7.74 (3H, multi) -7.37 (4H, multi) -3.32 (2H, q, $J(H_2CCH_3)$ = 7 Hz) -2.05 (3H, multi) -1.66 (3H, d, $J(H_3CP)$ = 13 Hz) -1.01 (3H, t, $J(H_3CCH_2)$ = 7 Hz) -0.85 (3H, dt, $J(H_3CCH_2)$ = 7 Hz) $J(H_3CCP)$ = 16 Hz) +0.54 (2H, d, $J(H_2CP)$ = 3 Hz)
	^{31}P[b]	+18.12 (multi)

d = doublet, t = triplet, q = quartet, multi = multiplet,
dt = doublet of triplets

a) chemical shifts measured relative to TMS

b) chemical shifts measured relative to external H_3PO_4

TABLE 2

Infrared Vibrational Frequencies for a Neat Film of $CH_2=P(C_2H_5)(CH_3)(C_6H_5)$

$\nu(cm^{-1})$	Possible Assignment
3070 m	
3050 m	ν(C-H aromatic)
2965 s	
2930 m	
2908 m	ν(C-H aliphatic)
2875 m	
1973 w	
1902 w	(C_6H_5 substitution
1835 w	pattern)
1775 w	
1590 w, br	
1485 w	ν(C=C)
1457 m	
1438 s	$\delta(C_6H_5)$-a
1427 m	δ(P-CH_3)
1379 w	
1360 m	
1310 m	
1291 m	δ(P-CH_3)
1238 w	
1100 s	$\delta(C_6H_5)$-b
1071 m	
1034 m	
1009 s	
998 s	$\delta(C_4$-P)
985 s	
950 vs	δ(P-CH_3)
902 s	ν(P=CH_2)
887 s	δ(P-CH_3)-c
748 vs	$\delta(C_6H_5)$-d
694 vs	
640 m	ν(P-C)
477 s	$\delta(C_6H_5)$-e
445 m	
392 w	

s = strong, m = medium, w = weak, v = very, br = broad

a) planar ring deformation of phenyl bonded to phosphorus
b) substituent sensitive C-H planar bending vibration
c) methyl rocking
d) substituent sensitive C-H out-of-plane bending vibration
e) substituent sensitive ring vibration

TABLE 3

Nuclear Magnetic Resonance Spectral Parameters
Several Lithiated Phosphorus Ylides

Compound	Nucleus	Chemical Shift (ppm)
$Li(CH_2)_2P(C_6H_5)_2$	^1H[a]	-7.66 (4H, multi) -7.08 (6H, multi) +0.32 (4H, d, $J(H_2CP)$ = 11 Hz)
	^{31}P[b]	+31.04 (quintet, $J(PCH_2)$ = 10 Hz)
$Li(CH_2)_2P(CH_3)(C_6H_5)$	^1H[a]	-7.74 (2H, multi) -7.13 (3H, multi) -1.23 (3H, d, $J(H_3CP)$ = 12 Hz) +0.58 (4H, d, $J(H_2CP)$ = 10 Hz)
	^{31}P[b]	+23.88 (octet, J(PCH) = 10 Hz)
$Li(CH_2)_2P(C_2H_5)(C_6H_5)$	^1H[a]	-7.75 (2H, multi) -7.18 (3H, multi) -1.49 (2H, multi) -0.81 (3H, dt, $J(H_3CCH_2)$ = 7 Hz, $J(H_3CCP)$ = 15 Hz) +0.61 (4H, d, $J(H_2CP)$ = 11 Hz)
	^{31}P[b]	+32.77 (broad multi)

d = doublet, dt = doublet of triplets, multi = multiplet

a) chemical shifts measured relative to TMS with THF-d_8 as the solvent

b) chemical shifts measured relative to external H_3PO_4

TABLE 4

Infrared Frequencies for Several
$Li(CH_2)_2P(C_6H_5)(R)$ Complexes

$\nu(cm^{-1})$			
R = CH_3	R = C_2H_5	R = C_6H_5	Possible Assignment
3072 w	3068 w	3068 m	
3066 w	3055 w	3059 m	ν(C-H aromatic)
3030 w		3042 m	
1956 w	1955 w	1950 w	
1894 w	1900 w	1899 w	
		1882 w	
1818 w	1820 w	1819 w	
1574 w	1560 w	1576 w	ν(C=C)
1482 m, sh	1480 m, sh	1482 m, sh	ν(C=C)
1438 s	1440 s	1438 vs	$\delta(C_6H_5)$-a
1415 m			$\delta(P-CH_3)$
		1330 w	
1308 w	1308 w	1306 m	
1285 m			$\delta(P-CH_3)$
	1239 w		
		1179 w	
1157 w		1155 w	
1107 s	1109 s	1103 vs	$\delta(C_6H_5)$-b
1029 w	1036 m	1026 m	
	1018 w		
	1000 m	998 m	$\delta(C_4-P)$
959 s			$\delta(P-CH_3)$
941 s			$\delta(P-CH_3)$
922 m	911 m	923 s	
910 s	889 s	901 s	$\nu(P-CH_2Li)$
		888 s	
866 s			$\delta(P-CH_3)$-c
833 s			$\delta(P-CH_3)$-c
805 s	806 s	804 s	$\nu(P-CH_2Li)$
	768 s		
720 vs, br	745 vs, br	731 vs, br	$\delta(C_6H_5)$-d
	713 s		
694 s	695 s	688 s	ν(P-C)
672 m	651 m		
517 w	512 w	523 m	ν(C-Li)
480 s	489 m	494 vs	$\delta(C_6H_5)$-e
450 m	445 m	445 m	
429 s			
392 w	390 w	398 w	ν(C-Li)
374 w		380 m	

s = strong, m = medium, w = weak, v = very, br = broad, sh = shoulder

a) planar ring deformation of phenyl bonded to phosphorus
b) substituent sensitive C-H planar bending vibration
c) methyl rocking
d) substituent sensitive C-H out-of-plane bending vibration
e) substituent sensitive ring vibration

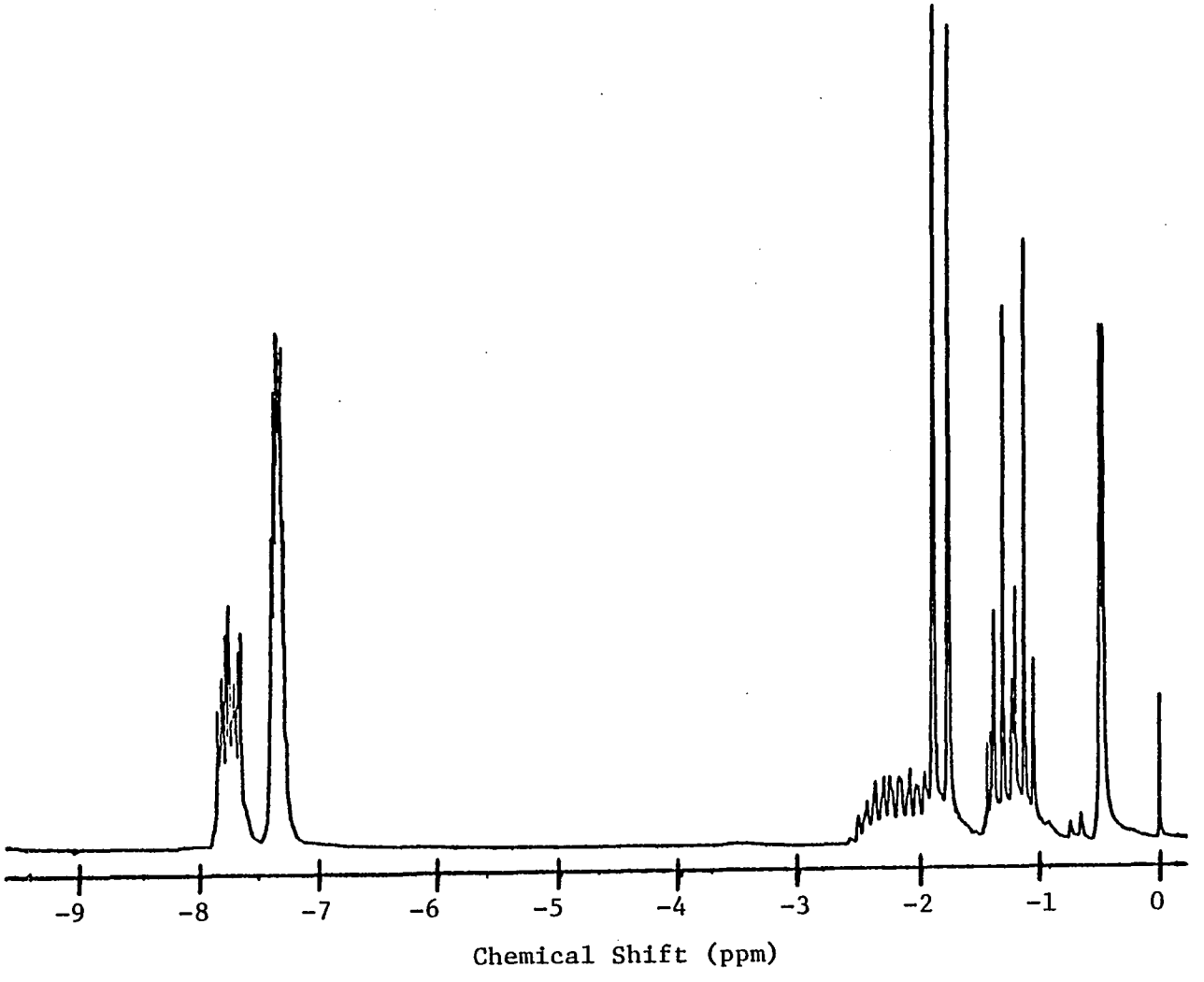


Figure 1. ^{1}H nmr spectrum of $CH_2=P(C_2H_5)(CH_3)(C_6H_5)$ obtained in C_6D_6.

information is readily available from this spectrum.

The infrared spectrum of $CH_2=P(C_2H_5)(CH_3)(C_6H_5)$ recorded over the range 4,000 - 300 cm^{-1} as a neat film is shown in Figure 2 and the data tabulated in Table 2. The most important feature of this spectrum is the band at 902 cm^{-1}. This has previously been assigned[56] in methylene triphenylphosphoranes to a $P=CH_2$ stretching vibration. Absorptions due to phosphorus-methyl vibrations are observed at 1427 cm^{-1}, 1291 cm^{-1}, 950 cm^{-1} and 887 cm^{-1}. Phosphorus-phenyl absorptions are seen at 1438 cm^{-1}, 1100 cm^{-1}, 748 cm^{-1} and 477 cm^{-1}. Aromatic carbon-hydrogen stretching is seen in the 3070 - 3050 cm^{-1} region and aliphatic carbon-hydrogen bands are observed in the 2970 - 2870 cm^{-1} region.

When either one or two equivalents of $LiCH_3$ is added to $((CH_3)_2P(C_2H_5)(C_6H_5))I$ one obtains the diethyl ether solvated lithium halide adduct of a methylene phosphorane, $((C_2H_5)(CH_3)(C_6H_5)PCH_2Li)I\cdot(C_2H_5)_2O$. The ^1H nmr spectrum of this compound is shown in Figure 3. The principle feature in the spectrum is the methylene doublet ($J(H_2CP)$ = 3 Hz) at +0.54 ppm. This coupling constant is in the range 1.5 - 3.0 Hz reported by Schmidbaur and co-workers[54] for lithium halide adducts of several methylene trialkyl phosphoranes. They concluded from their nmr measurements that the methylene carbon atom is in an sp^3 tetrahedral arrangement with the lithium atom and that a high portion of covalency is present in the Li-C bond.

The remainder of the spectrum is consistent with the above formulation. A methyl doublet ($J(H_3CP)$ = 13 Hz) is observed at -1.66 ppm and the methyl portion of the ethyl group is seen as a doublet of triplets ($J(H_3CCH_2)$ = 7 Hz and $J(H_3CCP)$ = 16 Hz) centered

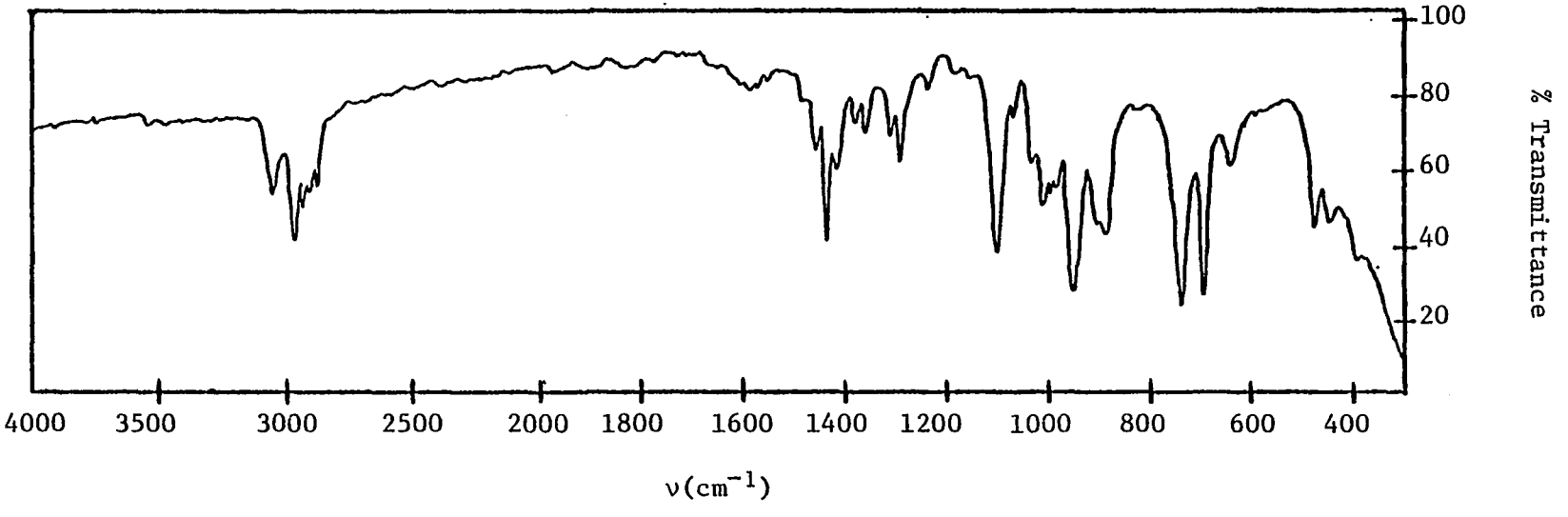


Figure 2. Infrared Spectrum of $CH_2=P(C_2H_5)(CH_3)(C_6H_5)$ obtained as neat film.

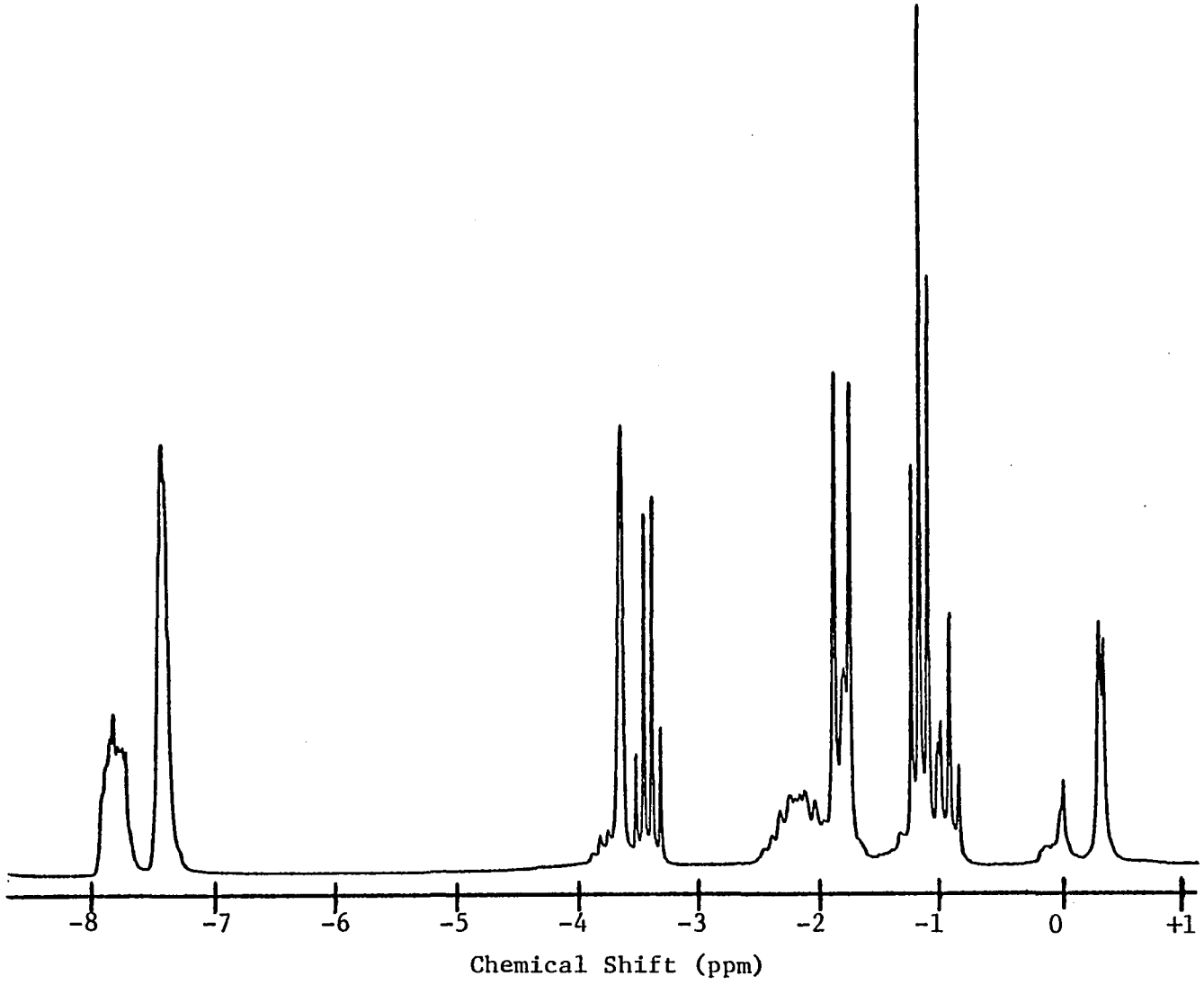


Figure 3. ^{1}H nmr spectrum of $[(C_2H_5)(CH_3)(C_6H_5)PCH_2Li]I\cdot(C_2H_5)_2O$ in THF-d_8.

at -0.85 ppm. A portion of it is obscured by the triplet ($J(H_3CCH_2)$ = 7 Hz) of the methyl group at -1.01 ppm of the ethyl group in the diethyl ether solvate. The methylene portion of the ethyl group on the phosphorane occurs at -2.05 ppm as a complex multiplet and the methylene portion of the diethyl ether solvate is a quartet ($J(H_2CCH_3)$ = 7 Hz) at -3.32 ppm. The phenyl group is seen as two complex multiplets in the -7.3 to -7.8 ppm region. From the relative intensities of the phosphorane and the diethyl ether resonances there is one diethyl ether solvate per lithium iodide phosphorane complex.

A comparison of the relative peak heights of the phenyl multiplets with the remainder of the spectrum indicates that secondary reaction products are present. This is more apparent in the ^{31}P nmr spectrum obtained at 40.5 MHz in THF/C_6D_6 shown in Figure 4. This spectrum shows three different phosphorus resonances, all of which are complex multiplets. The largest resonance at +18.12 ppm is due to the lithium iodide phosphorane complex and comprises 76% of the reaction mixture. The remaining two peaks are observed at +7.41 ppm (16%) and at +69.55 ppm (8%). We have not identified the materials which produce these two peaks.

The ^1H nmr of the lithiated phosphorus ylides, $Li(CH_2)_2P(C_6H_5)(R)$ (where R = CH_3, C_2H_5 or C_6H_5), obtained at 100 MHz in THF-d_8 are shown in Figures 5 - 7. In the spectrum of $Li(CH_2)_2P(C_6H_5)_2$ the methylene portion shows up as a doublet ($J(H_2CP)$ = 11 Hz) at +0.32 ppm. The doublet ($J(H_2CP)$ = 10 Hz) in the spectrum of $Li(CH_2)_2P(CH_3)(C_6H_5)$ is upfield at +0.58 ppm and a methyl doublet ($J(H_3CP)$ = 13 Hz) is present at -1.23 ppm. The spectrum of $Li(CH_2)_2P(C_2H_5)(C_6H_5)$ contains a

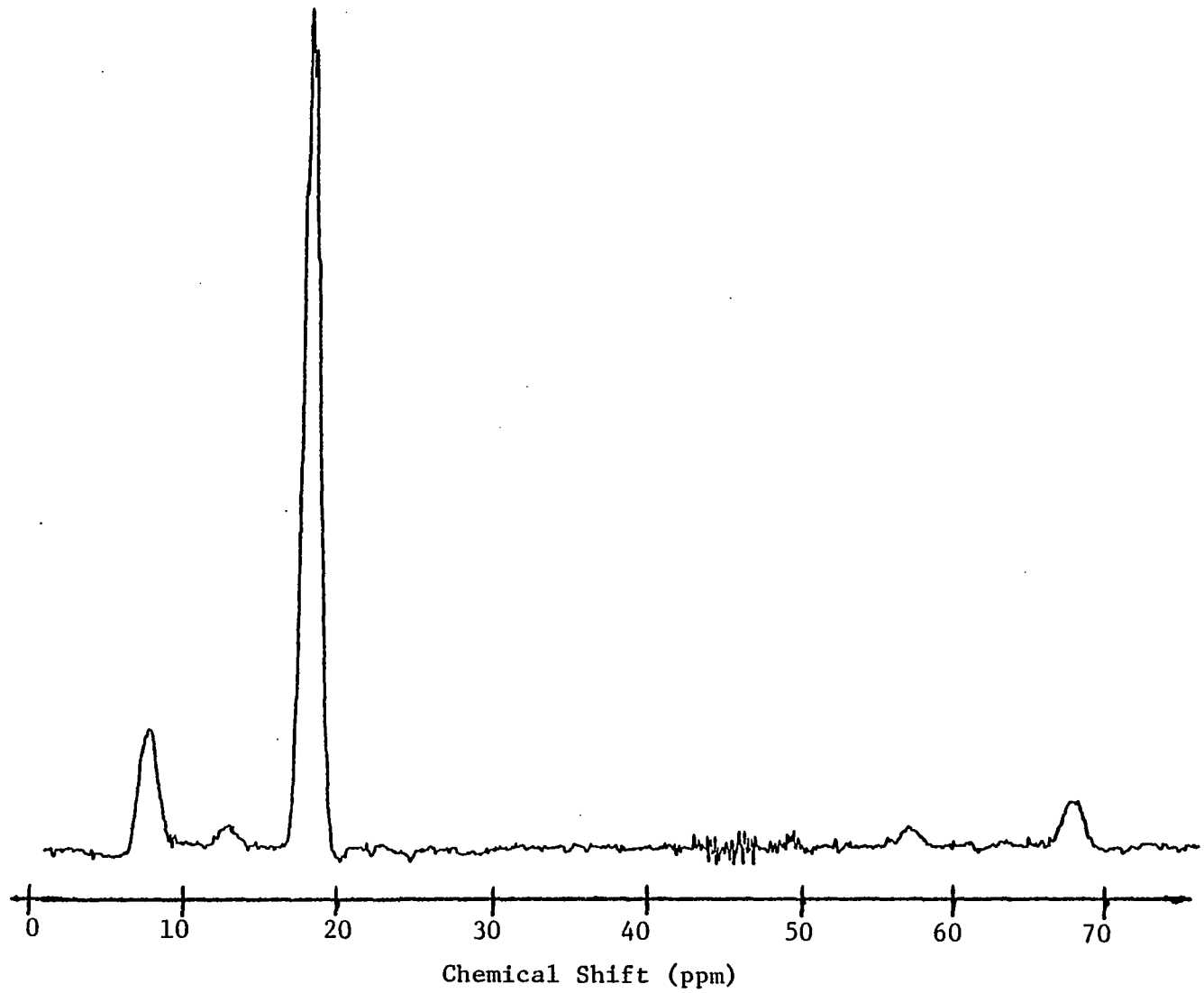


Figure 4. ^{31}P spectrum of $[(C_2H_5)(CH_3)(C_6H_5)PCH_2Li]I\cdot(C_2H_5)_2O$ in THF/C_6D_6.

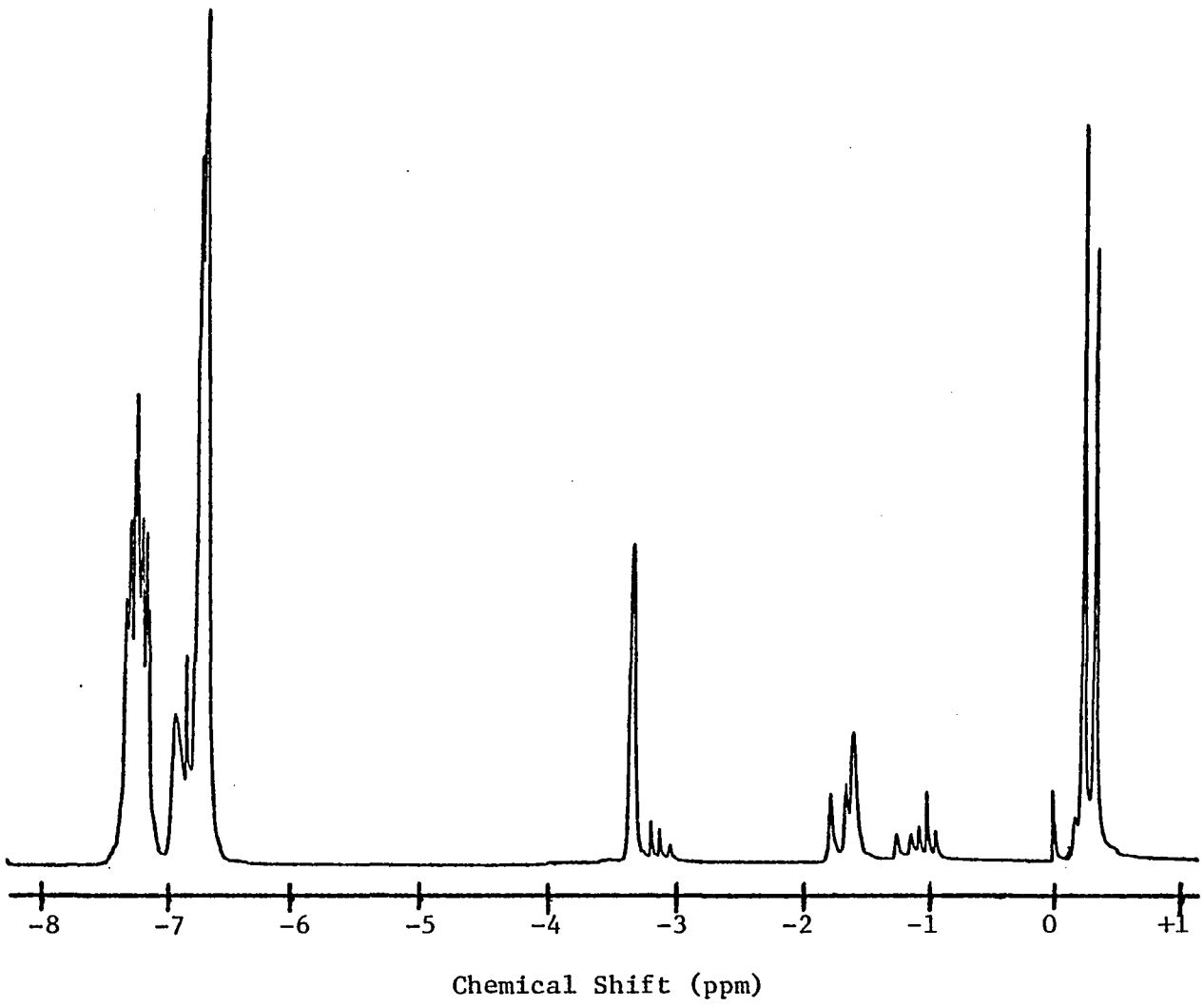


Figure 5. ^{1}H nmr spectrum of $Li(CH_2)_2P(C_6H_5)_2$ obtained in THF-d_8.

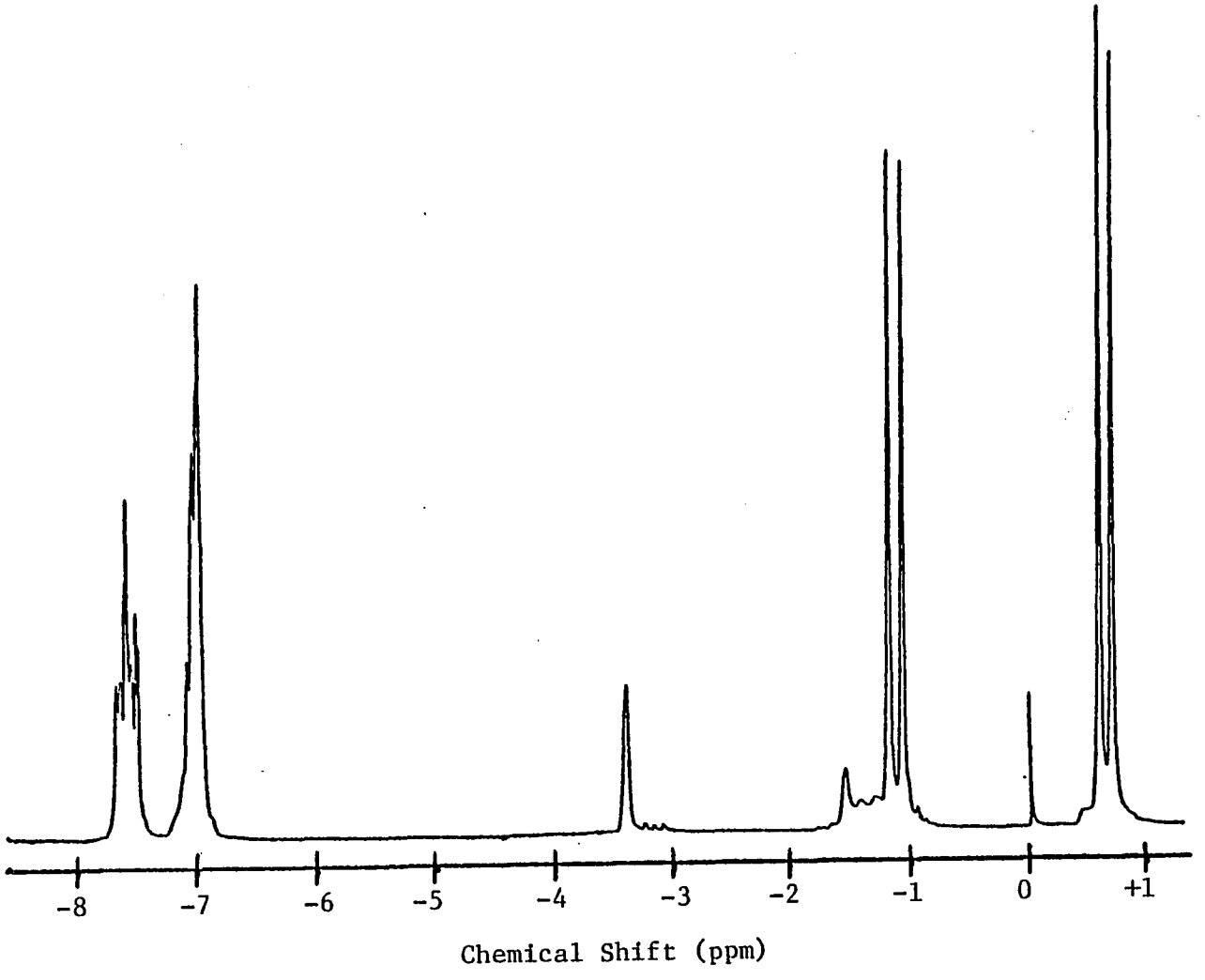


Figure 6. ^{1}H nmr spectrum of $Li(CH_2)_2P(CH_3)(C_6H_5)$ obtained in THF-d_8.

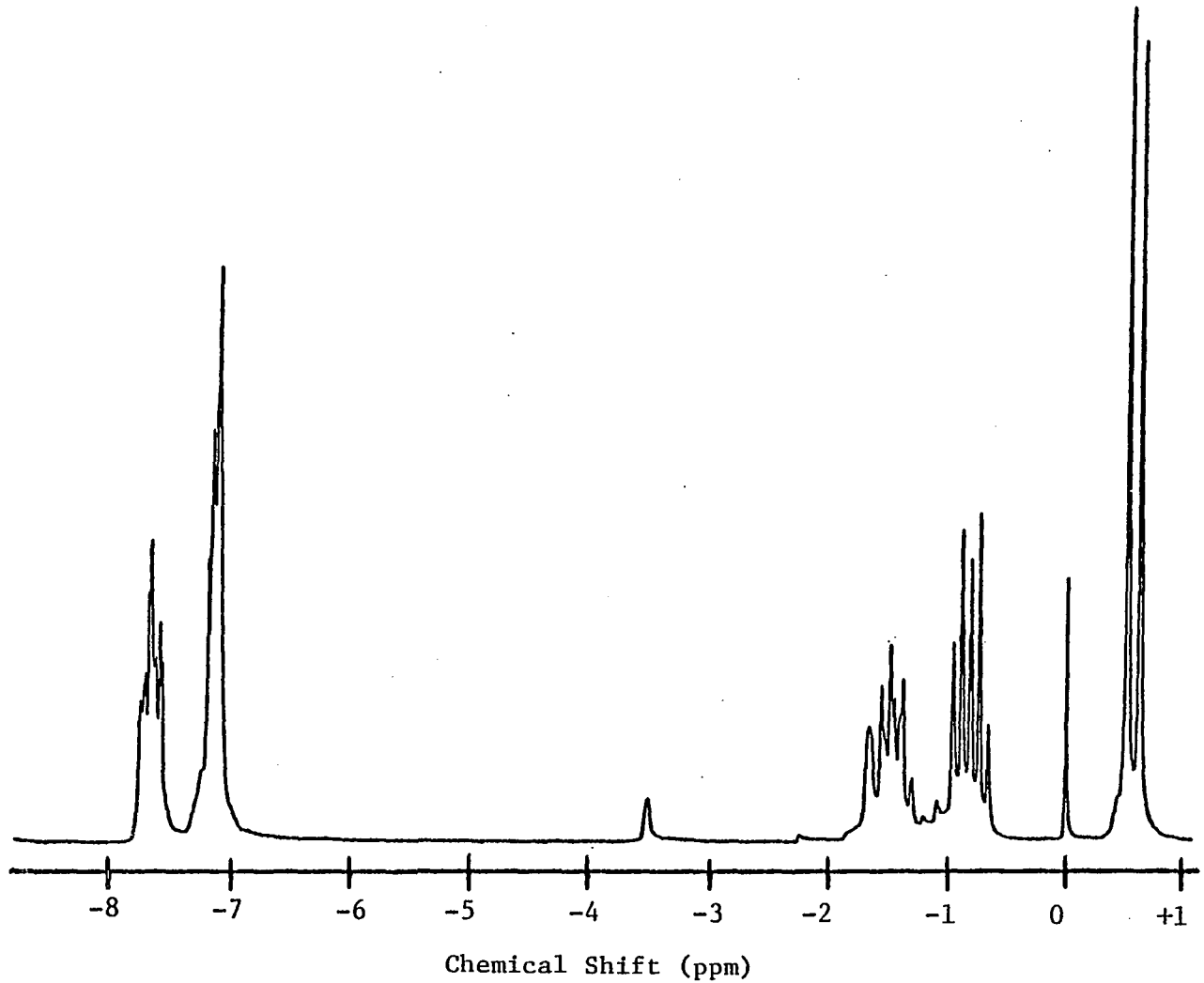
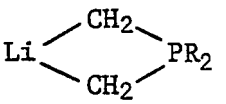
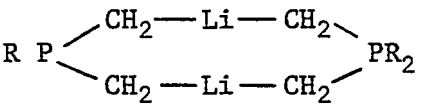


Figure 7. ^{1}H nmr spectrum of $Li(CH_2)_2P(C_2H_5)(C_6H_5)$ obtained in THF-d_8.

methylene doublet ($J(H_2CP)$ = 11 Hz) at +0.61 ppm. The methyl portion of the ethyl group is seen as an overlapping doublet of triplets ($J(H_3CCH_2)$ = 7 Hz and $J(H_3CCP)$ = 15 Hz) at -0.81 ppm and the methylene portion is a multiplet at -1.49 ppm. The coupling constants observed for the methylene resonances are in the same range (10 - 11 Hz) reported by Schmidbaur and co-workers[54] for $Li(CH_2)_2P(CH_3)_2$ and $Li(CH_2)_2P(C_2H_5)_2$. They concluded from their ^1H nmr investigation that a strong bonding interaction between the ylide carbon and lithium atom exists as in A or B:

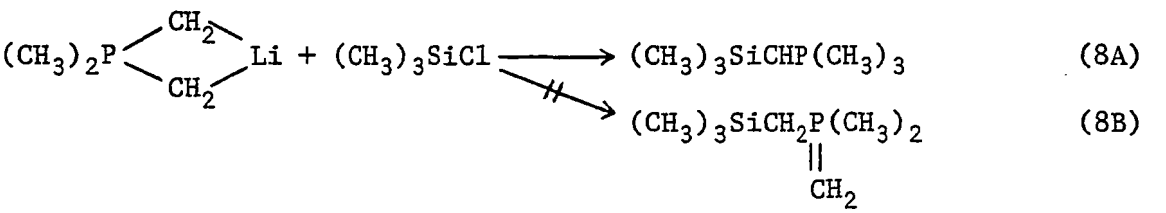


A



B

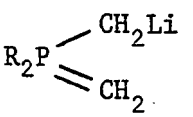
Furthermore they have found that lithiated ylides react with trimethylchlorosilane[57] to yield 8A rather than 8B:



(8A)

(8B)

A similiar reaction has been observed with dimethylchloroantimony[58], $M(CO)_5Br$ (where M = Mn or Re)[59] and, as will be shown later, also occurs with $(C_5H_5)_3UCl$. These results tend to eliminate a structure like C for the lithiated phosphoylides.



C

The ^{31}P nmr of the lithiated phosphorus ylides is shown in Figures 8 - 9. The spectrum of $Li(CH_2)_2P(C_6H_5)_2$ exhibits a quintet ($J(PCH_2)$ = 10 Hz) at +31.04 ppm. Each peak of the quintet appears to be further split into a poorly resolved quintet resulting from coupling of the four ortho phenyl protons with the phosphorus. The $Li(CH_2)_2P(CH_3)(C_6H_5)$ spectrum shows an octet (J(PCH) = 10 Hz) at +23.88 ppm with each peak showing no resolved coupling with the ortho phenyl protons. This apparent coupling of seven equivalent protons with the phosphorus is a result of the overlapped quintet of quartets due to coupling of the four methylene and three methyl protons to phosphorus. The ^{1}H nmr in Figure 6 clearly shows a distinct methyl resonance eliminating the possibility of a fast exchange process which averages the methyl and methylene protons. The $Li(CH_2)_2P(C_2H_5)(C_6H_5)$ spectrum shows a complex multiplet at +32.77 ppm.

The ^{31}P chemical shifts are 10 - 20 ppm upfield of the range reported for the alkylidenetrialkylphosphoranes.[55] A plausable explanation is that in going from an alkylidenetrialkylphosphorane, a formally neutral molecule, to the lithiated phosphoylide with the less electronegative lithium atom replacing a proton, an increase in electron density near the phosphorus occurs. This results in an increase in the shielding of the phosphorus and produces a larger upfield chemical shift. A similiar effect is observed for the $((C_2H_5)(CH_3)(C_6H_5)PCH_2Li)I$ complex, although its magnitude is smaller.

The infrared spectral data for the lithiated phosphoylides is collected in Table 4 and a spectrum of the $Li(CH_2)_2P(C_6H_5)_2$ complex is shown in Figure 10. The spectra are similar with the exception of the

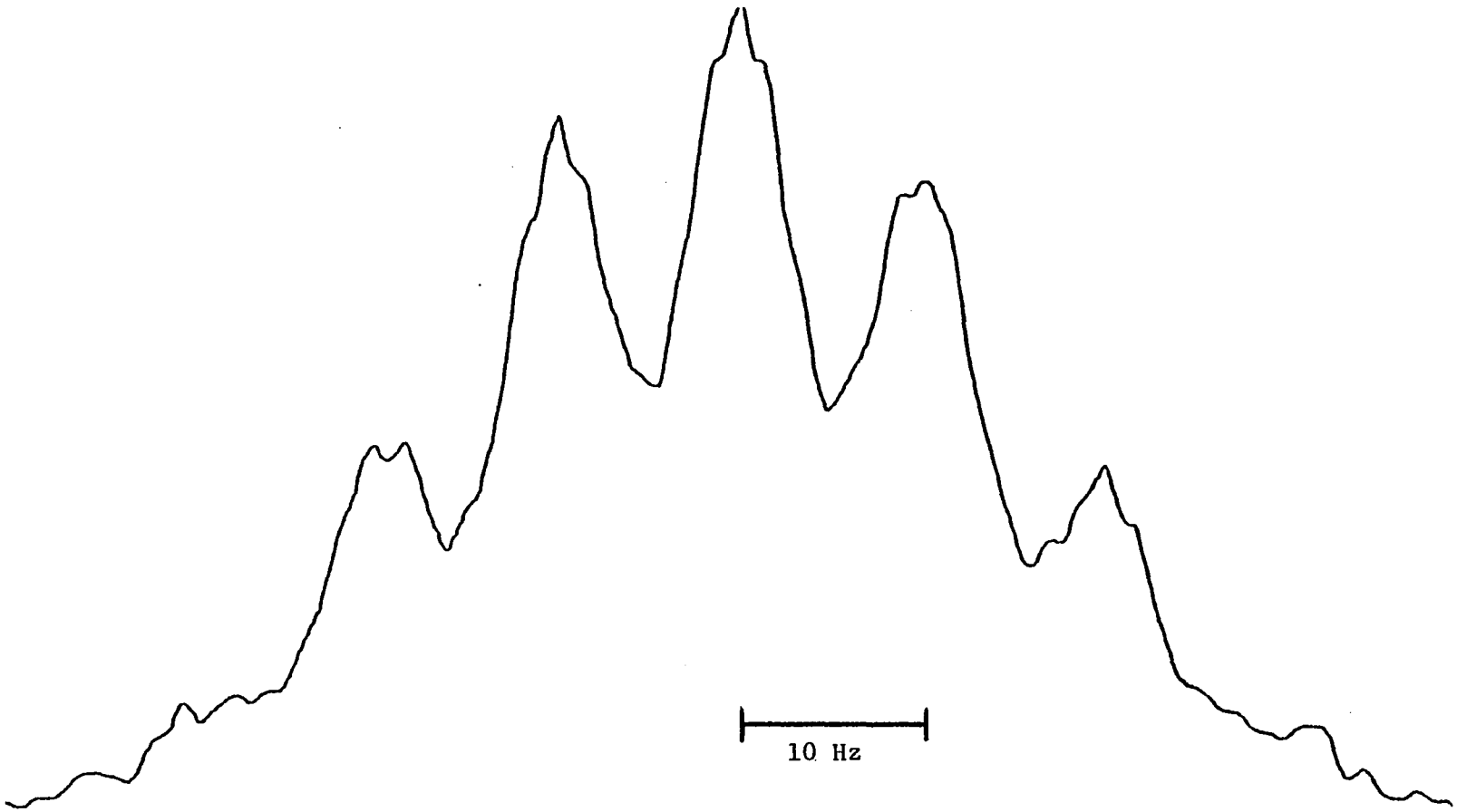


Figure 8. ^{31}P nmr spectrum of $Li(CH_2)_2P(C_6H_5)_2$ obtained in THF/C_6D_6.

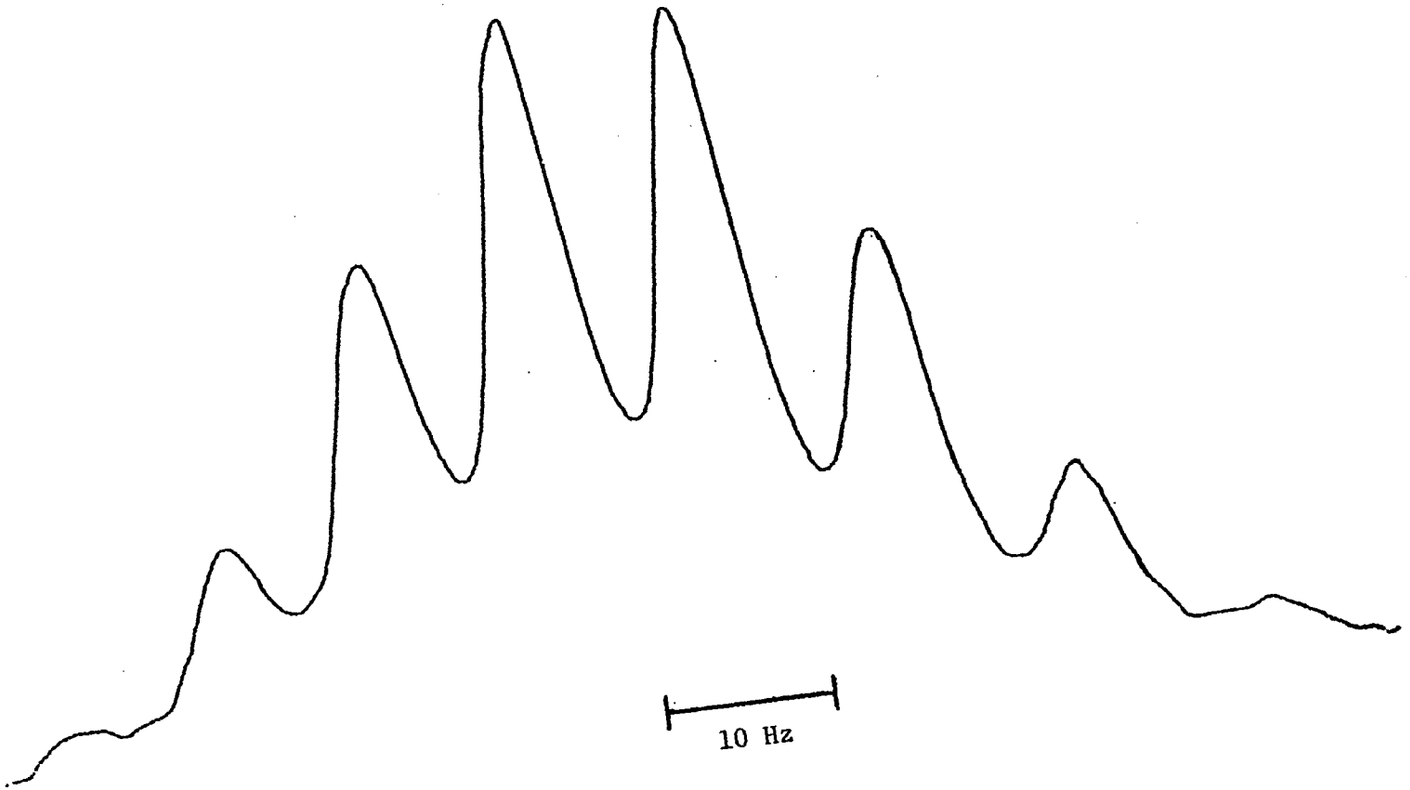


Figure 9. ^{31}P nmr spectrum of $Li(CH_2)_2P(CH_3)(C_6H_5)$ obtained in THF/C_6D_6.

bands[60] due to a phosphorus-methyl linkage in $Li(CH_2)_2P(CH_3)(C_6H_5)$. Vibrations due to phenyl groups attached to phosphorus are seen in the regions 1440 - 1435 cm^{-1} (a planar ring deformation), 1110 - 1100 cm^{-1} (a substituent sensitive C-H planar bending vibration), 745 - 720 cm^{-1} (a substituent sensitive ring vibration). The phosphorus-methyl group in $Li(CH_2)_2P(CH_3)(C_6H_5)$ shows bands at 1415 cm^{-1} (asymmetric bending), 1285 cm^{-1} (symmetric bending), 959 cm^{-1}, 941 cm^{-1}, 866 cm^{-1} (methyl rocking) and 833 cm^{-1} (methyl rocking).

Several bands are observed for aromatic hydrogens in the 3100 - 3000 cm^{-1} region. Some or all of the bands characteristic of mono-substituted benzene are seen in the 2000 - 1667 cm^{-1} region.

In the carbon-carbon double bond region are vibrations at 1590 - 1560 cm^{-1} and 1482 cm^{-1}. Phosphorus-carbon single bond vibrations are partly responsible for the broad absorptions seen about 725 cm^{-1} and 685 cm^{-1}. Bands due to the C_4-P group are observed at 1000 - 995 cm^{-1}.

In addition several new strong bands have appeared that are not present in the phosphonium salt starting material. These occur in the 910 - 890 cm^{-1} and 810 - 800 cm^{-1} region and are tentatively assigned to $P-CH_2Li$ vibrations. In addition weak to medium intensity bands are observed in the 525 - 510 cm^{-1} region and are due to carbon-lithium vibrations. This is in the region where the highest frequency vibration is seen for organolithium compounds.[61] In the spectra of the starting phosphonium salts no bands are observed near this region. Another band which may be due to a carbon-lithium vibration is observed in the 400 - 390 cm^{-1} region. However bands in the starting phosphonium salts are also seen near this region.

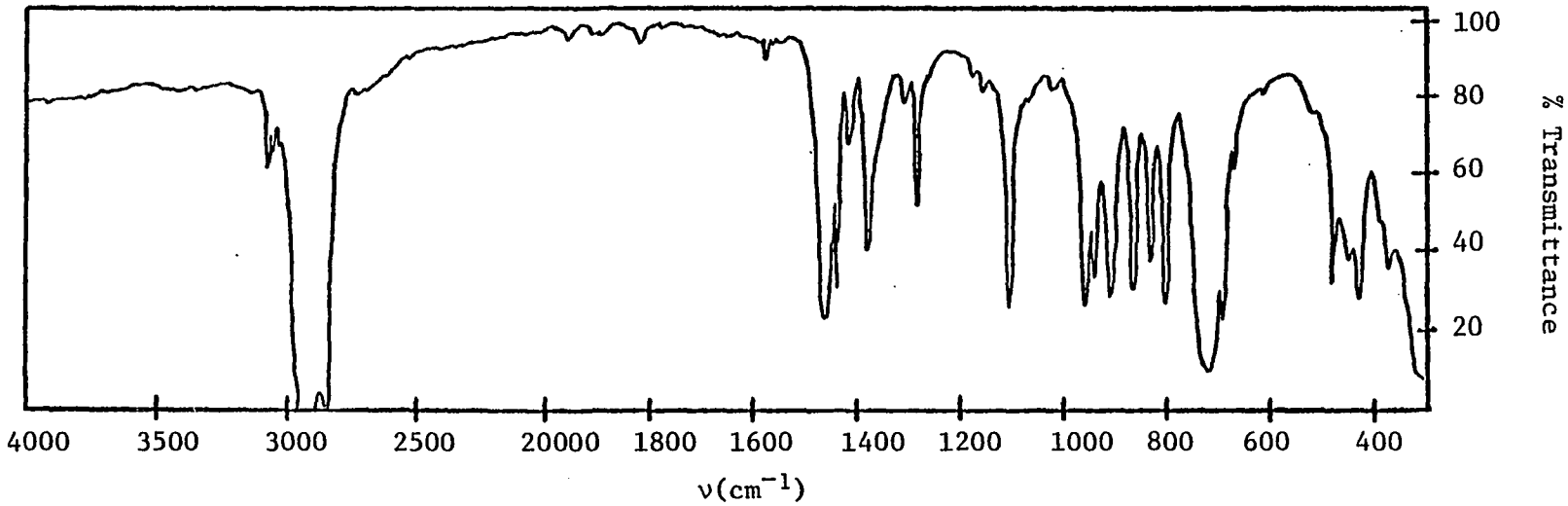


Figure 10. Infrared Spectrum of $Li(CH_2)_2P(C_6H_5)_2$ obtained as nujol mull.

A. THE TRISCYLCOPENTADIENYLURANIUMPHOSPHOYLIDE SYSTEM

When a lithiated phosphorus ylide is allowed to react with $(C_5H_5)_3UCl$ in a 1:1 molar ratio, dark green complexes result according to equation 9:

$$(C_5H_5)_3UCl + Li\begin{matrix}\diagup CH_2 \\ \diagdown CH_2\end{matrix}P(C_6H_5)(R) \xrightarrow[-50^\circ\ C.]{THF} (C_5H_5)_3UCHP(C_6H_5)(CH_3)(R) \qquad (9)$$

where R = CH_3, C_2H_5 or C_6H_5

The reaction of these lithiated phosphoylides with the organouranium moiety is analogous to that when lithiated phosphoylides react with $M(CO)_5Br$[59] (where M = Mn or Re), trimethylchlorosilane[57] or dimethylchloroantimony.[58]

We have found that optimium yields are obtained in strongly coordinating ethereal solvents (THF or 1,2-dimethoxyethane) cooled to -50° C. or lower. This is presumably due to the greater solubility of the starting materials in these solvents. If the reaction is run at room temperature or in a weakly coordinating solvent, such as diethyl ether, then an appreciable amount of the biscyclopentadienyluranium-phosphoylide dimer is formed as a side-product. Since standing for several hours at room temperature also produces some of the biscyclopentadienyluraniumphosphoylide dimer, it is necessary to immediately remove the solvent from the reaction mixture when the reaction is judged to be complete.

The triscyclopentadienyluraniumphosphoylide complexes are very soluble in diethyl ether, THF, 1,2-dimethoxyethane, benzene and toluene. They are sparingly soluble in aliphatic hydrocarbon solvents

with the solubility decreasing for the longer hydrocarbon chains. The best solvent combination we found for recrystallization is toluene-heptane.

These materials are very air and moisture sensitive. Upon exposure to the atmosphere they ignite and burn with considerable smoke. They are also susceptible to attack by solvents with acidic protons, carbonyl or nitrile functional groups.

The use of ^{1}H nmr spectroscopy has been of great value in the elucidation of the structure of the triscyclopentadienyluranium-phosphoylide complexes. The ^{1}H and ^{31}P nmr data for these complexes is summarized in Table 5 and their ^{1}H nmr spectra are shown in Figures 11 - 13. Since the U(IV) complexes are paramagnetic the ligands exhibit large displacements in the chemical shifts relative to those in a non-paramagnetic environment. The most important feature of these spectra is the relative intensities of the methine and methyl resonances. The $(C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$ complex exhibits a methyl doublet ($J(H_3CP)$ = 12 Hz) at +20.92 ppm with an intensity of 3 H's and the methine doublet (J(HCP) = 16 Hz) at +137.8 ppm with an intensity corresponding to 1 H. In the $(C_5H_5)_3UCHP(CH_3)_2(C_6H_5)$ complex the methyl doublet ($J(H_3CP)$ = 13 Hz) is observed at +15.52 ppm with an intensity corresponding to 6 H's and the methine doublet (J(HCP) = 16 Hz) at +123.7 ppm with an intensity of 1 H. The $(C_5H_5)_3UCHP(C_2H_5)(CH_3)(C_6H_5)$ complex shows a methyl doublet ($J(H_3CP)$ = 12 Hz) at +21.23 ppm with an intensity of 3 H's and the methine doublet (J(HCP) = 16 Hz) at +123.4 ppm with an intensity of 1 H. In addition this complex shows a multiplet consisting of the methylene

TABLE 5

Nuclear Magnetic Resonance Spectral Parameters for Several Triscyclopentadienyluraniumphosphoylide Complexes[a]

Compound	Nucleus	Chemical Shift (ppm)
$(C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$	^1H[b]	-3.69 (4H, dd, J(HCP) = 12 Hz, J(HCCH) = 7 Hz) -1.30 (4H, t, J(HCCH) = 7 Hz) -0.35 (2H, t, J(HCCH) = 7 Hz) +19.28 (15 H, s) +20.92 (3H, d, J(H_3CP = 12 Hz) +137.8 (1H, d, J(HCP) = 16 Hz)
	^{31}P[c]	+177.54 (broad multiplet)
$(C_5H_5)_3UCHP(CH_3)_2(C_6H_5)$	^1H[b]	-10.69 (2H, dd, J(HCP) = 12 Hz, J(HCCH) = 7 Hz) -3.95 (2H, t, J(HCCH) = 7 Hz) -1.96 (1H, t, J(HCCH) = 7 Hz) +15.52 (6H, d, J(H_3CP) = 13 Hz) +19.74 (15H, s) +123.7 (1H, d, J(HCP) = 16 Hz)
	^{31}P[c]	+213.65 (broad multiplet)
$(C_5H_5)_3UCHP(C_2H_5)(CH_3)(C_6H_5)$	^1H[b]	-10.23 (2H, t, J(HCCH) = 7 Hz) -3.80 (2H, t, J(HCCH) = 7 Hz) -1.93 (1H, t, J(HCCH) = 7 Hz) +6.85 (5H, multi) +19.80 (15H, s) +21.23 (3H, d, J(H_3CP) = 12 Hz) +123.4 (1H, d, J(HCP) = 16 Hz)
	^{31}P[c]	+173.10 (broad multiplet)

s = singlet, d = doublet, t = triplet, dd = doublet of doublets, multi = multiplet

a) spectra recorded at +25° C.

b) chemical shifts referenced relative to internal benzene

c) chemical shifts measured relative to external H_3PO_4

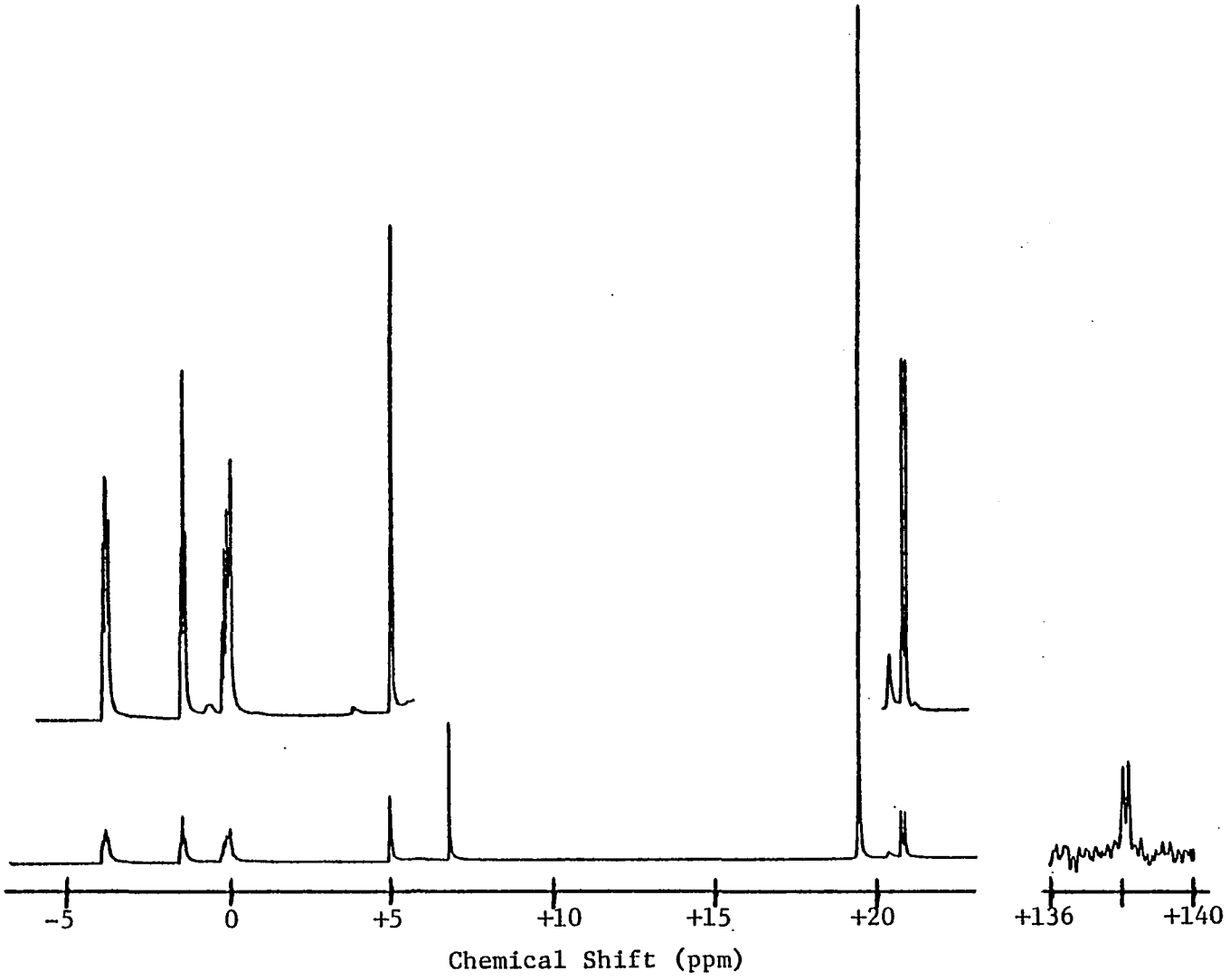


Figure 11. ^{1}H nmr spectrum of $(C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$ obtained in toluene-d_8.

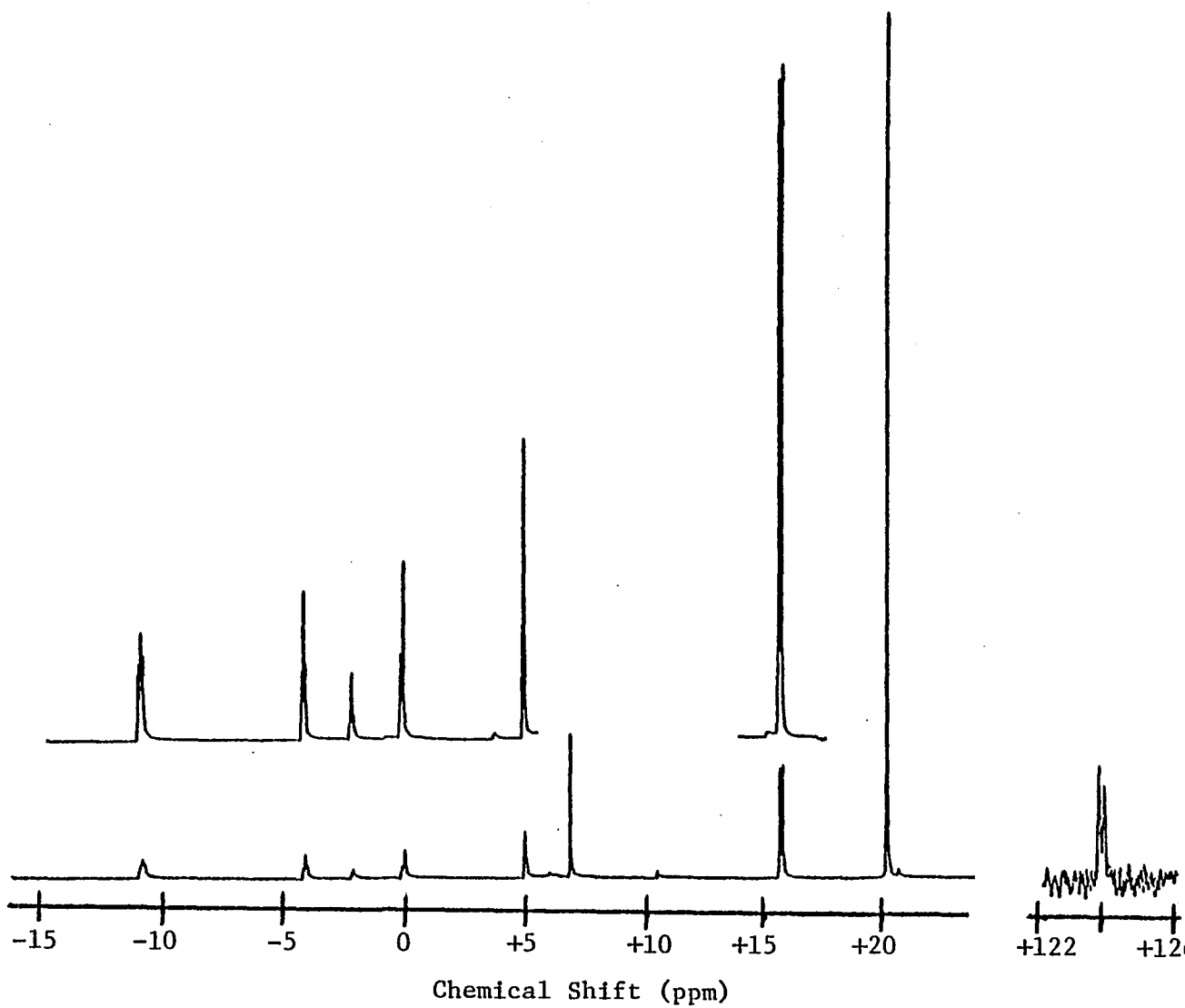


Figure 12. ^{1}H nmr spectrum of $(C_5H_5)_3UCHP(CH_3)_2(C_6H_5)$ obtained in toluene-d_8.

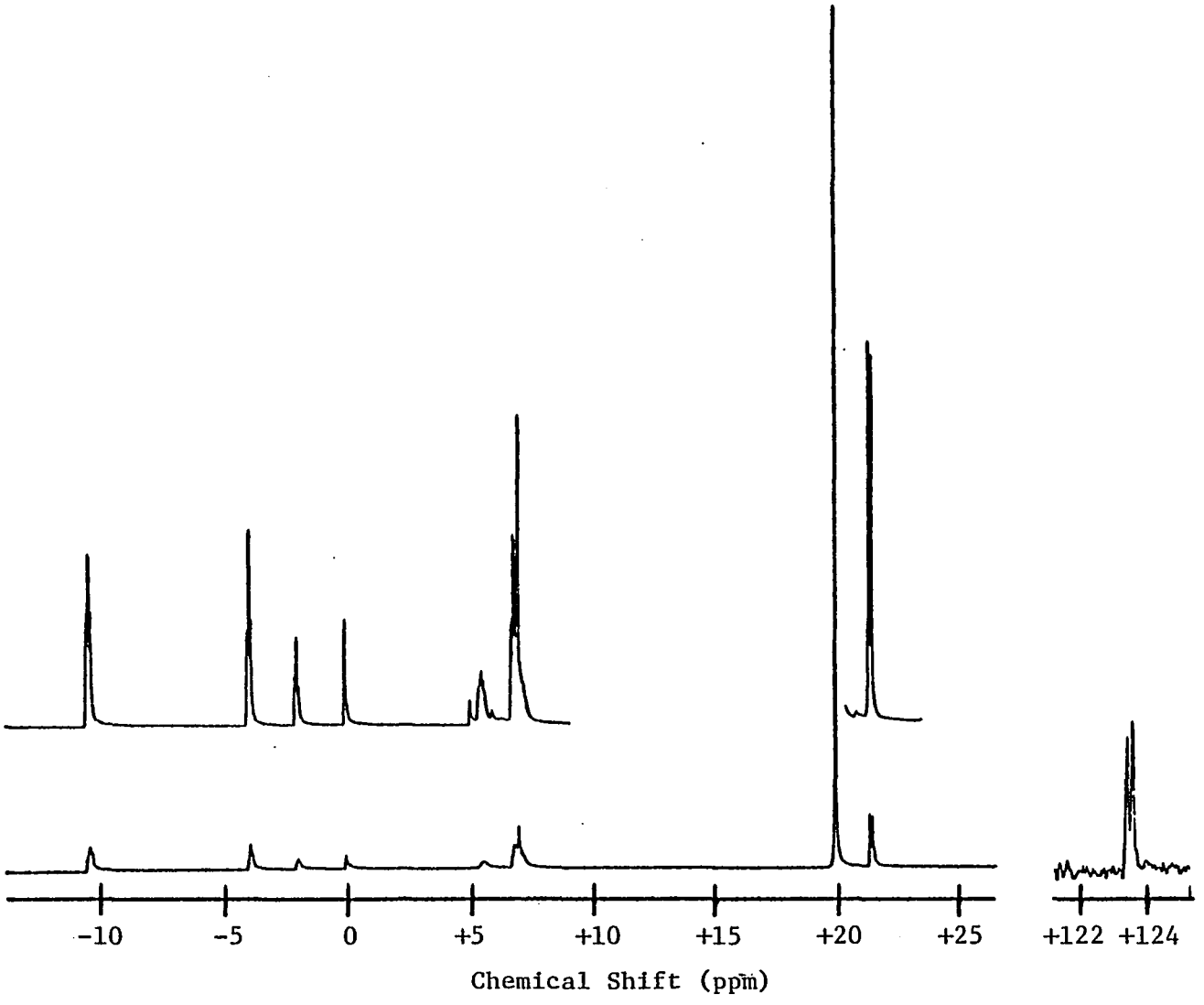


Figure 13. ^{1}H nmr spectrum of $(C_5H_5)_3UCHP(C_2H_5)(CH_3)(C_6H_5)$ obtained in C_6D_6.

and methyl resonances of the ethyl group centered at +6.85 ppm with an intensity of 5 H's.

This clearly indicates that the structure of the complexes is that shown in equation 9 rather than as indicated below.

$$(C_5H_5)_3UCH_2P(C_6H_5)(R)$$
$$\|$$
$$CH_2$$

With the methine resonance exhibiting such a large upfield shift it was necessary to observe it via the CW mode of the nmr spectrometer. As a result it is not to scale with the remaining portion of the spectra shown in Figures 11 - 13. Marks and co-workers[28] have noted similiar large upfield displacements in the ^1H nmr of the triscyclopentadienyluranium(IV) alkyl complexes.

The cyclopentadienyl resonances in these complexes are located at ~+20 ppm which is about 10 ppm upfield of the positions observed in the triscyclopentadienyl(IV) alkyl complexes. Apparently in the triscyclopentadienyluraniumphosphoylide complexes the cyclopentadienyl ligands are bound tighter to the uranium atom or there is more spin delocalization present, or a combination of both.

In the ^{31}P nmr spectra of these complexes all coupling information is lost due to paramagnetic broadening of the multiplet. Nevertheless the spectra show very large upfield displacements in the chemical shifts. The $(C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$ complex exhibits a resonance at +177.54 ppm, the $(C_5H_5)_3UCHP(CH_3)_2(C_6H_5)$ complex shows a resonance at +213.65 ppm and the $(C_5H_5)_3UCHP(C_2H_5)(CH_3)(C_6H_5)$ complex has a resonance at +173.10 ppm. These chemical shifts are on the order of

150 - 200 ppm upfield of the resonances seen in the lithiated phosphoylide starting materials.

The infrared spectral data for the organouraniumphosphoylide complexes recorded over the range 4000 - 300 cm^{-1} is summarized in Table 6 and a representative spectrum of $(C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$ is shown in Figure 14. The spectra of these three complexes are very similiar. The bands characteristic of a phosphorus-methyl group are seen in the regions 1295 - 1285 cm^{-1}, 960 - 930 cm^{-1} and 880 - 850 cm^{-1}. Absorptions arising from the phosphorus-phenyl group are observed in the regions of 1440 - 1435 cm^{-1}, 1100 - 1095 cm^{-1}, 740 - 730 cm^{-1} and 485 - 480 cm^{-1}. An additional band due to C-H out-of-plane bending on the phenyl group is observed in the 700 - 685 cm^{-1} region. Aromatic C-H are seen in the region 3080 - 3055 cm^{-1}. The phenyl substitution pattern occurring in the 2000 - 1667 cm^{-1} region is too weak in these complexes to be observed.

A carbon-carbon double bond stretching vibration is observed as a shoulder at 1480 cm^{-1} on the nujol mull abosrption. A phosphorus-carbon single bond stretching vibration is seen at 710 - 695 cm^{-1}.

In the 780 - 740 cm^{-1} region are two new bands of strong to very strong intensity not observed in the starting materials. It is believed that these are vibrations due to a phosphorus-carbon double bond. In the methylene triphenylphosphoranes[56] a band due to $P=CH_2$ stretching is observed at 900 cm^{-1}. Replacing one hydrogen atom with a uranium-carbon bond should lower this stretching vibration by at least 100 to 150 cm^{-1}.

TABLE 6

Infrared Frequencies for Several $(C_5H_5)_3UCHP(CH_3)(C_6H_5)(R)$ Complexes

$\nu(cm^{-1})$			
R = CH_3	R = C_2H_5	R = C_6H_5	Possible Assignment
3070 w	3055 w	3080 w	ν(C-H aromatic)
1480 m, sh	1480 m, sh	1480 m, sh	ν(C=C)
1438 s	1439 s	1440 s	$\delta(C_6H_5)$-a
1418 w	1418 w	1419 w	$\delta(P-CH_3)$
1310 w	1312 m	1314 m	
		1299 m	
1290 w	1294 m	1288 m	$\delta(P-CH_3)$
1262 w	1261 m	1252 w	
	1231 w		
	1159 w		
1100 s	1100 s	1098 m	$\delta(C_6H_5)$-b
1069 m	1071 m	1070 m	
1030 m, sh			
1005 vs	1010 vs	1011 vs	$\delta(C_5H_5)$
	1001 vs		
994 s	989 vs	997 s	$\delta(C_4-P)$
950 s	930 s	959 vs	$\delta(P-CH_3)$
		920 m	
878 w	875 m	852 w	$\delta(P-CH_3)$-c
791 vs	791 s, sh	794 s	$\delta(C_5H_5)$
772 vs	769 vs, br	770 vs	
742 s	750 vs	750 vs	ν(P=C)
731 s	740 s, sh	738 s	$\delta(C_6H_5)$-d
		708 m	
695 m	698 m	699 m	ν(P-C)
690 m			
	649 m		
	590 w		
500 w			ν(U-C)
480 m	484 m	480 w	$\delta(C_6H_5)$-e
415 w	418 m	427 m	ν(U-C)

s = strong, m = medium, w = weak, v = very, br = broad, sh = shoulder

a) planar ring deformation of phenyl bonded to phosphorus

b) substituent sensitive C-H planar bending vibration

c) methyl rocking

d) substituent sensitive C-H out-of-plane bending vibration

e) substituent sensitive ring vibration

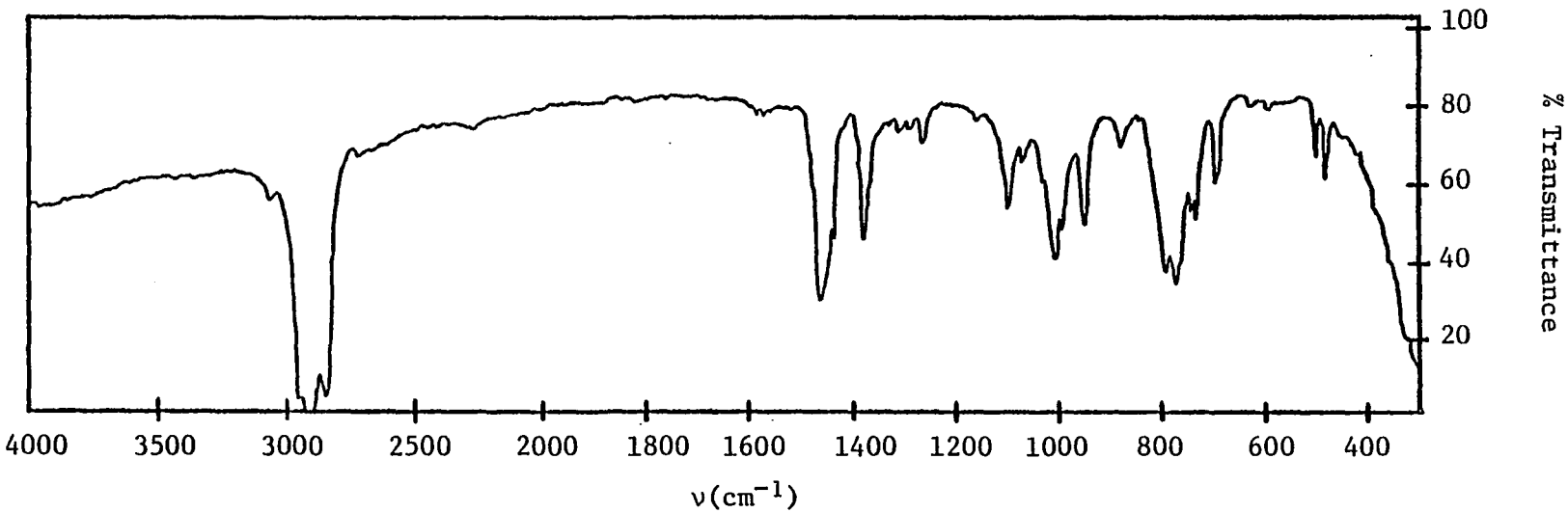


Figure 14. Infrared Spectrum of $(C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$ obtained as nujol mull.

The bands seen at 500 cm^{-1} in Figure 14 and in the 430 - 415 cm^{-1} region are assigned to uranium-carbon stretching vibrations. Heavy metal-carbon stretching vibrations have previously been assigned[62] to absorptions in these regions (ν (Hg-C) 577 - 515 cm^{-1}; ν (Pb-C) 496 - 420 cm^{-1}; ν (Pd-C) 534 - 435 cm^{-1}; ν (Pt-C) 576 - 508 cm^{-1}). In addition metal-carbon stretching vibrations have been assigned for tetrabenzylthorium.[62] The ν_{as}(Th-C) stretch occurs at 539 cm^{-1} and 516 cm^{-1} and a very weak ν_{s}(Th-C) stretch is observed at 463 cm^{-1}.

The spectral data for the visible region (25.0 - 13.0 kK) of the complexes is summarized in Table 7. A representative spectrum of the $(C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$ complex is shown in Figure 15. The three complexes give very similiar spectra. The bands observed in the visible region lie on the shoulder of a very intense band located in the ultraviolet region, due to either an electron-transfer band or a 5f-6d transition.

The near-infrared spectral data for the complexes recorded over the range 13.0 - 4.0 kK is tabulated in Table 8 and the spectrum of $(C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$ is presented in Figure 16. As expected the spectra are very similiar since the ligand environment about the uranium atom is almost identical. The observed bands are due to La Porte forbidden f→f transitions[63] and exhibit weak intensities (most $\varepsilon \leq 50$ liters/mole-cm).

The reaction of $((C_2H_5)(CH_3)(C_6H_5)PCH_2Li)I$ in a 1:1 or 2:1 molar ratio with $(C_5H_5)_3UCl$ was attempted. In each case a lime-green product was obtained, but it invariably decomposed during extractive work-up or upon standing for more than a day. ^1H nmr spectra showed

TABLE 7

Visible Spectral Parameters for Several
Triscyclopentadienyluraniumphosphoylide Complexes

ν max[a] (ε)[b]		
$(C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$	$(C_5H_5)_3UCHP(CH_3)_2(C_6H_5)$	$(C_5H_5)_3UCH(C_2H_5)(CH_3)(C_6H_5)$
19.8 (890)	19.9 (1150)	19.9 (1010)
17.2 (760)	17.3 (980)	17.3 (840)
16.7 (770)	16.6 (1000)	16.7 (880)
14.9 (460)	14.9 (660)	14.8 (590)
14.0 (255)	14.2 (390)	14.1 (340)
13.4 (160)	13.5 (200)	13.5 (190)

a) kK

b) ε = liter/mole-cm

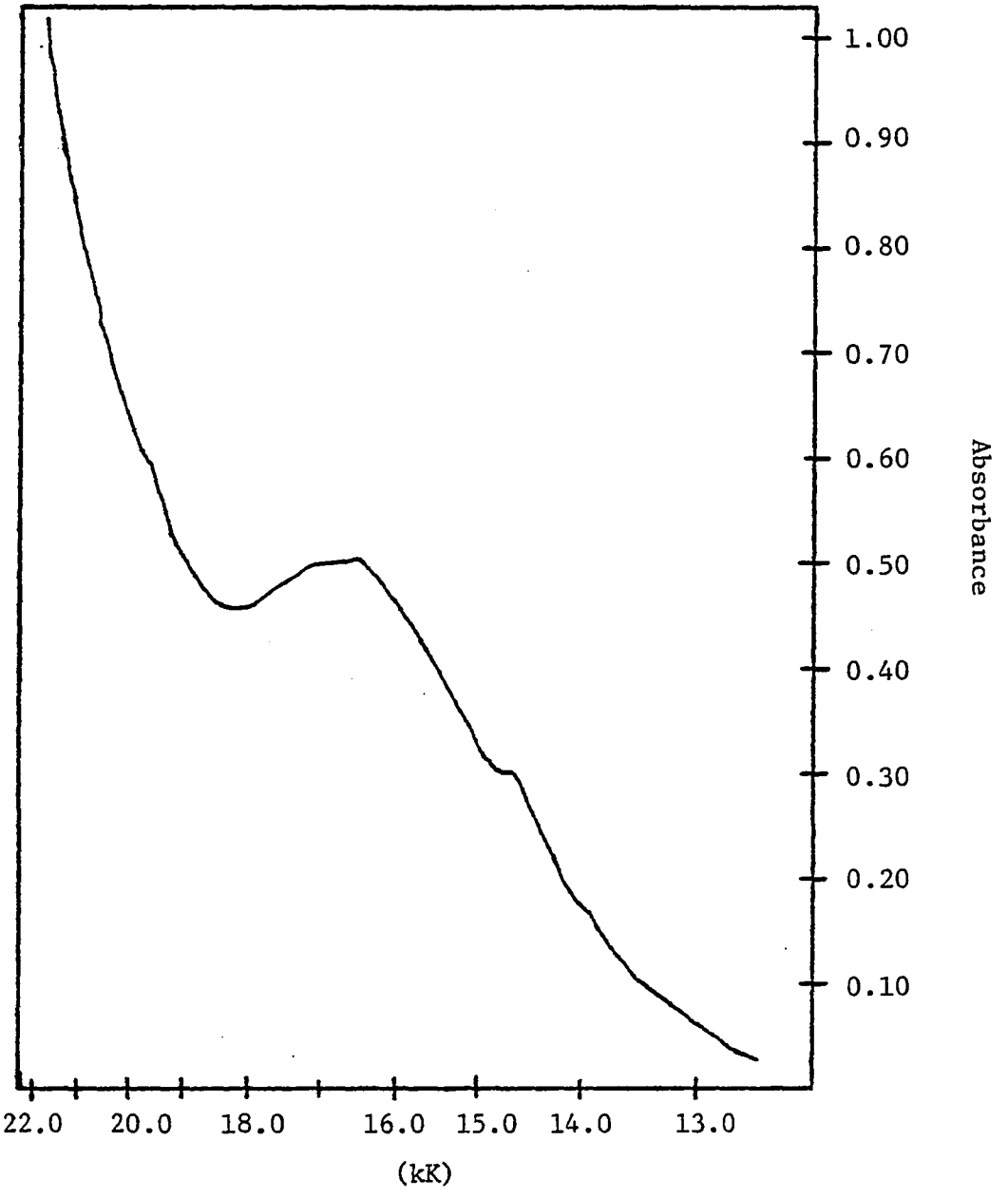


Figure 15. Visible Spectrum of $(C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$ obtained as a 6.6×10^{-4} M solution in THF.

TABLE 8

Near-Infrared Spectral Parameters for Several
Triscyclopentadienyluraniumphosphoylide Complexes

	ν max[a] (ϵ)[b]	
$(C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$	$(C_5H_5)_3UCHP(CH_3)_2(C_6H_5)$	$(C_5H_5)_3UCHP(C_2H_5)(CH_3)(C_6H_5)$
12.6 (52)	12.5 (52)	12.7 (61)
12.3 (40)	12.3 (38)	12.3 (44)
12.1 (30)	12.2 (30)	12.1 (33)
11.0 (22)	10.9 (16)	11.0 (18)
10.7 (18)		10.7 (19)
9.87 (43)	9.91 (43)	9.92 (48)
9.02 (34)	8.90 (45)	8.91 (51)
8.48 (55)	8.38 (59)	8.48 (62)
8.28 (68)		8.37 (81)
	7.59 (44)	7.60 (47)
7.43 (53)	7.30 (44)	7.33 (47)
		7.01 (43)
	6.67 (27)	6.71 (31)
6.58 (26)		6.59 (33)
		6.33 (21)
6.07 (13)	6.07 (16)	6.08 (18)
5.98 (16)		
5.66 (21)	5.68 (25)	5.66 (25)
5.38 (12)	5.38 (12)	5.38 (15)

a) kK

b) ϵ = liter/mole-cm

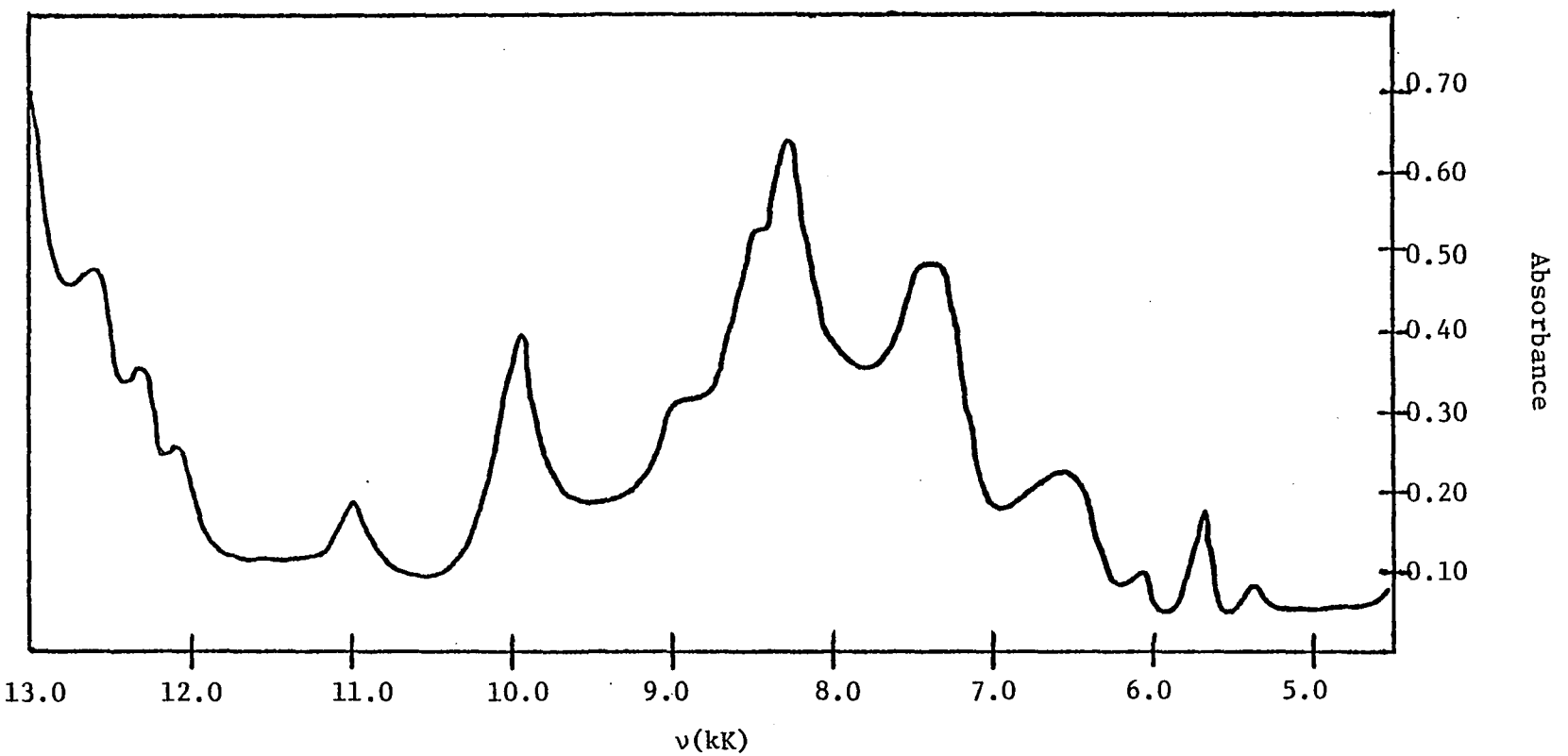


Figure 16. Near-infrared spectrum of $(C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$ obtained as a 9.8×10^{-3} M solution in THF.

it to be heavily solvated with THF but did not resemble spectra obtained for the other uranium phosphoylide complexes described below. At present this lime-green product is still uncharacterized.

B. THE BISCYCLOPENTADIENYLURANIUMPHOSPHOYLIDE SYSTEM

When two equivalents of lithiated phosphoylide are added to 1 equivalent of $(C_5H_5)_3UCl$, dark red complexes result according to equation 10:

$$(C_5H_5)_3UCl + 2Li\begin{matrix}CH_2\\ \diagup\quad\diagdown\\ CH_2\end{matrix}P(C_6H_5)(R) \xrightarrow[THF]{} \tfrac{1}{2}(\mu\text{-}(CH)(CH_2)P(C_6H_5)(R)U(C_5H_5)_2)_2 + LiCl + Li(C_5H_5) + CH_2{=}P(CH_3)(C_6H_5)(R)$$

where R = CH_3 or C_6H_5 (10)

With $Li(CH_2)_2P(C_6H_5)_2$ we are able to separate the dimeric product from the other side-products. When $Li(CH_2)_2P(CH_3)(C_6H_5)$ is used a dark red product is obtained which decomposes upon extractive work-up. However as long as it is kept in a coordinating solvent such as THF or 1,2-dimethoxyethane it remains stable. The reasons for this behavior will be explored in a later section.

As for the 1:1 complexes the best yields are obtained in a strongly coordinating solvent such as THF or 1,2-dimethoxyethane. The formation of the dimeric product is greatly enhanced if the reaction is run at an elevated temperature, such as boiling THF. If the reaction is run at -50° C. the products consist of a mixture of the green 1:1 complex and the 1:2 red dimeric complex.

The $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2$ complex is very soluble in THF, 1,2-dimethoxyethane and benzene. It is slightly soluble in toluene,

diethyl ether and pentane and totally insoluble in hexane or heptane. The best solvent combination for recrystallization is THF-heptane.

In addition to its preparation via equation 10, the red dimeric complex can also be prepared from $(C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$ via equation 11:

$$(C_5H_5)_3UCHP(CH_3)(C_6H_5)_2 + Li\begin{matrix}CH_2\\ \diagup\quad\diagdown\\ CH_2\end{matrix}P(C_6H_5)_2 \xrightarrow[THF]{}$$

$$(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2 + Li(C_5H_5) + CH_2{=}P(CH_3)(C_6H_5)_2 \quad (11)$$

This method is not as efficient as equation 10 since an appreciable amount of $(C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$ remains unreacted. A ^1H nmr of the mixture shows it consists of 39% $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2$ and 61% $(C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$. In terms of the red dimeric material this is only a 20% yield. But, this reaction demonstrates that the formation of the red dimer may go through $(C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$ as an intermediate.

When $Li(CH_2)_2P(CH_3)(C_6H_5)$ is used in place of $Li(CH_2)_2P(C_6H_5)_2$ in equation 11 a different reaction is seen to occur. The ^1H nmr indicates that a mixture consisting of 71% $(C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$ and 29% $(C_5H_5)_3UCHP(CH_3)_2(C_6H_5)$ is formed. No indication of $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2$ or a mixed dimer is seen in the ^1H nmr of this mixture. Rather than acting as a base and deprotonating a methyl group, as $Li(CH_2)_2P(C_6H_5)_2$ did in equation 11, the $Li(CH_2)_2P(CH_3)(C_6H_5)$ undergoes ligand exchange with the $(C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$ complex. The reason for this is not readily apparent to us.

We attempted the deprotonation reaction (equation 11) with $LiCH_3$. Upon addition of one equivalent of $LiCH_3$ to one equivalent of $(C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$ the ^1H nmr indicated only resonances for the starting materials. This same reaction was attempted again but with two equivalents of $LiCH_3$ to one equivalent of $(C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$. This time the color of the reaction mixture turned a dark red. However a ^1H nmr of this material showed no soluble paramagnetic species were present. It also showed no starting materials were present either, only an unidentified material which was not further characterized.

Of the three bases tried as deprotonating agents only $Li(CH_2)_2P(C_6H_5)_2$ proved to be successful in producing a biscyclopentadienyluraniumphosphoylide dimer.

An x-ray crystallographic study has been completed for $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2$ and the structure of the complex is shown in Figure 37. (See Page 135) A complete analysis of the structure is presented in a later section.

The ^1H nmr of $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2$ obtained at 100 MHz in C_6D_6 is presented in Figure 17 and the data tabulated in Table 9. The spectrum is in complete accordance with the x-ray structure in Figure 37. The methine and methylene protons exhibit large paramagnetically induced chemical shifts. The broadened methylene resonance is seen at -95.5 ppm and a broadened methine resonance is observed at +108.1 ppm. Resonances due to the phenyl protons are seen at -8.05 ppm (ortho), -3.07 ppm (meta) and -2.44 ppm (para). The cyclopentadienyl resonance is found upfield at +33.92 ppm. This is

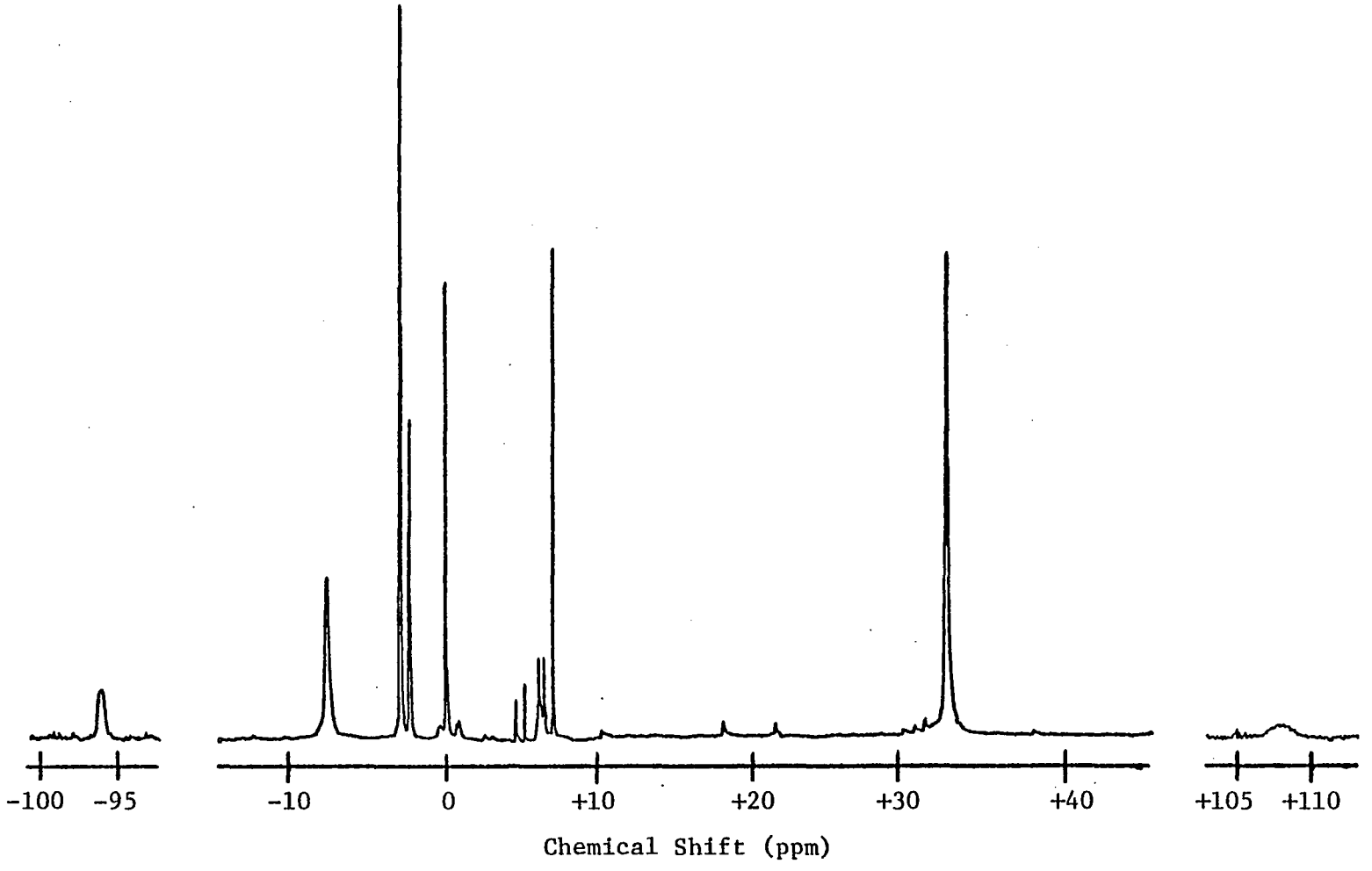


Figure 17. ^{1}H nmr spectrum of $[\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2$ obtained in C_6D_6.

TABLE 9

Nuclear Magnetic Resonance Parameters for a Biscyclopentadienyluraniumphosphoylide Dimer[a]

Compound	Nucleus	Chemical Shift (ppm)
$(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2$	^1H[b]	-95.5 (2H, broad)
		-8.05 (4H, broad)
		-3.07 (4H, t, J(HCCH) = 7 Hz)
		-2.44 (2H, t, J(HCCH) = 7 Hz)
		+33.92 (10H, s)
		+108.1 (1H, broad)
	^{31}P[c]	+140.44 (broad multiplet)

s = singlet, t = triplet

a) spectra recorded at +25° C.

b) chemical shifts referenced relative to internal benzene

c) chemical shifts measured relative to external H_3PO_4

greater than 10 ppm further upfield than the resonance observed for the cyclopentadienyl groups in the triscyclopentadienyluranium-phosphoylide complexes. Presumably this is due to a change in the orientation of the cyclopentadienyl groups relative to the dipolar field generated by the uranium atom, or to greater spin delocalization resulting from strong uranium cyclopentadienyl bonding, or both.

The ^1H nmr of this complex was found to be temperature dependent. The temperature dependence was studied in both a coordinating solvent (THF-d_8) and a noncoordinating solvent (toluene-d_8/C_6D_6). The spectrum over a +60° to -90° C. temperature range in toluene-d_8/C_6D_6 is shown in Figure 18. Upon cooling from +60° C. the cyclopentadienyl singlet begins to broaden and coalesces at ~-20° C. With further cooling to -45° C. two broad peaks emerge from the baseline and begin to sharpen at -60° C. However by -75° C. the downfield peak begins to broaden while the upfield peak continues to sharpen. This continues to -90° C. which is the lowest temperature we could achieve before solvent broadening and freezing of the sample occurred. A mechanism responsible for this latter broadening of the downfield resonance will be put forth in the discussion section.

The same temperature dependent behavior as seen in Figure 18 is also observed in THF-d_8 between +30° to -70° C. However we don't see broadening of the downfield resonance because we can't go to quite as low a temperature as with the toluene-d_8/C_6D_6 solvent mixture. The coalescence temperature in this spectrum is estimated to be at ~-30° C.

The loss of the broad peak at coalescence into the baseline makes it difficult to determine the coalescence temperature and we

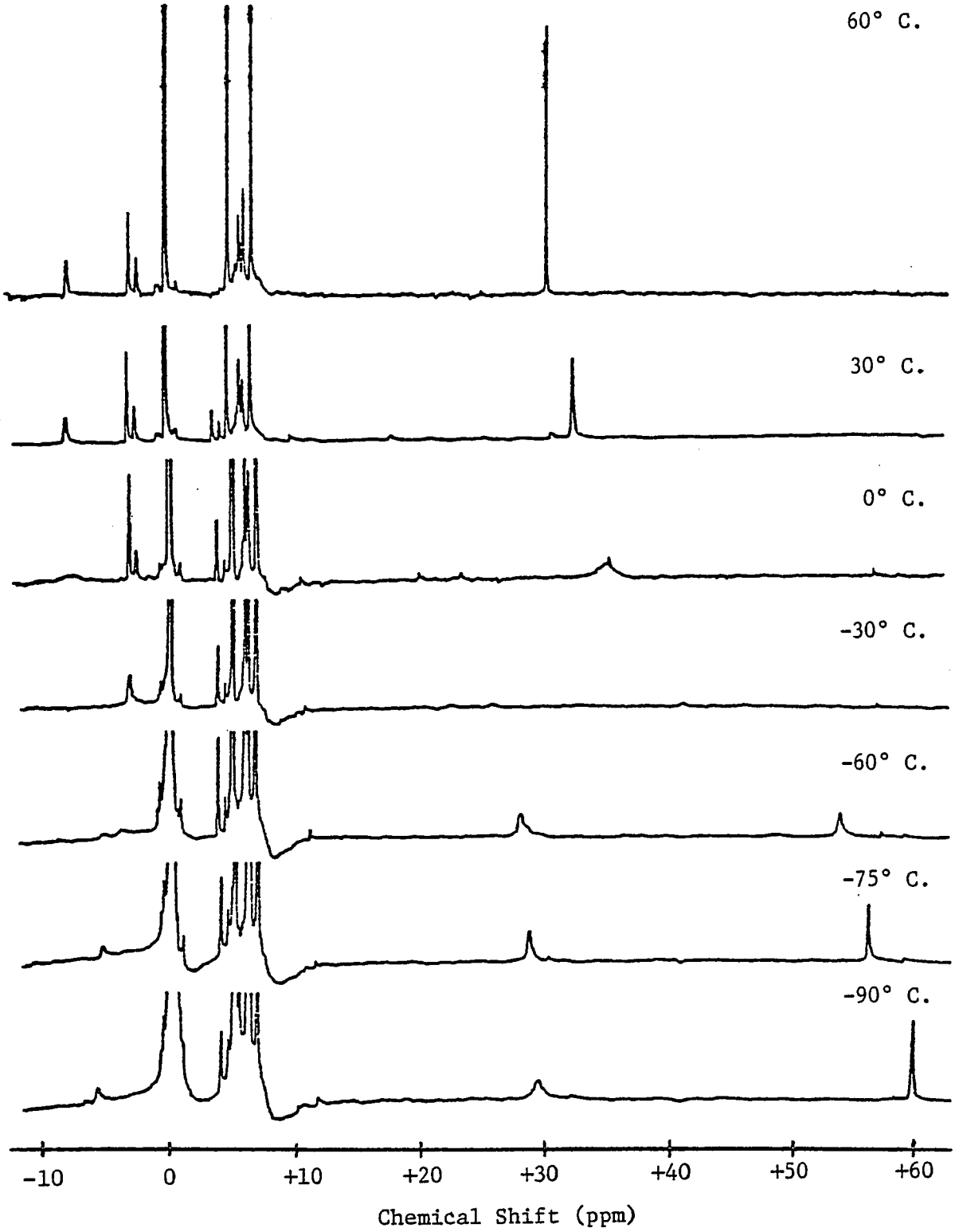


Figure 18. Variable temperature ^{1}H nmr of $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2$ obtained in toluene-d_8/C_6D_6.

estimate that it is accurate to no more than ±5° C. Since the two coalescence temperatures are within one standard deviation of each other, the 10° C. difference between the two estimated coalescence temperatures may not be significant.

A second problem associated with this broadening is that we lose the intermediate exchange information which precludes the use of line shape analysis by computer simulation to obtain thermodynamic parameters for the observed process. Although we can't determine ΔH_c or ΔS_c, we can still get an estimate of ΔG_c from equations 12 and 13:

$$k_r = \pi\Delta\nu/\sqrt{2} \tag{12}$$

$$k_r = KT/h \exp(-\Delta G_c/RT) \tag{13}$$

where k_r is the rate constant for the observed process, $\Delta\nu$ is the chemical shift separation in hertz at the coalescence temperature and the other symbols have their usual meaning

The chemical shift separation is determined by extrapolating the observed slow exchange peak positions back to the coalescence temperature and taking their difference. In toluene-d_8/C_6D_6 the chemical shift separation at 253° K. is 1,950 hertz which yields a ΔG_{253} = +10 ± 1 kcal/mole. In THF-d_8 the chemical shift separation is 1,920 hertz at 243° K. and this also gives a ΔG_{243} = +10 ± 1 kcal/mole.

The ^{31}P nmr spectrum of $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2$ exhibits a resonance at +140.44 ppm. Like the triscyclopentadienyluranium-phosphoylide complexes the coupling information is lost due to

paramagnetic broadening. The ^{31}P nmr was also studied as a function of temperature over the range +30° to -60° C. in THF/toluene-d_8. It was hoped that at a lower temperature the coupling constants would be observed and information pertaining to the rearrangement process would be obtained. Unfortunately the peak remains too broad, even at -60°C. to allow phosphorus-proton coupling to be resolved.

The infrared spectrum of $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2$ recorded over the range 4,000 - 300 cm^{-1} is shown in Figure 19 and the data summarized in Table 10. The bands characteristic of phenyl groups attached to phosphorus are seen at 1439 cm^{-1}, 1097 cm^{-1}, 735 cm^{-1} and 492 cm^{-1}. The weak but characteristic pattern of bands for mono-substituted benzene are observed in the 2000 - 1667 cm^{-1} region. Aromatic hydrogens are seen at 3070 cm^{-1} and 3050 cm^{-1}. The vibrational modes of π-bonded cyclopentadienyl groups are observed at 1010 cm^{-1} (C-H in-plane wagging) and at 791 cm^{-1} (out-of-plane wagging).

A carbon-carbon double bond stretching vibration is seen at 1480 cm^{-1} as a shoulder on the nujol peak. A band apparently due to phosphorus-carbon double bond stretching is seen at 776 cm^{-1}. The crystal structure of this complex indicates that an appreciable amount of double bond character is present in the phosphorus-methine and phosphorus-methylene bonds. Phosphorus-carbon single bond stretching is observed at 744 cm^{-1}.

The two absorptions occurring at 518 cm^{-1} and 467 cm^{-1} are assigned to uranium-carbon stretching vibrations for the reasons previously mentioned.

The visible spectrum of $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2$ recorded

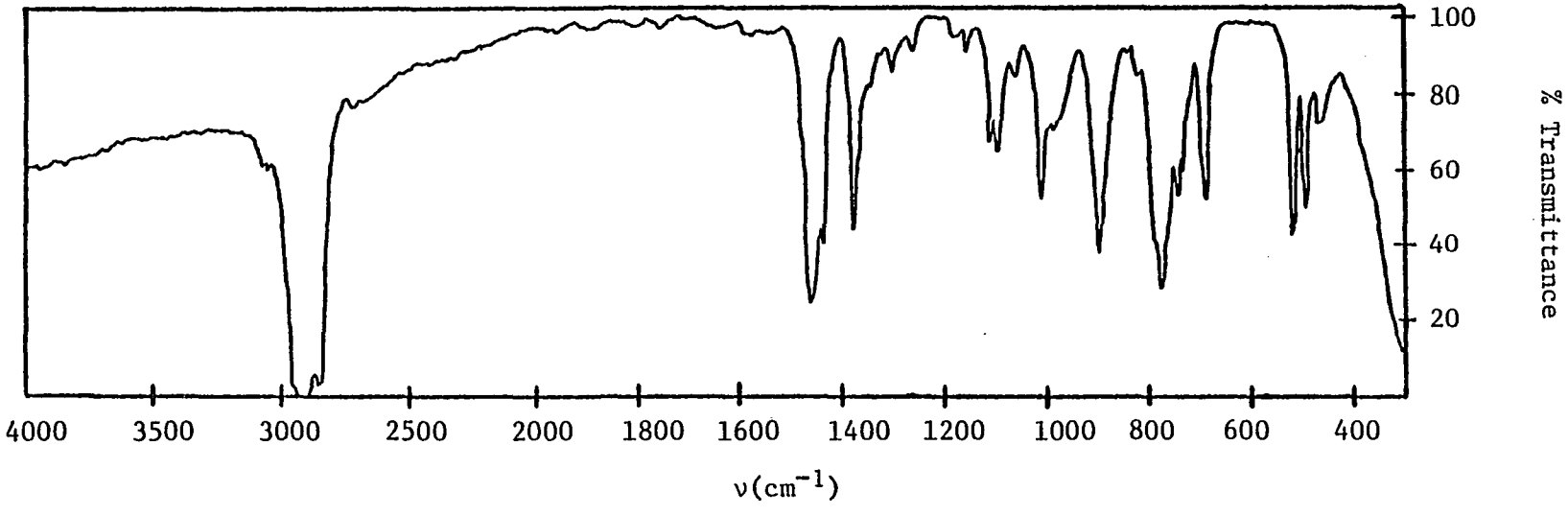


Figure 19. Infrared Spectrum of $[\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2$ as a nujol mull.

TABLE 10

Infrared Frequencies for
$(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2$

$\nu(cm^{-1})$	Possible Assignment
3070 w	
3050 w	ν(C-H aromatic)
1965 w	
1894 w	
1806 w	
1760 w	
1480 m. sh	ν(C=C)
1439 s, sh	$\delta(C_6H_5)$-a
1304 w	
1262 w	
1157 w	
1112 m	
1097 m	$\delta(C_6H_5)$-b
1010 s	$\delta(C_5H_5)$
985 m	$\delta(C_4\text{-}P)$
898 s	$\nu(P\text{-}CH_2)$
822 w	
791 s, sh	$\delta(C_5H_5)$
776 vs	ν(P=C)
744 s	$\delta(C_6H_5)$-c
735 m	
689 s	ν(P-C)
518 s	ν(U-C)
492 s	$\delta(C_6H_5)$-d
467 m	ν(U-C)

s = strong, m = medium, w = weak, v = very, sh = shoulder

a) planar ring deformation of phenyl bonded to phosphorus

b) substituent sensitive C-H planar bending vibration

c) substituent sensitive C-H out-of-plane bending vibration

d) substituent sensitive ring vibration

over the 25.0 - 13.0 kK region is shown in Figure 20 and the data summarized in Table 11. This spectrum is qualitatively very similiar to those observed for the triscyclopentadienyluraniumphosphoylide complexes. It consists of essentially one shoulder on an intense electron-transfer band or 5f-6d transition band present in the ultraviolet region. The main difference is a hypsochromic shift (blue shifted) of ~2,700 cm^{-1} of this feature for the $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2$ complex.

The near-infrared spectral data of $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2$ recorded over the 13.0 - 4.0 kK region is summarized in Table 11 and the spectrum shown in Figure 21. The most interesting feature of the spectrum are the two intense peaks at 8.81 kK (ε = 200 liter/mole-cm per molecule) and 6.57 kK (ε = 110 liter/mole-cm per molecule). This region is usually characterized by La Porte forbidden f→f transitions which are generally weak (ε < 50 liter/mole-cm), but occur because of vibronic coupling. The symmetry of the dimer is lower than the triscyclopentadienyluraniumphosphoylide complexes and this may allow greater intensity for these forbidden transitions. There may also exist a weak interaction between the two metal centers.

Other than these two relatively intense peaks the remainder of the spectrum is similiar to the near-infrared spectra of the triscyclopentadienyluraniumphosphoylide complexes. Here the peak positions have undergone a blue shift of ~500 cm^{-1} relative to those observed for the triscyclopentadienyluraniumphosphoylide complexes.

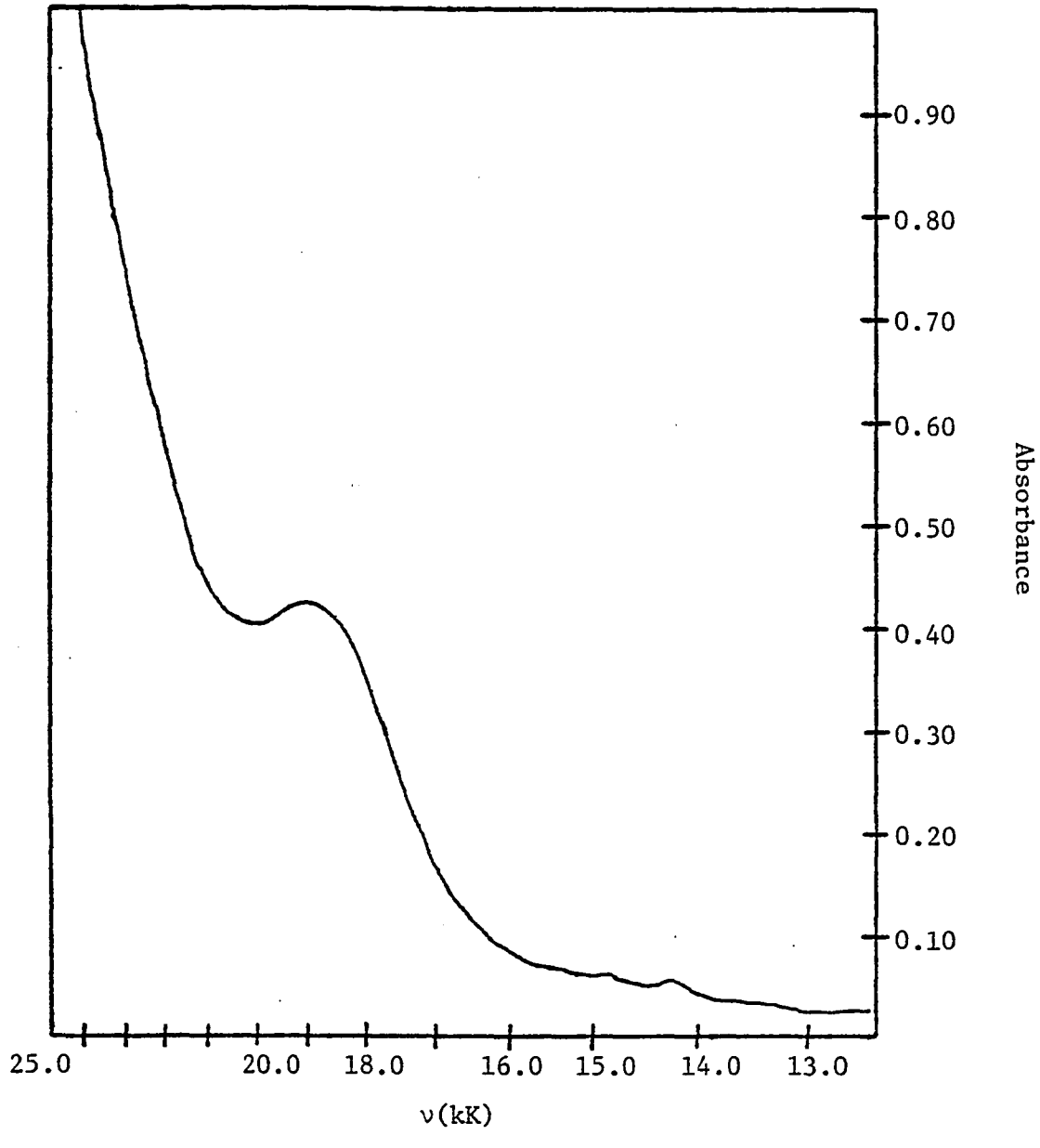


Figure 20. Visible spectrum of $[\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2$ obtained as a 2.9×10^{-4} M solution in THF.

TABLE 11

Electronic Spectral Parameters for
$(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2$

ν max[a] (ε)[b]	
Visible Region	Near-Infrared Region
19.3 (1430)	13.0 (36)
15.7 (240)	11.7 (33)
15.0 (210)	11.0 (35)
14.4 (190)	10.6 (40)
13.8 (120)	9.98 (62)
	9.36 (55)
	8.88 (190)
	8.81 (200)
	8.73 (190)
	7.42 (42)
	6.90 (40)
	6.73 (55)
	6.57 (110)
	6.32 (62)
	5.78 (27)
	5.65 (18)

a) kK

b) ε = liter/mole-cm per complex

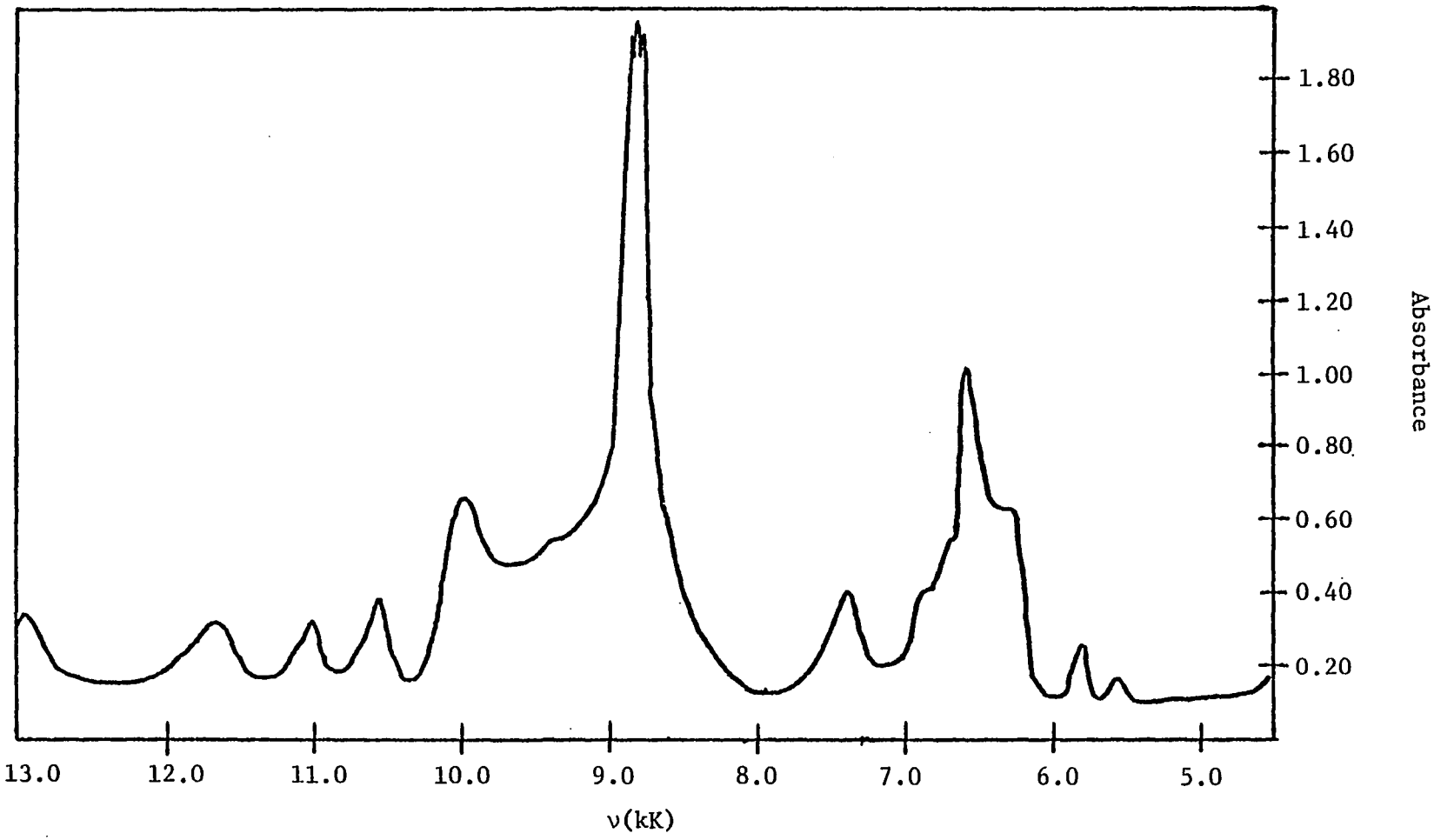
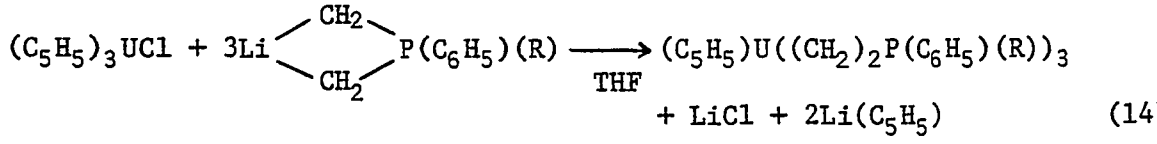


Figure 21. Near-infrared spectrum of $[\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2$ obtained as a 9.8×10^{-3} M solution in THF.

C. THE MONOCYCLOPENTADIENYLURANIUMTRISPHOSPHOYLIDE SYSTEM

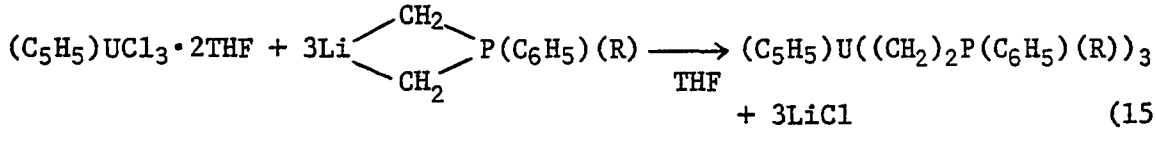
The addition of three equivalents of lithiated phosphoylide to one equivalent of triscyclopentadienyluranium chloride results in bright gold colored complexes according to equation 14:



$$(C_5H_5)_3UCl + 3Li\left(\begin{matrix}CH_2\\ \\ CH_2\end{matrix}\right)P(C_6H_5)(R) \xrightarrow[THF]{} (C_5H_5)U((CH_2)_2P(C_6H_5)(R))_3 + LiCl + 2Li(C_5H_5) \qquad (14)$$

where R = CH_3 or C_6H_5

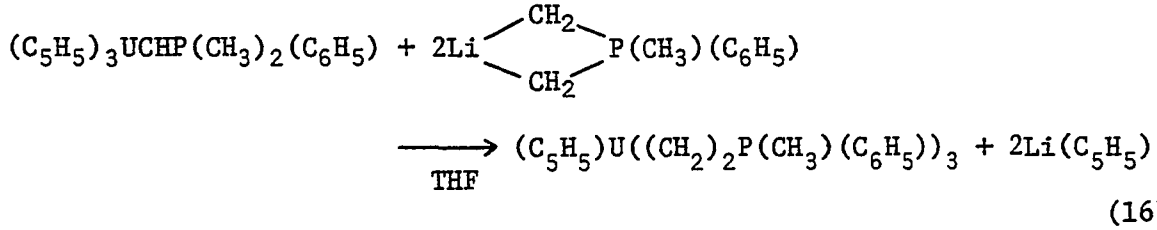
These complexes can also be prepared from $(C_5H_5)UCl_3 \cdot 2THF$ via equation 15:



$$(C_5H_5)UCl_3 \cdot 2THF + 3Li\left(\begin{matrix}CH_2\\ \\ CH_2\end{matrix}\right)P(C_6H_5)(R) \xrightarrow[THF]{} (C_5H_5)U((CH_2)_2P(C_6H_5)(R))_3 + 3LiCl \qquad (15)$$

where R = CH_3 or C_6H_5

In addition the triscyclopentadienyluraniumphosphoylide complexes can also serve as starting materials for the monocyclopentadienyluranium-trisphosphoylide complexes via equation 16:



$$(C_5H_5)_3UCHP(CH_3)_2(C_6H_5) + 2Li\left(\begin{matrix}CH_2\\ \\ CH_2\end{matrix}\right)P(CH_3)(C_6H_5) \xrightarrow[THF]{} (C_5H_5)U((CH_2)_2P(CH_3)(C_6H_5))_3 + 2Li(C_5H_5) \qquad (16)$$

Reactions 14 - 16 give essentially quantitative yield of crude gold colored product when THF is used as the solvent. The crude product prepared in this manner has repeatedly failed to recrystallize

using mixed solvent systems. However, substitution of diethyl ether for THF as the solvent produces, after filtering and standing for several hours, bright gold colored crystalline $(C_5H_5)U((CH_2)_2P(C_6H_5)_2)_3$. Unfortunately, this method fails in the case of $(C_5H_5)U((CH_2)_2P(CH_3)(C_6H_5))_3$ which is very soluble in diethyl ether.

Both complexes are very soluble in THF, 1,2-dimethoxyethane, benzene, and toluene. They are soluble in pentane and somewhat less soluble in heptane. These complexes can tolerate exposure to the air for several minutes before they begin to darken and catch fire. Exposure to water produces an immediate blackening. As with the previously discussed complexes these materials are also sensitive to solvents containing acidic protons.

One of the products we obtain in reactions 14 and 16 is lithium cyclopentadienide which was identified from its infrared spectrum. This was also seen as a side-product in the preparation of the biscyclopentadienyluraniumphosphoylide dimer complexes. The cyclopentadienyl ligands of the starting materials (except $(C_5H_5)UCl_3 \cdot 2THF$) react in an ionic fashion and are simply displaced by the ylide.

The ^1H nmr of $(C_5H_5)U((CH_2)_2P(C_6H_5)_2)_3$ and $(C_5H_5)U((CH_2)_2P(CH_3)(C_6H_5))_3$ obtained at 100 MHz in toluene-d_8 is shown in Figures 22 and 23 and the data tabulated in Table 12. The spectra shown were obtained at +95° C. since the methylene groups are in the intermediate exchange region at room temperature and are not observed. The principle features of interest in these spectra are the methylene and cyclopentadienyl resonances and in the case of

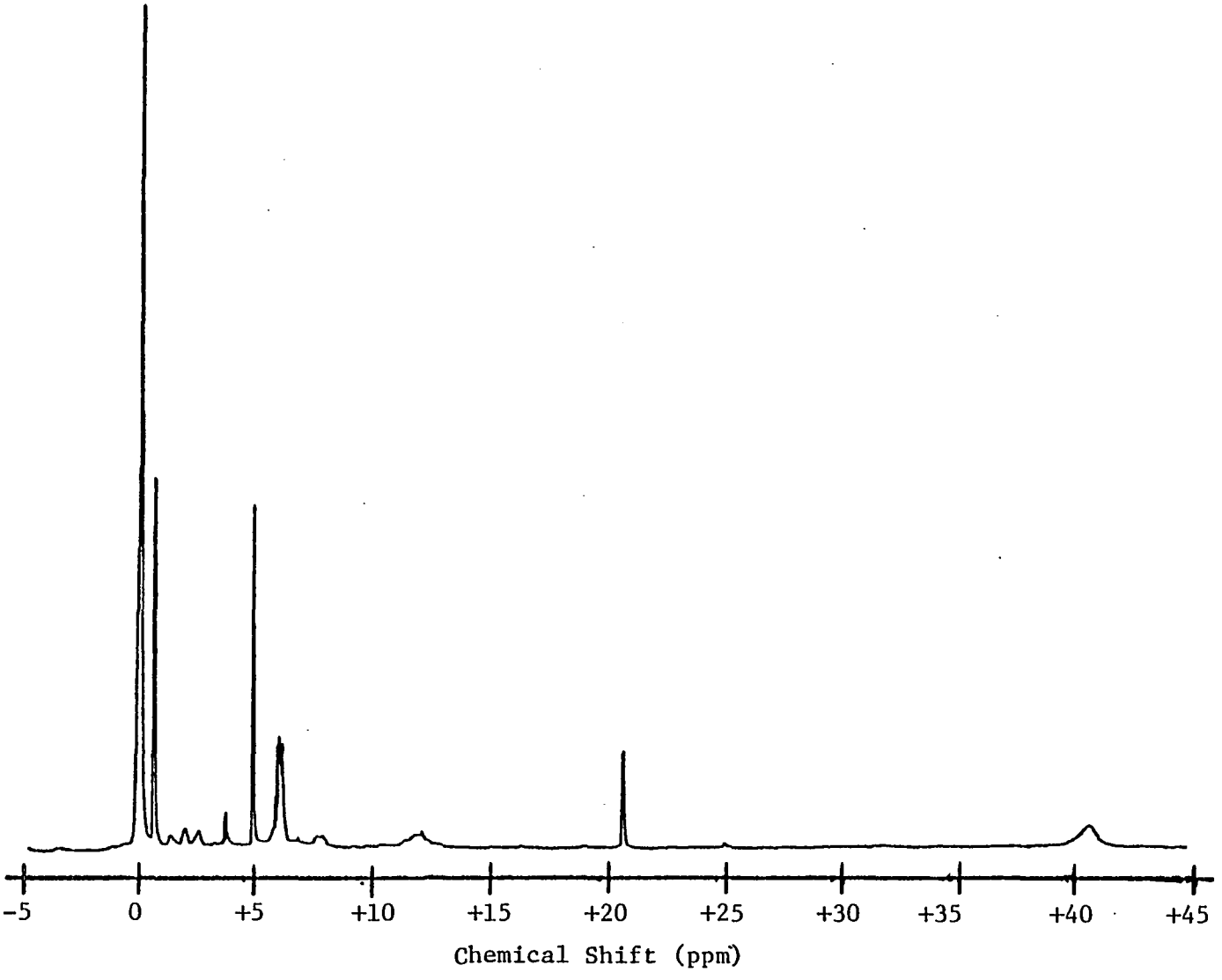


Figure 22. ^{1}H nmr spectrum of $(C_5H_5)U[(CH_2)_2P(C_6H_5)_2]_3$ obtained in toluene-d_8 at +95° C.

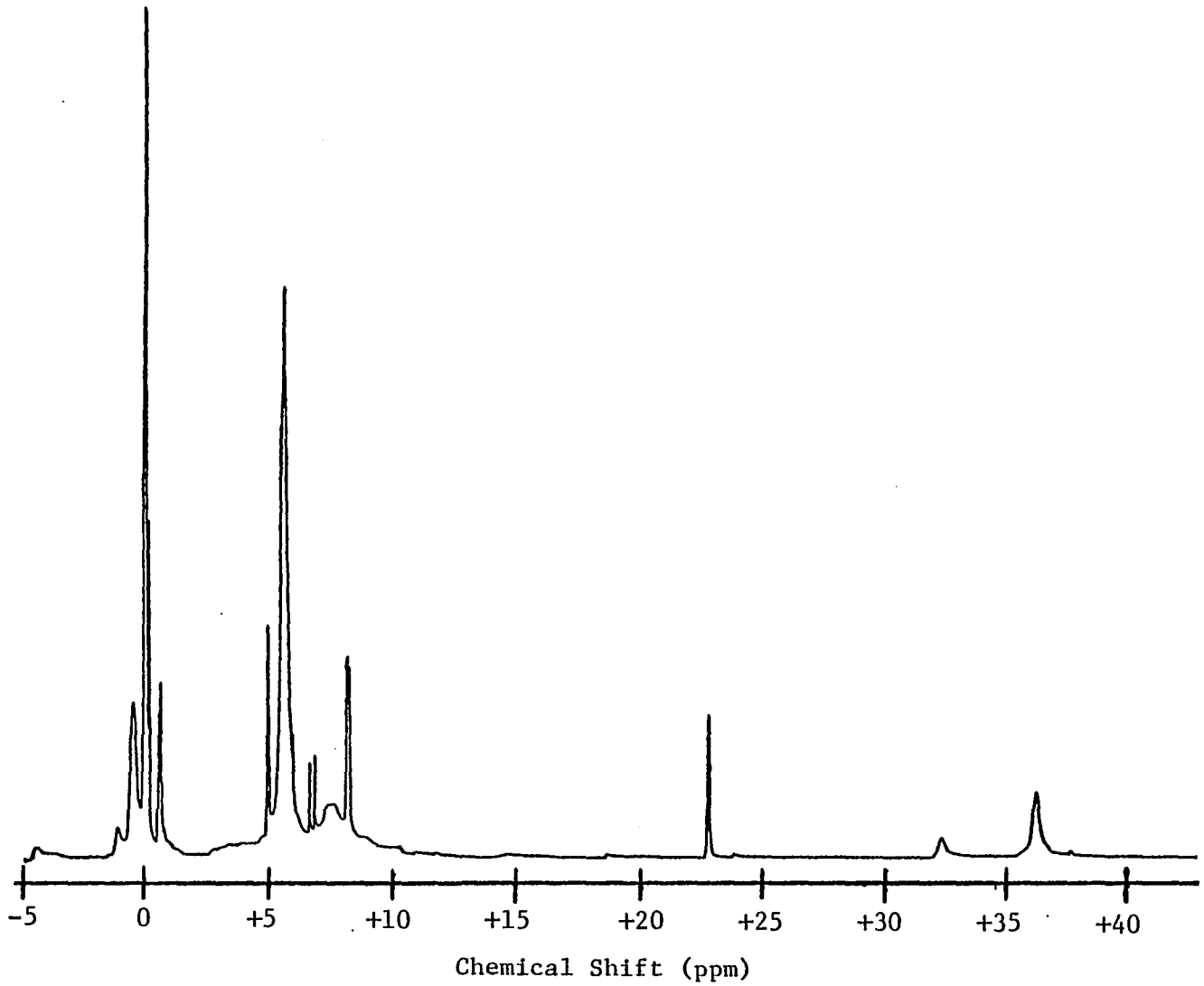


Figure 23. ^{1}H nmr spectrum of $(C_5H_5)U[(CH_2)_2P(CH_3)(C_6H_5)]_3$ obtained in toluene-d_8 at +95° C.

TABLE 12

Nuclear Magnetic Resonance Parameters for Several Monocyclopentadienyluraniumtrisphosphoylide Complexes

$(C_5H_5)U((CH_2)_2P(C_6H_5)_2)_3$	$(C_5H_5)U((CH_2)_2P(CH_3)(C_6H_5))_3$
^1H nmr at +95° C.[a]	
+0.62 (9H, multi, J(HCCH) = 7 Hz)[b]	+0.10 (6H, s)
+20.59 (5H, s)	+0.57 (9H, d, J(HCCH) = 7 Hz)
+40.54 (12H, broad s)	+8.31 (9H, d, $J(H_3CP)$ = 10 Hz)
	+23.47 (5H, s)
	+33.19 (2H, broad s)
	+37.20 (10H, broad s)
^1H nmr at +25° C.[a]	
+0.42 (6H, s)	+0.15 (6H, s)
+1.28 (9H, multi, J(HCCH) = 7 Hz)	+0.90 (9H, multi, J(HCCH) = 7 Hz)
+27.29 (5H, s)	+10.27 (9H, d, $J(H_3CP)$ = 10 Hz)
	+30.91 (5H, s)
^{31}P nmr at +25° C.[c]	
-11.02 (broad multi)	-14.42 (broad multi)

s = singlet, d = doublet, multi = multiplet

a) chemical shifts (ppm) measured relative to the methyl signal in toluene-d_8 and corrected to C_6H_6 via: δ(obs) + 4.93 ppm

b) a portion of the signal is obscured by the solvent signal

c) chemical shifts measured relative to external H_3PO_4

$(C_5H_5)U((CH_2)_2P(CH_3)(C_6H_5))_3$ the additional methyl resonance. The spectrum of the $(C_5H_5)U((CH_2)_2P(C_6H_5)_2)_3$ complex shows a cyclopentadienyl resonance at +20.59 ppm with an intensity corresponding to 5 H's and a broad methylene resonance at +40.54 ppm with an intensity of 12 H's. The spectrum of $(C_5H_5)U((CH_2)_2P(CH_3)(C_6H_5))_3$ exhibits a methyl doublet ($J(H_3P)$ = 10 Hz) at +8.31 ppm with an intensity of 9 H's, a cyclopentadienyl singlet at +23.47 ppm with an intensity of 5 H's and two broad peaks upfield. The downfield peak is at +33.19 ppm with an intensity of 2 H's and the upfield peak is at +37.20 ppm with an intensity corresponding to 10 H's. Apparently in this complex the process responsible for averaging the methylene protons still leaves one set of methylene protons different from the other five. The temperature dependence of these complexes will not be further discussed in this dissertation.

The ^{31}P nmr of these complexes is reported in Table 12. Instead of large upfield shifts, as seen for the other complexes, these show small downfield shifts relative to external H_3PO_4. The $(C_5H_5)U((CH_2)_2P(C_6H_5)_2)_3$ complex shows a broad multiplet at -11.02 ppm and the $(C_5H_5)U((CH_2)_2P(CH_3)(C_6H_5))_3$ complex exhibits a broad multiplet at -14.42 ppm.

The infrared spectrum of $(C_5H_5)U((CH_2)_2P(C_6H_5)_2)_3$ recorded over the range 4000 - 300 cm^{-1} is shown in Figure 24 and tabulated in Table 13. Bands characteristic of a π-bonded cyclopentadienyl group are seen at 1010 cm^{-1} (C-H in-plane wagging) and 805 cm^{-1} (C-H out-of-plane wagging). Absorptions due to phenyl groups attached to phosphorus are seen at 1437 cm^{-1}, 1096 cm^{-1}, 733 cm^{-1} and 470 cm^{-1}.

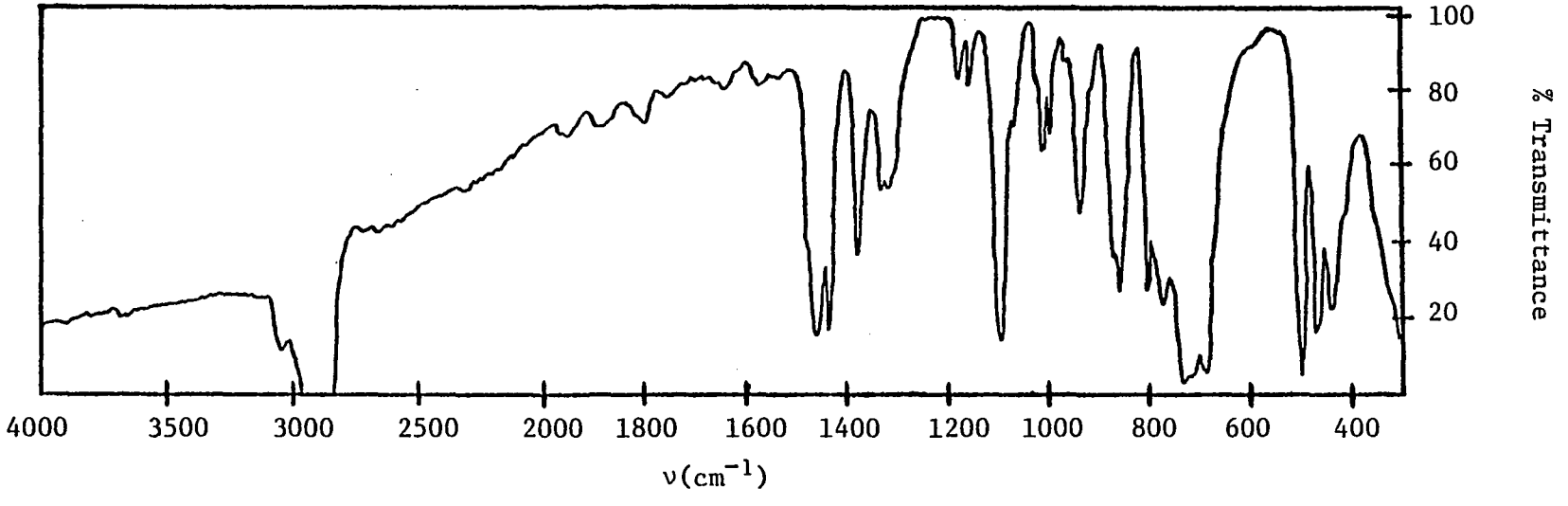


Figure 24. Infrared spectrum of $(C_5H_5)U[(CH_2)_2P(C_6H_5)_2]_3$ obtained as a nujol mull.

TABLE 13

Infrared Frequencies for
$(C_5H_5)U((CH_2)_2P(C_6H_5)_2)_3$

$\nu(cm^{-1})$	Possible Assignment
3049 w	ν(C-H aromatic)
1956 w	
1888 w	
1802 w	
1575 w	ν(C=C)
1479 m, sh	ν(C=C)
1437 s	$\delta(C_6H_5)$-a
1333 m	
1319 m	
1179 w	
1159 w	
1096 s	$\delta(C_6H_5)$-b
1070 m	
1010 m	$\delta(C_5H_5)$
999 m	$\delta(C_4$-P)
940 m	
871 s	
859 s	$\nu(P-CH_2)$
805 s	$\delta(C_5H_5)$
786 s	
772 s	ν(P=C)
733 vs	$\delta(C_6H_5)$-c
685 vs	ν(P-C)
500 vs	ν(U-C)
470 s	$\delta(C_6H_5)$-d
439 s	ν(U-C)

s = strong, m = medium, w = weak, v = very, sh = shoulder

a) planar ring deformation of phenyl bonded to phosphorus

b) substituent sensitive C-H planar bending vibration

c) substituent sensitive C-H out-of-plane bending vibration

d) substituent sensitive ring vibration

Aromatic hydrogens are seen at 3049 cm^{-1} and a partial mono-substituted benzene pattern is seen at 1956 cm^{-1}, 1888 cm^{-1} and 1802 cm^{-1}.

In the carbon-carbon double bond region are stretching vibrations at 1575 cm^{-1} and 1479 cm^{-1}. Bands arising from phosphorus-carbon double bond stretching are tentatively assigned to absorptions appearing in the 790 - 770 cm^{-1} region. In the 875 - 855 cm^{-1} region are two bands due to P-CH_2 stretching vibrations. Phosphorus-carbon single bond vibrations are also partly responsible for the broad absorptions at 733 cm^{-1} and 685 cm^{-1}.

The two bands occurring at 500 cm^{-1} and 439 cm^{-1} are assigned to uranium-carbon stretching for the reasons mentioned earlier.

The visible spectrum of $(C_5H_5)U((CH_2)_2P(C_6H_5)_2)_3$ recorded over the range 25.0 - 13.0 kK is shown in Figure 25 and the data tabulated in Table 14. The spectrum of this complex is different from those seen for the previous complexes. Its most interesting feature is the multiplet of peaks in the 15.4 - 13.9 kK region shown in Figure 26. These may be due to f→f transitions which have been blue shifted out of the near-infrared and into the visible region. As seen for the other complexes an intense band in the ultraviolet region tails off into the visible region with several shoulders.

The near-infrared spectra of $(C_5H_5)U((CH_2)_2P(C_6H_5)_2)_3$ recorded over the range 13.0 - 4.0 kK is shown in Figure 27 and summarized in Table 14. The most prominent feature in the spectrum is an intense peak located at 8.07 kK (ε = 195 liter/mole-cm) with an intense shoulder at 8.30 kK (ε = 160 liter/mole-cm). This peak is located in the same region as one of the two intense bands observed in the

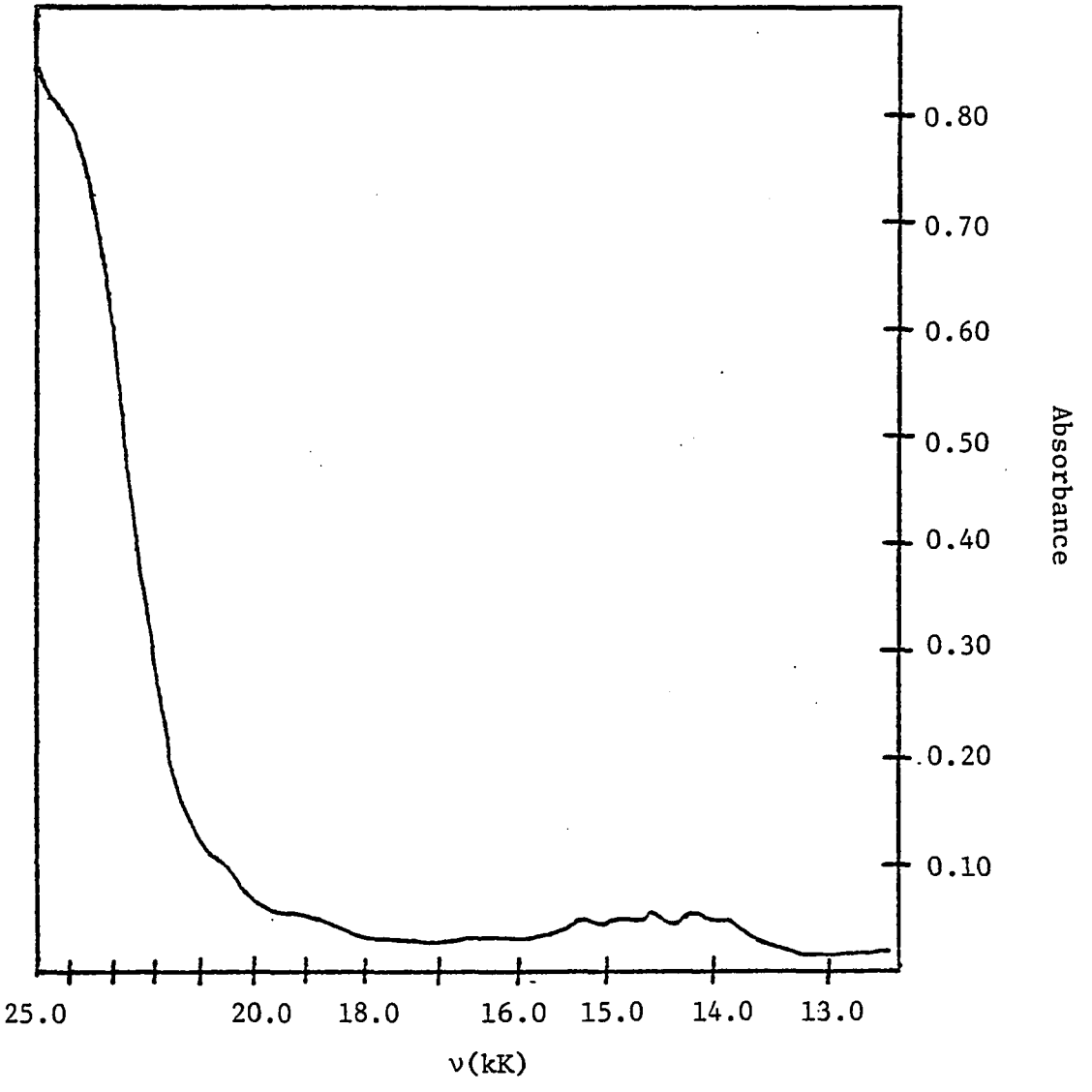


Figure 25. Visible spectrum of $(C_5H_5)U[(CH_2)_2P(C_6H_5)_2]_3$ obtained as a 4.7×10^{-4} M solution in THF.

TABLE 14

Electronic Spectral Parameters for
$(C_5H_5)U((CH_2)_2P(C_6H_5)_2)_3$

$\nu max^a (\varepsilon)^b$	
Visible Region	Near-Infrared Region
24.5 (1720)	10.5 (24)
20.8 (230)	9.59 (25)
19.3 (120)	9.22 (41)
17.9 (60)	9.05 (42)
16.6 (65)	8.70 (56)
15.4 (100)	8.30 (160)
15.0 (100)	8.07 (180)
14.7 (120)	7.04 (19)
14.3 (120)	6.62 (25)
14.0 (100)	6.16 (34)
	5.97 (38)
	5.70 (24)
	7.62 (23)

a) kK

b) ε = liter/mole-cm

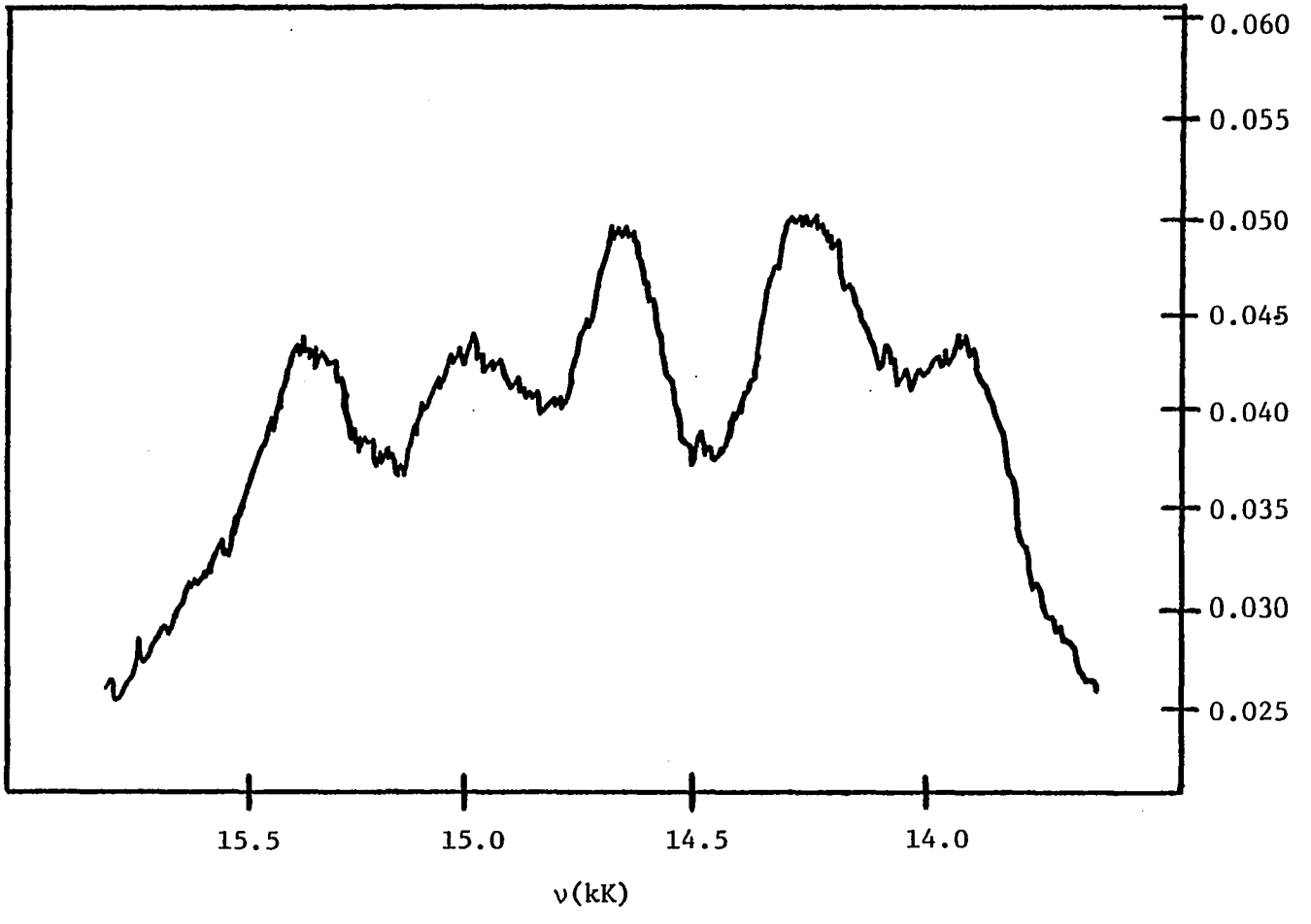


Figure 26. Possible f→f transitions shifted into the visible region for the $(C_5H_5)U[(CH_2)_2P(C_6H_5)_2]_3$ complex. See Figure 27 for details.

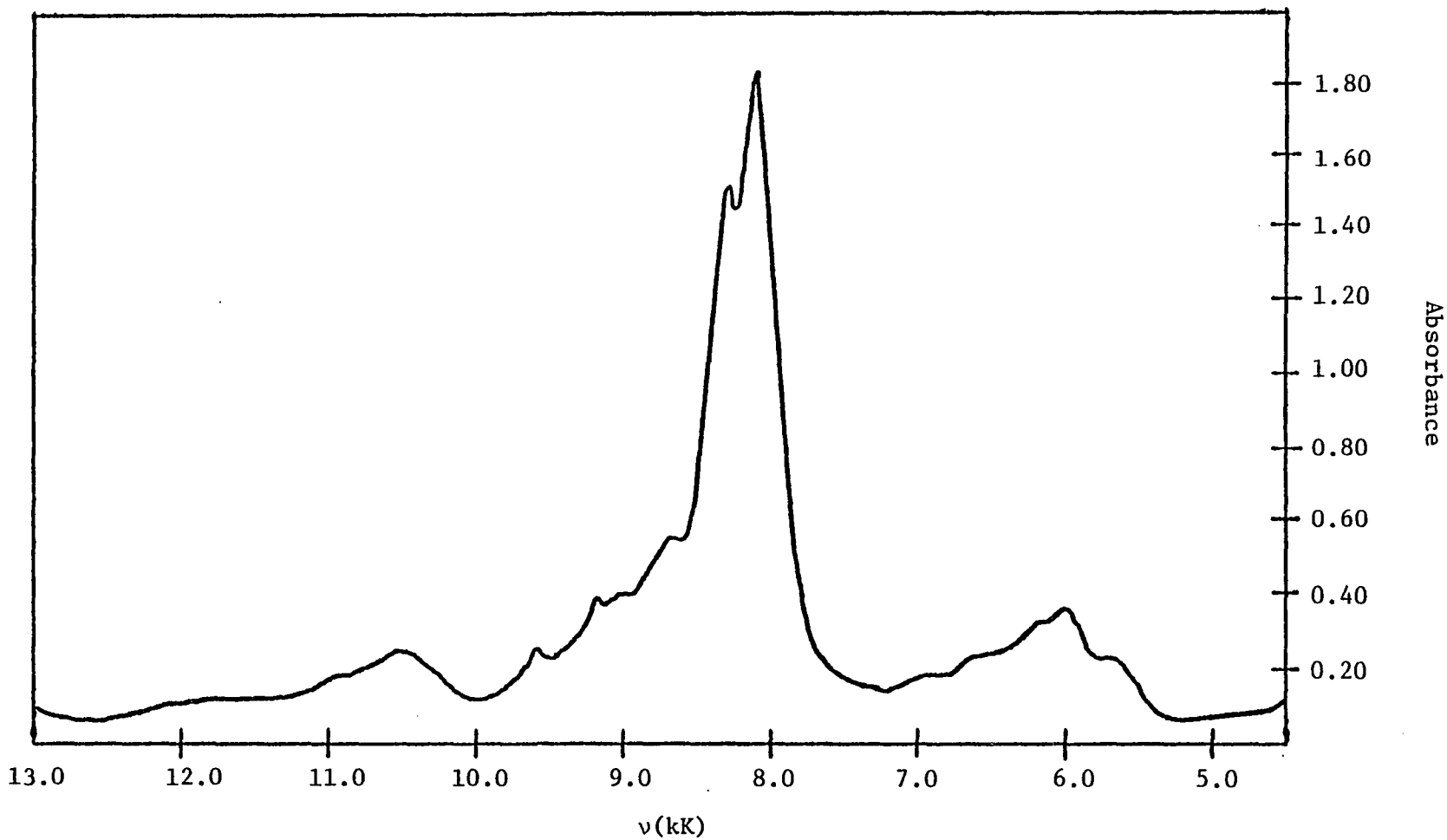


Figure 27. Near-infrared spectrum of $(C_5H_5)U[(CH_2)_2P(C_6H_5)_2]_3$ obtained as a 9.5×10^{-3} M solution in THF.

near-infrared spectrum of $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2$. Lowering of the symmetry of the complex may allow one of the f→f transitions to become more allowed. Also seen in the spectrum are La Porte forbidden f→f transitions of much weaker intensity.

D. REACTIONS OF ORGANOURANIUMPHOSPHOYLIDE COMPLEXES WITH CARBON MONOXIDE

When carbon monoxide is passed over either a benzene or toluene solution of a triscyclopentadienyluraniumphosphoylide complex at room temperature the color of the solution changes from dark green to dark reddish-orange and a reaction according to equation 17 occurs:

$$(C_5H_5)_3UCHP(CH_3)(C_6H_5)(R) + CO \longrightarrow (C_5H_5)_3U(CO)CHP(CH_3)(C_6H_5)(R)$$
$$\text{where } R = CH_3,\ C_2H_5,\ \text{or } C_6H_5 \qquad (17)$$

We have found that the rate of this reaction is highly dependent upon temperature. At room temperature it is complete in 30 - 60 minutes, while at -50° C. no color change is apparent after several hours.

The reaction gives essentially quantitative yield of crude product that is easily recrystallized in 85 - 90% yields. The products in which $R = C_2H_5$ or C_6H_5 are soluble in THF, benzene and toluene, and insoluble in saturated hydrocarbon solvents. The complexes are easily recrystallized from a toluene-heptane solvent mixture. The complex obtained when $R = CH_3$ is soluble in THF and benzene, but only slightly soluble in toluene. It is totally insoluble in saturated hydrocarbon solvents and conveniently recrystallized from THF-heptane. The complexes are pyrophoric when exposed to air and decompose in the presence of acidic solvents.

A molecular weight determination by osmometry was carried out for

the $(C_5H_5)_3U(CO)CHP(CH_3)(C_6H_5)_2$ complex. The data (calc: 675, found: 719 ± 10%) strongly indicates that the complex is a monomer, at least in benzene. Presumably the same holds true for the other two complexes as well.

The ^1H nmr of the complexes obtained in C_6D_6 at 100 MHz are shown in Figures 28 - 30 and summarized in Table 15. The complexes give very similiar spectra and are in accord with the tentatively formulated product. The methine proton in $(C_5H_5)_3U(CO)CHP(CH_3)(C_6H_5)_2$ is observed as a doublet (J(HCP) = 35 Hz) at -53.64 ppm, in the $(C_5H_5)_3U(CO)CHP(CH_3)_2(C_6H_5)$ complex as a doublet (J(HCP) = 36 Hz) at -56.30 ppm and in $(C_5H_5)_3U(CO)CHP(C_2H_5)(CH_3)(C_6H_5)$ as a doublet (J(HCP) = 33 Hz) at -54.47 ppm. This is quite a different chemical shift compared to the methine proton in the starting material which was found upfield in the range +120 - 140 ppm. Quite clearly a drastic relocation of this proton with respect to the uranium atom has occurred. In addition, the coupling constant is more than twice that found in the starting material (J(HCP) = 16 Hz).

In $(C_5H_5)_3U(CO)CHP(CH_3)(C_6H_5)_2$ a methyl doublet ($J(H_3CP)$ = 14 Hz) with an intensity of 3 H's is located at +6.88 ppm. The $(C_5H_5)_3U(CO)CHP(CH_3)_2(C_6H_5)$ complex shows a methyl doublet ($J(H_3CP)$ = 14 Hz) at +6.07 ppm corresponding in intensity to 6 H's. In the $(C_5H_5)_3U(CO)CHP(C_2H_5)(CH_3)(C_6H_5)$ complex a methyl doublet ($J(H_3CP)$ = 13 Hz) is seen at +5.58 ppm with an intensity of 3 H's. In addition the methyl doublet of triplets of the ethyl group ($J(H_3CCP)$ = 19 Hz, J(HCCH) = 7 Hz) is observed at +8.20 ppm. The methylene portion of the ethyl group lies beneath the methyl doublet at +5.58 ppm. The

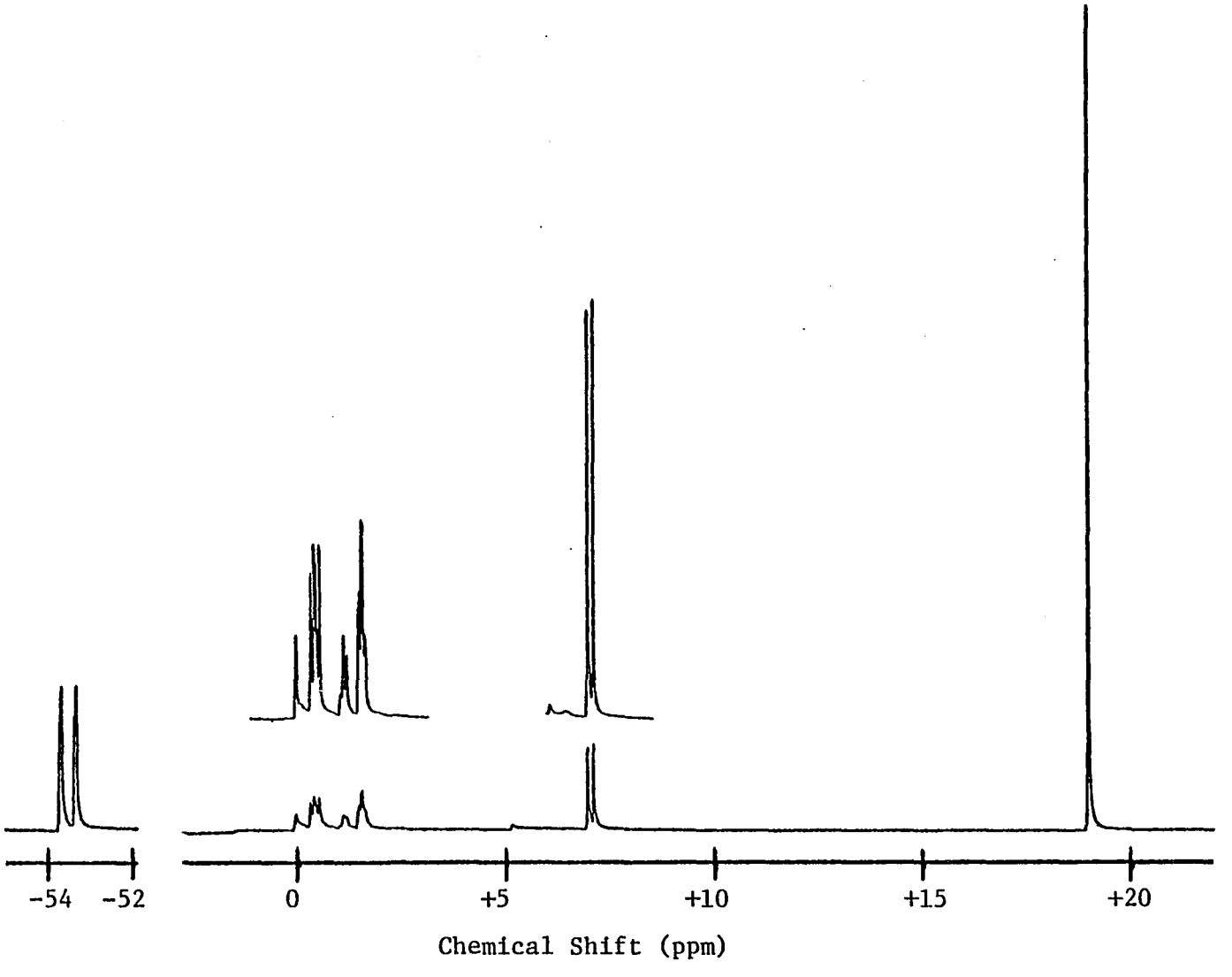


Figure 28. ^{1}H nmr spectrum of $(C_5H_5)_3U(CO)CHP(CH_3)(C_6H_5)_2$ obtained in C_6D_6.

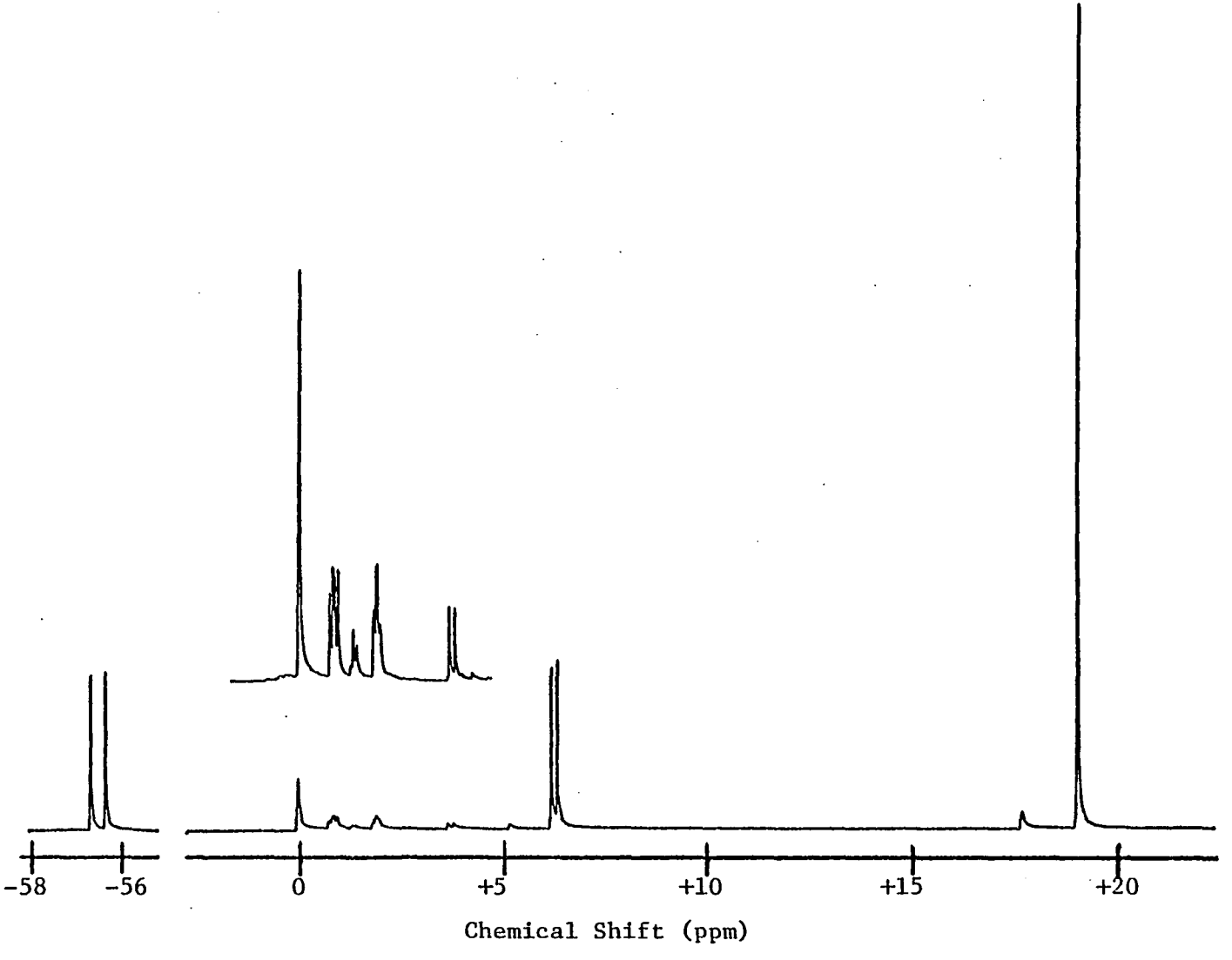


Figure 29. ^{1}H nmr spectrum of $(C_5H_5)_3U(CO)CHP(CH_3)_2(C_6H_5)$ obtained in C_6D_6.

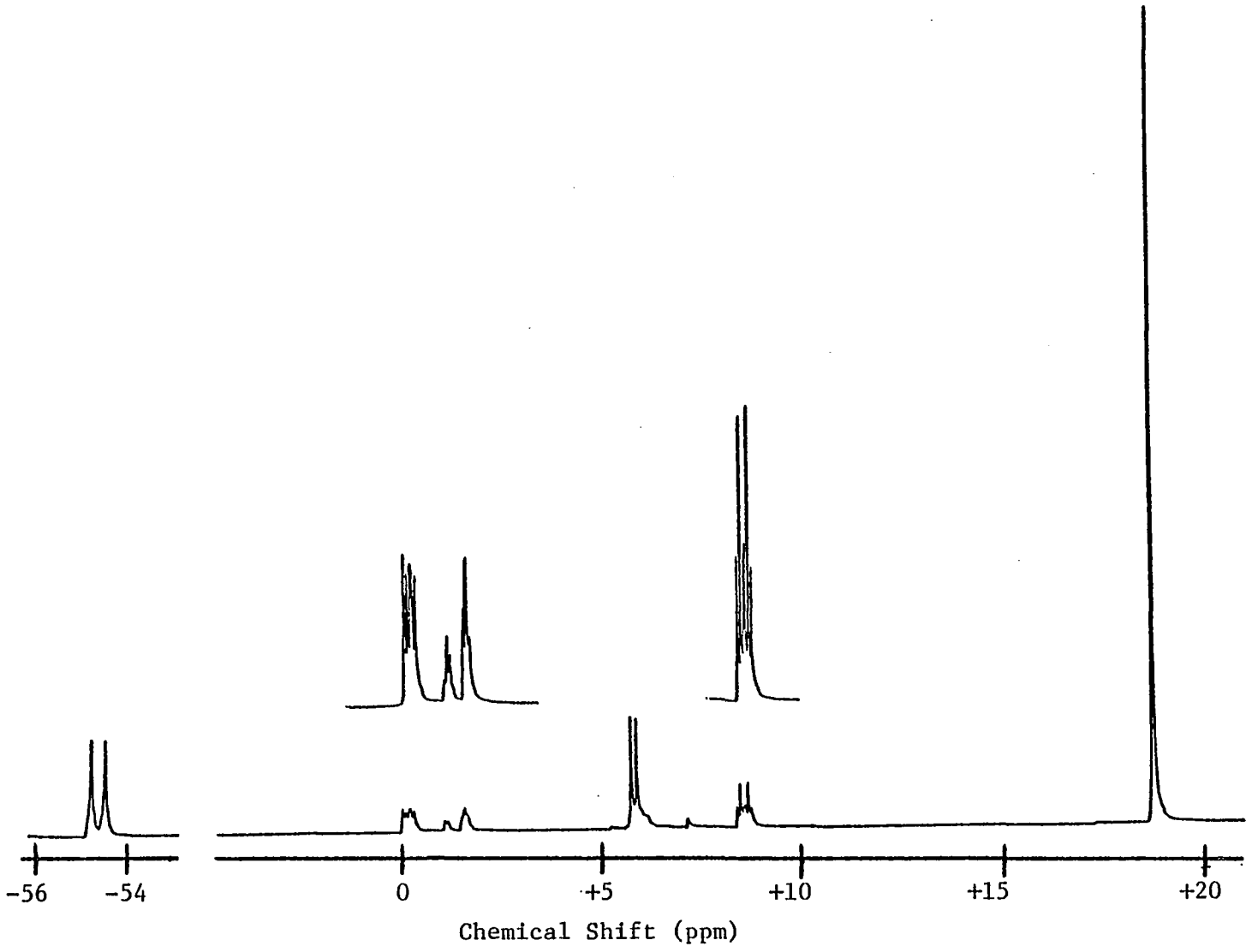


Figure 30. ^{1}H nmr spectrum of $(C_5H_5)_3U(CO)CHP(C_2H_5)(CH_3)(C_6H_5)$ obtained in C_6D_6.

TABLE 15

Nuclear Magnetic Resonance Parameters for the Reaction Product of Several Triscyclopentadienyluraniumphosphoylide Complexes with Carbon Monoxide[a]

Compound	Nucleus	Chemical Shift (ppm)
$(C_5H_5)_3U(CO)CHP(CH_3)(C_6H_5)_2$	^1H[b]	-53.64 (1H, d, J(HCP) = 35 Hz) +0.40 (4H, dd, J(HCP) = 12 Hz, J(HCCH) = 7 Hz) +1.09 (2H, t, J(HCCH) = 7 Hz) +1.51 (4H, t, J(HCCH) = 7 Hz) +6.88 (3H, d, J(H_3CP) = 14 Hz) +18.61 (15H, s)
	^{31}P[c]	+126.30 (broad multiplet)
$(C_5H_5)_3U(CO)CHP(CH_3)_2(C_6H_5)$	^1H[b]	-56.30 (1H, d, J(HCP) = 36 Hz) +0.80 (2H, dd, J(HCP) = 12 Hz, J(HCCH) = 7 Hz) +1.31 (1H, t, J(HCCH) = 7 Hz) +1.85 (2H, t, J(HCCH) = 7 Hz) +6.07 (6H, d, J(H_3CP) = 14 Hz) +18.58 (15H, s)
	^{31}P[c]	+133.04 (broad multiplet)
$(C_5H_5)_3U(CO)CHP(C_2H_5)(CH_3)(C_6H_5)$	^1H[b]	-54.47 (1H, d, J(HCP) = 33 Hz) +0.20 (2H, dd, J(HCP) = 12 Hz, J(HCCH) = 7 Hz) +1.02 (1H, t, J(HCCH) = 7 Hz) +1.51 (2H, t, J(HCCH) = 7 Hz) +5.58 (3H, d, J(H_3CP) = 13 Hz) +5.58 (2H, multiplet)-d +8.20 (3H, dt, J(H_3CCP) = 19 Hz, J(HCCH) = 7 Hz) +18.12 (15H, s)
	^{31}P[c]	+123.62 (broad multiplet)

s = singlet, d = doublet, t = triplet, dd = doublet of doublets

a) spectra recorded at +25° C.

b) chemical shifts referenced relative to internal benzene

c) chemical shifts measured relative to external H_3PO_4

d) methine multiplet is under the methyl doublet

cyclopentadienyl resonances for the complexes are located in the range +18.1 - 18.6 ppm with an intensity corresponding to three cyclopentadienyl groups. This is close to the position observed for the starting triscyclopentadienyluraniumphosphoylide complexes (~+20 ppm).

The ^{31}P spectra obtained at 40.5 MHz in THF/C_6D_6 also supports this view and is presented in Table 15. Although the coupling information is lost due to the paramagnetism of the uranium, the spectra exhibit large upfield chemical shifts compared to the starting lithiated phosphorus ylides. The $(C_5H_5)_3U(CO)CHP(CH_3)(C_6H_5)_2$ complex shows a broad multiplet at +126.30 ppm, the $(C_5H_5)_3U(CO)(CH_3)_2(C_6H_5)$ complex has a broad multiplet +133.04 ppm and in the $(C_5H_5)_3U(CO)CHP(C_2H_5)(CH_3)(C_6H_5)$ complex the broad multiplet is seen at +123.62 ppm. These chemical shifts are about 60 ppm downfield of the resonances observed in the triscyclopentadienyluraniumphosphoylide complexes.

The spectra of the complexes indicates that the environment about the phosphorus atom is the same as it was in the starting complexes. The major difference is the smaller chemical shifts presumably due to the ylide moiety being located further from the paramagnetic influence of the uranium atom than it was in the starting complex.

The infrared spectral data for these complexes recorded over the range 4000 - 300 cm^{-1} is summarized in Table 16 and a representative spectrum of $(C_5H_5)_3U(CO)CHP(CH_3)(C_6H_5)_2$ is shown in Figure 31. The infrared spectra reveal several important features concerning the insertion of the carbon monoxide into the complex. In the 1660 - 1640 cm^{-1} region is a weak band due to an oxygen-carbon double bond. These

TABLE 16

Infrared Frequencies for the Reaction Product of Several $(C_5H_5)_3UCHP(CH_3)(C_6H_5)(R)$ Complexes with Carbon Monoxide

$\nu(cm^{-1})$			
R = CH_3	R = C_2H_5	R = C_6H_5	Possible Assignment
3090 w	3090 w		ν(C-H aromatic)
3042 w	3050 w	3048 w	
1765 w	1772 w	1770 w	
1655 w	1660 w	1770 w	ν(C=O)
	1642 w		
1590 w	1590 w	1591 w	ν(C=C)
1555 w	1551 w	1578 w	
1480 m, sh	1480 m, sh	1480 m, sh	ν(C=C)
1434 vs	1441 vs	1437 vs	δ(C_6H_5)-a
1411 s			
1397 s	1399 s	1399 s	δ(P-CH_3)
	1328 m		
1312 m	1319 m	1317 m	
1305 m	1305 m		
1292 m	1290 w	1291 w	δ(P-CH_3)
	1263 m	1260 w	
1255 m	1257 w		ν(C-O)
1190 m		1190 w	
1160 w		1160 w	
1119 m			
1103 s	1104 s	1110 s	δ(C_6H_5)-b
1068 s	1070 m	1070 m	ν(C-O)
1009 s	1011 s	1009 s	δ(C_5H_5)
957 s			δ(P-CH_3)
927 s	918 s		
884 m	890 s	897 s	
868 m		846 m	δ(P-CH_3)-c
	839 m	832 m	
797 vs, sh	790 s, sh	791 s, sh	δ(C_5H_5)
768 vs	765 vs, br	770 vs	ν(P=C)
746 vs	742 vs	741 vs	δ(C_6H_5)-d
715 m	707 s		
690 s	692 s	689 s	ν(P-C)
658 m	651 m	663 m	
643 m		623 w	
501 m	506 m	503 m	ν(U-C)
		479 m	
471 m	473 m	471 m	δ(C_6H_5)-e
401 s	433 m	438 m	ν(U-C)
391 s	395 s	390 s	ν(U-O)
372 m	374 s	378 s	(U-O)

s = strong, m = medium, w = weak, v = very, sh = shoulder, br = broad

a) planar ring deformation of phenyl bonded to phosphorus
b) substituent sensitive C-H planar bending vibration
c) methyl rocking
d) substituent sensitive C-H out-of-plane bending vibration
e) substituent sensitive ring vibration

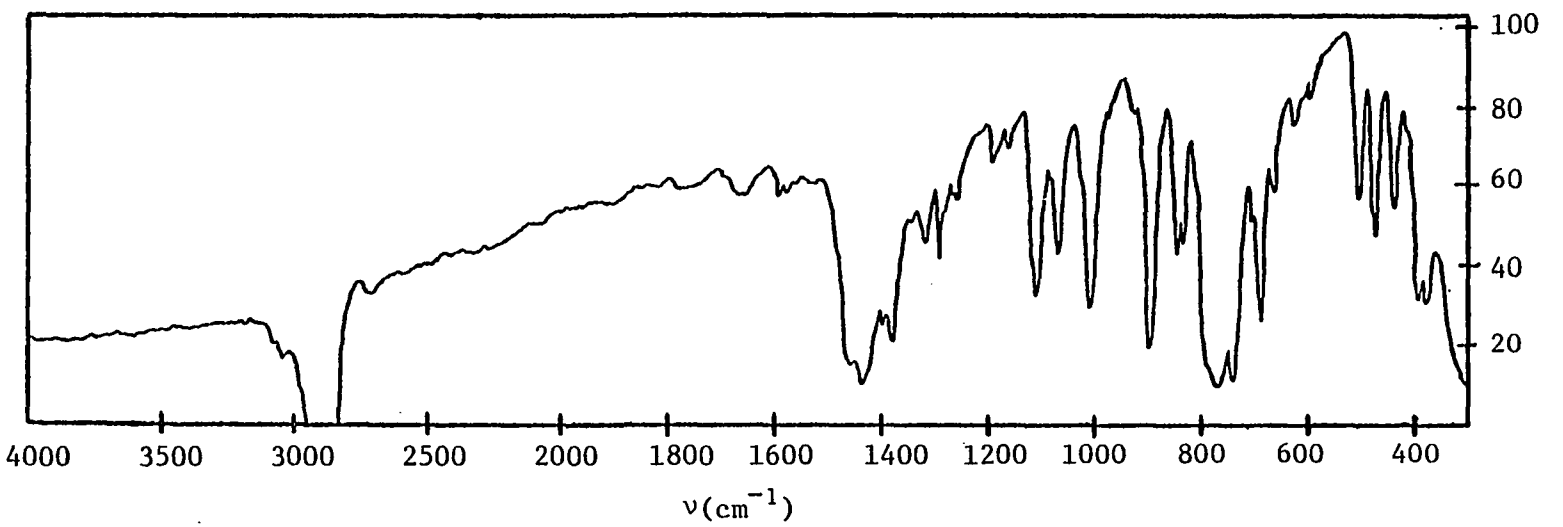
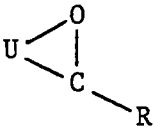


Figure 31. Infrared spectrum of $(C_5H_5)_3U(CO)CHP(CH_3)(C_6H_5)_2$ obtained as a nujol mull.

are generally quite strong in intensity. However this double bond may have been weakened because of bonding of the oxygen atom to the uranium. Absorptions due to uranium-oxygen stretching have been assigned to the bands in the 395 - 370 cm^{-1} region. These are in the range of metal-oxygen stretching frequencies observed[65] for heavy metal alkoxide complexes. Also seen are bands due to carbon-oxygen single bond stretching in the 1265 - 1250 cm^{-1} and 1070 - 1065 cm^{-1} regions. The absorptions seen for uranium-carbon stretching seen in the starting complexes are seen in these complexes at 510 - 500 cm^{-1} and 440 - 400 cm^{-1}. These data appear to indicate that the carbon-oxygen group is side-bonded in a dihapto fashion to the uranium atom as shown below:



Recently Marks and co-workers[66,67] have reported a bispentamethylcyclopentadienyl uranium complex which contains a side-bonded carbon-oxygen group (1620 cm^{-1}).

The remaining absorptions in the infrared are consistent with our formulation of these complexes. The bands characteristic of π-bonded cyclopentadienyl groups are seen at 1015 - 1005 cm^{-1} and 800 - 790 cm^{-1}. Absorptions due to a phenyl group attached to phosphorus are observed at 1445 - 1430 cm^{-1}, 1110 - 1100 cm^{-1}, 750 - 740 cm^{-1} and 475 - 470 cm^{-1}. Methyl-phosphorus stretching and bending vibrations are seen at 1400 - 1395 cm^{-1}, 1296 - 1290 cm^{-1}, 957 cm^{-1} cand 870 - 845 cm^{-1}.

The carbon-carbon double bond stretching of the aromatic groups are observed at 1595 - 1590 cm^{-1} and 1480 cm^{-1}. A phosphorus-carbon

double bond stretch occurs at 770 - 765 cm^{-1}. The broad absorptions at 750 - 740 cm^{-1} and 690 - 680 cm^{-1} are in part caused by phosphorus-carbon single bond stretching.

The visible spectral data is tabulated in Table 17 and a representative spectrum of $(C_5H_5)_3U(CO)CHP(CH_3)(C_6H_5)_2$ is shown in Figure 32. The complexes give qualitatively similiar spectra with the bands somewhat less intense for the $(C_5H_5)_3U(CO)CHP(CH_3)_2(C_6H_5)$ complex. As for the starting triscyclopentadienyluraniumphosphoylide complexes the spectra consist of several shoulders on an intense band located in the ultraviolet region. The main difference between these two classes of compounds is the blue shift of ~2.5 kK that has occurred in the visible spectra of the $(C_5H_5)_3U(CO)CHP(CH_3)(C_6H_5)(R)$ complexes and the disappearance of the band at about 17 kK. This is about the same amount of hypsochromic shift that occurred for the $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2$ complexes. This results in the reddish-orange color seen for dilute solutions of the $(C_5H_5)_3U(CO)CHP(CH_3)(C_6H_5)(R)$ complexes.

The near-infrared spectral data of these complexes recorded over the range 13.0 - 4.0 kK is summarized in Table 18 and the spectrum of $(C_5H_5)_3U(CO)CHP(CH_3)(C_6H_5)_2$ is shown in Figure 33. As for the visible spectra the complexes give very similiar near-infrared spectra. Qualitatively they are similiar to the starting triscyclopentadienyl-uraniumphosphoylide complexes with one exception. In the starting complexes the 5.2 - 4.0 kK region is clear of any bands. However the product complexes contain an intense band at ~5.0 kK (ε = 150 liter/mole-cm) with several shoulders of lesser intensity out to 4.6 kK.

TABLE 17

Visible Spectral Parameters for the Reaction Product of Several Triscyclopentadienyluraniumphosphoylide Complexes with Carbon Monoxide

$\nu max^a(\varepsilon)^b$		
$(C_5H_5)_3U(CO)CHP(CH_3)(C_6H_5)_2$	$(C_5H_5)_3U(CO)CHP(CH_3)_2(C_6H_5)$	$(C_5H_5)_3U(CO)(C_2H_5)(CH_3)(C_6H_5)$
21.4 (540)	21.7 (430)	21.7 (510)
19.2 (360)	19.2 (310)	19.5 (350)
		18.0 (230)
17.5 (230)	17.3 (150)	17.3 (170)
16.0 (110)	16.1 (95)	16.1 (110)
	14.9 (36)	14.8 (50)
14.4 (31)	14.4 (27)	
	13.8 (22)	
13.2 (21)	13.2 (24)	13.2 (32)

a) kK

b) ε = liter/mole-cm

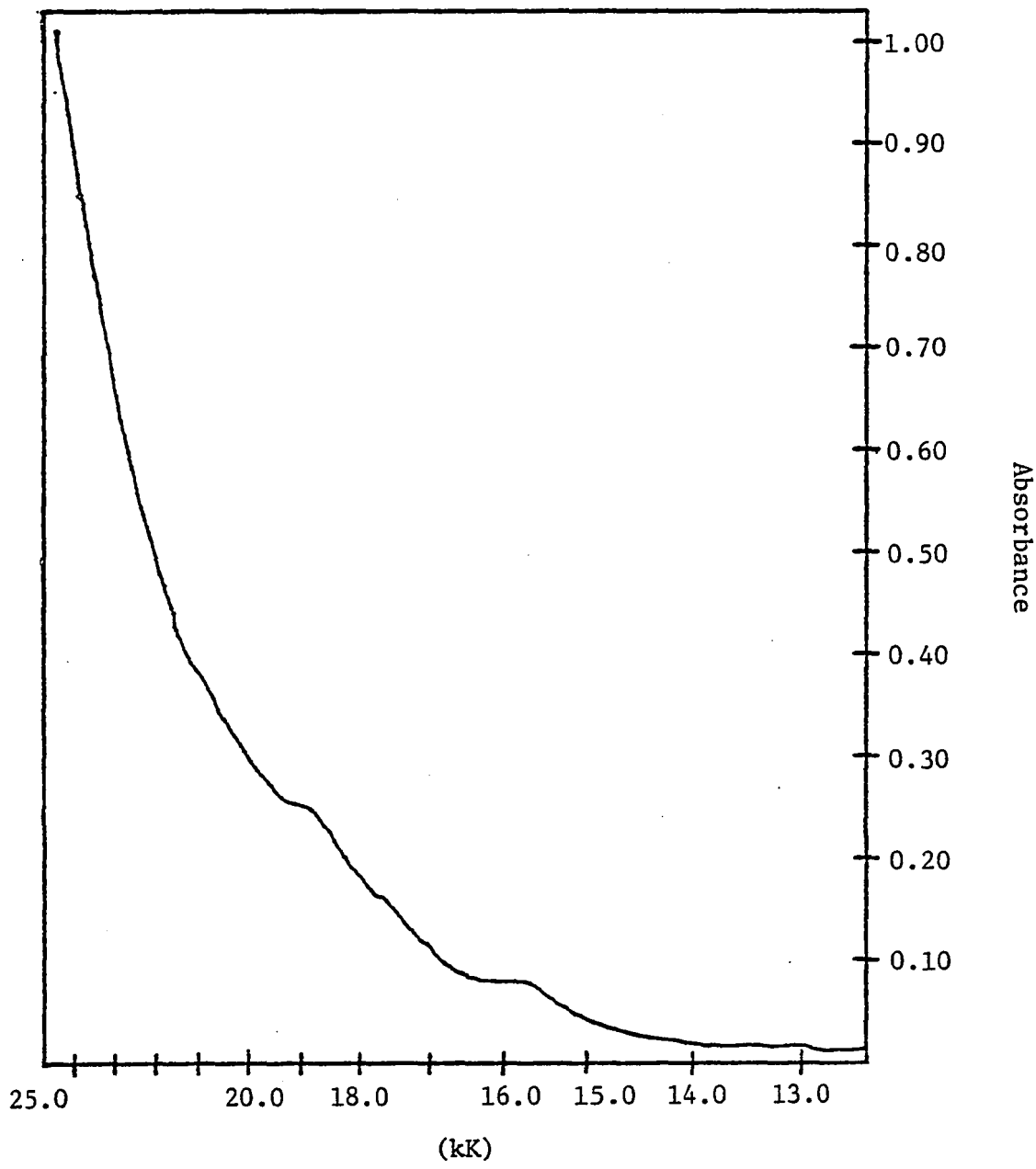


Figure 32. Visible spectrum of $(C_5H_5)_3U(CO)CHP(CH_3)(C_6H_5)_2$ obtained as a 7.1 x 10^{-4} M solution in THF.

TABLE 18

Near-Infrared Spectral Parameters for the Reaction Product of Several Triscyclopentadienyluraniumphosphoylide Complexes with Carbon Monoxide

ν max[a] (ε)[b]		
$(C_5H_5)_3U(CO)CHP(CH_3)(C_6H_5)_2$	$(C_5H_5)_3U(CO)(CH_3)_2(C_6H_5)$	$(C_5H_5)_3U(CO)CHP(C_2H_5)(CH_3)(C_6H_5)$
10.7 (30)	10.7 (23)	10.7 (27)
9.44 (38)	9.43 (39)	9.56 (35)
9.02 (43)	8.93 (48)	9.01 (38)
8.44 (37)	8.47 (44)	8.46 (37)
7.97 (24)	8.07 (26)	8.06 (26)
7.40 (38)	7.41 (36)	7.43 (37)
6.98 (27)	6.98 (21)	
6.02 (24)	6.02 (20)	6.21 (21)
5.67 (28)	5.65 (21)	5.66 (25)
5.04 (150)	5.03 (150)	5.05 (130)
4.88 (65)	4.94 (83)	
4.77 (50)	4.81 (46)	4.89 (49)
4.69 (46)		
4.61 (36)	4.65 (34)	4.68 (34)

a) kK

b) ε = liter/mole-cm

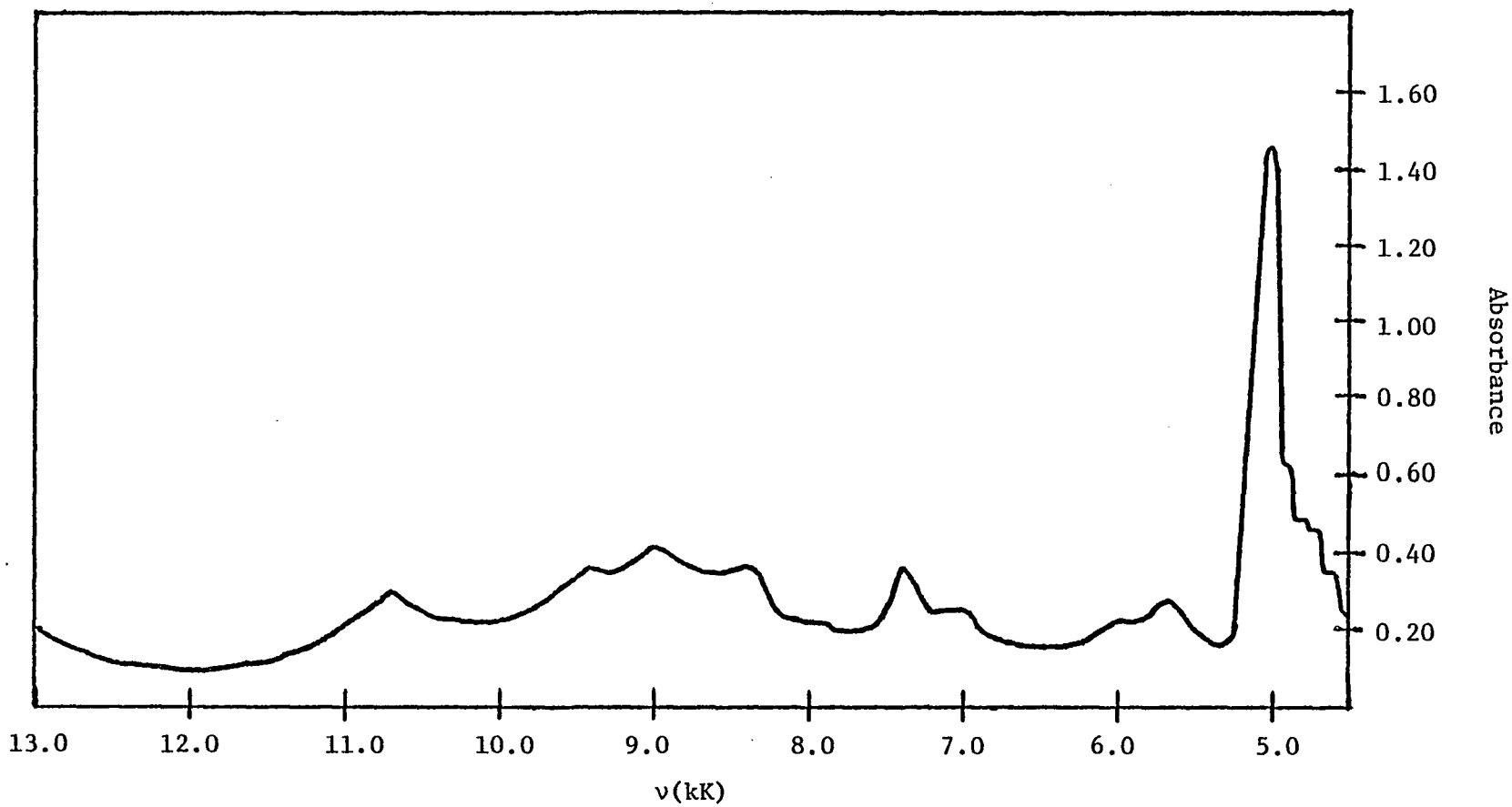


Figure 33. Near-infrared spectrum of $(C_5H_5)_3U(CO)CHP(CH_3)(C_6H_5)_2$ obtained as a 9.8×10^{-3} M solution in THF.

This may be due to a lowering of the symmetry in these complexes about the uranium atom which results in a La Porte forbidden f→f transition becoming allowed.

The red dimeric $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2$ complex was refluxed under a carbon monoxide atmosphere for ten hours. At the end of this time a light brown material had precipitated. This compound's infrared spectrum is shown in Figure 34. The insolubility of this material in all common solvents prevented further characterization and it was not studied any further.

Allowing the gold colored $(C_5H_5)U((CH_2)_2P(C_6H_5)(R))_3$ complexes to stir under carbon monoxide gave a light greenish-yellow material. A ^1H nmr of this material showed only resonances characteristic of a methylene phosphorane. No evidence of paramagnetically shifted species was seen. No further characterization of this material was attempted.

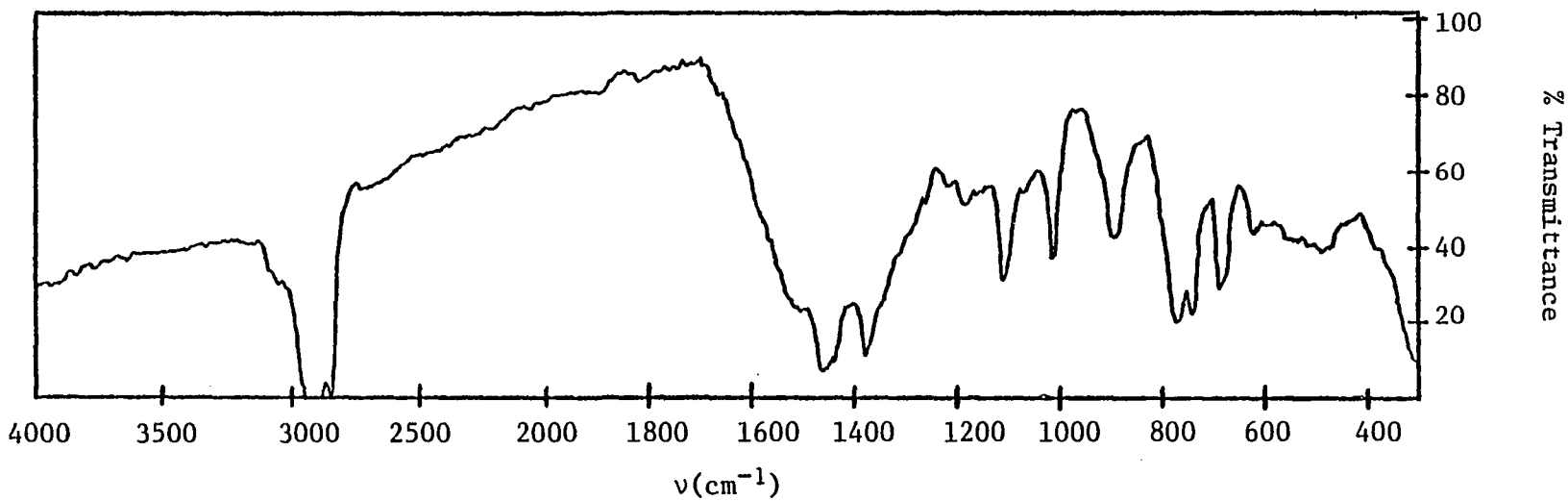


Figure 34. Infrared spectrum of the product obtained from the reaction of carbon monoxide with $[\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2$ obtained as a nujol mull.

III. GENERAL DISCUSSION

The principle accomplishment of this work was the synthesis and characterization of a new and novel class of organouranium complexes containing phosphorus ylides as ligands. In addition the reaction of these organouraniumphosphoylide complexes with carbon monoxide has been studied.

Several of the lithiated phosphorus ylides, $Li(CH_2)_2P(C_6H_5)_2$ and $Li(CH_2)_2P(CH_3)(C_6H_5)$, have been previously prepared, but no data concerning their characterization was reported. Manzer's paper[53] describing his preparation of lithiated phosphoylides led us to believe that the method was a general one. However we found this <u>not</u> to be the case. While the addition of two equivalents of $LiCH_3$ to either $((CH_3)_2P(C_6H_5)_2)I$ or $((CH_3)_3P(C_6H_5))I$ does yield the corresponding diethyl ether insoluble lithiated phosphorus ylide, this is <u>not</u> what is obtained if other phosphonium salts are used. Rather one obtains the diethyl ether soluble iodide salt of the corresponding lithiated phosphorane. In Manzer's paper he describes the preparation of diethyl ether soluble "$Li(CH_2)(CH_3CH)P(C_2H_5)_2$" from the addition of two equivalents of lithium alkyl to one equivalent of $((CH_3)P(C_2H_5)_3)I$. We believe that instead of preparing $Li(CH_2)(CH_3CH)P(C_2H_5)_2$, he prepared $((C_2H_5)_3PCH_2Li)I$ which would be diethyl ether soluble. In addition, the yields for the metal phosphoylide complexes he prepared from $Li(CH_2)_2P(C_6H_5)_2$ and $Li(CH_2)_2P(CH_3)(C_6H_5)$ are on the order of 80 - 95%. With his "$Li(CH_2)(CH_3CH)P(C_2H_5)_2$" starting material a yield of only 41% was realized. A reduction in yield of about one half is expected if $((C_2H_5)_3PCH_2Li)I$ is the starting material, since a second

equivalent of this base is needed to deprotonate the coordinated first equivalent to yield the reported complex as shown in equations 18 and 19:

$$(C_5H_5)_2TiCl + ((C_2H_5)_3PCH_2Li)I \longrightarrow ((C_5H_5)_2TiCH_2P(C_2H_5)_3)I + LiCl \quad (18)$$

$$((C_5H_5)_2TiCH_2P(C_2H_5)_3)I + ((C_2H_5)_3PCH_2Li)I \longrightarrow$$

$$(C_5H_5)_2Ti\begin{array}{l}\diagup CH_2 \\ \diagdown CH\end{array}\!\!\begin{array}{l}\diagdown \\ \diagup\end{array}\!\!P(C_2H_5)_2 + LiI + (CH_3P(C_2H_5)_3)I \quad (19)$$

$$\begin{array}{c} \\ CH_3 \end{array}$$

From the stoichiometry of the overall reaction, the maximum yield of desired product is 50%.

Our attempts to react a similiar compound, $((C_2H_5)(CH_3)(C_6H_5)PCH_2Li)I$, with $(C_5H_5)_3UCl$ were unsuccessful. Apparently reaction (18) occurs, but for reasons not apparent to us the second reaction (19) does not occur, even with an excess of $((C_2H_5)(CH_3)(C_6H_5)PCH_2Li)I$. Since the product we obtained defied our attempts to isolate it we subsequently did nothing more with it.

We did find that we could thermolyze $((C_2H_5)(CH_3)(C_6H_5)PCH_2Li)I$ and obtain the salt-free compound, $CH_2{=}P(C_2H_5)(CH_3)(C_6H_5)$. These salt-free phosphoranes have been previously shown[54] to react with lithium alkyls to produce the corresponding lithiated phosphorus ylide. This method allows preparation of the authentic $Li(CH_2)_2P(C_2H_5)(C_6H_5)$, and should allow one to prepare any lithiated phosphorus ylide.

The reactions between $(C_5H_5)_3UCl$ and $(C_5H_5)UCl_3 \cdot 2THF$ and varying equivalents of lithiated phosphorus ylide, $Li(CH_2)_2P(C_6H_5)(R)$, are evidenced by changes in the color of the reaction mixtures. The

reactions and products obtained are summarized below:

$$(C_5H_5)_3UCl + Li\begin{matrix}CH_2\\CH_2\end{matrix}P(C_6H_5)(R) \xrightarrow[-50^\circ\ C.]{THF} (C_5H_5)_3UCHP(CH_3)(C_6H_5)(R) + LiCl$$

green colored complexes (20)

where R = C_2H_5, CH_3 or C_6H_5

$$(C_5H_5)_3UCl + 2Li\begin{matrix}CH_2\\CH_2\end{matrix}P(C_6H_5)(R) \xrightarrow[THF]{} \tfrac{1}{2}(\mu\text{-}(CH)(CH_2)P(C_6H_5)(R)U(C_5H_5)_2)_2$$

red colored complexes

$$+ LiCl + Li(C_5H_5) + CH_2{=}P(CH_3)(C_6H_5)(R) \quad (21)$$

where R = CH_3 or C_6H_5

$$(C_5H_5)_3UCl + 3Li\begin{matrix}CH_2\\CH_2\end{matrix}P(C_6H_5)(R) \xrightarrow[THF]{} (C_5H_5)U((CH_2)_2P(C_6H_5)(R))_3$$

gold colored complexes

where R = CH_3 or C_6H_5

$$+ LiCl + 2Li(C_5H_5) \quad (22)$$

$$(C_5H_5)UCl_3\cdot 2THF + 3Li\begin{matrix}CH_2\\CH_2\end{matrix}P(C_6H_5)(R) \xrightarrow[THF]{} (C_5H_5)U((CH_2)_2P(C_6H_5)(R))_3$$

gold colored complexes

where R = CH_3 or C_6H_5

$$+ 3LiCl \quad (23)$$

In addition the triscyclopentadienyluraniumphosphoylide complexes can be used to prepared the other cyclopentadienyluraniumphosphoylide complexes as shown in equations 24 and 25:

$$(C_5H_5)_3UCHP(CH_3)(C_6H_5)_2 + Li\begin{matrix}CH_2\\CH_2\end{matrix}P(C_6H_5)_2 \xrightarrow[THF]{}$$

$$\tfrac{1}{2}(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2 + Li(C_5H_5) + CH_2{=}P(CH_3)(C_6H_5)_2 \quad (24)$$

$$(C_5H_5)_3UCHP(CH_3)_2(C_6H_5) + 2Li\begin{matrix}\diagup CH_2 \\ \\ \diagdown CH_2\end{matrix}P(CH_3)(C_6H_5) \longrightarrow$$

$$(C_5H_5)U((CH_2)_2P(CH_3)(C_6H_5))_3 + 2Li(C_5H_5) \quad (25)$$

From the above reactions we envisage the general scheme shown in Figure 37 for the reaction pathway of the formation of our cyclopentadienyluraniumphosphoylide complexes. Central to this scheme is the intermediate biscyclopentadienyluraniumbisphosphoylide complex. Its existence seems tenuous at best since even the ^1H nmr spectra of crude $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2$ shows little if any indication of its presence. Its instability is rather remarkable considering it would be ten coordinate and presumably coordinatively saturated. However this may not be too surprising considering that the $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2$ complex is one of only a few examples of a biscyclopentadienyluranium complex containing simple cyclopentadienyl groups.

A novel feature of these reactions is the ease with which cyclopentadienyl groups are displaced by the phosphorus ylides in the preparation of the bis or monocyclopentadienyluraniumphosphoylide complexes. Normally the cyclopentadienyl groups in uranium (IV) complexes are highly resistant to displacement even when reactions at the C-H portion of the ring occur.[68] The only other ligand shown to displace cyclopentadienyl groups[24] is the cyclooctatetraene dianion, $C_8H_8^{2-}$, which forms the very stable uranocene complex, $U(C_8H_8)_2$.[17] It would be interesting to see if a phosphorus ylide could displace one of the cyclooctatetraene ligands in uranocene to form a mixed ligand complex. At the present time only one, the recently prepared

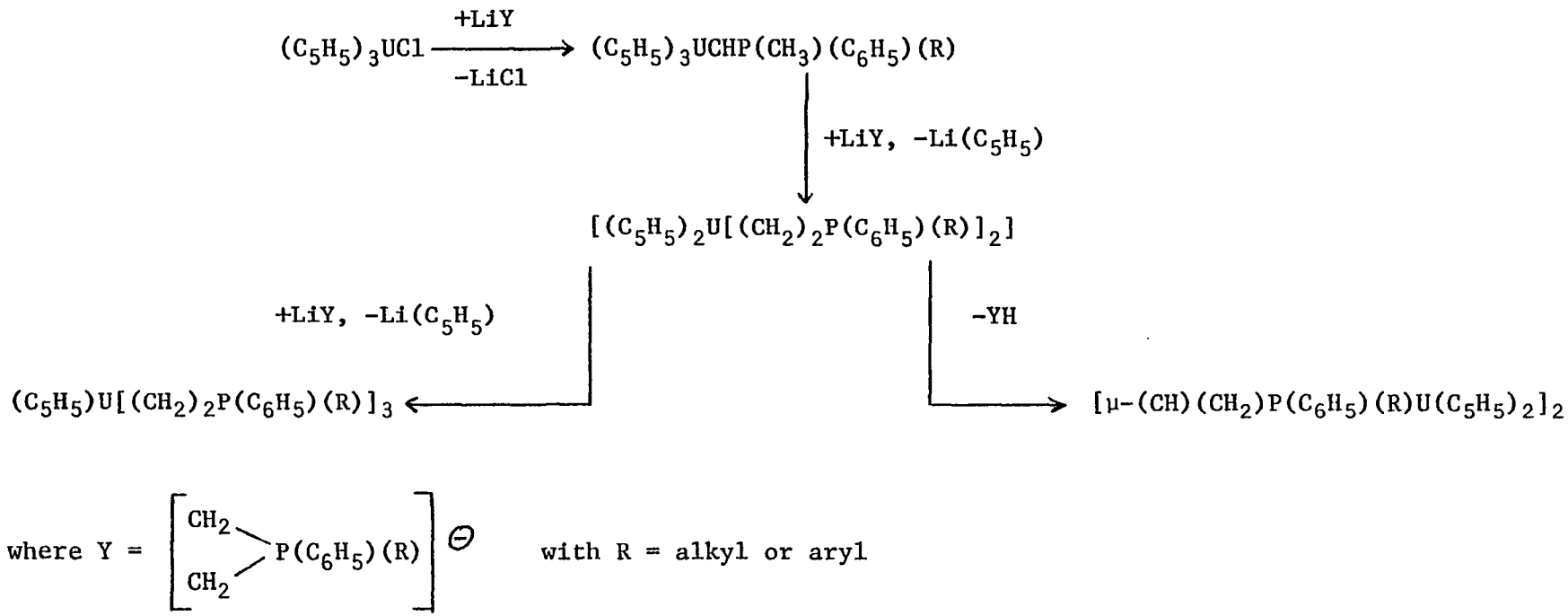


Figure 35. Proposed general reaction scheme for the cyclopentadienyluraniumphosphoylide system.

$(C_8H_8)UCl_2 \cdot 2THF$,[69] is known.

The series of organouraniumphosphoylide complexes obtained with varying equivalents of lithiated phosphorus ylides has unique features which set them apart from previously studied organouranium compounds.

In the dark green triscyclopentadienyluraniumphosphoylide complexes, obtained from the reaction of one equivalent of lithiated phosphoylide with one equivalent of $(C_5H_5)_3UCl$, a proton transfer occurs from one methylene group to the other to give a methyl group and the coordinated methine group. Apparently because of the size of the ligands involved, a reorganization of the ligands about the uranium atom is not possible to form an eleven coordinate complex. Instead a proton transfer occurs and in this way a coordination number of ten is preserved. To a first approximation these complexes might be viewed as analogs of the triscyclopentadienyluranium alkyl complexes.[25-28] However, as will be shown later, the triscyclopentadienyluraniumphosphoylide complexes possess a much greater reactivity toward small molecules such as carbon monoxide than the triscyclopentadienyluranium alkyl complexes and have the potential for a large derivative chemistry.

The reaction of two equivalents of lithiated phosphorus ylide with one equivalent of $(C_5H_5)_3UCl$ produces unique and quite unexpected complexes. These red biscyclopentadienyluraniumphosphoylide dimeric complexes have several novel features. They are the first examples of nine-coordinate organouranium (IV) species and as such could be considered to be coordinatively unsaturated. While we have not extensively studied their chemistry with Lewis bases, limited

experiments which we have tried indicate they may possess interesting catalytic or reagent properties.

As previously mentioned these are one of only a few examples of biscyclopentadienyluranium complexes in which the cyclopentadienyl groups have not been manipulated in some fashion, such as replacing the hydrogens with bulkier methyl groups[38-40] or bridging the two cyclopentadienyl groups together,[37] to increase the stability of the complex. However we have found that the steric bulk of the groups attached to the phosphorus is important to the stability of the dimer. When two phenyl groups are attached to each phosphorus the dimer is stable for weeks in an inert atmosphere. But when one phenyl group is replaced by a methyl group the dimer is stable only in the presence of a strongly coordinating ether solvent. Apparently when the steric bulk of the ligating phosphoylide is reduced, a strongly coordinating solvent molecule is necessary to increase the congestion about the uranium atom and enhance the stability of the dimer. The solvent molecule may coordinate in a bridging fashion between the two uranium atoms. Although this complex is of limited stability, it may be possible to photochemically substitute the coordinating solvent molecule (THF) with a more strongly bonding ligand and consequently enhance the stability of the dimer or resulting complex.

The novel fashion in which the ylide moiety bonds to the uranium atoms is also of interest. This is the first example where a phosphorus ylide both chelates to one metal center and at the same time bridges two metal centers through a methine carbon. A bridging methine group is also unique to actinide chemistry. The closest analog

to this is the $((C_5H_5)_2Th(\eta^5, \eta^1-(C_5H_4))_2$ complex[68] where one cyclopentadienyl group is pentahapto to one thorium atom and σ-bonded through one carbon of the ring to the other thorium atom.

The ^1H nmr of the $(\mu-(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2$ complex is temperature dependent and its behavior as a function of temperature in toluene-d_8/C_6D_6 is shown in Figure 18. (See Page 50) Unfortunately, this system has several problems which limit the amount of useful information concerning the observed process. As seen in Figure 18 the intermediate exchange information is lost into the baseline due to paramagnetic broadening and thus precludes computer simulation to obtain $\Delta H^\dagger$ and $\Delta S^\dagger$ parameters. The phenyl, methylene and methine protons also undergo severe paramagnetic broadening at low temperature and are lost into the baseline. In addition the solubility of the $(\mu-(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2$ complex drastically decreases with temperature even in THF-d_8.

However even with these problems some information and conclusions can be drawn concerning the observed process. In the fast-exchange region single resonances for ortho, meta, and para phenyl protons and cyclopentadienyl protons are observed. When the slow exchange region is reached and dynamic processes have slowed, the spectrum is consistent with the static structure of the complex shown in Figure 36. (See Page 123) The dynamic process involved consists of the averaging of the diastereotopic cyclopentadienyl groups and inversion of configuration at the methine carbons. Both of these processes appear to have the same activation energy and we estimate[64] $\Delta G_{253} = 10 \pm 1$ kcal/mole in toluene-d_8 and $\Delta G_{243} = 10 \pm 1$ kcal/mole in THF-d_8.

The mechanism responsible for the observed dynamic process could be either an intra- or intermolecular process. An intramolecular process would probably involve the averaging of the methylene and methine protons in the fast exchange region. However the elevated temperature ^1H nmr spectrum of the dimer clearly shows distinct methylene and methine resonances. Thus it would appear that perhaps an intermolecular process is more likely.

At present dissociation of the dimer (26) seems to best

$$(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2 \rightleftharpoons 2\ (C_5H_5)_2U(CH)(CH_2)P(C_6H_5)_2 \qquad (26)$$

describe the observed behavior. The thermodynamic parameters involving an intermolecular process should be dependent upon and reflect the coordinating ability (solvation) of the solvent. Unfortunately because of the accuracy involved and the inability to determine ΔS parameters, we cannot draw a valid conclusion from our estimated ΔG_c parameters determined in a coordinating and non-coordinating solvent. For this system it may be better to study the diamagnetic thorium analog which would not suffer from the severe broadening present in the uranium complex. With the thorium analog it may also prove possible to resolve proton-phosphorus coupling to provide additional evidence for the nature of the observed process.

As the temperature is lowered from -60° to -90° C. it becomes apparent from the spectrum that another process responsible for averaging cyclopentadienyl proton resonances is beginning to slow. This occurs for the downfield cyclopentadienyl groups whose resonance begins to broaden, while the resonance of the other continues to

sharpen. The only process of which we are aware which adequately describes this behavior is the slowing of the rotation of one-half of the cyclopentadienyl groups. Such rotational barriers are low and for ferrocene are on the order of 1 - 2 kcal/mole. However with bulkier substituents on the cyclopentadienyl groups of substituted ferrocenes this barrier has been observed as high as ~5 kcal/mole. This is the first example of such a process observed for actinide or lanthanide complexes containing cyclopentadienyl groups.

We believe a steric interaction between one of the cyclopentadienyl groups and a phenyl group of the phosphoylide is responsible for raising the rotational barrier enough to allow it to be partially observed. An examination of the crystal structure of the complex reveals such an interaction as seen in Figure 37. (See Page 135) Several of the carbon to carbon contacts between these groups are in the range 3.66 - 3.74 Å which is at the limit of van der Waals contact (3.7 Å). In addition a close contact of the two cyclopentadienyl rings occurs at 3.22 Å.

The addition of three equivalents of lithiated phosphorus ylide to one equivalent of either $(C_5H_5)_3UCl$ or $(C_5H_5)UCl_3 \cdot 2THF$ results in golden-brown colored monocyclopentadienyluraniumtrisphosphoylide complexes. These complexes can also be prepared from the triscyclopentadienyluraniumphosphoylide complexes by the addition of two equivalents of lithiated phosphorus ylide. These are the first examples of monocyclopentadienyl organouranium complexes other than the $(C_5H_5)UCl_3 \cdot 2THF$ starting material. From the spectroscopic and analytical data the three phosphorus ylide ligands are bonding through

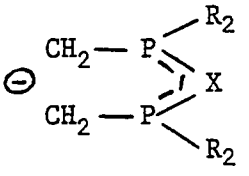
methylene groups in a chelating fashion which is a common mode of bonding observed in transition metal complexes containing phosphorus ylide ligands.

These monocyclopentadienyluraniumtrisphosphoylide complexes could be considered analogous[72] to the group IVB monocyclopentadienyltris(N,N-dialkyldithiocarbamato) metal complexes, $(C_5H_5)M(S_2CNR_2)_3$ (M = T, Zr, Hf), which have attracted interest as seven-coordinate chelates that are stereochemically rigid on the nmr time scale. The monocyclopentadienyluraniumtrisphosphoylide complexes also exhibit temperature dependent nmr behavior. However in order to adequately describe the mechanism responsible, the static structure of one of these complexes must be determined. It is for this reason that the discussion of the temperature dependence of the ^1H nmr spectra must await a further date.

If we consider the cyclopentadienyl group to occupy three coordination sites and each chelating ylide ligand to occupy two sites, then these complexes represent the second example of a class of nine-coordinate organouranium (IV) complexes. Being nine-coordinate, they might be considered to be coordinatively unsaturated and may possess interesting catalytic or reagent properties. They are observed to react with carbon monoxide. However the only presently identifiable product is methylene phosphorane. The fate of the organouranium moiety is unknown at the present time.

The six uranium-carbon σ bonds of the monocyclopentadienyluranium-trisphosphoylide complexes are the most observed at the present time for any organouranium complex. These complexes are the nearest example of an organouranium complex composed solely of U-C σ bonds. Indeed, evidence

exists[73] that with phosphorus ylides as ligands it may not be easy to prepare a uraniumphosphoylide complex composed solely of σ bonding phosphorus ylide ligands. Manzer has noted[74] that paramagnetic organometallic complexes of the early transition metals are generally less stable than their diamagnetic counterparts except in those instances where a ligand such as a cyclopentadienyl group or a β-diketone are present to delocalize some of the electron density away from the metal center. Nevertheless, it may be possible to prepare stable uraniumphosphoylide complexes by using bulkier phosphorus ylides such as $Li(CH_2)_2P(t\text{-}C_4H_9)_2$ or by using double ylides[75] such as



where X = N, CH or BH_2

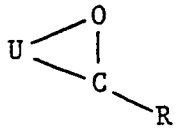
which could also delocalize electron density away from the uranium center.

As mentioned previously organouranium complexes with a coordination number of ten have been considered to be coordinatively saturated. Since the triscyclopentadienyluraniumphosphoylide complexes are ten coordinate they would not be expected, from this point of view, to further react with substrate molecules and perhaps, even increase their coordination number. We have found quite the opposite to be true. The triscyclopentadienyluraniumphosphoylide complexes readily react with carbon monoxide at room temperature to yield reddish-orange complexes according to equation 27:

$$(C_5H_5)_3UCHP(CH_3)(C_6H_5)(R) \xrightarrow{CO} (C_5H_5)_3U(CO)CHP(CH_3)(C_6H_5)(R) \qquad (27)$$

where R = C_2H_5, CH_3 or C_6H_5

The spectroscopic and analytical data suggests that the carbon monoxide has undergone an insertion reaction between the U-C bond to form an acyl complex. However, from the infrared data the acyl portion appears to be side-bonded to the uranium as shown below:



The "side-on" coordination of an acyl group had been postulated[76] as early as 1971 for several ruthenium(II) complexes of general formula RCO-RuCl(CO)$(P(C_6H_5)_3)_2$ mainly based on infrared results. Other than several dinuclear manganese complexes[77,78] containing a side-bonded bridging carbonyl group, the only other metal complexes to contain side-bonding acyl groups are the group IVB metals (Ti, Zr and Hf). Several groups[79-82] have found that a great variety of biscyclopentadienyl or bispentamethylcyclopentadienyl titanium and zirconium complexes contain side-bonded or dihapto acyl groups. It has even been suggested[79,82] that this form of acyl coordination to a metal atom may be more widespread than suspected and may account for the very low CO stretching frequencies seen for acyl complexes of early transition metals.

Marks and co-workers have postulated[39] side-bonded acyl intermediates in the carbonylation reactions of bispentamethylcyclopentadienylthorium and uranium complexes. Recently they have succeeded[66,67] in

isolating and structurally characterizing a side-bonded acyl group in the $((CH_3)_5C)_2ThCl(CO)$neopentyl complex. Undoubtably one of the important factors in the formation of Th(IV) or U(IV) side-bonded acyl complexes is the high affinity of these metals for oxygen-containing ligands. As such, when carbon monoxide insertion reactions occur in organoactinide complexes the side-bonded acyl product or intermediate may well be a general and often observed feature of these systems.

Aside from the novel product obtained in reaction 27, the really unique feature is the expansion of the coordination number of this complex from ten to eleven. It is the second example[36] of a triscyclopentadienyluranium complex increasing its coordination number above ten by reacting with a coordinatively unsaturated small molecule. Apparently with the right choice of ligand a triscyclopentadienyluranium complex can react in the manner of a coordinatively unsaturated complex. Perhaps, the time has come to reevaluate the notion of a ten-coordinate uranium(IV) complex as being coordinatively saturated.

The ability of a metal complex to increase its coordination number is important if that complex is to exhibit catalytic activity. While the complexes already discussed show this ability or have the potential for it, their actual use in a catalytic cycle may be hampered or severely limited because of their sensitivity to oxygen and water. For this reason they may find wider use as reagents for organic synthesis.

Transition metal complexes containing phosphorus ylide ligands have already been shown[53] to react in the manner of Wittig reagents in the transformation of carbonyl functional groups to olefins. The

novel mode of coordination exhibited by some of the organouranium-phosphoylide complexes and the high affinity of uranium for oxygen may well produce some novel and unique organic transformations, both in the substrate molecule and the organouranium moiety.

IV. EXPERIMENTAL

A. CHEMICALS AND EXPERIMENTAL CONDITIONS

All reactions involving organometallics were carried out under a dry dinitrogen atmosphere using Schlenk techniques, a Vacuum Atmospheres glove box equipped with a HE-493 Dri-train or a high vacuum line. Elemental analysis were performed by Schwarzkopf Microanalytical Laboratories, Woodside, New York.

Uranium tetrachloride, 1.7M $LiCH_3$, phenyldichlorophosphine and diphenylchlorophosphine were obtained from Research Organic/Inorganic Corporation. Thallous cyclopentadienide was obtained from Aldrich Chemical Company. Ethyl and methyl iodide were obtained from Eastman Kodak. All of the above materials were used as received.

Diethyl ether, tetrahydrofuran, 1,2-dimethoxyethane, benzene and toluene were dried and deoxygenated by distillation under high purity dinitrogen from blue sodium benzophenone ketyl. Saturated hydrocarbons were refluxed over calcium hydride for several hours and distilled under high purity dinitrogen.

The organouranium reagents, $(C_5H_5)_3UCl$ and $(C_5H_5)UCl_3 \cdot 2THF$ were prepared by literature procedures.[51,52]

The necessary phosphines were prepared from the appropriate halophosphines via the method used in the preparation of $(n\text{-}C_4H_9)_3P$.[83] They were then placed in diethyl ether and stirred with an excess of the appropriate aklyl iodide until no further precipitation of phosphonium salt was observed. The phosphonium salts were recrystallized from either methanol or ethanol. A second batch of crystalline phosphonium salt could be obtained by reducing the solvent in volume

and adding diethyl ether. These were then used in the preparation of the lithiated phosphorus ylides.

The reagents, $Li(CH_2)_2P(C_6H_5)_2$ and $Li(CH_2)_2P(CH_3)(C_6H_5)$, were prepared by literature methods.[53] The preparation of $Li(CH_2)_2P(C_2H_5)(C_6H_5)$ was also attempted by this same method. However, the product obtained was $LiI \cdot CH_2=P(C_2H_5)(CH_3)(C_6H_5) \cdot (C_2H_5)_2O$ rather than $Li(CH_2)_2P(C_2H_5)(C_6H_5)$. An alternate route was used to prepare $Li(CH_2)_2P(C_2H_5)(C_6H_5)$ and is described on Page 108.

B. INSTRUMENTATION

All ^1H (100.1 MHz) and ^{31}P (40.5 MHz) spectra were obtained on a Varian XL-100-15 spectrometer with variable temperature accessory interfaced to a Digilab Nova 1200 mini-computer operating in Fourier transform mode, except where noted. Temperatures were measured with a thermocouple in an nmr tube that was placed into the probe. They are considered to be accurate to ±2° C.

The lithiated phosphorus ylide H spectra were recorded in THF-d_8 with TMS as the internal reference. The ^{31}P spectra were obtained in ~75% THF and 25% toluene-d_8 as the internal look. The samples were referenced to external H_3PO_4.

The ambient temperature organouranium ^1H spectra were obtained in benzene-d_6 or toluene-d_8 which also served as the internal reference. Toluene-d_8 and THF-d_8 were used as the solvents for variable temperature ^1H studies. The CH_3 resonance in toluene-d_8 was used as an internal reference. Benzene or TMS was used as the internal reference when THF-d_8 was the solvent. The ^{31}P spectra of the organouranium complexes were obtained in the same manner as that used for the lithiated phosphorus

ylides.

Samples that were to be run at ambient temperature were prepared in the dry box and sealed with Para-Film. Variable temperature samples were prepared in the dry box in nmr tubes fitted with a standard taper ground glass joint and a vacuum stop-cock. These were frozen in liquid dinitrogen, evacuated and sealed.

Infrared spectra were recorded on a Perkin-Elmer 467 grating spectrometer. The samples were prepared as nujol mulls between KBr plates that were sealed with stopcock grease. The spectra were calibrated with the 1601 cm^{-1} absorption of polystyrene film.

A Cary 14 recording spectrophotometer was used to obtain the near-infrared spectra. The visible spectra were recorded on a Beckman Acta CIII spectrophotometer. The samples were run in matched 1.000 cm quartz cells with greased teflon stoppers. The solvent used for all electronic spectra was THF.

C. SYNTHESIS AND REACTION CHEMISTRY

Preparation of tris(pentahaptocyclopentadienyl)(methinidylphosphoniumdimethylphenyl) uranium, $(C_5H_5)_3UCHP(CH_3)_2(C_6H_5)$

A 30 ml THF solution containing 0.321 g (2.03 mole) $Li(CH_2)_2P(CH_3)(C_6H_5)$ was added to 0.950 g (2.03 mmole) $(C_5H_5)_3UCl$ in 50 ml of THF cooled to -50° C. over a period of one hour. After the addition was complete the dark green solution was stirred for several hours at -50° C., allowed to warm to -10° C. and the solvent immediately removed *in vacuo*. The dark green residue was extracted with 40 ml of benzene, filtered and the solvent removed *in vacuo*. The material was

recrystallized from a 1:1 solution of toluene:heptane to yield 0.729 g (62%) of dark-green long needles of $(C_5H_5)_3UCHP(CH_3)_2(C_6H_5)$. The needles are pyrophoric in the presence of air or water. Anal. Calc. for $U_1P_1C_{24}H_{27}$: C, 49.31; H, 4.67; P, 5.30. Found: C, 49.53; H, 4.91; P, 5.22.

Reaction of tris(pentahaptocyclopentadienyl)(methinidylphosphoniumdimethylphenyl)uranium with carbon monoxide

A solution of 0.888g (1.52 mmole) of $(C_5H_5)_3UCHP(CH_3)_2(C_6H_5)$ in 30 ml of toluene was placed in a 300 ml reaction vessel equipped with a gas inlet tube. A slow steam of carbon monoxide, passed through a -78° C. trap, was passed over the solution for 30 minutes with stirring at room temperature. A dark red precipitate gradually formed and the solution became a very pale red color. The mixture was filtered and washed with 10 ml of toluene. The dark red material was washed through the filter with 30 ml of THF. The THF solution was reduced in volume to ca. 10 ml and heptane was added until the solution became slightly cloudy. This solution was cooled overnight at -15°C. to give 0.707 g (85% based on starting material) of dark red air and moisture sensitive needles. Anal. Calc. for $U_1P_1O_1C_{25}H_{27}$: C, 49.02; H, 4.45; P, 5.06. Found: C, 48.90; H, 4.47; P, 5.05.

Attempted preparation of tris(pentahaptocyclopentadienyl)(methinidylphosphoniumethylmethylphenyl)uranium from $LiI \cdot CH_2=P(C_2H_5)(CH_3)(C_6H_5)$

A solution of 0.942 g (2.01 mmole) of $(C_5H_5)_3UCl$ in 40 ml of THF

was placed into a 300 ml reaction vessel. The solution was cooled to -50° C. and a 20 ml THF solution containing 4.02 mmole of $LiI \cdot CH_2=P(C_2H_5)(CH_3)(C_6H_5)$ was slowly added. After completion of the addition, the solution was maintained at -50° C. for 1 hour, allowed to warm to -10° C. and the solvent was immediately removed in vacuo to give a lime-green gummy product. Upon extraction of this material with benzene or allowing it to stand for more than 1 day it turned brown. This material was insoluble in ethers and aromatic and saturated hydrocarbons. Several attempts were made using THF or diethyl ether as the solvent with the product decompsoing each time.

Preparation of $Li(CH_2)_2P(C_2H_5)(C_6H_5)$ from $LiI \cdot CH_2=P(C_2H_5)(CH_3)(C_6H_5)$

A 5.04 g (16.8 mmole) sample of $LiI \cdot CH_2=P(C_2H_5)(CH_3)(C_6H_5)$ was placed in a short-path molecular still and thermolyzed. At ~180°C./ 0.5 Torr a dark orange liquid was collected. From ^1H nmr and infrared spectra this material was identified as $CH_2=P(C_2H_5)(CH_3)(C_6H_5)$. This liquid is air and moisture sensitive. We obtained 1.56 g (56%) of this material.

The entire amount of $CH_2=P(C_2H_5)(CH_3)(C_6H_5)$ collected was placed in 20 ml of diethyl ether and a 15 ml diethyl ether solution containing 5.6 ml of 1.7M $LiCH_3$ was slowly added. After cessation of CH_4 production, the white solid was filtered, washed with 10 ml of diethyl ether and dried in vacuo for 2 hours to give 1.21 g (75%) of $Li(CH_2)_2P(C_2H_5)(C_6H_5)$.

Preparation of tris(pentahaptocyclopentadienyl)(methinidylphosphonium ethylmethylphenyl)uranium, $(C_5H_5)_3UCHP(C_2H_5)(CH_3)(C_6H_5)$

A 10 ml THF solution containing 0.414 g (2.40 mmole) of $Li(CH_2)_2P(C_2H_5)(C_6H_5)$ was slowly added to 1.127 g (2.40 mmole) of $(C_5H_5)_3UCl$ in 25 ml of THF cooled to -50° C. When the addition was complete, the solution was maintained at -50° C. for 1 hour, allowed to warm to -10° C. and the THF immediately removed *in vacuo*. The dark green residue was extracted with 40 ml of benzene, filtered and the solvent removed *in vacuo*. The material was recrystallized from a 1:1 solution of toluene:heptane to give 0.982 g (68%) of dark green crystalline material. The product is pyrophoric in the presence of air or moisture. *Anal*. Calc. for $U_1P_1C_{25}H_{29}$: C, 50.15; H, 4.89; P, 5.17. Found: C, 50.25; H, 4.92; P, 5.10.

Reaction of tris(pentahaptocyclopentadienyl)(methinidylphosphonium-ethylmethylphenyl)uranium with carbon monoxide

A solution of 0.732 g (1.22 mmole) of $(C_5H_5)_3UCHP(C_2H_5)(CH_3)(C_6H_5)$ in 30 ml of benzene was placed in a 50 ml reaction vessel equipped with a gas inlet tube. A slow stream of carbon monoxide, passed through a -78° C. trap, was passed over the solution with stirring at room temperature for about 1 hour. The solution slowly turned from dark green to dark reddish-orange. The benzene was removed *in vacuo* and the dark colored residue dissolved in a minimum volume of toluene. Heptane was layered on top of the solution until it became cloudy. It

was placed in a freezer (-15° C). overnight to give 0.687 g (90%) of red feathery material.

Preparation of tris(pentahaptocyclopentadienyl)(methinidylphosphonium-diphenylmethyl)uranium, $(C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$

A 30 ml THF solution containing 0.528 g (2.40 mmole) of $Li(CH_2)_2P(C_6H_5)_2$ was slowly added to 1.123 g (2.40 mmole) of $(C_5H_5)_3UCl$ in 40 ml of THF cooled to -50° C. Upon completion of the addition, the solution was stirred at -50° C. for several hours, allowed to warm to -10° C. and the solvent immediately removed *in vacuo*. The dark green solid was extracted with 50 ml of benzene, filtered and the solvent removed *in vacuo*. The material was recrystallized from a 1:2 toluene: heptane solution to give 0.885 g (57%) of dark green microcrystalline material which decomposes immediately upon exposure to the atmosphere. *Anal*. Calc. for $U_1P_1C_{29}H_{29}$: C, 53.87; H, 4.53; P, 4.79. Found: C, 51.03, H, 4.94; P, 4.87.

Reaction of tris(pentahaptocyclopentadienyl)(methinidylphosphonium-diphenylmethyl)uranium with $Li(CH_2)_2P(C_6H_5)_2$

A 20 ml THF solution containing 0.225 g (1.16 mmole) of $Li(CH_2)_2P(C_6H_5)_2$ was rapidly added to 0.748 g (1.16 mmole) of $(C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$ in 30 ml of THF. The dark colored solution was refluxed for 4 hours and the THF removed *in vacuo*. The dark colored material was extracted with 40 ml of benzene, filtered and the solvent removed *in vacuo*. A ^1H-nmr of this material showed a mixture

consisting of 39% $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2$ and 61% $(C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$ from relative ^{1}H-nmr peak heights.

Reaction of tris(pentahaptocyclopentadienyl)(methinidylphosphonium-diphenylmethyl)uranium with $Li(CH_2)_2P(CH_3)(C_6H_5)$

This reaction was performed in a manner analogous to that described above with $Li(CH_2)_2P(CH_3)(C_6H_5)$ used in place of $Li(CH_2)_2P(C_6H_5)_2$. The darkly colored reaction product was analyzed by ^{1}H-nmr. The mixture consisted of 71% $(C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$ and 29% $(C_5H_5)_3UCHP(CH_3)_2(C_6H_5)$ from relative peak height ratios.

Reaction of tris(pentahaptocyclopentadienyl)(methinidylphosphonium-diphenylmethyl)uranium with $LiCH_3$

A solution of 0.413 g (0.64 mmole) of $(C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$ in 20 ml of THF was placed in a 50 ml reaction vessel. To this was slowly added a 10 ml THF solution containing 0.37 ml of 1.7M $LiCH_3$. This was refluxed for several hours whereupon it turned a dark color. The THF was then removed in vacuo. A ^{1}H-nmr of this material showed it to consist essentially of starting material. No peaks due to $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_6H_5)_2)_2$ were seen.

A second reaction similiar to the first was performed in which 2 equivalents of $LiCH_3$ was used. This produced a dark red material whose ^{1}H-nmr showed no paramagnetically displaced resonances. The remaining product was not identified.

Reaction of tris(pentahaptocyclopentadienyl)(methinidylphosphonium-diphenylmethyl)uranium with carbon monoxide

A solution of 0.692 g (1.07 mmole) of $(C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$ in 30 ml of toluene was placed in a 300 ml reaction vessel equipped with a gas inlet tube. A slow stream of carbon monoxide, passed through a -78° C. trap, was passed over the solution with stirring at room temperature for 30 minutes. The solution slowly turned from dark green to dark red. It was filtered and the filtrate reduced in volume to ca. 10 ml. Heptane was layered on top of the solution until it became cloudy. It was placed in a freezer (-15° C.) overnight to give 0.635 g (88% based on starting material) of red prisms. Anal. Calc. for $U_1P_1O_1C_{30}H_{29}$: C, 53.41; H, 4.34; P, 4.59; mol wt, 675 g/mol. Found: C, 53.65; H, 4.45; P, 4.60; mol wt, 719 10% g/mol.

Preparation of bis(pentahaptocyclopentadienyl)(μ-methinidylmethylene-phosphoniumdiphenyl)uranium dimer, $[\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2$

A solution containing 1.339 g (6.08 mmole) of $Li(CH_2)_2P(C_6H_5)_2$ in 50 ml of THF was added to 1.422 g (3.03 mmole) of $(C_5H_5)_3UCl$ in 50 ml of THF at room temperature. After addition, the reddish-brown solution was heated to near THF reflux for 2 hours. The dark red solution was allowed to cool to room temperature and the solvent was removed in vacuo. The material was recrystallized from a 1:1 solution of THF:hexane and dried overnight under vacuo to give 0.775 g (44%) based on starting $(C_5H_5)_3UCl$) of red microcrystalline $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2 \cdot THF$. Anal. Calc. for $U_2P_2O_1C_{52}H_{54}$:

C, 50.65; C, 4.42; P, 5.02. Found: C, 48.02; H, 4.36; P, 4.76.

Reaction of bis(pentahaptocyclopentadienyl)(μ-methinidylmethylene-phosphoniumdiphenyl)uranium dimer with carbon monoxide

A solution of 0.317 g (0.27 mmole) of $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2$ in 20 ml of THF was placed into a 50 ml reaction vessel equipped with a gas inlet tube. A slow stream of carbon monoxide, passed through a -78° C. trap, was passed over the solution with stirring overnight. A light brown precipitate formed which was insoluble in ethers and aromatic and saturated hydrocarbon solvents. This product has not been further characterized.

Attempted preparation of bis(pentahaptocyclopentadienyl)(μ-methinidyl-methylenephosphoniummethylphenyl)uranium dimer, $[\mu\text{-}(CH)(CH_2)P(CH_3)(C_6H_5)U(C_5H_5)_2]_2$

A 35 ml THF solution containing 0.621 g (3.93 mmole) of $Li(CH_2)_2P(CH_3)(C_6H_5)$ was added to 0.919 g (1.96 mmole) of $(C_5H_5)_3UCl$ in 40 ml of THF cooled to -50° C. When the addition was complete, the mixture was maintained at -50° C. for an additional hour and warmed to reflux for 1 hour. The solution was now a deep red color and the THF was removed in vacuo. It was extracted with 10 ml of toluene, filtered and 10 ml of heptane layered on top. The solution turned a brown color and the material was found to be decomposed.

This reaction was attempted several times in THF including the addition of the $Li(CH_2)_2P(CH_3)(C_6H_5)$ at room temperature. Substituting

1,2-dimethoxyethane for THF produced the same results.

Preparation of mono(pentahaptocyclopentadienyl)tris(dimethylene-phosphoniumdiphenyl)uranium, $(C_5H_5)U[(CH_2)_2P(C_6H_5)_2]_3$

A) From $(C_5H_5)_3UCl$:

A 30 ml THF solution containing 0.760 g (3.45 mmole) of $Li(CH_2)_2P(C_6H_5)_2$ was slowly added to 0.538 g (1.15 mmole) of $(C_5H_5)_3UCl$ in 40 ml of THF at -50° C. When the addition was complete the solution was allowed to warm to room temperature and stirred for several hours. The THF was removed *in vacuo* leaving a dark orange-red material. This was extracted with 40 ml of benzene, filtered and the solvent removed *in vacuo* to give a gold colored material.

All attempts at crystallization from various solvents failed. However the following modification of the procedure did produce a crystalline product.

A 100 ml schlenk flask was charged with 0.576 g (2.62 mmole) of $Li(CH_2)_2P(C_6H_5)_2$ and 0.407 g (0.89 mmole) of $(C_5H_5)_3UCl$ and 50 ml of diethyl ether cooled to -50° C. was added. This was stirred for several hours and then warmed to room temperature. The mixture was filtered and the golden-brown solution reduced in volume to *ca.* 20 ml. It was cooled to -15° C. overnight whereupon gold rod-like crystals formed. These were collected and washed with 5 ml of diethyl ether and dried under *vacuo* for 30 minutes to give 0.774 g (58%) of product. *Anal.* Calc. for $U_1P_3C_{47}H_{47}$: C, 59.87; H, 5.03; P, 9.85. Found: C, 59.97; H, 5.06; P, 9.80.

The ^1H nmr of the material from both of the above methods was

virtually identical except for some small impurity peaks and stopcock grease in the material prepared from THF.

B) From $(C_5H_5)UCl_3 \cdot 2THF$:

A 25 ml THF solution containing 0.983 g (4.46 mmole) of $Li(CH_2)_2P(C_6H_5)_2$ was added to 0.825 g (1.49 mmole) of $(C_5H_5)UCl_3 \cdot 2THF$ in 40 ml of THF at -50° C. This mixture was stirred at -50° C. for 30 minutes and color changed from green to orange to dark red. After warming to room temperature, the THF was removed in vacuo. The material was extracted with 40 ml of benzene, filtered and the solvent removed in vacuo to give a quantitative yield of golden-brown solid. The ^1H nmr of this material showed it to be identical to that prepared from $(C_5H_5)_3UCl$.

Reaction of mono(pentahaptocyclopentadienyl)tris(dimethylenephosphonium-diphenyl)uranium with carbon monoxide

A 300 ml reaction vessel equipped with a gas inlet tube was charged with 0.937 g (0.99 mmole) of $(C_5H_5)U((CH_2)_2P(C_6H_5)_2)_3$ in 40 ml of benzene. This was stirred for 5 hours under a slow stream of carbon monoxide passed through a -78° C. trap. The solvent was removed in vacuo to give a light brown colored solid. The ^1H nmr of this material showed it to be a methylene phosphorane with no indication of any paramagnetic material.

Preparation of mono(pentahaptocyclopentadienyl)tris(dimethylene-phosphoniummethylphenyl)uranium, $(C_5H_5)U[(CH_2)_2P(CH_3)(C_6H_5)]_3$

A 20 ml THF solution containing 0.646 g (4.09 mmole) of $Li(CH_2)_2P(CH_3)(C_6H_5)$ was added to 0.637 g (1.36 mmole) of $(C_5H_5)_3UCl$ in 40 ml of THF at -50° C. When the addition was complete the solution was maintained at -50° C. for 30 minutes and allowed to warm to room temperature. After stirring at room temperature for several hours the solvent was removed in vacuo. The material was extracted with 35 ml of benzene, filtered and the solvent removed in vacuo to give a quantitative yield of golden-brown material.

All attempts at crystallization of this material, including the modification of using diethyl ether as the reaction medium failed. The ^1H nmr of this material showed it to be almost free of any impurities except for stopcock grease and a small amount of starting ylide.

B) From $(C_5H_5)UCl_3 \cdot 2THF$:

A 20 ml THF solution containing 6.86 g (4.34 mmole) of $Li(CH_2)_2P(CH_3)(C_6H_5)$ was added to 0.797 g (1.44 mmole) of $(C_5H_5)UCl_3 \cdot 2THF$ in 40 ml of THF cooled to -50°C. After the addition was complete the solution was allowed to warm to room temperature and stirred there for several hours whereupon the THF was removed in vacuo. The solid was extracted with 40 ml of benzene, filtered and the solvent removed in vacuo to give a quantitative yield of golden-brown material.

A ^1H nmr of this material showed it to be identical to that prepared from $(C_5H_5)_3UCl$. However this material was not as clean of impurities as that prepared from $(C_5H_5)_3UCl$.

C) From $(C_5H_5)_3UCHP(CH_3)_2(C_6H_5)$:

A 10 ml THF solution containing 0.233 g (1.47 mmole) of $Li(CH_2)_2P(CH_3)(C_6H_5)$ was added in one addition to 0.432 g (0.74 mmole) of $(C_5H_5)_3UCHP(CH_3)_2(C_6H_5)$ at room temperature. After stirring for several hours the THF was removed in vacuo. The golden-brown solid was extracted with 30 ml of benzene, filtered and the benzene removed in vacuo to give an essentially quantitative yield of golden-brown material.

A ^1H nmr of the material confirmed its identity as $(C_5H_5)U((CH_2)_2P(CH_3)(C_6H_5))_3$.

V. X-RAY CRYSTALLOGRAPHY

During our attempt to characterize the product of the addition of two equivalents of $Li(CH_2)_2P(C_6H_5)_2$ to one equivalent of $(C_5H_5)_3UCl$ it became clear that the available physical data would not allow us to assign a reasonable structure for the red product. Thus it was necessary to undertake an x-ray crystallographic study to determine the structure of the complex. In addition, no previous structural data existed for lanthanide or actinide complexes with phosphorus ylides.

A. Experimental

X-ray diffraction quality crystals were obtained by preparing $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2$ in an analogous fashion to that mentioned in the Experimental section except diethyl ether was used in place of THF. Allowing the dark red diethyl ether solution to stand for several days produced deep red crystals of $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2\cdot(C_2H_5)_2O$ (I). Shoxlet extraction of crude $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2$ with pentane for 24 hours produced very deep red crystals of $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2\cdot C_5H_{12}$ (II).

A high resolution mass spectrum run on a Varian MAT-311 mass spectrometer using crystals of I which had been washed with a large amount of hexane and dried under vacuum for 12 hours at 30° C. did not show a parent ion but contained fragments resulting from the loss of one or more cyclopentadienyl groups. The formulation of the compound as an ether solvate was indicated by the presence of $C_4H_{10}O^+$ (m/e: 74.0732 (calc.); 74.0728 (obs.)) and $C_3H_7O^+$ (m/e: 59.0497 (calc.); 59.0497 (obs.)). NMR spectra obtained by dissolving crystals of I in C_6D_6 also

indicated the presence of diethyl ether.

Crystals of I and II were mounted with Corning high-vacuum stopcock grease in thin-walled glass capillaries under nitrogen. A plate-like crystal of I measuring 0.39 mm x 0.06 mm x 0.29 mm and a crystal of II with 0.26 mm x 0.22 mm x 0.15 mm dimensions were selected by microscopic examination and found to be suitable for x-ray diffraction.

A Syntex four-circle computer-controlled diffractometer with graphite monochromatized Mo K_α radiation ($K_{\alpha 1}$, λ = 0.70930 Å; $K_{\alpha 2}$, λ = 0.71359 Å) and a scintillation detector with pulse height analyzer was used for preliminary experiments and the measurement of diffraction intensities. Except as otherwise noted, the procedure used has been described. [84,85] The cell constants were determined by least-squares methods from the centered angular coordinates of 15 intense reflections with 2θ values between 4° and 17° for I and between 4° and 19° for II. Crystal data, data collection and refinement parameters are listed in Table 19. Atomic scattering factors for U°, P° and C° were used.[86] Anomalous dispersion corrections[87] to the scattering factors were made for all non-hydrogen atoms except in structure I where only the real part of anomalous dispersion was applied.

A three-dimensional Patterson map yielded the coordinates for the uranium atoms in structure I. Subsequent Fourier maps and full-matrix[88] least squares refinement with anisotropic thermal parameters for uranium and phosphorus and isotropic thermal parameters for the carbon atoms converged at R_1 = 0.095 and R_w = 0.115. Although absorption is undoubtedly important for this crystal, orientation of the crystal was

TABLE 19

Summary of Crystal Data, Data Collection and Refinement

	Structure I	Structure II
Compound	$[\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2(C_2H_5)_2O$	$M\text{-}[\mu\text{-}(S\text{-}CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2 \cdot C_5H_{12}$
Formula weight	1235.01 g/mole	1233.11 g/mole
	monoclinic	orthorhombic
Space group	$P2_1/c$ (No. 14)	$P2_12_12_1$ (No. 19)
a	12.676(8) Å	16.026(12) Å
b	16.462(8) Å	23.453(13) Å
c	25.837(25) Å	12.679(3) Å
β	124.43(5°)	
Volume	4447(6) Å	4799(4) Å
Z	4	4
Density	1.84 g/cm^3 (calcd)	1.71 g/cm^3 (calcd)
Absorption grid	4 x 6 x 10	6 x 10 x 4
μ	70.37 cm^{-1}	64.83 cm^{-1}
Transmission		
Coefficients	0.181-0.629	0.428-0.527
Scan rate	variable/5° min^{-1}-24° min^{-1}	variable/5° min^{-1}-24° min^{-1}
2θ range	3°-50°	3°-40°
Total no. of		
Observations (m)	8126	2584
Data with		
$I_o > 3\ (\sigma_I)$	3993	1874
p	0.05	0.05
R_1	.092	.047
R_w	.110	.052
Goodness-of-fit	2.44	1.29
parameters (s)	296	326
Overdetermination		
Ratio (m/s)	13.5	5.8

lost and an absorption correction was not possible.

At this point a difference Fourier map revealed the positions of 3 atoms of a diethyl ether solvate. Several cycles of refinement with each of these assigned as oxygen or carbon all produced similiar R values and occupancy factors. As a result it was not possible to identify the oxygen atom and in the final model all three were refined as carbon atoms. Since the other two atoms of the solvate could not be located, it is not possible to establish that the solvate is $(C_2H_5)_2O$ from crystallographic evidence, but the high resolution mass spectrum confirms its identity. These three solvate atoms lowered the error indices to $R_1 = 0.092$ and $R_w = 0.110$. No attempt was made to locate hydrogen atoms.

Examination of the final difference Fourier map with an estimated standard deviation ≈ 0.4 e/Å^3 revealed that the largest peak has a height of 1.0 e/Å^3 and is associated with one of the solvate atoms. All others with the exception of ripples around the uranium atoms are less than 0.9 e/Å^3. In the final cycle of least squares refinement no parameter shifted by more than 30% of its estimated standard deviation.

Structure II was routinely solved by heavy atom methods. However since $P2_12_12_1$ is a noncentric space group it was necessary to determine the correct enantiomer for the crystal examined. Refinement with anisotropic thermal parameters for uranium and phosphorus and isotropic thermal parameters for the carbon atoms of the original, arbitrarily chosen, enantiomer converged at $R_1 = 0.049$ and $R_w = 0.056$. Refinement of the other enantiomer yielded $R_1 = 0.055$ and $R_w = 0.063$. The R factor ratio is 1.12 and is greater than the limiting value of 1.07

calculated for a 99% confidence level.[89] Thus the initial enantiomer chosen was judged to be correct.

Finally, the four carbon atoms bound to both uranium and phosphorus were given anisotropic thermal parameters and all atoms were allowed to refine for three more cycles, producing final values of $R_1 = 0.047$ and $R_w = 0.052$. No attempt was made to locate hydrogen atoms. A final difference Fourier with an estimated standard deviation of ≈ 0.2 e/Å^3 showed no peaks greater than 0.5 e/Å^3, roughly 25% of a carbon atom, other than noise peaks in the region of the uranium atoms. In the final cycle of least squares refinement no parameter shifted more than 10% of its estimated standard deviation, except for the pentane carbons where shifts were less than 50% of their estimated standard deviation.

The final positional and thermal parameters for structures I and II are listed in Tables 20 and 21. The bond lengths and bond angles are shown in Tables 22-26. A listing of observed and calculated structure factors for I and II are found in Appendices A and B respectively.

B. RESULTS AND DISCUSSION

Since the molecular structures of I and II are almost identical, the bond distances and angles to be discussed here were obtained by averaging corresponding parameters in the two structures as well as those which are made equivalent by the approximate C_2 site symmetry of the molecule.

A perspective drawing of $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2$ is shown in Figure 36. The structure contains several interesting features, the most obvious being the manner in which the ylide is incorporated

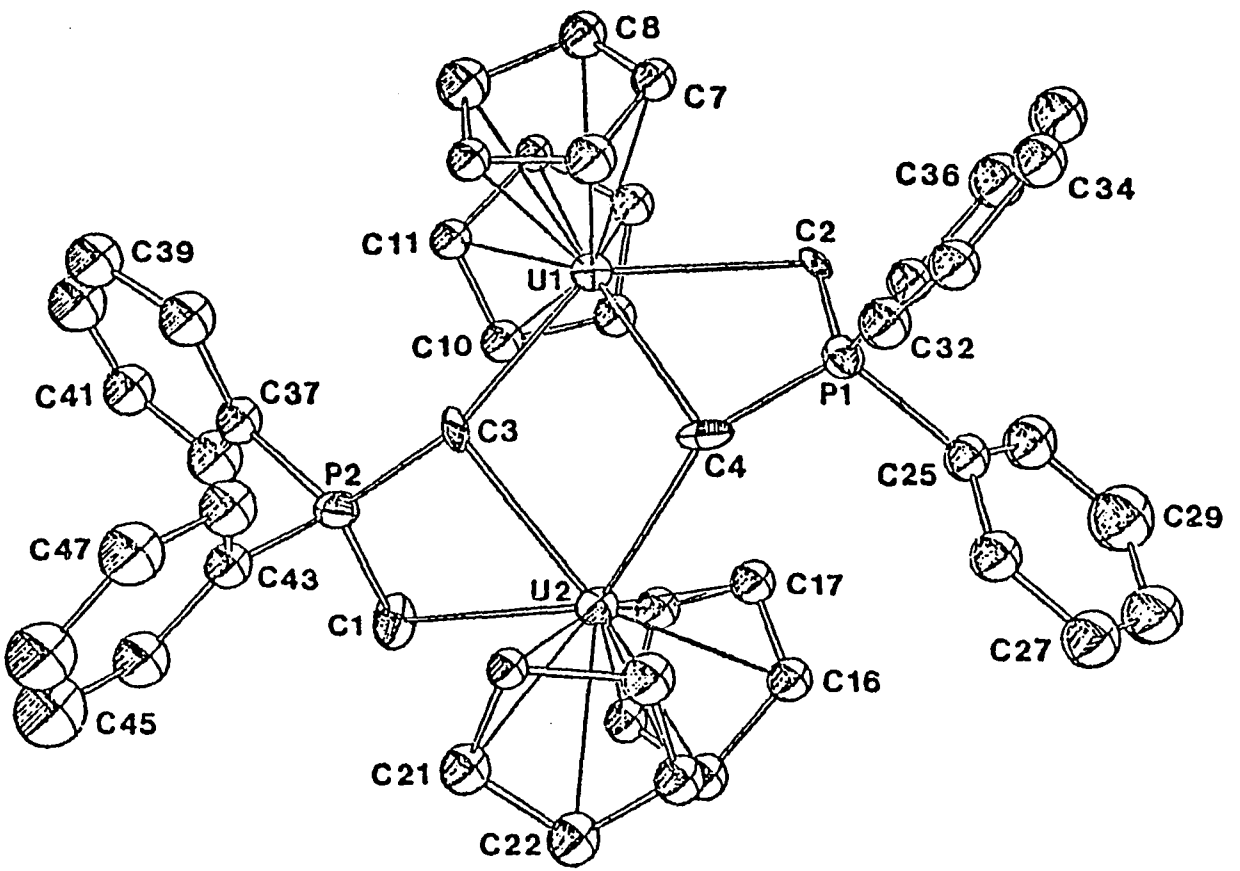


Figure 36. Perspective view of the M-(μ-(S-CH)(CH_2)P(C_6H_5)$_2$U(C_5H_5)$_2$)$_2$molecule. Thermal ellipsoids as drawn by ORTEP-II at the 20% probability level.

TABLE 20

Positional and Thermal Parameters[a] with Standard Deviations for $[\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2 \cdot (C_2H_5)_2O$

ATOM	X	Y	Z	β11	β22	β33	β12	β13	β23
U 1	0.03845(12)	0.33792(7)	0.39289(6)	723(13)	191(5)	218(3)	-181(15)	598(12)	-55(8)
U 2	-0.20680(12)	0.24506(8)	0.23327(6)	684(13)	236(5)	219(3)	16(16)	537(11)	-37(8)
P 1	0.1692(8)	0.2752(5)	0.3259(4)	76(9)	25(4)	23(2)	-6(9)	60(8)	-4(5)
P 2	-0.3143(8)	0.2634(5)	0.3178(4)	68(9)	27(4)	28(2)	-2(9)	65(8)	0(5)

a) The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Uranium thermal parameters $x10^5$ are given and phosphorus thermal parameters $x\ 10^4$ are given.

Table 20 continued

ATOM	X	Y	Z	B,Å^2
C 1	-0.394(3)	0.301(2)	0.242(1)	3.0(6)
C 2	0.198(3)	0.370(2)	0.359(2)	5.0(8)
C 3	-0.158(3)	0.257(2)	0.340(1)	4.3(7)
C 4	0.021(3)	0.243(2)	0.310(1)	3.2(6)
C 5	0.232(4)	0.345(3)	0.517(2)	6.0(9)
C 6	0.122(4)	0.323(3)	0.515(2)	5.9(9)
C 7	0.090(4)	0.242(3)	0.492(2)	5.5(9)
C 8	0.181(3)	0.214(2)	0.478(2)	4.7(8)
C 9	0.265(4)	0.287(3)	0.494(2)	6.6(11)
C10	0.054(3)	0.506(2)	0.390(1)	3.6(7)
C11	0.036(4)	0.493(3)	0.440(2)	5.6(9)
C12	-0.102(3)	0.465(2)	0.400(2)	4.1(7)
C13	-0.150(3)	0.458(2)	0.335(1)	4.0(7)
C14	-0.050(3)	0.488(2)	0.330(1)	4.0(7)
C15	-0.345(4)	0.352(2)	0.135(2)	5.5(9)
C16	-0.304(4)	0.296(3)	0.105(2)	6.2(10)
C17	-0.168(4)	0.306(3)	0.146(2)	6.0(10)
C18	-0.135(4)	0.374(3)	0.190(2)	5.5(9)
C19	-0.247(4)	0.398(2)	0.184(2)	4.7(8)
C20	-0.154(4)	0.083(3)	0.219(2)	5.7(9)
C21	-0.228(4)	0.076(3)	0.249(2)	5.6(9)
C22	-0.349(4)	0.100(2)	0.207(2)	5.4(9)
C23	-0.363(4)	0.125(3)	0.152(2)	6.8(11)
C24	-0.245(4)	0.115(3)	0.160(2)	7.0(11)
C25	0.179(3)	0.284(2)	0.258(1)	3.0(6)
C26	0.141(3)	0.208(2)	0.219(2)	4.0(7)
C27	0.145(4)	0.213(2)	0.163(2)	5.2(9)
C28	0.200(4)	0.281(3)	0.157(2)	5.3(9)
C29	0.233(3)	0.347(2)	0.196(2)	5.1(8)
C30	0.229(3)	0.352(2)	0.248(2)	4.3(8)
C31	0.296(3)	0.199(2)	0.375(1)	2.5(6)
C32	0.268(3)	0.123(2)	0.382(1)	3.6(7)
C33	0.364(4)	0.065(3)	0.417(2)	5.6(9)
C34	0.492(4)	0.093(3)	0.450(2)	5.5(9)
C35	0.522(4)	0.167(2)	0.443(2)	5.2(8)
C36	0.425(3)	0.222(2)	0.405(2)	4.6(8)
C37	-0.379(3)	0.167(2)	0.325(1)	3.3(6)
C38	-0.514(3)	0.158(2)	0.288(2)	4.7(8)
C39	-0.568(4)	0.081(3)	0.289(2)	6.0(10)
C40	-0.491(4)	0.022(2)	0.324(2)	5.3(9)
C41	-0.356(4)	0.028(2)	0.362(2)	5.2(8)
C42	-0.304(3)	0.106(2)	0.360(2)	4.5(8)
C43	-0.339(3)	0.321(2)	0.368(2)	4.6(8)
C44	-0.259(3)	0.311(2)	0.438(2)	4.4(8)
C45	-0.275(4)	0.355(2)	0.480(2)	5.1(8)
C46	-0.364(4)	0.417(3)	0.453(2)	5.7(9)
C47	-0.438(4)	0.432(2)	0.391(2)	5.4(9)
C48	-0.428(3)	0.388(2)	0.344(2)	4.6(8)
EC 1	-0.006(7)	0.029(4)	0.487(3)	11.1(19)
EC 2	-0.052(13)	0.034(10)	0.535(6)	21.6(50)
EC 3	-0.092(17)	0.037(13)	0.559(8)	34.1(90)

TABLE 21

Positional and Thermal Parameters[a] with Standard Deviations for $[\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2 \cdot C_5H_{12}$

ATOM	X	Y	Z	β11	β22	β33	β12	β13	β23
U 1	0.13013(8)	0.15453(4)	0.23341(9)	398(6)	120(2)	635(11)	68(7)	-49(15)	-49(8)
U 2	0.29331(8)	0.16871(5)	0.45035(10)	506(7)	120(2)	598(10)	-53(7)	-85(15)	-91(9)
P 1	0.0912(6)	0.0722(4)	0.4223(8)	43(5)	19(2)	76(8)	-6(5)	6(10)	-7(7)
P 2	0.3529(6)	0.2263(3)	0.2377(8)	50(5)	22(2)	69(8)	-17(5)	-30(12)	7(7)
C 1	0.358(2)	0.262(1)	0.360(3)	9(3)	1(1)	10(3)	-3(2)	4(5)	0(2)
C 2	0.016(1)	0.115(1)	0.365(2)	1(1)	3(1)	7(3)	-2(2)	-2(4)	3(3)
C 3	0.280(1)	0.174(1)	0.250(2)	4(1)	1(0)	8(3)	-2(2)	1(4)	3(2)
C 4	0.190(2)	0.102(1)	0.389(2)	4(2)	3(1)	3(2)	0(2)	-7(3)	-2(2)

a) The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Uranium thermal parameters $x10^5$, phosphorus thermal parameters $x10^4$ and carbon thermal parameters $x10^3$ are given.

Table 21 continued

ATOM	X	Y	Z	B,Å^2
C 5	0.196(2)	0.092(1)	0.070(2)	4.3(7)
C 6	0.158(2)	0.052(1)	0.133(3)	5.8(9)
C 7	0.071(2)	0.061(1)	0.124(2)	4.6(8)
C 8	0.048(2)	0.106(1)	0.062(3)	5.5(8)
C 9	0.131(2)	0.127(1)	0.025(3)	6.8(9)
C10	0.132(2)	0.272(1)	0.255(2)	5.4(7)
C11	0.112(2)	0.265(1)	0.146(2)	5.0(8)
C12	0.030(2)	0.237(1)	0.136(2)	4.1(7)
C13	0.000(2)	0.230(1)	0.237(3)	5.8(8)
C14	0.059(2)	0.252(1)	0.310(2)	5.5(9)
C15	0.290(2)	0.214(1)	0.657(2)	5.6(8)
C16	0.211(2)	0.180(1)	0.640(2)	5.4(8)
C17	0.158(2)	0.206(1)	0.566(3)	5.7(8)
C18	0.196(2)	0.258(1)	0.538(3)	5.9(8)
C19	0.276(2)	0.260(1)	0.590(2)	5.1(8)
C20	0.422(2)	0.096(1)	0.395(2)	3.7(7)
C21	0.462(2)	0.144(1)	0.448(3)	5.6(8)
C22	0.439(2)	0.144(1)	0.559(3)	6.2(8)
C23	0.386(2)	0.094(1)	0.568(3)	5.5(8)
C24	0.373(2)	0.067(1)	0.476(3)	6.2(8)
C25	0.074(2)	0.063(1)	0.565(3)	5.2(8)
C26	0.135(2)	0.035(1)	0.624(3)	6.4(9)
C27	0.130(3)	0.026(1)	0.735(3)	8.3(10)
C28	0.060(3)	0.045(2)	0.782(4)	9.3(13)
C29	-0.004(3)	0.074(2)	0.723(4)	11.3(15)
C30	0.004(2)	0.085(1)	0.616(3)	7.4(11)
C31	0.081(2)	-0.004(1)	0.385(2)	4.7(7)
C32	0.149(2)	-0.036(1)	0.378(3)	5.9(9)
C33	0.142(2)	-0.098(1)	0.358(2)	5.2(8)
C34	0.060(2)	-0.118(1)	0.342(3)	5.9(9)
C35	-0.011(2)	-0.087(1)	0.345(3)	6.9(10)
C36	-0.007(2)	-0.025(1)	0.373(3)	7.1(10)
C37	0.333(2)	0.276(1)	0.131(3)	5.5(9)
C38	0.327(2)	0.249(1)	0.029(3)	7.7(11)
C39	0.321(2)	0.294(1)	-0.062(3)	8.2(11)
C40	0.321(2)	0.347(2)	-0.039(3)	8.9(11)
C41	0.325(2)	0.369(1)	0.056(3)	7.2(10)
C42	0.331(2)	0.334(2)	0.152(3)	8.1(11)
C43	0.455(2)	0.200(1)	0.197(2)	5.0(8)
C44	0.528(2)	0.238(1)	0.213(3)	7.1(10)
C45	0.606(3)	0.213(2)	0.184(4)	10.6(15)
C46	0.611(2)	0.157(2)	0.133(3)	9.3(12)
C47	0.537(3)	0.127(1)	0.117(3)	8.1(11)
C48	0.459(2)	0.146(1)	0.149(3)	6.8(9)
PC1	0.746(9)	0.065(6)	0.370(12)	28.5(64)
PC2	0.674(8)	0.054(5)	0.394(11)	30.8(55)
PC3	0.729(8)	0.076(5)	0.510(10)	26.1(44)
PC4	0.644(6)	0.056(4)	0.557(9)	24.2(39)
PC5	0.711(8)	0.043(4)	0.648(9)	28.5(47)

TABLE 22

Bond Lengths for $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2$

Atoms	Distance, Å		Atoms	Distance, Å	
	Structure I	Structure II		Structure I	Structure II
U(1)-C(2)	2.66(4)	2.65(3)	U(2)-C(19)	2.73(4)	2.79(3)
U(1)-C(3)	2.45(4)	2.45(2)	U(C)-C(20)	2.81(4)	2.77(3)
U(1)-C(4)	2.55(4)	2.53(3)	U(2)-C(21)	2.86(4)	2.77(3)
U(2)-C(1)	2.67(4)	2.67(3)	U(2)-C(22)	2.84(4)	2.78(3)
U(2)-C(3)	2.48(4)	2.57(3)	U(2)-C(23)	2.76(5)	2.74(3)
U(2)-C(4)	2.41(4)	2.40(3)	U(2)-C(24)	2.71(5)	2.74(3)
U(1)-C(5)	2.73(5)	2.77(3)	P(1)-C(2)	1.72(4)	1.74(3)
U(1)-C(6)	2.72(5)	2.77(3)	P(1)-C(4)	1.76(4)	1.79(3)
U(1)-C(7)	2.74(5)	2.78(3)	P(1)-C(25)	1.83(4)	1.86(3)
U(1)-C(8)	2.79(4)	2.80(3)	P(1)-C(31)	1.85(3)	1.85(3)
U(1)-C(9)	2.70(5)	2.74(4)	P(2)-C(1)	1.73(4)	1.78(3)
U(1)-C(10)	2.78(3)	2.77(2)	P(2)-C(3)	1.72(4)	1.70(2)
U(1)-C(11)	2.84(4)	2.83(3)	P(2)-C(37)	1.84(4)	1.82(3)
U(1)-C(12)	2.82(4)	2.80(3)	P(2)-C(43)	1.78(4)	1.83(3)
U(1)-C(13)	2.79(4)	2.73(3)	groups[a]		
U(1)-C(14)	2.82(4)	2.73(3)	U(1)-11	2.53	2.49
U(2)-C(15)	2.76(4)	2.84(3)	U(1)-12	2.46	2.49
U(2)-C(16)	2.92(5)	2.77(3)	U(2)-21	2.51	2.52
U(2)-C(17)	2.76(5)	2.76(3)	U(2)-22	2.52	2.47
U(2)-C(18)	2.79(5)	2.84(3)			

a. Group 11 = cp ring C(5)-C(9), group 12 = cp ring C(10)-C(14), group 21 = cp ring C(15)-C(19) and group 22 = cp ring C(20)-C(24).

TABLE 23

Selected Bond Angles for $[\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2$

Atoms	Angles, deg.		Atoms	Angles, deg.		Groups[a]	Angles, deg.	
	Structure I	Structure II		Structure I	Structure II		Structure I	Structure II
C(2)-U(1)-C(3)	130(1)	133.4(9)	C(2)-P(1)-C(4)	106(12)	107(1)	11-U(1)-12	119	119
C(4)-U(2)-C(1)	130(1)	131(1)	C(3)-P(2)-C(1)	103(12)	106(1)	11-U(1)-C(2)	104	103
C(2)-U(1)-C(4)	65(1)	66.4(9)	C(2)-P(1)-C(31)	114(2)	113(1)	11-U(1)-C(3)	106	104
C(1)-U(2)-C(3)	63(1)	64.2(8)	C(1)-P(2)-C(43)	114(2)	112(2)	11-U(1)-C(4)	112	109
C(4)-U(1)-C(3)	68(1)	69.4(9)	C(4)-P(1)-C(25)	116(2)	114(1)	12-U(1)-C(2)	95	95
C(4)-U(2)-C(3)	70(1)	69.5(8)	C(3)-P(2)-C(37)	114(2)	114(1)	12-U(1)-C(3)	103	104
U(2)-C(3)-U(1)	101(1)	99.2(9)	C(25)-P(1)-C(31)	101(2)	98(1)	12-U(1)-C(4)	128	131
U(2)-C(4)-U(1)	100(1)	102(1)	C(37)-P(2)-C(43)	97(2)	99(1)	21-U(2)-22	116	119
P(1)-C(4)-U(1)	93(1)	92(1)	C(2)-P(1)-C(25)	108(2)	112(1)	21-U(2)-C(1)	96	94
P(2)-C(3)-U(2)	97(2)	94(1)	C(1)-P(2)-C(37)	114(2)	112(1)	21-U(2)-C(3)	134	133
P(1)-C(4)-U(2)	144(2)	142(1)	C(4)-P(1)-C(31)	111(2)	113(1)	21-U(2)-C(4)	104	106
P(2)-C(3)-U(1)	140(2)	143(1)	C(3)-P(2)-C(43)	116(2)	114(1)	22-U(2)-C(1)	105	104
P(1)-C(2)-U(1)	90(2)	89(1)				22-U(2)-C(3)	108	107
P(2)-C(1)-U(2)	90(1)	89(1)				22-U(2)-C(4)	105	104

a) See footnote in Table 22

TABLE 24

Cyclopentadienyl and Phenyl C-C Bond Distances(Å)
and Standard Deviations

Atoms	Structure I	Structure II
C 5-C 6	1.42 (7)	1.38 (4)
C 6-C 7	1.42 (6)	1.43 (5)
C 7-C 8	1.45 (6)	1.38 (4)
C 8-C 9	1.51 (7)	1.49 (5)
C 9-C 5	1.32 (7)	1.45 (4)
C10-C11	1.45 (6)	1.43 (4)
C11-C12	1.51 (6)	1.48 (4)
C12-C13	1.44 (6)	1.39 (5)
C13-C14	1.44 (6)	1.42 (5)
C14-C10	1.40 (6)	1.44 (5)
C15-C16	1.46 (7)	1.51 (5)
C16-C17	1.43 (7)	1.42 (4)
C17-C18	1.49 (7)	1.40 (4)
C18-C19	1.40 (7)	1.44 (5)
C19-C15	1.40 (6)	1.40 (4)
C20-C21	1.52 (7)	1.46 (4)
C21-C22	1.35 (7)	1.46 (5)
C22-C23	1.39 (7)	1.44 (4)
C23-C24	1.40 (8)	1.35 (5)
C24-C20	1.40 (7)	1.47 (4)
C25-C26	1.50 (5)	1.40 (5)
C26-C27	1.47 (6)	1.44 (6)
C27-C28	1.37 (6)	1.36 (6)
C28-C29	1.37 (6)	1.44 (7)
C29-C30	1.39 (6)	1.40 (7)
C30-C25	1.38 (5)	1.39 (5)
C31-C32	1.34 (5)	1.33 (4)
C32-C33	1.40 (6)	1.49 (4)
C33-C34	1.42 (7)	1.40 (5)
C34-C35	1.31 (6)	1.36 (5)
C35-C36	1.39 (6)	1.50 (5)
C36-C31	1.40 (6)	1.51 (5)
C37-C38	1.42 (6)	1.46 (5)
C38-C39	1.45 (6)	1.58 (5)
C39-C40	1.30 (7)	1.29 (5)
C40-C41	1.42 (7)	1.31 (6)
C41-C42	1.47 (6)	1.48 (5)
C42-C37	1.33 (5)	1.38 (5)
C43-C44	1.49 (6)	1.45 (5)
C44-C45	1.42 (6)	1.42 (6)
C45-C46	1.38 (6)	1.46 (6)
C46-C47	1.35 (7)	1.39 (6)
C47-C48	1.47 (6)	1.40 (6)
C48-C43	1.44 (6)	1.41 (4)

TABLE 25

Cyclopentadienyl and Phenyl C-C Bond Angles(Deg.)
and Standard Deviations

Atoms	Structure I	Structure II
C 9-C 5-C 6	111 (4)	107 (3)
C 7-C 6-C 5	107 (4)	107 (3)
C 8-C 7-C 6	110 (4)	115 (3)
C 9-C 8-C 7	102 (4)	101 (3)
C 8-C 9-C 5	110 (4)	110 (3)
C14-C10-C11	116 (4)	105 (3)
C12-C11-C10	98 (4)	110 (3)
C13-C12-C11	113 (4)	106 (3)
C14-C13-C12	106 (3)	110 (3)
C13-C14-C10	107 (4)	110 (3)
C19-C15-C16	114 (4)	101 (3)
C17-C16-C15	101 (4)	111 (2)
C18-C17-C16	110 (4)	106 (3)
C19-C18-C17	108 (4)	108 (3)
C18-C19-C15	106 (4)	113 (3)
C24-C20-C21	103 (4)	106 (2)
C22-C21-C20	108 (4)	109 (2)
C23-C22-C21	110 (4)	104 (3)
C24-C23-C22	108 (5)	114 (3)
C23-C24-C20	111 (5)	107 (3)
C30-C25-C26	123 (3)	119 (3)
C27-C26-C25	116 (3)	124 (3)
C28-C27-C26	117 (4)	116 (4)
C29-C28-C27	122 (4)	121 (4)
C30-C29-C28	126 (4)	122 (4)
C29-C30-C25	114 (4)	118 (4)
C36-C31-C32	119 (3)	125 (3)
C33-C32-C31	121 (4)	120 (3)
C34-C33-C32	117 (4)	116 (3)
C35-C34-C33	122 (4)	126 (3)
C36-C35-C34	120 (4)	120 (3)
C35-C36-C31	120 (4)	113 (3)
C42-C37-C38	120 (4)	127 (3)
C39-C38-C37	119 (4)	111 (3)
C40-C39-C38	119 (4)	119 (4)
C41-C40-C39	125 (4)	126 (4)
C42-C41-C40	115 (4)	124 (3)
C41-C42-C37	122 (4)	113 (3)
C48-C43-C44	116 (4)	124 (3)
C45-C44-C43	125 (4)	117 (3)
C46-C45-C44	115 (4)	120 (4)
C47-C46-C45	124 (4)	118 (4)
C48-C47-C46	124 (4)	124 (4)
C47-C48-C43	115 (4)	116 (3)

TABLE 26

Bond Lengths and Angles for the Solvate Molecules

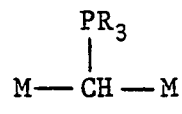
Pentane

Atoms	Distance, Å	Atoms	Angle, deg.
C(1)-C(2)	1.2(2)	C(1)-C(2)-C(3)	70(11)
C(2)-C(3)	1.8(2)	C(2)-C(3)-C(4)	78(8)
C(3)-C(4)	1.6(2)	C(3)-C(4)-C(5)	76(8)
C(4)-C(5)	1.6(2)		

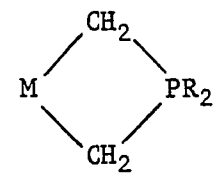
Diethyl Ether

C(1)-C(2)	1.7(2)	C(1)-C(2)-C(3)	172(20)
C(2)-C(3)	1.0(3)		

into the molecule. Each ylide is bonded to both uranium atoms, chelating one and bridging to the second with a single carbon. This mode of ylide attachment is unique in phosphorus ylide chemistry but might be considered as a hybrid of A and B



A



B

which are bonding schemes seen in other metal-ylide complexes.

The U-C bonds in the M-C-M bridge, 2.43(1) Å and 2.53(2) Å, are both within the range found for U-C σ bonds in several triscyclopentadienyluranium alkyl complexes: $(C_5H_5)_3U((CH_2)_2CH_3)$,[90] 2.48(3) Å; $(C_5H_5)_3U\text{-}C_4H_9$,[91] 2.43(2) Å; and $(C_5H_5)_3U\text{-}CH_2(p\text{-}CH_3C_6H_4)$;[92] 2.54(2) Å. Thus the bridging carbon can be considered to be σ bonded to both uranium atoms. Such an arrangement is unique in organoactinide chemistry. The most similiar case is $(\eta^5\text{-}(C_5H_5)_2Th(\eta^5, \eta^1\text{-}C_5H_4)_2$[68] where a cyclopentadienyl group bridges between two thorium atoms, being bonded to one via a Th-C σ bond, but in a pentahapto fashion to the second. In contrast to the uranium-methine bonds, the uranium bond to the non-bridging methylene group is somewhat longer, 2.662(5) Å and, in fact, is closer to the bond length observed between uranium and pentahaptocyclopentadienyl groups (range 2.68 to 2.74 Å, Table 27).

The conformation of the U-C-P-C ring is also significant with respect to the nature of the uranium-methylene bond. As shown in Figure 37, the C-U-C plane is folded by about 27° (Table 28) with

TABLE 27

Average Bond Distances (Å) in
Organouranium (IV) Complexes

Compound	U-C(C_5H_5 ring)	Ref.
structure I	2.78(1)	This work
structure II	2.776(7)	This work
$(C_5H_5)_3U[CH_3C(CH_2)_2]$	2.74(1)	90
$(C_5H_5)_3U$(n-butyl)	2.736(8)	91
$(C_5H_5)_3U[CH_2(p\text{-}CH_3C_6H_4)]$	2.722(4)	91
$(C_5H_4CH_2C_6H_5)_3UCl$	2.733(1)	92
$(C_5H_5)_3U(C_2C_6H_5)$	2.68	93
$(C_5H_5)_3UF$	2.74	94
$(C_5H_5)_3UCl$	2.74	95
$LiU_2Cl_5[CH_2(C_5H_4)_2]_2 \cdot 2THF$	2.72	37
$(C_5H_5)_4U$	2.81	96

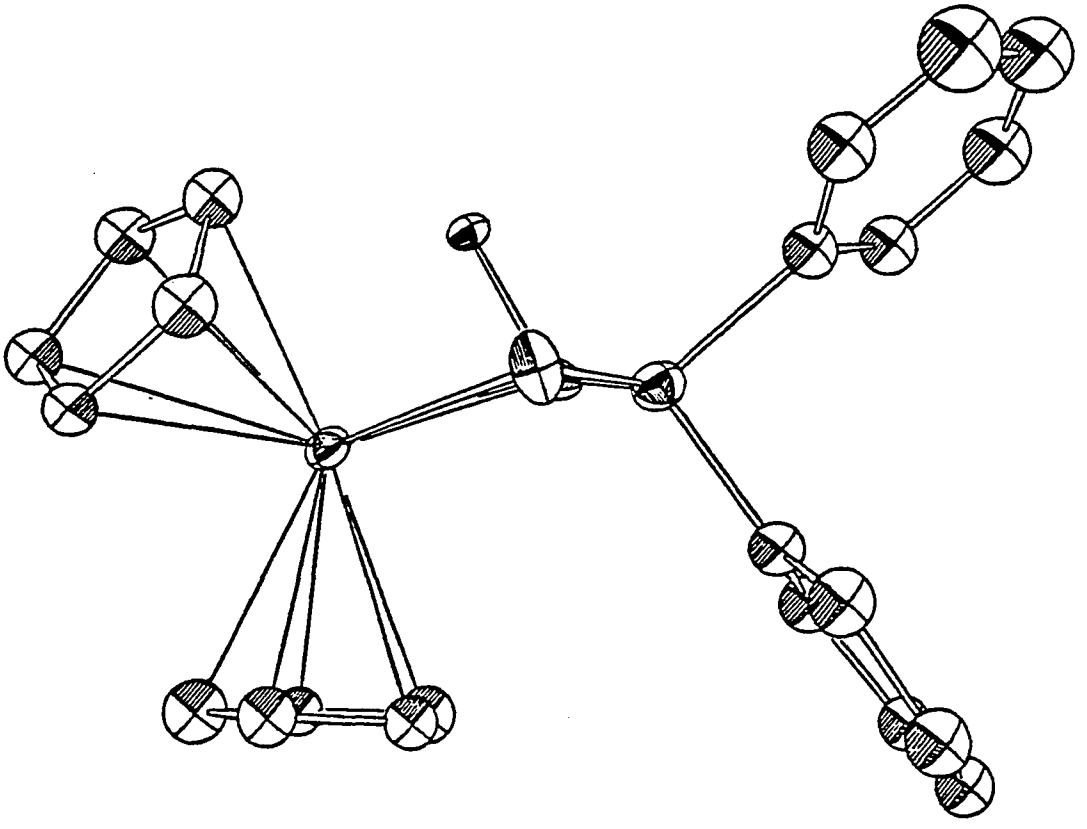


Figure 37. A view showing the fold angle about the C-U-C and C-P-C planes. A portion of the molecule has been removed for clarity. Ellipsoids of 20% probability are shown.

TABLE 28

Fold Angle about the U-C-P-C Ring

Atoms Defining plane (I)	Atoms Defining plane (II)	Fold angle, deg.	
		Structure I	Structure II
C(2),P(1),C(4)	C(2),U(1),C(4)	27	25
C(1),P(2),C(3)	C(1),U(2),C(3)	28	27

respect to the C-P-C plane. This has been observed before in a nickel complex[97] where the fold angle is 44° and the ylide was described as bonding in a "pseudo-phosphaallyl" fashion. The P-C methine and P-C methylene bonds are both 1.74(1) Å, typical for such groups in other ylides, and are shorter than the typical 1.87 Å P-C single bond length in phosphorus alkyls,[98] and the 1.83(1) Å P-C bonds to the phenyl rings. Thus it is likely that the U-C methylene bond should not be considered as a σ bond, but rather to have formed via interaction of metal orbitals with a π system on the ylide. The disparity in fold angles between I and II and the nickel complex mentioned above are probably the result of steric interactions between C_5H_5 and phenyl groups which preclude the formation of a more acute angle in I and II.

Within the uranium ylide chelate ring most of the bond angles and distances are similiar to those found in transition metal phosphoylide[44] structures. The main exception is the C-U-C angle (64.6(6)°) which is about 15° less than typical values in other chelating structures. This probably is the result of the larger size of the actinide and, perhaps, to steric interactions between cyclopentadienyl and phenyl moieties which prevent a closer approach of the ylide. The C(phenyl)-P-C(phenyl) angle (98.8(1)°) is somewhat collapsed[98] and may indicate such a steric interaction. It is also noteworthy that the U-C(methine)-P angle is highly distorted from tetrahedral to an average bond angle of 142.5(8)° which is indicative of the strains introduced upon complexation of the ylide.

The average U-C(cyclopentadienyl) distance is 2.78(1) Å in I and 2.776(7) Å in II. These are somewhat longer than the average U-C bond

in the triscyclopentadienyluranium complexes (Table 27) and may also reflect large steric interactions within the molecule. However, they are shorter than the 2.81 Å U-C bond length in $U(C_5H_5)_4$,[96] a severely crowded molecule. The average ring centroid-U-ring centroid angle of 118° is essentially the same as that found in the triscyclopentadienyl-uranium complexes[90] and indicates that steric strains are not relieved by compression of these groups.

The overall geometry about each uranium is approximately tetrahedral if the two η^5-C_5H_5 groups, the chelating ylide, and the bridging methine carbon atom on the remaining ylide are considered to define the vertices of a polyhedron. The U-U separation (3.810(2) Å in I and 3.824(2) Å in II) is at the limit of van der Waals' interactions for neutral uranium atoms, 3.8 Å, indicating that a U-U bond is highly unlikely. Thus if each cyclopentadienyl group is considered to occupy three coordination sites, the chelating phosphoylide to occupy two sites and the bridging methine carbon to occupy one site, then each uranium is nine coordinate. This is the first example of a nine coordinate U(IV) organometallic compound. This is noteworthy because organoactinides tend to be ten coordinate.[35,100]

The complex is chiral. The space group of I, however, is achiral and the crystal is thus racemic. On the other hand, crystals of II contain only a single enantiomer, and the one present in the crystal studied here is shown in Figure 36. Both methine carbon atoms are centers of chirality and are of the same absolute configuration. Using standard sequence-rule procedures[101,102] we have been unable to assign priorities to the two uranium containing substituents, even though

relative to an individual methine carbon atom, they are clearly distinct in a topological sense. We have therefore assigned the uranium atom which is not chelated by the ylide containing the carbon atom whose configuration is being sought a higher priority than the one which is chelated by this ylide. Making this assignment gives both methine carbons the S configuration. There is also a helical axis of chirality colinear with the molecular twofold axis. The helix is left-handed and therefore M.

The solvate molecule in both structures does not associate with the uranium dimer. This can be seen in the stereoviews of the two structures in Figure 38 and 39. In structure I the closest interatomic contact of the partial diethyl ether solvate within the asymmetric unit is 4.45 Å distance to a phenyl carbon. The closest contact to the dimmer in an adjacent cell is 3.55 Å to a cyclopentadienyl carbon. In structure II the pentane molecule would not be expected to interact with the dimer and is not found to do so. The closest contact is 3.88 Å with a cyclopentadienyl carbon. Both of the solvate molecules are poorly determined with high thermal parameters. As a result their structural parameters are characterized by large errors and are of little merit.

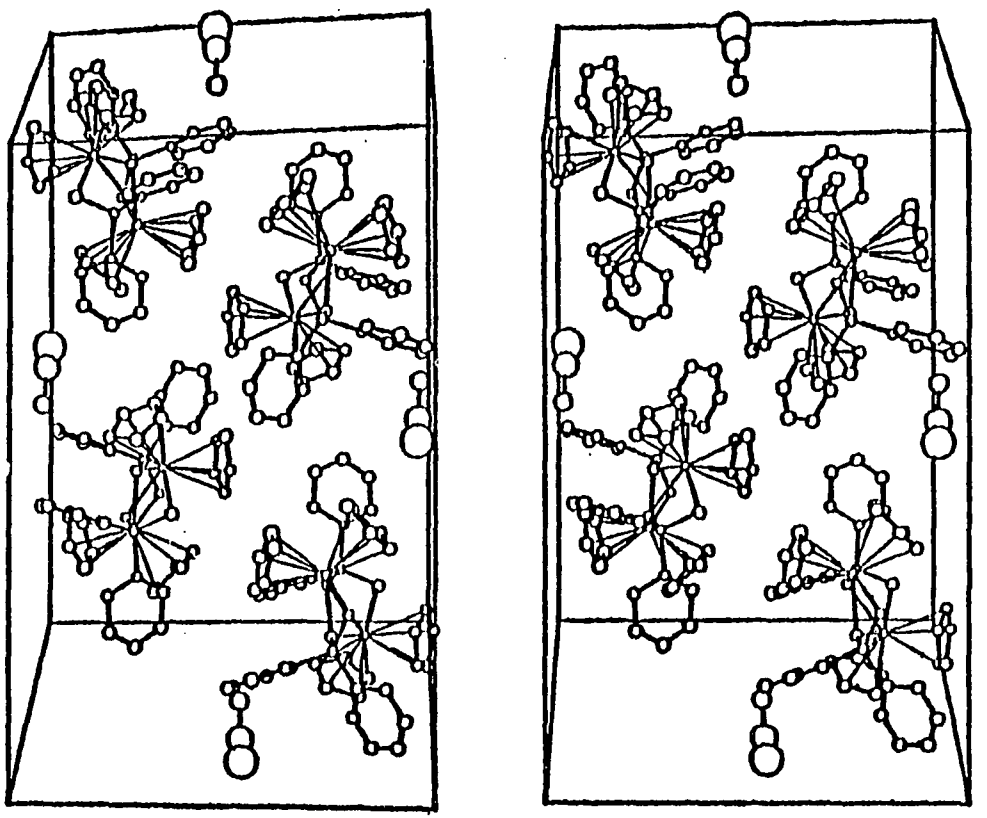


Figure 38. A stereoview (ORTEP-II) of the contents of a unit cell of $[\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2 \cdot (C_2H_5)_2O$. The b axis is horizontal, the c axis is vertical and the view is along the a axis. Ellipsoids of 20% probability are used.

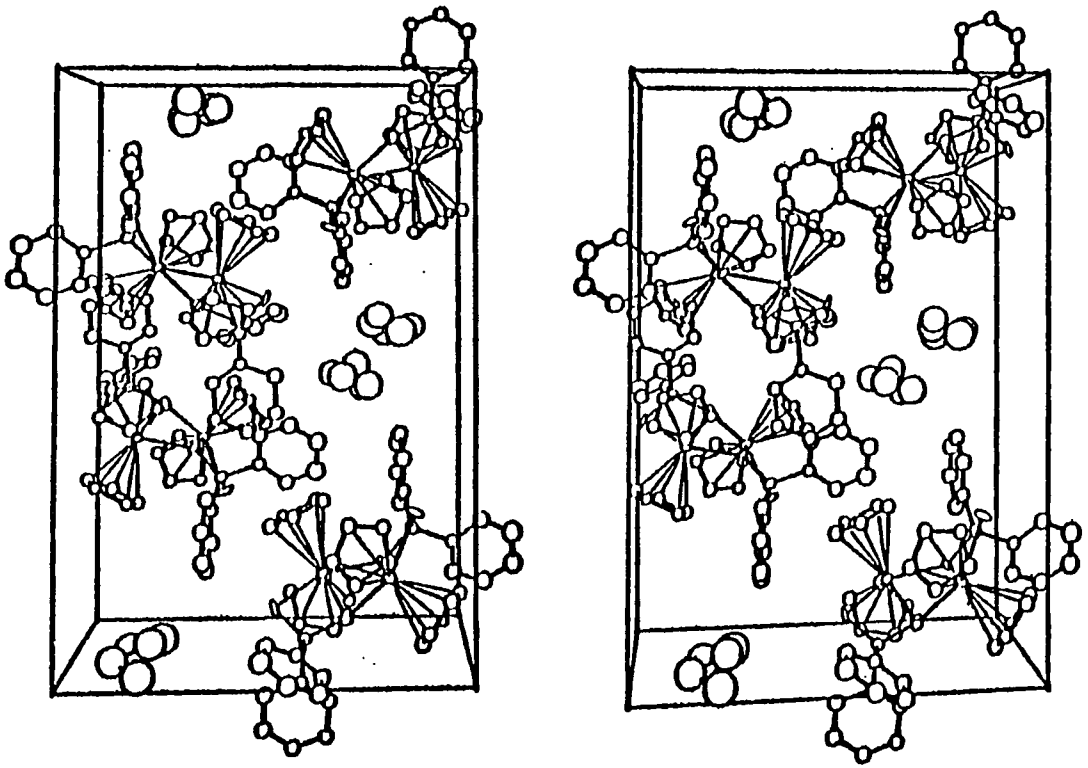


Figure 39. A stereoview (ORTEP-II) of the contents of a unit cell of $[\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2]_2 \cdot C_5H_{12}$. The a axis is horizontal, the b axis is vertical and the view is along the c axis. Ellipsoids of 20% probability are used.

VI. FUTURE WORK

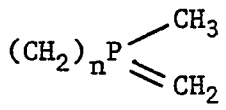
This investigation has shown that phosphorus ylides can serve as suitable ligands for the snythesis of stable organouranium complexes containing σ bonds. Since this study was the first of its kind it is by no means comprehensive. Rather it should be considered as a source of motivation for further developement of this new and novel class of organoactinide compounds.

Several of the complexes already prepared bear further study. For example, a structural determination via x-ray crystallography should be done on at least one of the triscyclopentadienyluraniumphosphoylide complexes. We previously attempted a structural determination on $(C_5H_5)_3UCHP(CH_3)(C_6H_5)_2$; unfortunately, these crystals were plagued by twinning and a structural determination was not possible. Recently we have prepared and mounted crystals of $(C_5H_5)_3UCHP(CH_3)_2(C_6H_5)$ and hopefully these will prove to be of x-ray diffraction quality. It would be interesting to compare the structure of this complex to that of the triscyclopentadienyluranium alkyl complexes. Perhaps this may give an indication of the greater reactivity of the triscyclopentadienyluraniumphosphoylide complexes toward coordinatively unsaturated molecules such as carbon monoxide.

In this regard, a structural determination of the carbon monoxide insertion product of these complexes would be illuminating. This would establish the manner of coordination of the insertion product which we have assigned as a side-bonded acyl group. In addition if our assignment is correct it would be interesting to see how the cyclopentadienyl groups have reoriented themselves to allow an eleventh

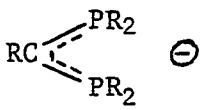
coordination site to become available for bonding. We have prepared crystalline material of $(C_5H_5)_3U(CO)CHP(CH_3)(C_6H_5)_2$ and $(C_5H_5)_3U(CO)CHP(CH_3)_2(C_6H_5)$ and expect a structure determination to begin in the near future.

During this study we limited ourselves to using only several phosphorus ylides. However, there are several different types of phosphorus ylides which could be used as ligands. In addition to the double ylides mentioned previously, heterocyclic ylides (A) or bisphosphinomethanide ylides (B) could be used.[75] The use of lithiated



n = 5 or 6

A



B

ylides containing the bulkier tert-butyl group in place of the phenyl groups should allow the preparation of more complexes similiar to $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2$.

The ylides thus far described all contain phosphorus as the heteroatom. However ylides containing other heteroatoms such as arsenic, sulfur or selenium are also known. It should prove to be a straightforward extension of our previous work to use these ylides as ligands.

Besides using different ylides one could also use different organouranium starting materials. Several attractive compounds are $(C_2B_9H_{11})_2UCl_2^{2-}$ [24], $(CH_2(C_5H_4)_2)U_2Cl_5^{1-}$ [37] or $((CH_3)_5C)_2UCl_2$ [38]. Extension of this work to thorium would provide diamagnetic compounds

of similiar chemical properties which would alleviate some of the problems associated with paramagnetic broadening in the uranium system.

Aside from preparing new organoactinidephosphoylide complexes the chemistry of those already prepared should be studied further. In particular, the reactivity toward small molecules such as hydrogen, silanes or olefins should be investigated. The high affinity of uranium for oxygen would make molecules such as carbon dioxide and sulfur and nitrogen oxides attractive candidates for insertion reactions of the type already seen for carbon monoxide. In addition their interaction with carbonyl functional groups of organic compounds in a Wittig type manner also bears investigation.

APPENDIX A

Listing of the Observed and Calculated Structure Factors for $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2 \cdot (C_2H_5)_2O$ After Full Matrix Least Squares Refinement

Data is given in four columns per page in groupings of common h and k Miller indices for running values of the l Miller indices. For each h, k, l datum the input structure factor $10(F_o)$ is given first followed by the calculated structure factor $10(F_c)$.

H= 0. K= 0			7	1531	1953
4	570	-764	10	1278	-1614
6	1246	-1688	11	756	-967
8	2317	2863	12	1380	1437
10	547	626	13	562	-658
12	646	676	15	718	693
14	1873	-2043	17	678	502
18	1368	1331	20	831	-778
24	1255	-813	21	575	-550
			22	889	709
H= 0. K= 1					
3	510	-873	H= 0. K= 5		
4	1688	2375	1	852	954
5	1128	-1528	2	1581	-1661
6	2110	-2994	3	407	-646
9	898	1111	4	616	-880
10	1271	-1478	6	482	676
12	3028	3488	7	446	-595
14	1478	-1581	8	2595	3344
15	794	-906	9	509	650
18	1101	-921	10	2247	-2850
19	565	653	11	459	477
20	1282	1135	12	491	645
			14	953	-1085
H= 0. K= 2			16	2018	1940
0	5025	-6328	17	594	604
1	1454	1669	22	963	-744
2	2276	3598	24	687	478
3	1783	2732			
4	1226	-1773	H= 0. K= 6		
5	925	-1167	2	4313	3635
6	1062	1611	4	3206	-4259
7	1500	-1995	7	566	785
8	1716	-2159	8	413	461
11	1102	1255	10	1859	2240
12	688	-827	11	445	-509
13	920	1129	12	966	-976
14	1019	995	14	883	-948
15	990	-1051	18	509	474
17	705	-705	20	990	758
18	779	-625	22	1069	-788
21	756	640			
24	854	584	H= 0. K= 7		
			1	1273	1351
H= 0. K= 3			2	2358	2147
1	2865	-2469	5	1763	-2346
2	587	739	7	542	611
5	1054	1537	8	2021	-2696
8	1515	-1934	9	944	1130
9	1552	-1991	10	1442	1832
10	1899	2359	13	873	-854
11	522	-681	14	1063	1132
12	1773	-2066	16	1651	-1666
13	658	686	19	752	684
14	1145	1396	22	940	607
15	1089	1077			
16	1060	-1165	H= 0. K= 8		
18	682	487	0	1646	1894
19	700	-635	1	1621	1710
20	610	-449	2	2566	-2548
22	712	469	3	1632	1465
23	778	498	4	1559	1937
			7	1969	-2678
H= 0. K= 4			10	775	-1072
0	1466	1721	11	1099	1354
1	2207	-2144	15	610	-410
2	2409	-2853	17	871	-779
3	1132	-1578	20	677	-480
4	2469	3609	21	846	571
5	568	816	22	714	414

H= 0. K= 9		
1	1169	-1375
2	545	531
5	2039	2538
6	955	-1285
8	766	980
9	1198	-1656
10	859	-1166
12	1373	1621
13	1150	1302
14	777	-830
18	742	-638
19	966	-806
20	765	650
H= 0. K= 10		
0	2259	-2930
1	584	-765
2	1258	1386
3	1172	-1035
6	1276	1699
7	1432	1988
8	1153	-1481
11	775	-839
14	810	921
18	706	-606
H= 0. K= 11		
2	1372	-1480
3	504	503
4	1130	-1036
5	660	-931
6	1334	1748
12	1735	-2112
14	751	847
17	628	-387
18	891	900
20	1043	-852
H= 0. K= 12		
0	2283	2900
2	952	-971
3	880	-867
5	883	977
6	1619	-1892
8	916	1177
10	584	644
11	511	-580
14	944	-922
18	646	739
H= 0. K= 13		
1	851	1113
2	654	835
3	783	-888
4	599	699
5	800	-664
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-19	942	-986	-2	664	723				5	848	811
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-12	767	688	-24	810	843	H= 8, K= 0			-26	703	607
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-1	766	-716	0	1147	-1178	-16	944	823	-17	838	-835
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6	893	854	-16	755	708	0	1349	-1297	-10	490	332
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-14	1222	-1210	-2	642	-407	-21	676	-603	2	991	-1036
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-10	1744	-1809				-15	865	816	6	561	-563
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-20	631	556	-8	1214	-1205	-4	1040	1116	-20	1989	-2007
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-18	631	535	-4	2188	2187	2	903	-829	-14	2397	2456
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-9	1527	1626				-8	1108	1119	H=	9, K=	1
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1	948	969	-15	587	510	H=	8, K=	12	-19	624	-567
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-2	2457	-2426	6	813	707				-2	904	951
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-21	544	-551	-13	1256	-1205	-9	822	849	-21	1017	1078
-20	1122	-1174	-12	2039	2030	-8	1080	-975	-19	990	1020
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-15	1563	-1547
-14	1296	-1352
-12	1357	1330
-11	1773	1858
-10	1267	-1397
-8	885	954
-7	1114	-1187
-6	933	-1018
-5	1067	-1142
-4	1527	1533
-3	803	765
-2	1328	-1416
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2	643	-776
3	789	-822

H= 9, K= 4

-30	653	609
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-24	1715	-1586
-23	944	-902
-22	1410	1283
-21	604	-568
-18	1094	1016
-17	1282	1260
-16	1921	-1935
-14	966	915
-13	1281	-1355
-12	563	-609
-10	1658	1720
-9	990	1066
-8	622	-517
-7	774	804
-6	1282	-1278
-5	711	-718
-3	893	-918
0	870	762
1	988	1005
2	1086	-1054
6	662	-472
8	819	813

H= 9, K= 5

-28	911	810
-22	1465	-1419
-18	1700	1756
-16	698	-683
-15	818	826
-12	2380	-2482
-11	1002	-1091
-10	1605	1748
-6	1026	1055
-5	583	671
-4	2314	-2320
-2	713	646
2	1198	1203
4	711	-578

H= 9, K= 6

-24	1853	1754
-22	1232	-1164
-18	1110	-1104
-16	2295	2261
-10	2068	-2082
-8	853	774
-6	1526	1534
0	1215	-1253
2	1088	1080
8	1003	-958

H= 9, K= 7

-25	592	531
-22	906	917
-21	923	-891
-18	1175	-1255
-15	878	916
-12	1960	1979
-10	1903	-1891
-9	801	-716
-7	879	953
-6	823	-924
-4	1730	1720
-2	637	-621
-1	594	-782
2	994	-1007

H= 9, K= 8

-27	723	-620
-26	677	510
-24	1236	-1003
-23	709	696
-22	900	948
-21	656	742
-20	561	-535
-19	908	-979
-18	667	789
-17	848	-797
-16	1058	-1077
-14	845	817
-13	1057	1244
-12	596	-522
-10	852	873
-9	1007	-1056
-7	678	-543
-6	699	-537
-5	841	909
-3	980	985
-2	584	-530
-1	625	-638
0	783	798
1	579	-445
5	827	739
6	621	-509

H= 9, K= 9

-25	671	-682
-23	673	-498
-21	954	958
-19	619	583
-17	630	-578
-16	864	-823
-15	1288	-1286
-14	1386	1376
-12	757	-774
-10	723	736
-9	875	939
-8	1029	-1134
-7	1359	-1334
-6	1243	1228
-5	653	-593
-4	726	-830
-2	873	887
-1	879	952
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3	612	-414

H= 9, K= 10

-26	997	-862
-22	735	-617
-21	904	-827
-20	1498	1402
-19	816	891
-18	748	-629
-14	1076	-1079
-13	767	-836
-12	1299	1323
-9	776	680
-7	783	702
-6	627	-628
-3	766	-731
-2	1147	1137
4	877	-831

H= 9, K= 11

-22	891	-758
-18	755	653
-16	901	898
-14	1741	-1777
-9	593	-762
-8	1697	1813
-7	796	612
-6	923	-887
-2	1052	-1019
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H= 9, K= 12

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-12	998	-1113
-10	681	-553
-9	588	367
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-2	1317	-1137

H= 9, K= 13

-19	647	-648
-16	674	-722
-15	616	640
-14	1131	1054
-11	1040	-1115
-9	637	258
-8	1277	-1359
-6	688	641
-5	678	723
-2	907	825
0	620	-745

H= 9, K= 14

-17	982	-1057
-13	815	781
-9	671	-750
-2	707	356

H= 9, K= 15

-12	846	768
-11	908	1022
-10	795	-932

H= 10, K= 0

-28	1194	-1090
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-20	1283	-1355
-18	633	-581
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-10	2305	-2442
-8	1457	1577
-4	1363	1427
-2	1427	-1577
4	1304	1256

H= 10, K= 1

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-28	828	-793
-24	679	-620
-22	2210	2183
-20	1091	-1125
-19	793	-777
-16	1780	-1930
-15	866	921
-14	1766	1891
-11	610	-640
-8	1721	-1819
-4	873	999
-1	581	-573
2	1016	-1055

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-27	832	-742
-26	749	-734
-23	999	929
-21	769	835
-20	763	769
-19	618	-567
-17	853	-918
-16	885	-920
-14	513	285
-13	1282	1343
-12	666	-795
-11	597	509
-10	1701	1809
-9	1058	-1093
-8	1337	-1462
-7	757	-815
-6	593	461
-4	960	-1053
-3	840	757
-2	1220	1274
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1	928	-815
4	951	-860

H= 10, K= 3

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-24	910	806
-23	667	-639
-22	1080	-1126
-21	694	785
-20	1351	1360
-19	1109	1165
-18	1313	-1292
-16	928	999
-15	1107	-1239
-14	858	-877
-12	1128	1098
-11	1322	1372
-10	937	-953
-9	964	953
-7	1039	-1051
-5	864	-990
-1	938	934
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H= 10, K= 4

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-24	816	-891
-23	885	-823

-21	732	-850	-12	817	862	-24	2019	1983	-26	821	-652
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-13	911	-1011	-4	800	640	-12	886	995	-20	1616	1714
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-11	526	-605	-2	709	-597	-10	2184	-2463	-17	721	817
-9	951	966	0	951	885	-8	711	786	-16	534	486
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-12	1753	-1901	-8	553	-748	-6	1228	-1397	-14	749	-967
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-19	581	-520	-20	903	-963	-19	781	1041	-5	889	899
-18	1643	-1810	-16	979	1003	-15	1189	-1244	-2	1083	1086
-15	1133	1216	-10	1342	-1470	-14	805	787	0	801	-795
-12	1374	1525	-5	671	-669	-12	731	-828			
-11	824	-837	-4	997	1040	-11	829	903	H=	11.	K= 8
-10	741	-912	-2	1262	-1161	-10	762	748	-22	997	-920
-7	560	586				-9	1070	1090	-21	710	656
-5	582	643	H=	10.	K= 13	-8	744	-779	-20	1011	1044
-2	901	790	-19	699	-773	-7	530	-609	-17	1540	-1646
-1	610	-590	-16	874	-1032	-6	859	871	-16	641	596
0	889	-868	-14	1055	1001	-5	962	-920	-14	1153	-1192
			-11	896	-868	-4	802	-812	-13	587	802
H=	10.	K= 8				-2	823	898	-12	960	856
-27	681	-739	H=	10.	K= 14	-1	774	763	-8	737	896
-23	624	556	-13	756	957	0	844	-915	-7	748	-756
-21	763	726	-7	725	-845	2	800	643	-6	720	-694
-17	1295	-1361							-3	850	798
-14	709	-806	H=	11.	K= 0	H=	11.	K= 4	1	695	-654
-13	902	949	-26	601	-343	-27	729	626			

H= 11. K= 9
-23 660 -629
-19 1043 1035
-15 1073 -1127
-12 695 579
-11 774 910
-10 754 -751
-5 1043 -1026
-4 687 802
0 598 403

H= 11. K= 10
-24 935 -1011
-22 666 529
-18 1134 945
-17 1232 1195
-16 1097 -1167
-10 1335 1318
-3 625 -556

H= 11. K= 11
-22 963 -1134
-12 1232 -1204
-6 694 796
-4 1024 -1054

H= 11. K= 12
-18 1005 -1093
-16 966 1097
-10 1171 -1293

H= 11. K= 13
-15 813 664
-12 737 782

H= 12. K= 0
-26 702 -788
-24 1577 1613
-18 1258 -1503
-14 911 1004
-8 1160 -1250
-6 1217 1351
0 1054 -1060

H= 12. K= 1
-26 1073 -987
-23 650 510
-20 1302 1365
-19 652 -633
-18 1468 -1638
-14 610 -740
-12 1540 1702
-9 539 -490
-6 1226 -1305
-4 877 923

H= 12. K= 2
-26 668 682
-25 605 -623
-24 1056 -1044
-22 678 527
-21 961 1008
-18 759 936
-17 990 -1130
-16 650 -634
-13 744 724
-11 706 838
-8 823 896
-7 820 -796
-6 883 -946
0 721 731

H= 12. K= 3
-25 664 -540
-23 936 -1002
-22 709 738
-20 638 -720
-19 900 1049
-18 899 899
-16 967 -1067
-15 969 -1076
-14 746 1018
-12 682 -724
-10 762 841
-9 962 1020
-8 916 -915
-6 724 788
-5 716 -793

H= 12. K= 4
-28 1005 1054
-26 695 -757
-22 722 -734
-21 928 -905
-20 963 1079
-17 763 886
-14 793 -860
-13 567 -747
-11 600 -678
-10 1114 1257
-7 589 711
-4 901 -776
-3 667 -682

H= 12. K= 5
-26 698 620
-23 621 606
-22 1388 -1372
-16 1667 1871
-14 1163 -1223
-10 869 -958
-8 1401 1544

H= 12. K= 6
-26 630 643
-22 938 1007
-20 1257 -1318
-14 1109 1177
-10 1135 -1381
-5 607 -226
-4 1070 1031
-2 756 -706

H= 12. K= 7
-22 1091 1196
-19 649 -719
-16 1385 -1534
-14 1061 991
-13 733 665
-11 718 -763
-10 727 1032
-8 1093 -1210

H= 12. K= 8
-25 616 -715
-22 759 -753
-21 700 670
-20 724 692
-17 612 -723
-13 744 859
-10 627 645

H= 12. K= 9
-20 713 766
-19 939 1045
-18 1047 -1048
-13 855 -846
-12 920 969
-11 841 851
-10 721 -802
-5 640 -656

H= 12. K= 10
-18 760 846
-8 641 517
-6 743 -864

H= 12. K= 11
-18 1048 1139
-12 1378 -1467

H= 13. K= 0
-22 1067 1167
-20 1176 -1383
-14 1225 1481
-8 1464 -1550
-6 1000 1115

H= 13. K= 1
-26 1174 -1255
-23 640 638
-20 1335 1516
-19 781 -587
-18 1022 -1198
-12 602 652
-10 632 632
-8 799 -890

H= 13. K= 2
-25 896 -760
-22 716 -793
-21 699 804
-20 935 985
-17 805 -932
-14 874 -961
-12 676 783
-11 784 731
-8 1009 1143
-6 841 -873

H= 13. K= 3
-23 977 -984
-22 664 807
-19 751 921
-15 750 -775
-13 638 -674
-9 640 785

H= 13. K= 4
-24 651 -678
-18 1005 1180
-17 769 898
-16 906 -918
-12 903 -893
-11 729 -795
-10 1103 1384

H= 13. K= 5
-24 945 993
-23 637 496
-22 1308 -1367
-16 1003 1262
-12 811 -882
-6 655 762

H= 13. K= 6
-24 826 954
-18 1287 -1446
-16 609 744
-12 971 979
-10 1259 -1479

H= 13. K= 7
-24 759 -850
-22 963 1153
-19 603 -571
-16 886 -1032

H= 13. K= 8
-21 683 828
-18 898 755
-15 843 -832
-13 902 826
-12 705 -806
-10 773 906

H= 13. K= 9
-20 646 716
-19 717 691
-13 616 -755

H= 14. K= 0
-22 1269 1430
-20 824 -1071
-16 765 -817
-14 1284 1466
-10 635 -453

H= 14. K= 1
-16 1410 -1575
-10 748 975
-8 841 -945

H= 14. K= 2
-22 903 -965
-21 725 753
-20 691 857
-16 641 740
-15 699 -589
-14 793 -1008
-11 643 650
-7 605 -591

H= 14. K= 3
-19 737 843
-17 607 568
-16 722 675

H= 14. K= 4
-24 898 -1067
-18 943 1129
-17 680 599
-11 625 -480
-10 628 434

H= 14. K= 5
-14 679 770
-12 1064 -1186

```
 H= 14, K=  6
-18 1130 -1464

 H= 14, K=  7
-14  673  -744

 H= 15, K=  0
-18  972 -1125

 H= 15, K=  1
-18  646   804
-16 1221 -1498
```

APPENDIX B

Listing of the Observed and Calculated Structure Factors for $(\mu\text{-}(CH)(CH_2)P(C_6H_5)_2U(C_5H_5)_2)_2 \cdot C_5H_{12}$ After Full Matrix Least Squares Refinement

Data is given in four columns per page in groupings of common h and k Miller indices for running values of the l Miller indices. For each h, k, l datum the input structure factor $10(F_o)$ is given first followed by the calculated structure factor $10(F_c)$.

H=	0,	L=	0
2	3799		3660
4	3133		3040
6	2577		2513
8	921		944
10	4000		3781
12	3967		3664
16	2314		2250
18	1718		1723
22	976		1043

H=	1,	L=	0
2	1224		1131
3	5393		4979
4	577		578
5	1334		1383
6	460		482
7	2647		2343
8	1103		1095
9	4138		3684
11	1347		1248
12	1349		1297
13	1839		1866
15	2174		2155
16	480		578
18	735		788
19	1384		1316
21	1102		1125
22	550		644

H=	2,	L=	0
0	2169		2034
1	986		1004
2	2044		2232
3	1936		1929
4	475		519
5	350		336
6	3201		2957
7	569		582
8	1800		1730
9	1573		1484
10	758		820
11	1455		1417
12	1835		1795
13	943		963
14	1233		1267
15	1423		1446
16	660		658
18	1294		1342
19	1109		1074
20	774		725
21	1337		1341

H=	3,	L=	0
1	2542		2574
2	863		868
3	779		800
4	497		452
5	1975		1839
6	1787		1651
8	1370		1277
9	381		311
10	896		989
11	1550		1503
12	1115		1089
13	981		985
15	1041		1030
16	1611		1598
17	1363		1371
18	1267		1348
21	760		741
22	1065		1156

H=	4,	L=	0
0	2393		2482
1	2912		2920
3	965		949
4	648		737
5	456		538
6	769		784
7	1437		1415
8	652		686
10	1913		1860
11	1666		1638
13	1293		1250
14	1661		1659
15	494		432
16	1408		1418
17	518		706
19	1272		1350
20	1122		1257

H=	5,	L=	0
1	514		606
2	2641		2837
3	500		561
4	2368		2323
7	1021		1083
8	3572		3581
9	726		683
10	2435		2288
11	835		824
12	754		761
13	1146		1137
14	1640		1672
16	791		833
17	994		1031
19	800		827
20	1217		1132

H=	6,	L=	0
0	1637		1551
1	3963		3928
2	1092		1044
5	4584		4678
6	493		350
7	3575		3511
8	440		409
9	1233		1245
10	448		462
11	2762		2908
13	1108		1112
15	1087		1196
16	847		725
17	1700		1647
19	531		576

H=	7,	L=	0
1	550		473
2	3167		3297
4	3495		3403
6	960		973
8	3180		3192
10	1629		1605
11	433		427
12	554		562
13	678		689
14	1795		1811
16	848		906
17	709		666
18	801		749
20	1017		1063

H=	8,	L=	0
0	651		721
1	1296		1309
4	432		505
5	1733		1745
6	467		424
7	1319		1400
8	556		641
10	1086		1052
11	877		907
13	1250		1315
14	924		1040
16	983		1000
17	895		939
19	624		604

H=	9,	L=	0
3	561		512
4	408		443
6	760		763
7	801		890
10	776		749
11	1163		1269
12	767		757
13	604		536
16	725		850
17	1092		1073

H=	10,	L=	0
0	695		671
1	844		908
5	1167		1183
6	538		598
8	815		842
9	1158		1268
11	625		529
12	888		1004
14	555		562
15	953		1009

H=	11,	L=	0
1	818		790
2	500		457
3	1845		1870
4	578		609
5	601		544
6	677		645
7	1075		1085
8	1337		1270
9	1379		1376
11	659		553
13	672		654
14	714		696
15	745		854

H=	12,	L=	0
0	2110		2120
2	1157		1195
4	1312		1298
5	733		690
6	2060		2019
7	651		649
10	1180		1226
11	594		480
12	1176		1191

H=	13,	L=	0
1	1110		1089
3	1973		1925
5	810		749
7	1127		1114
9	1330		1326

H=	14,	L=	0
0	1112		1204
2	545		405
6	806		810
9	632		640

H=	0,	L=	1
1	2580		2336
2	4355		4105
3	880		821
4	4000		3756
5	704		811
6	1602		1413
7	2491		2192
8	2642		2526
9	1186		1164
10	1436		1340
11	2192		2020
12	2009		2053
13	1743		1712
14	1961		1988
17	576		698
18	1073		1136
19	1230		1256
20	857		970

H=	1,	L=	1
0	1812		1758
1	3233		3366
2	2900		2847
3	1445		1388
4	3706		3505
5	2638		2478
6	924		881
7	1504		1402
8	1916		1841
9	1381		1284
10	2609		2429
11	2576		2434
12	949		952
13	722		664
14	1270		1261
15	1220		1194
16	1483		1442
17	1196		1206
20	1179		1160
21	636		641
22	1186		1228

H=	2,	L=	1
0	904		848
1	3014		3151
2	1284		1306
3	2545		2509
4	1709		1616
5	1651		1623
6	1488		1485
7	3245		2992
8	1040		931
9	1784		1592
10	1278		1154
11	1298		1213

12	1129	1095
13	2341	2347
14	771	805
15	525	474
16	670	684
17	1579	1481
18	610	745
19	1589	1611

H= 3, L= 1

0	969	1034
1	2619	2663
2	1165	1163
3	2374	2467
4	3171	3202
5	721	852
6	1005	1069
7	824	798
8	1647	1578
9	2016	1978
10	1595	1618
11	1592	1465
12	619	602
13	801	784
14	1358	1311
15	1464	1460
16	1531	1492
17	688	636
19	735	682
20	1311	1328
21	1151	1139
22	817	878

H= 4, L= 1

0	891	966
1	1614	1642
2	1917	2044
3	781	699
4	1288	1340
5	1807	1706
6	2314	2184
7	979	956
8	2472	2414
9	410	347
10	999	986
11	900	838
12	2442	2401
13	684	717
14	1313	1300
16	791	700
17	832	899
18	1769	1749
20	946	982

H= 5, L= 1

0	2260	2261
1	2265	2310
2	1098	1155
3	2276	2226
4	1533	1520
5	2168	2191
6	1935	1863
7	662	624
8	764	775
9	2288	2277
10	1570	1550
11	1655	1695
12	1412	1406
13	889	798
15	1569	1596
16	680	713
17	1331	1263
21	1225	1207

H= 6, L= 1

0	1800	1808
1	1794	1806
2	765	810
3	2999	2925
4	1015	1049
5	776	784
6	1749	1718
7	2171	2233
8	1158	1161
9	2557	2629
10	401	452
11	438	340
12	1366	1338
13	1503	1551
14	841	941
15	775	791
16	573	510
17	719	721
18	981	1001
19	1033	1070
20	723	772

H= 7, L= 1

0	2039	2027
1	927	1023
2	1027	1022
3	1667	1651
4	2153	2159
5	1179	1221
6	2357	2420
7	611	590
8	889	867
9	1231	1272
10	1448	1511
11	1112	1135
12	1119	1198
15	1439	1406
16	1133	1155

H= 8, L= 1

0	1382	1400
1	1053	1024
2	1532	1613
3	952	959
4	1369	1409
5	998	1041
6	1508	1533
7	1133	1153
8	1567	1561
9	833	880
11	832	826
12	1542	1572
13	619	663
14	988	1055
15	754	691
16	529	484
17	558	534
18	1111	1125

H= 9, L= 1

0	796	780
1	1194	1220
2	1443	1502
3	767	808
4	1031	1080
5	1173	1208
7	562	503
8	920	909
9	1201	1218
10	1252	1166
11	1096	996
14	935	975
15	1084	1106
16	820	809
17	511	660

H= 10, L= 1

0	1187	1280
1	1373	1443
2	627	548
3	1149	1201
5	808	831
7	1422	1401
9	851	757
11	1012	973
12	568	681
13	1216	1245
17	957	899

H= 11, L= 1

0	829	857
1	730	680
2	1098	1081
4	1201	1208
5	970	934
6	922	935
7	600	530
8	807	802
9	524	451
10	1358	1286
11	658	599
12	608	636
14	654	651

H= 12, L= 1

1	770	779
2	1391	1316
3	634	470
4	1156	1077
5	653	623
7	945	1019
8	1252	1244
9	541	487
10	508	474
11	532	539
13	771	755
14	793	794

H= 13, L= 1

1	1083	1089
4	742	712
5	1111	1122
8	665	609
10	633	586
11	910	928

H= 14, L= 1

0	671	713
1	667	641
3	699	675
4	655	638
7	739	747
8	537	467

H= 15, L= 1

0	795	650
3	628	543

H= 0, L= 2

0	431	401
1	656	684
2	1104	1074
4	774	728
6	441	369
7	558	522
8	1437	1452
9	689	673
10	1386	1324
11	1345	1344
12	581	589
14	1659	1617
15	846	857
16	1391	1381
17	866	883
18	652	560
20	1459	1448
21	612	713

H= 1, L= 2

0	540	519
1	774	768
2	2085	2115
3	725	686
4	1580	1591
5	587	479
6	1589	1547
7	1079	988
8	3125	2898
9	659	612
10	1002	992
11	1898	1776
12	1338	1324
13	995	972
14	1529	1510
15	464	593
17	1440	1439
18	1283	1172
20	702	814
21	866	871

H= 2, L= 2

0	2680	2745
1	3161	3305
2	2494	2576
3	1738	1756
4	941	956
5	3621	3664
6	898	979
7	2436	2313
8	1608	1584
9	2206	2123
10	736	762
11	2799	2735
12	1262	1301
13	1096	1060
14	1156	1102
15	1568	1544
16	616	648
17	1568	1533
18	785	768
21	1124	1151

H= 3, L= 2

0	507	535
1	1762	1815
2	2491	2719

3	2398	2617
4	2080	2133
5	1786	1909
6	1812	1739
7	2766	2633
8	3454	3283
9	2208	2135
10	2277	2142
11	910	858
12	868	807
13	1390	1348
14	1818	1762
15	1433	1396
16	660	774
17	609	605
18	1068	1033
19	931	968
20	1070	1036

H= 4. L= 2

0	2982	3102
1	1694	1634
2	2179	2280
3	1121	1191
4	2042	2092
5	1953	2062
6	3045	3141
7	2077	1996
8	1290	1238
9	878	907
10	2607	2554
11	1268	1312
12	1554	1599
13	1056	1026
14	739	801
15	524	607
16	1807	1831
17	773	722
18	927	795
19	869	904
20	743	655

H= 5. L= 2

0	746	804
1	1756	1747
3	2155	2187
4	752	750
5	795	821
6	1052	1072
7	2062	2090
9	1575	1648
10	1110	1083
11	972	961
12	695	743
13	1868	1866
15	850	818
16	1197	1199
18	1074	1072
19	989	1042

H= 6. L= 2

0	586	624
2	617	579
3	804	798
4	700	784
5	581	603
7	478	453
9	941	960
10	880	919
11	441	412
12	482	379
13	985	967
14	484	521
15	1320	1342
16	899	920
18	526	703
19	1172	1203

H= 7. L= 2

1	742	767
2	399	510
3	1362	1410
4	799	710
5	1104	1122
6	880	937
7	1472	1479
8	647	616
9	1094	1140
10	416	332
12	985	1030
13	953	1041
15	818	798
16	1083	1068
17	590	499
18	894	997
19	900	907

H= 8. L= 2

0	3117	3111
1	783	835
2	1354	1332
3	1000	1052
4	1601	1653
5	614	571
6	1954	2028
7	796	814
8	659	600
9	619	708
10	1739	1771
12	1400	1429
13	747	779
14	631	539
15	693	656
16	1392	1461
18	646	630

H= 9. L= 2

0	1273	1244
1	1582	1543
2	1471	1495
3	2213	2168
4	1220	1268
5	940	971
6	860	886
7	1280	1357
8	1113	1124
9	1680	1750
10	712	692
11	536	500
12	877	874
13	1478	1477
14	782	799
15	1123	1045

H= 10. L= 2

0	1743	1744
1	1679	1622
2	1016	892
3	865	828
4	687	703
5	1388	1453
6	1117	1054
7	948	963
8	778	763
9	903	923
10	707	787
11	1395	1376
12	1093	1104
15	887	863
16	559	554

H= 11. L= 2

0	644	503
1	471	388
2	1345	1258
3	565	520
4	733	661
6	770	818
8	1342	1414
10	603	695
11	659	624
12	766	674
14	682	712

H= 12. L= 2

10	512	564

H= 13. L= 2

1	523	360
2	696	634
4	504	410
8	586	518

H= 14. L= 2

1	1009	1003
2	523	435
5	1076	935
7	671	702

H= 15. L= 2

1	701	545
2	1114	1011

H= 0. L= 3

1	2954	3009
3	375	325
4	1047	1020
5	1677	1701
6	552	554
7	2178	1921
8	688	674
9	456	379
10	1636	1556
11	1779	1802
12	1662	1663
13	836	799
14	573	543
16	1264	1232
17	1023	1068
18	1523	1536
19	573	649

H= 1. L= 3

0	1149	1200
1	1342	1276
2	2546	2640
3	1074	968
4	1931	1987
5	365	206
6	2523	2367
7	658	687
8	1838	1741
9	1509	1380
10	2200	2114
12	1185	1146
13	1253	1252
14	1083	1039
15	1322	1321
16	1218	1278
19	1262	1224
20	794	858
21	728	917

H= 2. L= 3

1	816	848
2	1160	1206
3	3267	3428
4	1670	1560
5	1710	1611
6	618	584
7	2923	2839
8	976	961
9	3032	2911
10	1337	1261
11	992	944
13	1913	1883
14	1023	1084
15	1124	1123
16	944	946
17	933	958
19	1402	1443
20	588	654

H= 3. L= 3

0	3011	2991
1	2087	2162
2	1569	1636
3	350	341
4	1806	1932
5	2965	3010
6	3091	3111
7	1785	1709
8	692	693
9	953	931
10	1929	1990
11	1585	1578
12	1875	1893
13	859	850
15	951	984
16	1200	1260
17	1384	1412
18	777	884
21	539	528

H= 4. L= 3

0	1060	994
1	1119	1149
2	2990	3017
3	1909	1955
4	2413	2478
5	1089	1059
6	1328	1367
7	835	874
8	2419	2422
9	1774	1775
10	845	765
11	877	923
12	1542	1516
13	732	714
14	1817	1794

15	867	944
16	501	524
18	1356	1288
19	486	463
20	754	814
21	910	904

H= 5, L= 3

0	605	630
1	2330	2402
3	1661	1674
5	1598	1623
6	569	532
7	1243	1296
8	1043	1057
9	1558	1611
11	1420	1458
12	806	776
13	637	627
14	964	981
15	1463	1430
16	613	592
17	1015	1106
18	859	857
20	1071	1184

H= 6, L= 3

0	1801	1828
2	1272	1235
4	1282	1301
5	760	829
6	1889	1902
7	1100	1144
8	395	478
10	763	870
11	1100	1088
12	1341	1364
13	760	782
14	549	533
15	615	592
16	631	570
17	1403	1447
18	597	659
19	661	751

H= 7, L= 3

0	420	374
1	1456	1460
3	1723	1763
4	672	721
5	1655	1720
7	1150	1191
8	744	719
9	1307	1432
10	779	767
11	1044	1076
13	803	796
14	1204	1259
15	938	916
16	682	605
17	767	799
18	512	569

H= 8, L= 3

0	772	718
2	2433	2453
3	808	802
4	1548	1563
5	510	666
6	1026	1075
8	1747	1696
10	988	983
12	1159	1181
14	1535	1595
15	880	876
17	620	680
18	963	994

H= 9, L= 3

0	1397	1339
1	2066	2131
2	721	659
3	472	522
4	759	799
5	1671	1723
6	1329	1340
7	1258	1258
9	595	596
10	929	867
11	1561	1617
12	885	761
13	565	643
15	864	931
17	1110	1124

H= 10, L= 3

1	1067	1097
2	1386	1368
3	1427	1433
4	1070	1039
5	481	412
7	1210	1242
8	925	923
9	1290	1295
10	858	917
13	1291	1213
14	886	900
16	616	593

H= 11, L= 3

0	1218	1183
1	510	473
2	504	497
3	487	276
4	1214	1190
6	1066	1033
8	680	666
9	510	365
10	1088	1039
12	705	692
13	582	685
14	587	652

H= 12, L= 3

1	880	820
5	907	883
7	681	541
11	677	628
12	638	689
13	550	412

H= 13, L= 3

0	717	690
1	594	476
2	806	764
4	814	628
6	674	601
8	627	508
9	573	560
10	752	671

H= 14, L= 3

1	760	668
3	1154	957
7	824	787

H= 0, L= 4

0	1409	1567
1	1614	1648
2	2316	2243
3	3291	3280
4	1502	1484
5	2206	2006
6	3065	2831
7	1323	1296
9	2839	2653
10	2331	2247
11	536	623
12	1401	1440
13	1631	1642
14	664	674
15	1573	1563
16	1526	1492
17	662	664
18	694	694
21	939	1003

H= 1, L= 4

0	2934	2926
1	1111	1196
2	1845	1887
3	2919	2834
4	1695	1653
5	1062	1054
6	3407	3228
7	1749	1666
8	2336	2327
9	1612	1610
10	1228	1172
12	2096	2068
13	1634	1641
14	802	817
15	1093	1109
16	1033	942
18	1617	1593
19	740	794
20	704	648
21	558	383

H= 2, L= 4

0	1315	1277
1	1578	1583
3	1866	1919
4	825	895
5	2145	2144
6	927	873
7	967	1008
9	2079	2014
10	461	430
11	1363	1327
12	953	961
15	1771	1809
16	679	827
17	1134	1089
18	666	647
19	809	777
21	1104	1211

H= 3, L= 4

0	912	942
1	854	924
2	1143	1127
3	1130	1200
4	553	547
5	559	597
6	1735	1579
7	1459	1461
8	1438	1406
9	801	775
11	834	866
12	883	859
13	1153	1095
14	1148	1185
15	612	397
16	603	658
17	878	872
18	1231	1230
19	958	995
20	565	639

H= 4, L= 4

0	1825	1872
1	460	351
2	1501	1571
3	417	403
4	1894	1963
5	845	789
6	1289	1241
7	524	468
8	1151	1182
10	1769	1818
11	583	580
12	449	490
13	741	690
14	1371	1327
15	498	440
16	1536	1452
17	786	753
20	870	891

H= 5, L= 4

0	491	464
1	2445	2477
2	1827	1892
3	1625	1692
4	1570	1598
5	1807	1907
6	759	772
7	1869	1929
8	1418	1413
9	418	470
10	867	878
11	1745	1738
12	464	469
13	1933	1978
14	1147	1160
17	924	983
18	515	599
19	959	997
20	637	558

H= 6, L= 4

0	511	497
1	2020	2076
2	2478	2594
3	714	730
4	1790	1792
5	2366	2405
7	1248	1276
8	1844	1843

9	878	892
10	1658	1723
11	1515	1544
13	658	673
14	1392	1431
15	949	942
16	804	853
17	813	943

H= 7. L= 4

1	1869	1944
2	1832	1864
3	869	849
4	1164	1186
5	1651	1612
6	876	935
7	1571	1634
8	1815	1940
9	477	448
10	1076	1110
11	1336	1399
12	634	556
13	1320	1371
14	1103	1113
17	1036	1062
18	754	734

H= 8. L= 4

0	1455	1449
1	620	615
2	970	1013
4	1507	1585
5	859	918
6	846	900
7	825	820
8	1085	1110
10	1273	1272
11	961	959
13	521	495
14	1057	1103
16	1204	1201
17	605	623

H= 9. L= 4

1	733	732
3	898	925
5	530	603
7	838	873
8	626	633
11	543	370
12	813	864
13	1061	1008
14	592	648

H= 10. L= 4

1	965	909
3	958	867
5	936	947
6	484	295
9	1092	1084
11	1041	993
15	909	898

H= 11. L= 4

0	1334	1243
2	1033	1089
3	654	607
4	728	684
6	1247	1324
7	690	682
8	1025	1008
9	786	837
10	680	615
12	936	893

H= 12. L= 4

0	1394	1330
1	737	610
3	1403	1361
4	938	853
5	798	838
6	1045	1004
7	733	669
9	1041	1026
10	803	789
12	647	642

H= 13. L= 4

0	1046	849
1	816	662
2	771	647
3	961	989
6	1063	1066
7	691	718
9	772	716

H= 14. L= 4

0	685	499
3	754	635
5	632	622

H= 0. L= 5

1	1567	1568
2	4460	4339
4	3824	3641
5	932	853
7	370	235
8	2838	2730
10	2100	1967
11	736	798
12	1056	994
14	2647	2700
16	1204	1227
20	1126	1082

H= 1. L= 5

1	3421	3541
2	1177	1123
3	667	717
4	1326	1321
5	3339	3147
6	889	884
7	2566	2508
8	517	497
9	827	755
10	786	798
11	2268	2261
12	497	464
13	1594	1572
14	971	924
15	723	639
16	656	708
17	1477	1464
19	927	894
20	675	726

H= 2. L= 5

0	1272	1280
2	2135	2108
3	452	562
4	2297	2337
5	1170	1079
6	1052	1031
7	1472	1453
8	1488	1457
9	576	543
10	1692	1641
11	603	619
13	960	913
14	1257	1250
15	576	452
16	1349	1317
17	1263	1299
19	552	551
20	675	669

H= 3. L= 5

1	620	660
2	1171	1211
3	1040	1029
4	759	739
7	1050	1075
8	891	886
9	1012	1046
10	620	605
12	544	579
13	1159	1216
14	1155	1177
15	1022	998
16	495	518
18	782	817
19	921	959
20	1046	1051

H= 4. L= 5

1	1251	1324
2	887	923
3	1920	1916
4	481	409
5	1462	1527
6	863	893
7	439	486
8	618	675
9	1283	1304
11	1062	1061
12	1407	1404
14	584	594
15	1293	1334
16	743	724
17	764	780
18	887	916

H= 5. L= 5

0	3171	3209
1	1014	1048
2	1386	1437
4	1820	1897
5	587	593
6	2249	2331
8	866	945
9	1092	1143
10	1348	1382
11	957	889
12	1899	1853
13	568	553
14	723	729
15	1012	972
16	929	907
18	902	995

H= 6. L= 5

0	1162	1149
1	1681	1676
2	603	613
3	3094	3238
4	758	734
5	986	1014
6	561	581
7	1943	1968
9	2407	2511
10	676	707
11	492	488
13	1400	1407
14	567	607
15	1370	1355

H= 7. L= 5

0	2442	2480
1	657	631
2	1266	1366
3	692	741
4	1416	1467
6	2472	2548
7	606	669
8	734	752
9	566	607
10	1448	1484
12	1740	1732
14	522	468
15	525	596
16	843	886

H= 8. L= 5

1	882	826
2	436	524
3	1298	1309
5	892	874
6	508	483
7	1009	1065
8	456	537
9	1442	1483
11	1013	932
12	877	970
15	839	900
16	620	682
17	578	461

H= 9. L= 5

2	479	493
4	617	650
6	502	543
8	748	834
9	753	755
12	559	534
13	624	760
14	774	754
15	553	722

H= 10. L= 5

0	609	532
2	721	635
3	493	520
4	803	766
6	647	631
7	683	723
8	613	536
10	1017	1021
11	551	529
13	673	630

H= 11. L= 5			4	1650	1659	17	657	713	7	623	559
0	555	538	5	1474	1424				8	920	896
1	1198	1169	6	979	938	H= 6. L= 6			9	1089	1100
3	566	531	7	727	769	1	1312	1410	11	748	687
4	598	639	8	1632	1636	2	769	784	13	667	445
5	1284	1269	9	1357	1305	3	434	348			
6	770	709	10	947	995	4	522	539	H= 11. L= 6		
7	1273	1342	11	1372	1402	5	1436	1517	0	807	688
10	763	716	12	689	650	6	482	456	1	593	509
11	1061	990	14	1224	1151	7	1061	1125	2	742	697
			15	1474	1416	9	677	645	4	602	553
H= 12. L= 5			17	620	743	10	839	876	5	660	677
2	1478	1446	18	540	470	11	1298	1381	6	754	756
3	619	400				12	796	817	7	522	619
4	1277	1257	H= 3. L= 6			16	1056	971	8	1008	907
7	717	656	0	2088	2097				11	539	556
8	1323	1350	1	1977	2061	H= 7. L= 6					
9	538	486	2	1093	1112	0	874	900	H= 12. L= 6		
10	717	833	3	460	542	1	784	730	0	797	700
			4	1308	1369	2	1199	1181	4	657	620
H= 13. L= 5			5	1824	1863	3	565	493	5	576	569
1	1360	1307	6	2134	2141	4	1156	1132	6	887	884
5	1293	1212	7	1513	1592	6	1075	1076			
7	1000	851	8	938	963	7	710	710	H= 13. L= 6		
			10	500	569	8	1422	1421	1	532	458
H= 14. L= 5			11	1532	1584	9	508	544	3	705	789
2	646	707	12	1328	1319	10	847	991	5	565	398
			13	1384	1355	12	651	598			
H= 0. L= 6			14	571	439	13	952	1012	H= 0. L= 7		
0	3045	3012	16	909	931	14	757	723	5	549	512
2	738	740	17	1043	1084	16	517	512	6	698	732
3	536	564	18	1119	1141				9	640	700
4	1287	1304	19	757	616	H= 8. L= 6			10	800	790
5	780	741				0	866	783	12	1179	1050
6	1464	1461	H= 4. L= 6			1	855	905	13	675	600
8	413	398	0	1481	1567	2	847	741	15	809	797
9	1703	1580	1	1047	1062	3	1354	1370	16	939	830
10	1328	1288	2	1477	1558	4	796	804	18	768	726
11	1041	991	3	1915	2026	5	861	899			
12	1344	1275	4	1418	1492	6	739	769	H= 1. L= 7		
15	700	646	5	762	772	7	987	980	0	1226	1291
16	1097	1070	6	852	809	8	633	573	1	670	717
17	1186	1240	7	1151	1207	9	1055	1091	2	466	497
19	515	361	8	1156	1152	10	1132	1070	3	1167	1212
			9	1097	1169	11	491	281	4	637	667
H= 1. L= 6			10	1622	1618	13	815	873	6	1205	1275
0	807	853	12	490	484	14	655	662	7	1504	1514
1	1529	1626	13	957	983	15	742	684	9	650	692
2	1430	1471	14	1144	1142				10	1088	1116
3	1719	1801	15	937	946	H= 9. L= 6			12	1001	947
5	2037	2028	16	1271	1211	0	1567	1463	13	1143	1057
6	1233	1194				1	879	876	15	1016	981
7	1129	1111	H= 5. L= 6			2	788	834	16	752	712
8	1583	1519	0	1389	1423	3	503	617	18	664	719
9	1259	1264	1	1272	1376	4	869	873			
10	494	414	2	1443	1460	5	872	767	H= 2. L= 7		
11	888	842	3	1194	1213	6	1345	1421	0	1418	1348
12	1265	1175	4	1030	1039	7	1032	993	1	1295	1319
13	1177	1180	5	807	814	8	512	566	2	1016	1043
14	1108	1035	6	841	849	10	833	761	3	1731	1713
15	815	868	7	1073	1097	11	901	901	4	1615	1610
17	523	595	8	1214	1266	12	1003	1007	5	773	697
18	1080	1021	9	745	652	13	776	670	6	1694	1759
19	600	478	10	1231	1227				7	1483	1540
			11	764	715	H= 10. L= 6			8	864	781
H= 2. L= 6			12	883	904	1	788	682	9	1834	1764
0	545	604	13	1329	1329	2	999	997	10	1203	1206
1	1261	1265	14	601	574	3	1259	1211	12	976	940
2	1631	1682	15	670	611	4	808	685	13	1237	1269
3	1735	1815	16	562	573	5	1059	1027	14	791	665

15	632	608
16	1148	1138
H=	3, L=	7
0	1907	1891
1	1598	1675
2	924	1009
3	1389	1480
4	1757	1859
5	1427	1454
6	1431	1496
7	1316	1301
8	1202	1203
9	1302	1294
10	1269	1205
11	1360	1325
12	1340	1265
13	962	893
14	697	658
15	930	915
16	806	804
17	672	759
18	597	655
H=	4, L=	7
0	1049	1079
1	1178	1193
2	1592	1643
3	1181	1181
4	1356	1355
5	1364	1430
6	810	802
7	1010	1079
8	1581	1627
9	1262	1311
10	796	888
11	1146	1183
12	1234	1224
14	1080	1133
15	863	1011
17	632	645
H=	5, L=	7
0	509	593
1	1257	1278
2	956	998
3	455	410
4	795	772
5	965	961
6	532	532
7	589	576
8	968	991
9	671	694
11	1179	1124
12	882	988
14	1108	1169
15	544	571
17	774	829
H=	6, L=	7
5	445	499
8	490	417
11	766	767
14	681	710
15	530	513
16	536	509
H=	7, L=	7
1	776	722
2	640	563
4	853	860
5	875	923
7	477	557
8	834	905
11	778	809
12	642	556
13	587	516
14	619	716
H=	8, L=	7
1	1068	1082
2	1128	1107
4	1169	1220
5	1029	1088
6	519	467
7	667	718
8	1165	1184
9	610	616
11	930	1030
12	604	643
14	901	929
H=	9, L=	7
0	1122	1025
1	1179	1134
2	1330	1264
3	637	649
4	872	853
5	1084	1176
6	830	744
7	836	839
8	830	832
9	628	643
10	909	867
11	1035	964
12	671	682
H=	10, L=	7
0	985	889
1	934	776
2	774	747
3	1082	1040
4	999	1033
7	901	933
8	632	662
9	710	772
10	675	723
11	550	593
H=	11, L=	7
0	579	531
1	662	578
4	548	615
6	698	659
7	549	566
9	687	627
H=	12, L=	7
6	523	324
H=	0, L=	8
1	1004	1062
3	2096	2099
5	599	677
7	1126	1191
8	1023	1021
9	1434	1361
10	588	580
12	574	509
13	1247	1143
14	779	805
15	1078	1080
16	512	554
H=	1, L=	8
0	1497	1588
2	1062	1160
4	1333	1330
5	793	809
6	1658	1589
8	960	977
9	714	694
10	1043	1037
11	1083	987
12	1142	1109
15	673	633
16	852	849
17	732	781
H=	2, L=	8
0	889	889
1	1227	1284
2	501	580
3	818	782
4	623	620
5	1795	1821
6	1019	992
7	1222	1206
8	832	806
9	1057	1055
11	1059	1078
12	916	914
13	576	544
14	616	647
15	695	696
H=	3, L=	8
1	587	596
2	1161	1196
3	1042	1128
4	1080	1039
5	693	720
7	872	860
8	1574	1529
9	1071	1015
10	914	921
13	612	643
14	857	674
15	902	852
16	578	519
H=	4, L=	8
0	1536	1515
1	807	855
2	654	873
3	679	687
4	691	789
5	794	822
6	1250	1245
7	1120	1051
10	1131	1091
11	966	907
12	576	688
13	889	976
14	502	392
16	841	850
H=	5, L=	8
0	830	789
1	1196	1311
2	492	544
3	825	859
4	503	600
5	1233	1300
7	1047	1075
9	687	755
10	903	951
11	1015	970
12	571	517
13	855	777
H=	6, L=	8
1	499	474
4	1203	1223
8	1504	1512
9	705	632
10	821	852
13	767	677
14	941	948
H=	7, L=	8
1	1174	1181
3	663	764
4	548	560
5	1304	1293
6	619	494
7	1080	1134
11	1131	1111
12	574	508
13	615	652
H=	8, L=	8
0	1554	1542
1	669	618
2	841	916
3	621	550
4	818	815
6	938	940
7	617	484
8	655	677
10	1075	1043
12	773	650
H=	9, L=	8
1	856	698
2	547	722
3	1070	1051
4	591	638
7	519	547
8	542	478
9	968	943
H=	10, L=	8
0	927	844
1	679	782
2	686	543
6	694	622
8	554	519
H=	11, L=	8
0	604	596
2	581	536
5	625	557
H=	0, L=	9
1	2106	2121
2	1038	1046
4	1074	1022
5	1869	1750
6	579	516
7	1736	1716

8	1233	1193
9	560	545
11	1759	1714
12	679	695
13	781	734
14	696	649

H= 1. L= 9

1	1020	1045
2	1736	1822
4	1805	1764
5	755	786
7	534	490
8	1512	1528
9	604	599
10	1195	1126
11	909	825
12	510	441
13	577	471
14	1094	1098

H= 2. L= 9

1	1032	954
3	551	540
4	708	690
5	932	900
7	1091	1086
10	832	791
11	790	694
13	903	852
14	667	711

H= 3. L= 9

4	662	604
5	474	412
9	539	410
11	524	565
12	717	681

H= 4. L= 9

0	953	1047
1	543	418
2	545	570
4	661	481
5	488	472
6	687	658
8	680	755
11	618	484
12	915	810
14	602	558

H= 5. L= 9

0	705	714
1	1150	1137
2	707	793
3	1562	1594
4	704	641
5	575	513
6	842	831
7	682	711
9	1303	1273
10	521	501
12	686	675
13	670	687

H= 6. L= 9

0	1783	1732
1	548	549
2	740	777
3	1097	1058
4	1221	1241
6	1618	1681
7	881	928
8	561	518
9	835	877
10	854	884
12	1172	1263

H= 7. L= 9

0	898	944
1	759	716
3	1601	1584
4	724	623
5	701	692
6	779	726
7	836	936
9	1144	1167
10	523	600

H= 8. L= 9

0	914	828
2	692	645
4	569	523
6	949	946

H= 0. L= 10

0	2132	2202
1	639	551
2	1017	1098
3	954	936
4	966	903
6	1550	1499
7	578	549
8	582	423
9	635	741
10	977	944
12	963	1067
13	847	800

H= 1. L= 10

0	755	730
1	1030	968
2	547	370
3	1665	1592
5	678	767
6	576	531
7	795	762
9	1276	1226
10	586	612
11	722	788
13	655	568

H= 2. L= 10

0	1013	1072
2	1214	1195
6	1000	995
8	1217	1113
12	900	983

H= 3. L= 10

0	872	746
1	577	518
3	511	590
4	513	631
5	939	890
9	674	657
10	723	670
11	746	831

H= 4. L= 10

1	1047	1053
3	857	870
7	874	972
8	595	490
9	734	692

H= 5. L= 10

0	882	834
2	1093	1146
4	1095	1043
6	622	618
8	965	945
10	970	1000

H= 6. L= 10

1	1214	1187
2	858	836
5	1201	1267
7	992	1018
8	726	686

H= 7. L= 10

2	1019	994
4	1002	1050
5	620	596
8	964	977

H= 8. L= 10

1	722	656
3	594	651
5	530	584

H= 9. L= 10

0	625	555

H= 0. L= 11

2	544	468
8	585	560
9	563	545

H= 1. L= 11

1	648	661
3	724	787
5	530	436
9	738	711

H= 2. L= 11

0	1239	1221
1	866	691
2	560	479
4	982	898
5	781	600
6	1116	1088
7	686	649

H= 3. L= 11

1	725	684
2	1040	1099
3	1238	1202
4	752	782
7	830	803
8	682	776
9	1096	1056

H= 4. L= 11

0	564	566
1	1172	1090
5	1097	1044
6	838	896
7	650	679

H= 5. L= 11

0	561	546
2	870	755
3	550	412
4	715	691
5	542	480

H= 0. L= 12

0	523	467

H= 1. L= 12

1	619	589

H= 2. L= 12

1	614	447
2	788	859
4	803	730

H= 3. L= 12

0	890	800
1	782	734
2	648	608

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where A_i is the electron-nuclear hyperfine coupling constant, χ is the magnetic susceptibility, g_j the Lande g factor and the other terms have their usual meaning.

34) $$\frac{\Delta H_i^{dip}}{H} = -D_1 \frac{3\cos^2\theta_i - 1}{r_i^3} - D_2 \frac{\sin^2\theta_i \cos 2\Omega_i}{r_i^3}$$

where $D_1 = \frac{1}{3N}(\chi_z - \frac{1}{2}(\chi_x + \chi_y))$; $D_2 = \frac{1}{2N}(\chi_x - \chi_y)$

and r, θ, and Ω are spherical polar coordinates; the χ's are principal molecular susceptibilities. For molecules with threefold or higher symmetry axes, $D_2 = 0$.

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