The Synthesis and Reactivity of New Niobium (V) Polyhydrides

Thesis by

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In Partial Fulfillment of the Requirements
for the Degree of
Master of Science

California Institute of Technology
Pasadena, California
1983
(Submitted August 10, 1982)

for John

Acknowledgements

I wish to thank John Bercaw for his guidance and support, and Dean Roddick, Jimmy Mayer, and all the members of the Bercaw group for their help in making me something of a synthetic organometallic chemist. Financial support from the National Science Foundation is gratefully acknowledged.

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Abstract

The synthesis of new niobium polyhydrides by high pressure hydrogenation of Cp^*NbMe_4 in the presence of trapping phosphines is reported. The complexes $Cp^*NbL_2H_4$, L=PMe_3, PMe_2Ph, PMe_2Cy, and L_2=bis(dimethylphosphino)ethane, are described. They exchange D_2 into the hydride positions, and react hydridically with methanol and acetone to give alkoxide species. Reactions with CO give reduced metal carbonyl phosphine complexes. All these reactions (except the reaction with methanol) appear to proceed with loss of phosphine as the rate limiting step. Reactions of the hydride species with group VI carbonyls, and with ethylene, are presented. The novel reactivity of $Cp^*Nb(PMe_2Ph)_2H_4$ with H_2 to give $Cp^*Nb(PMe_2Cy)_2H_4$ is discussed.

Introduction

The objective of this research was originally to parallel with niobium some of the work that had been done in the Bercaw group on tantalum polyhydrides,[1-3] to explore differences in reactivity between the second and third row transition metals, and to try to fulfill some of the goals set for but not reached by the tantalum system. One of the primary goals of that initial research had been to make a d^0, 16-electron tantalum hydride that would mimic some of the chemistry of $Cp^*_2ZrH_2$.[4,5] This aspect of the research was not realized; although many new tantalum polyhydrides were synthesized, they underwent substitution reactions with CO, yielding reduced tantalum centers instead of reduced CO species. It was thought that perhaps in going from the third to the second row of group V the increase in reactivity generally accompanying such a move[6] might produce more active hydrides.

From a broader point of view, the tantalum research has opened up a new class of compounds with interesting chemistry. The corresponding niobium chemistry is largely untouched[7] and similarly promising.

There is no questioning the importance of transition metal hydrides in numerous processes, either as starting materials or as intermediates, especially in catalytic systems. They are invoked in the mechanisms for olefin and arene hydrogenation, olefin metathesis, CO reduction, and many other cycles.[8] Many of the practical homogeneous catalysis systems involve late transition metals, and most of the well-studied hydrides are group VIII complexes.[9] But there are some problems with the study of these catalyst intermediates--key steps involving the hydrides may be too buried in a complicated mechanism for anything to be detailed about their reactions, or the hydride species themselves may be too transient to isolate or even observe.

One advantage that early transition metal hydrides have to offer at this point is that often their reactions are stoichiometric rather than catalytic,[4,10] and hence compounds may be isolated which were only postulated in late metal systems. Early transition metal systems can serve as "model compounds" for late metal catalysts.[4a]

Also, there are some fundamental chemical differences in early versus late transition metal systems, and these can have important influences on their roles in organic synthesis. Whereas late transition metal "hydrides" are usually more protic than hydridic, behaving in some cases as strong acids (e.g. $HCo(CO)_4$, $pK_a < 2$),[11] the d^0 early transition metal hydrides are genuinely hydridic.[2,11] Some of the reaction chemistry takes advantage of the difference in behavior between early and late transition metals, such as the "hydrozirconation" reactions of Schwartz's reagent.[12]

There are not many early transition metal hydrides known and well studied, relative to the late metal hydrides. For niobium, there are only a few polyhydrides known, and some monohydride deriviatives of these. The polyhydrides are

Cp_2NbH_3,[13] $NbH_5(dmpe)_2$,[14] $NbH_5(PMe_3)_4$;[15][†] the transient species $\{Cp_2NbH_2(CO)_2\}^+$[16] and $\{Cp_2NbH_2(PR_3)_2\}^+$[17]; the paramagnetic species Cp_2NbH_2[18] and $Cp_2NbH_2(olefin)$[18]; and several polynuclear species with bridging hydrides, $\{CpNb(dmpe)H(\mu H)\}_2$[19] and $Cp_2Nb_2(\mu H)_2(\mu C_5H_4)_2$.[20] Only the first three of these are stable Nb(V), d^0 complexes. The analogous tantalum compounds Cp_2TaH_3[21] and $TaH_5(dmpe)_2$[22] are known.

A series of complexes $Cp^*TaL_2H_4$ has been made,[1-3] with $L=PMe_3$, $P(OMe)_3$, PMe_2Ph, and L_2=dmpe, as well as $Cp^*Ta(PMe_3)_2H_3Cl$. The chemistry of these complexes is provided as needed for comparison to the niobium systems. The compounds $Cp^*NbL_2H_4$ ($L=PMe_3$, PMe_2Ph, PMe_2Cy, and L_2=dmpe), their syntheses and reactivities are now reported.

The niobium system is being explored for a variety of reasons, among them the scarcity of known, stable niobium polyhydrides. It was hoped that the increase of reactivity would produce a change in some of the chemistry of the polyhydrides, as some changes are observed in going from Hf to Zr.[23] One of the differences expected is the greater accessibility of the +3 and +1 formal oxidation states of Nb over those of Ta.[24] This may be reflected in the greater tendency of Nb(V) complexes to reductively eliminate H_2.

[†] $Cp=(\eta^5C_5H_5)$, $Cp^*=(\eta^5C_5Me_5)$; dmpe=bis(dimethylphosphino)ethane, $(CH_3)_2PCH_2CH_2P(CH_3)_2$

The Synthesis and Reactivity of Nb^*Me_3Cl and Nb^*Me_4[†]

While the syntheses of Ta^*Me_3Cl and Ta^*Me_4 have been studied by several workers,[1,2,27,28] the analogous Nb compounds have not been reported. There are several routes into the Cp*-Nb chemistry which was of interest. Malcolm Green has made $CpNbCl_4$ from $NbCl_5$ by treatment in dichloromethane with σ-Cp-$^nBu_3Sn$. This has been done recently with Cp* also.[25] The method chosen, however, was that which was very successful for tantalum: to alkylate the metal chloride first, then add the ring:

$$MCl_5 + 3/2\ ZnMe_2 \longrightarrow MMe_3Cl_2 + 3/2\ ZnCl_2,\ M{=}Nb,\ Ta \quad \text{(ref. 26)}$$

$$MMe_3Cl_2 + M'Cp^* \longrightarrow Cp^*MMe_3Cl + M'Cl,\ M'{=}Li,\ K \quad \text{(ref. 27)}$$

A fourth methyl group can easily be added with methyllithium[28] to make the fully alkylated metal suitable for hydrogenation:

$$M^*Me_3Cl + LiMe \longrightarrow M^*Me_4 + LiCl$$

Whereas the tantalum products Ta^*Me_3Cl and Ta^*Me_4 are quite stable and can be stored for years at 0° in an inert atmosphere, the niobium products are only metastable, and some adjustments to the procedure were necessary for their synthesis. $TaMe_3Cl_2$ is stable enough to sublime easily from the reaction mixture containing the side-product $ZnCl_2$. This is important, as the reaction is done in diethyl ether, and $ZnCl_2$ is soluble in ether to an appreciable degree. $NbMe_3Cl_2$,

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[†] Throughout this paper, the abbreviation "M*" is used for a metal-permethylcyclopentadienyl fragment, $(\eta^5\text{-}C_5Me_5)M$.

however, is much less stable and the ethereal solutions begin to darken and evolve a non-condensable (at 77 K) gas, presumably methane,[29] within minutes at room temperature. The $ZnCl_2$ cannot be separated by removal of the diethyl ether and addition of a solvent such as petroleum ether (hexanes). The compound is a yellow solid which forms beautiful needle-like crystals, but it is very volatile, and attempts to remove the ether under vacuum result in large losses of product as well. Added dioxane,[30] however, coordinates with and precipitates the unwanted $ZnCl_2$, allowing filtration of the solution. The solution of $NbMe_3Cl_2$ is rapidly added to the Cp^{*-} source.

Originally LiCp* was used, the usual reagent for such reactions. The lithium reagent was found to be quite reactive toward the $NbMe_3Cl_2$; the two reacted violently enough at RT in the solid state to explode and incinerate the Cp*. Reasonable results could be attained when cold solutions of $NbMe_3Cl_2$ were added to LiCp* wetted with cold ether. Even so, 30-50% of the niobium ended up in black, gas-emitting side-products, frequently difficult to remove from the desired Nb^*Me_3Cl. Yields were variable, and impurities accelerated the decomposition of the product. Nb^*Me_3Cl is indefinitely stable at 0^o when very clean, but solution half-lives decrease to less than two hours, and solid half-lives to less than a day when the product is contaminated. One of the reasons for the difficulty in obtaining clean Nb^*Me_3Cl was due to solubility problems again. The side-product LiCl is soluble in diethyl ether, so the solvent had to be removed and petroleum ether condensed in. Nb^*Me_3Cl is not soluble enough in cold pet. ether to allow separation of the product from the finely-divided LiCl without numerous washings. The reaction mixture continues to evolve gas during all the manipulations, complicating solvent transfers. Benzene and toluene were tried, being better solvents for the product, but these less-volatile liquids do not "move" well when even several millitorr of gas are present.

All these difficulties were overcome with the move to KCp*[31] as the ring-adding reagent. K^+ is not as prone to side-reaction producing electron transfer reactions as Li^+, and has the primary advantage that the KCl formed in the reaction with $NbMe_3Cl_2$ is not soluble in ether, and the product can be rapidly filtered from KCl and then recovered from the ether with no time lost changing solvents or washing solids. The reaction still proceeds with an overall isolated yield of less than 50%, due to the decomposition of $NbMe_3Cl_2$ and recovery losses, but the product is much more pure, and reasonably stable when stored at 0° C.

Adding the final methyl group to make Nb^*Me_4, the starting material for the polyhydrides, is simple chemically. The resulting product, however, is very soluble in pet. ether, and the solid is not stable at room temperature for more than half an hour, nor at 0° for more than a day. The product is therefore made as efficiently as possible and used immediately. When the solid is allowed to stand in an inert atmosphere at RT for several hours it gradually darkens and evolves gas. This compound effectively demonstrates the reactivity difference between Ta and Nb; the analogous Ta compound is stable indefinitely. The similar, though much less stable, compounds

$TaMe_5$ and $NbMe_5$ demonstrate this also, and give clues to the decomposition of Nb^*Me_4.[29]

$TaMe_5$ can be isolated and handled at 0° for short periods of time. It decomposes in minutes at 25° C, releasing methane. $NbMe_5$ decomposes rapidly above -30°. These compounds and their occasionally violent autocatalytic decompositions have been studied by Schrock,[29] and are postulated to decay by intramolecular α-hydrogen atom abstraction pathways that yield methane and metal-carbon-hydrogen fragments in the best cases, and additionally dihydrogen in the violent detonations. It is reasonable to assume that Nb^*Me_4 decomposes by similar mechanisms. No major Cp*-containing products are seen in the NMR spectra of the decomposing and decomposed samples.

The decomposition of Nb^*Me_4 is vastly accelerated by the presence of H_2. A frozen benzene solution of Nb^*Me_4 sealed under H_2 in an NMR tube[32] turns from red to black as the benzene melts, and no starting material peaks are visible in the ^1H NMR spectrum within three minutes of warming to RT. A large peak due to methane is seen at δ 0.2. When Nb^*Me_4 is sealed under H_2 in the presence of three equivalents of trimethylphosphine, however, better results are obtained. The initial NMR spectrum is broad and shapeless between δ 1-2.5. Within 45 minutes, though, several Cp* peaks emerge. One of these Cp* resonances, along with the appropriate peaks for the phosphine methyls and the hydrides, clearly belongs to $Nb^*(PMe_3)_2H_4$ (by comparison to an isolated sample, prepared as described later).

In the presence of the ligand PMe_3 the decay/hydrogenation products of Nb^*Me_4 are trapped, and a new niobium polyhydride is formed under only ca. three atomspheres of H_2 at room temperature--rather gentle conditions. The reaction is by no means quantitative, due to the rapid decomposition of Nb^*Me_4 to a number of products and to there being only about 3.5 equivalents of hydrogen per niobium in the sample. It is important, however, in showing that these niobium polyhydrides can be formed without resorting to brutal conditions.

Nb^*Me_4 also reacts very rapidly with CO to form a transitory species thought to be $Nb^*(\eta^2\text{-}C(O)Me_2)$ by analogy to the tantalum reaction.[28] The compound forms as the benzene melts, and is essentially gone within one hour. When the reaction is done in the presence of PMe_3, the acetone complex is formed more slowly, but no cleaner nor longer lived. No methane is seen in the NMR of either case.

Spectral data are found in Table I.

Table I

Compound	^{1}H NMR data,† chemical shifts, δ		
1 Nb*Me Cl	Cp*	1.55 s	
	Me	1.23 s	
2 Nb*Me	Cp*	1.52 s	
	Me	1.18 s	
Ta*Me	Cp*	1.69 s	(ref. 1)
	Me	0.66 s	

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† Data from ambient-temperature spectra. Chemical shifts reported in ppm downfield from internal TMS.

The Synthesis and Characterization of New Niobium Polyhydrides, $Nb^{*}L_2H_4$

A convenient, versatile, high yield pathway to new tantalum polyhydrides has been obtained in the high pressure hydrogenation of $Ta^{*}Me_4$ in the presence of trapping phosphines.[1] Attempts to produce $Ta^{*}H_4$ had given only black oils with no characterizable metal-containing products. Since the $Ta^{*}H_4$ species was clearly not stable, neutral ligands were added to try to obtain single products. Phosphines were the ligands of choice: they are often successful as ligands in metal hydrides;[11] they are good σ donors, helpful in stabilizing high oxidation states; and there are a large number to choose from, with widely varying steric and electronic properties.[33] The strategy worked for most of the phosphines tried, to give species of the form $Ta^{*}L_2H_4$, L=PMe_3, $P(OMe)_3$, PMe_2Ph, and L_2=dmpe.[1,2] Tricyclohexylphosphine and triphenylphosphine did not work, presumably due to large steric bulk (cone angles 170°, 145° respectively[33]) and the low basicity of PPh_3. $Ta^{*}(PMe_3)_2H_3Cl$ has also been made, by hydrogenation of $Ta^{*}Me_3Cl$ with PMe_3.[1] Yields of the hydrides were generally limited only by the high solubility of the products.

The same approach works for niobium as well, and $Nb^{*}L_2H_4$, L=PMe_3, PMe_2Ph, and L_2=dmpe, have been isolated and characterized. The reactions are not as clean as with tantalum, however; yields of approximately 30% are usual, with brown oils the major reaction products. Another complex, $Nb^{*}(PMe_2Cy)_2H_4$, has been synthesized in a novel manner, to be detailed later in this report. Attempts to hydrogenate $Nb^{*}Me_3Cl$ in the presence of dmpe results in a mixture of uncharacterizable products; in the presence of PMe_3 a mixture of products including ca. 10% $Nb^{*}(PMe_3)_2H_4$.[34] The new niobium hydrides are nearly white when washed very clean, though due to their high solubility in hydrocarbon solvents, they are generally used in colored, dirty-appearing forms, which are still pure by NMR. ^1H NMR and IR spectra of the hydrides are completely analogous to those for the tantalum compounds, and support their formulation as $Nb^{*}L_2H_4$.

Exhaustive NMR studies--^1H and ^{31}P, 90 and 500 MHz, high and low temperature--have been done by Mayer on the tantalum hydrides $Ta^{*}L_2H_3X$ (X=H, L=PMe_3, $P(OMe)_3$, L_2=dmpe; X=Cl, L=PMe_3) and used with symmetry arguments to determine their stoichiometries and their ground state solution structures. Some of the simpler studies have been done for the Nb hydrides (L=PMe_3, L_2=dmpe) also.[3]

Stoichiometries were determined at ambient temperatures by observing the multiplicities of selectively decoupled ^{31}P spectra (quintets show phosphines are split by four hydrides) and proton spectra (triplets show hydrides are split by two phosphines) and by careful integration of the spectra. More elaborate work was done to determine structures. Briefly, it was found that at very low temperatures the monodentate phosphine hydrides all adopt a similar geometry, visualized as derived from a tricapped trigonal prism, as seen in figure 1a. The Cp* occupies one triangular face, the two phosphine phosphoruses and a hydrogen or chlorine atom the other face, with the rest of the hydrogens capping the rectangular faces. The low temperature 500 MHz ^1H spectra show three types of hydrides, in the ratio of 2:1:1, and the ^{31}P spectra show equivalent phosphines. Only a structure with a mirror plane such as the one shown will explain the data. The proton NMR patterns are clear for the tantalum hydrides at -70° C; the $Nb^*(PMe_3)_2H_4$ spectrum does not resolve well until -100°.[3]

The bidentate dmpe hydrides adopt a different structure, indicated by two types of hydrides in the low temperature proton spectra, and by inequivalent phosphines in the ^{31}P spectra. The structure assigned can also be placed on a tricapped trigonal prism, with the Cp* now spanning two corners of one triangular face and capping a rectangular face, and the dmpe placed with one P on the third corner of the Cp*'s triangular face, and the other P on the corresponding corner of the opposite triangular face. The hydrides fill in the remaining places (figure 1b). The reason for the different structures is related to the constraints of the chelating dmpe ligand, which has a bite angle of only ca. 75° for group V compounds.[35] The monodentate phosphine structure seems to be the preferred one, but dmpe cannot attain it.[3]

These group V polyhydrides are highly fluxional at RT, of course, and give simple proton NMR spectra: the Cp* resonance appears as a singlet about 2 ppm downfield from TMS, the alkyl hydrogens from the phosphines between 1 and 2 ppm downfield, and the hydride resonances appear as lovely binomial triplets centered about 1 ppm upfield of TMS, with phosphorus-hydrogen coupling constants of 45-60 Hz. Figure 2 shows a typical ^1H NMR spectrum of one of the hydrides. These simple spectra make monitering of reactions by NMR quite simple: as reactions proceed, the original Cp* disappears and a new one grows in; the hydride signals disappear; the phosphine alkyl signals disappear and reappear in slightly different positions as different bound or free phosphines, distinguishable by their multiplicities and coupling constants.[36] The IR spectra of the hydrides show two moderately strong bands near 1600 and 1700 cm^{-1}, assigned to the M-H stretches. Detailed spectral data for these and similar compounds are found in Table II.

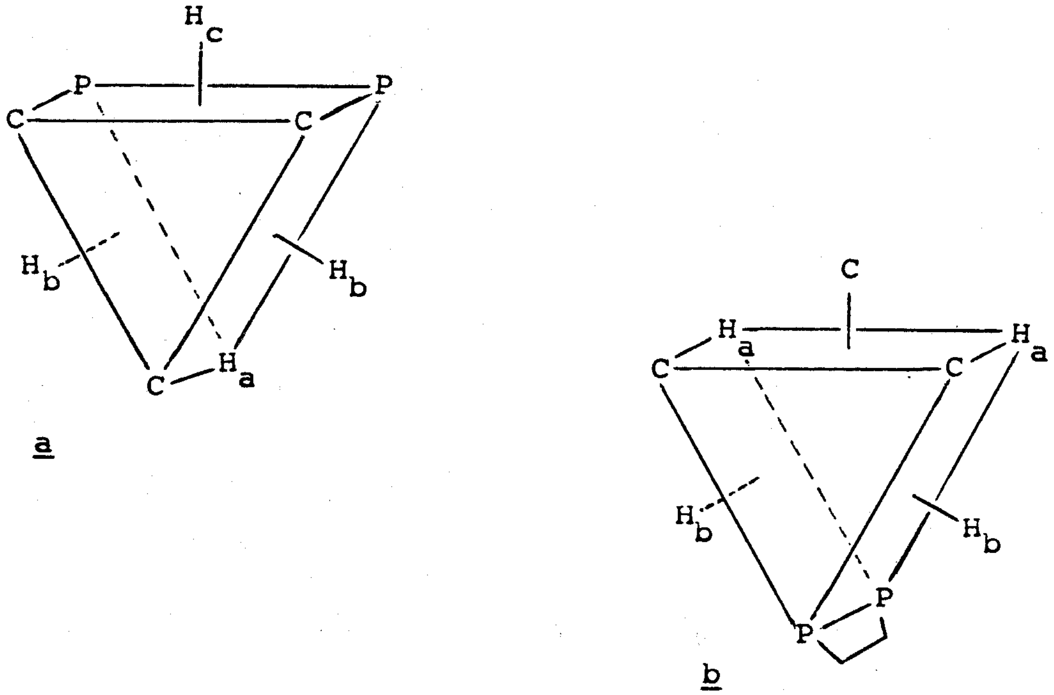


Figure 1.

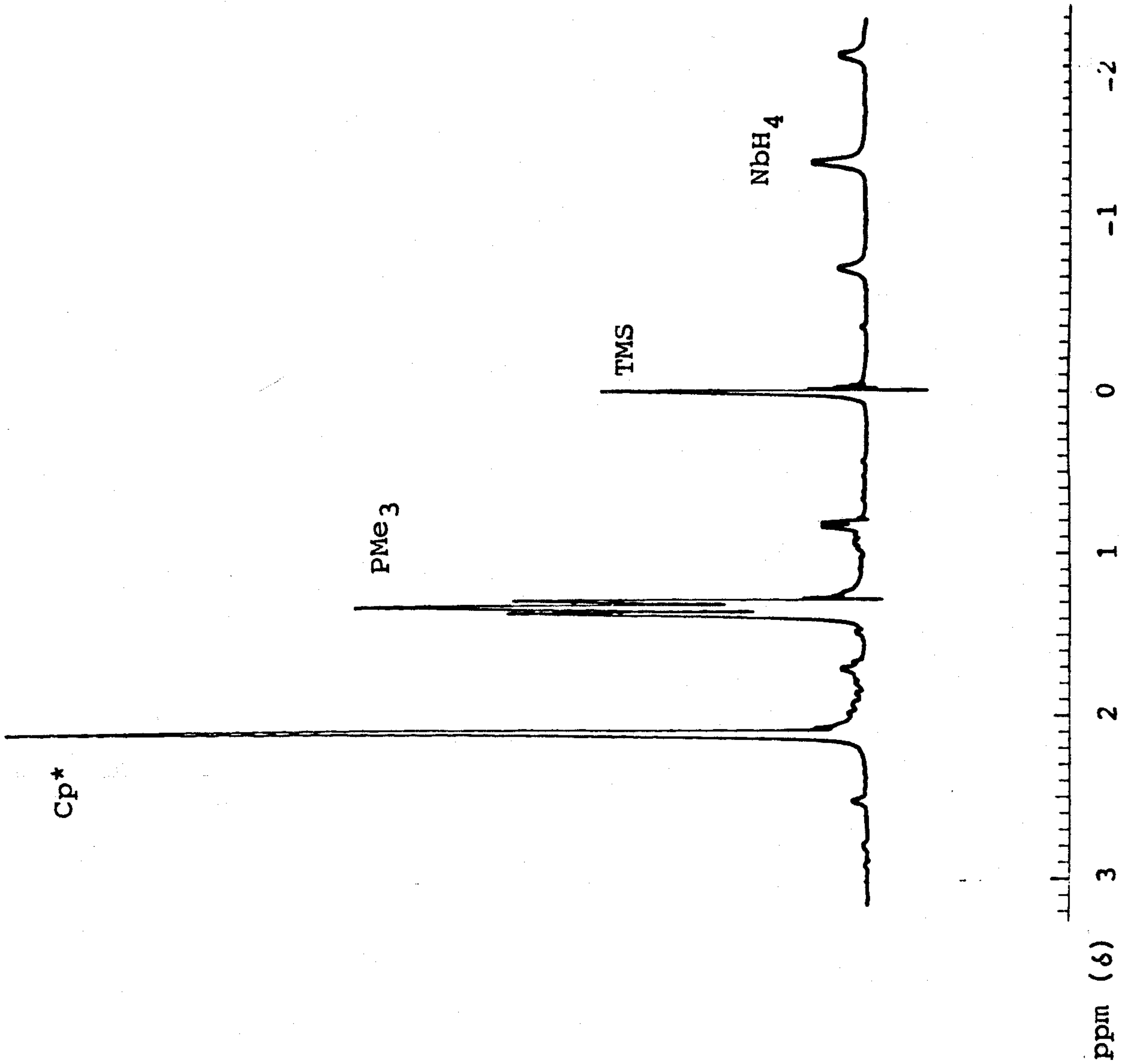


Figure 2. Nb*(PMe$_3$)$_2$H$_4$

Table II

Compound		IR (cm^{-1}) a	^1H NMR Data			
			Assignment	Chemical Shift (δ)	Coupling (Hz)	(Reference)
3	Nb*(dmpe)H_4	MH 1680 br	Cp*	2.23 s		
		1570 br	$\underline{Me}_2PCH_2CH_2P\underline{Me}_2$	1.23 "t"		
			$Me_2PC\underline{H}_2C\underline{H}_2PMe_2$	1.10 "d"		
			$Nb\underline{H}_4$	-1.35 t	$^2J_{PH}=45$	
4	Nb*$(PMe_3)_2H_4$	MH 1670 br	Cp*	2.10 s		
		1580 br	$P\underline{Me}_3$	1.33 "t"		
		^{b}MD 1205 br	$Nb\underline{H}_4$	-1.38 t	$^2J_{PH}=58$	
		1135 br				
5	Nb*$(PMe_2Ph)_2H_4$		Cp*	1.80 s		
		MH 1650 br	$P\underline{Me}_2Ph$	1.65 "t"		
		1600 br	$PMe_2\underline{Ph}$	7.85 m, 7.20 m		
			$Nb\underline{H}_4$	-1.05 t	$^2J_{PH}=57$	
6	Nb*$(PMe_2Cy)_2H_4$		Cp*	2.13 s		
		MH 1680 br	$P\underline{Me}_2Cy$	1.30 "t"		
		1600 br	$PMe_2\underline{Cy}$	1.8, 1.3 br		
			$Nb\underline{H}_4$	-1.73 t	$^2J_{PH}=59$	
8	Nb*$(OMe)_4$		Cp*	1.88 s		
			$O\underline{Me}$	4.17 s		
	Nb(dmpe)H_5	MH 1520	$Nb\underline{H}_5$	-2.09 quint		(14)
	$Nb(PMe_3)_4H_5$		$P\underline{Me}_3$	1.30 d	$J_{PH}=32.4$	(15)
			$Nb\underline{H}_5$	-0.67 quint	$J_{PH}=43.2$	

a. Nujol mull   b. Benzene solution

Table II

Compound	IR (cm^{-1}) ^{a}		^{1}H NMR Data		
		Assignment	Chemical Shift (δ)	Coupling (Hz)	(Reference)
Ta*(dmpe)H_4	MH 1715	Cp*	2.33 s		(2)
	1624	$\underline{Me}_2PCH_2CH_2P\underline{Me}_2$	1.32 m		
	^{b}MD 1250	$Me_2PC\underline{H}_2C\underline{H}_2PMe_2$	1.16 "d"		
	1160	$Ta\underline{H}_4$	0.19 t	$^{2}J_{PH}=37$	
Ta*$(PMe_3)_2H_4$	MH 1725	Cp*	2.16 s		(2)
	1640	$P\underline{Me}_3$	1.42 "t"		
	MD 1225	$Ta\underline{H}_4$	1.08 t	$^{2}J_{PH}=52.5$	
	1095				
Ta*$(PMe_2Ph)_2H_4$	MH 1730	Cp*	1.94 s		(2)
	1700	$P\underline{Me}_2Ph$	1.73 m		
	1655	$PMe_2\underline{Ph}$	7.11 m, 7.70 m		
		$Ta\underline{H}_4$	1.44 t	$^{2}J_{PH}=50$	
Ta*$(OMe)_4$		Cp*	2.00 s		(2)
		$O\underline{Me}$	4.22 s		
Ta*$(OCHMe_2)_4$		Cp*	1.91 s		(2)
		$OC\underline{H}Me_2$	4.58 sep	$J_{HH}=6$	
		$OCH\underline{Me}_2$	1.17 d	$J_{HH}=6$	

The Reactivity of $Nb^*L_2H_4$

The thermal stability of the polyhydride complexes and the lability and hydridic character of their hydride ligands have been investigated.

$Nb^*(dmpe)H_4$ (**3**) is quite stable both in the solid state and in solution. A benzene solution sealed under vacuum can be heated at 80° for approximately ten hours without appreciable decomposition. When **3** is sealed under H_2, it can be kept at 80° for over a month with only a small amount of free phosphine appearing in the NMR spectrum to indicate decomposition. After three months at 80°, the spectrum still shows over 90% **3**, a small new singlet about one-half ppm upfield of the Cp*, and a small amount of free dmpe.

3 has also been sealed under D_2 to moniter any D exchange into the hydride positions and possibly into the phosphine or ring methyl groups. (See experimental section for a description of this type of NMR experiment.) No reaction is observed in two weeks at room temperature. After three hours at 80°, however, the relative intensity of the hydride resonance decreases from 4H/Cp* to 3H/Cp*; after seven hours it is 1H/Cp*, and by nine hours at 80° the hydride signal is no longer visible. After several days at 80° there appears to be no exchange of deuterium into the dmpe or the ring methyls. After three months the solution decays to give ca. 70% starting material and 30% of the new singlet and free dmpe, with no other clear resonances apparent in the spectrum (figure 3).

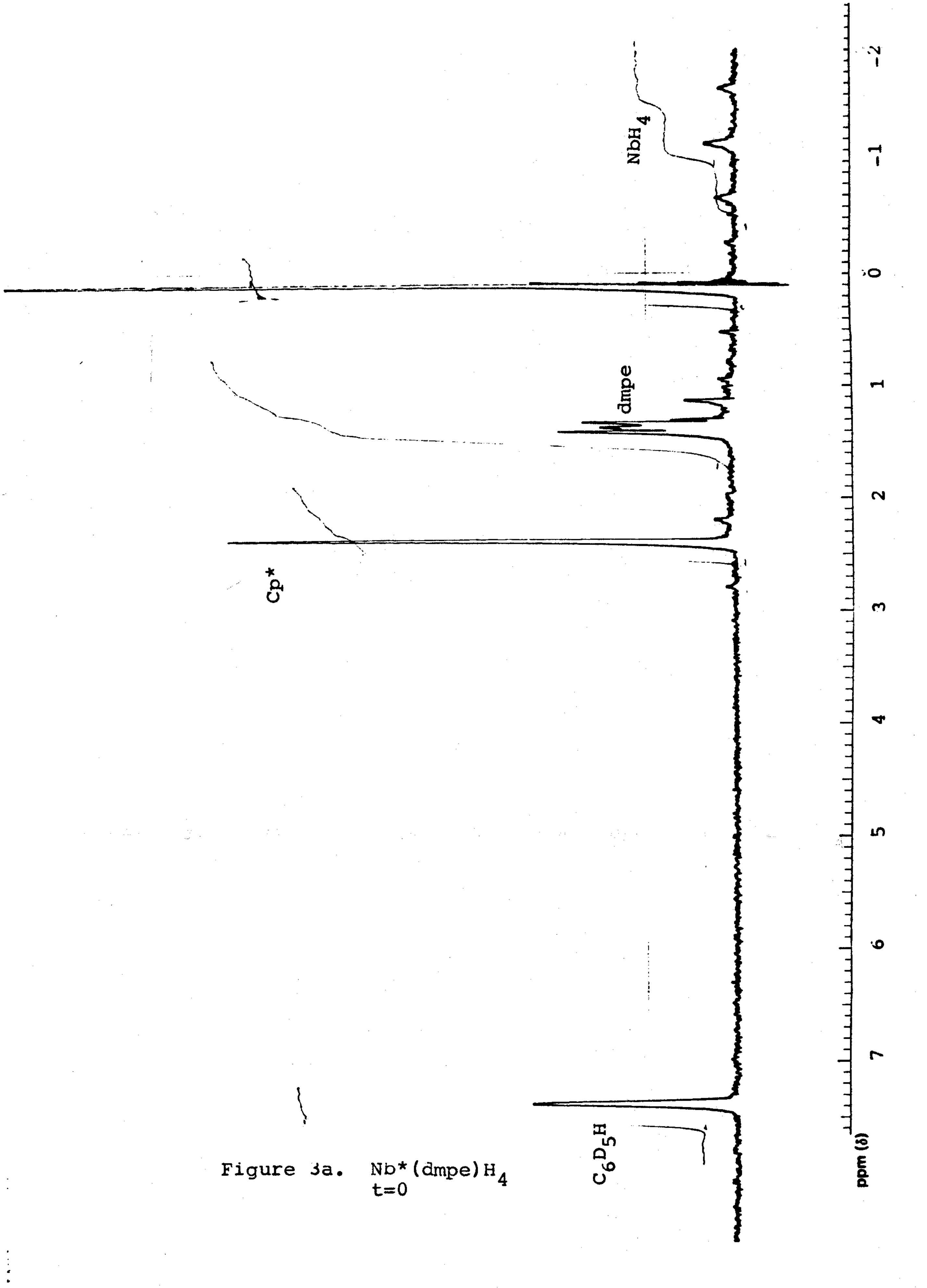


Figure 3a. Nb*(dmpe)H_4
t=0

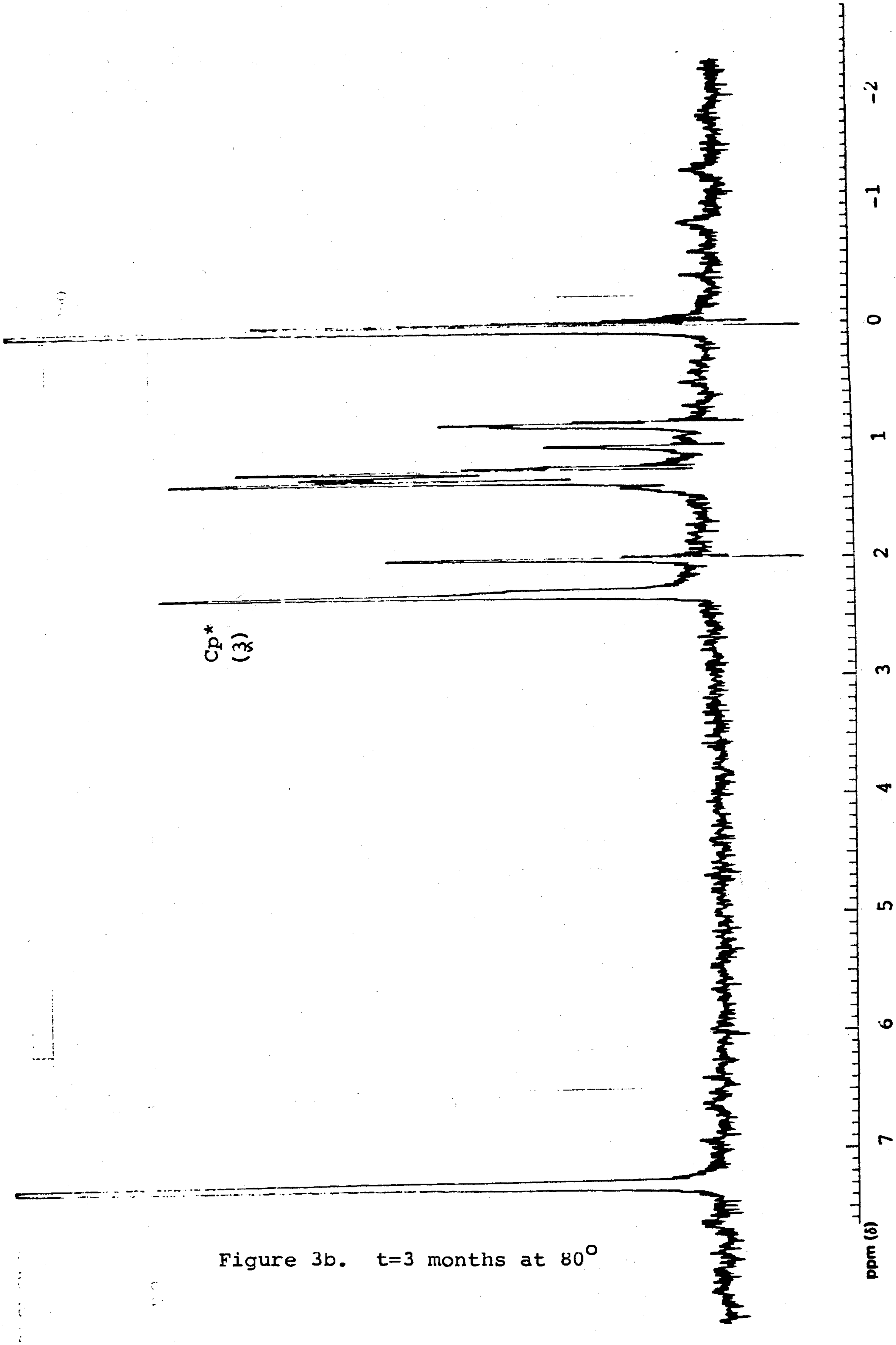


Figure 3b. t=3 months at 80°

$Nb^*(PMe_3)_2H_4$ (4) is considerably less stable than 3. The initial spectrum of a sample of 4 sealed in a tube with benzene under vacuum shows a small amount of free PMe_3, and this is seen in nearly all samples of 4. As PMe_3 is very volatile and is completely removed from the original reaction mixture with the solvent, the PMe_3 seen in the spectra comes from dissociation from the complex. After three and a half days at RT, a small peak is seen just upfield of the Cp* resonance in the NMR. The growth of this peak, accompanied by an increase in the amount of free phosphine seen, is greatly accelerated by heating the solution to 80°. After five minutes the new peak has tripled in size; decomposition to a number of products and free phosphine is seen in less than an hour at 80°.

A sample of 4 sealed under N_2 gives the same upfield peak, presumably a new Cp* resonance, and free phosphine. After one and a half days at 40°, this new peak reaches about half the total Cp* intensity, with no new features seen but free phosphine and a slight buildup of intensity between δ 1-2 (figure 4). Attempts to push the reaction further to the new Cp* product results in more general decomposition. This primary decay product has not yet been isolated or characterized. A similar initial decay product and free phosphine are seen for all the niobium polyhydride investigated here.

When sealed under H_2, 4 shows no sign of decomposition for ten days at RT, although a small amount of free PMe_3

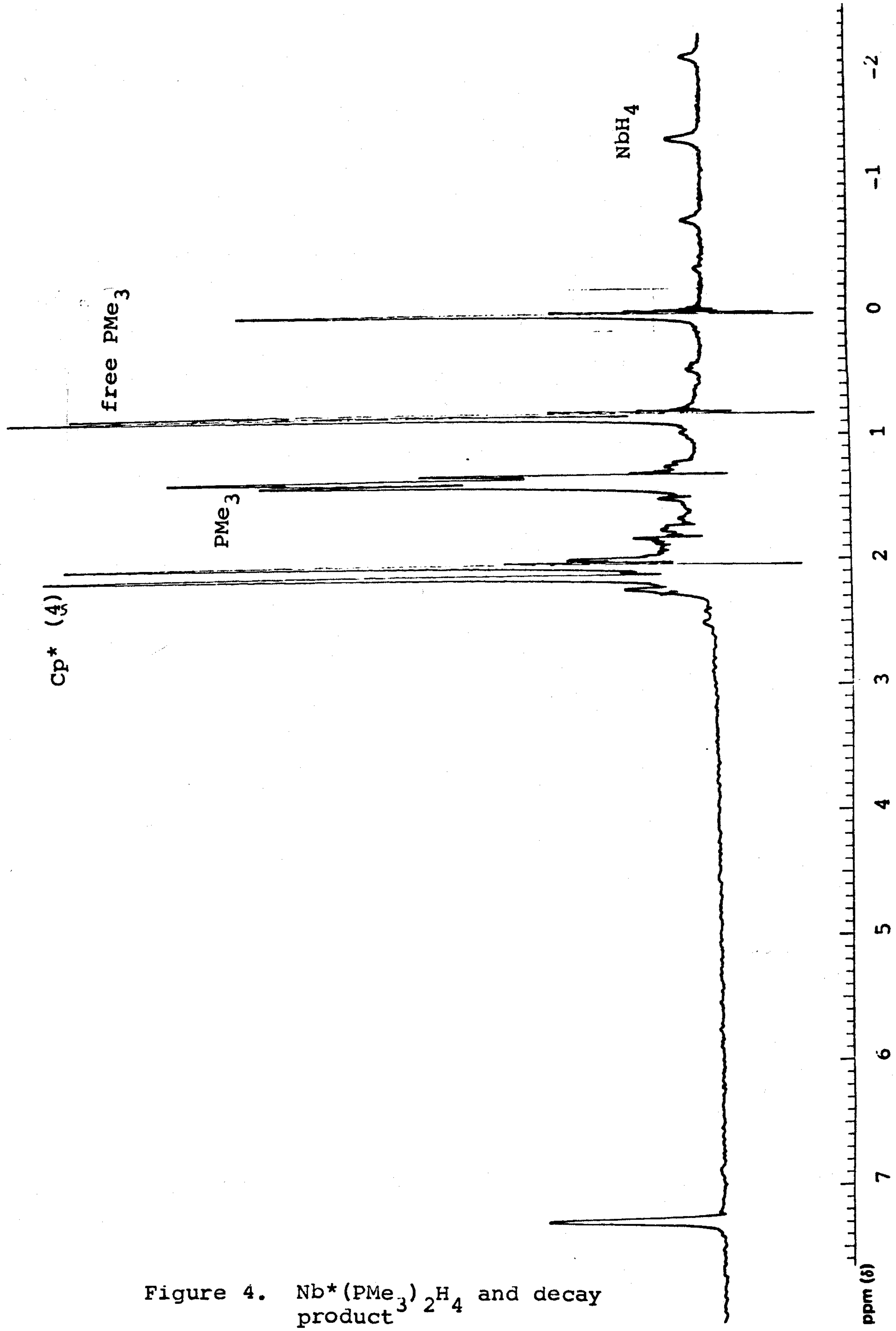


Figure 4. Nb*$(PMe_3)_2H_4$ and decay product

is seen. The solution shows only **4** when heated at 80° for five hours; within 24 hours extensive decomposition to a number of products occurs.

A sample of **4** sealed under D_2 exchanges deuterium into the hydride positions at room temperature within days. The hydride resonance decreases to 2H/Cp* within 22 hours; within ten days the intensity evens out at 1H/Cp*, apparently in equilibrium.[37] This does not change after five hours at 80°. No deuterium exchange into other groups on the niobium is seen.

It has been convincingly demonstrated in the $Ta^*L_2H_4$ systems that the general rate-determining-step for the reaction of those polyhydrides with CO, acetone, and ethylene is loss of phosphine (e.g. the relative rates of reaction go in the order of the phosphine lability; rates are depressed by addition of excess phosphine).[1,2] This appears to be true for the reactions of **3** and **4** with D_2 also: the bidentate dmpe ligand is much harder to dislodge (see comments in the discussion section for a fuller treatment), and the reaction of **3** with D_2 requires heating to 80° to proceed, whereas **4**, which is seen to lose phosphine readily, reacts with D_2 at room temperature. To test this, **4** was sealed under D_2 with excess PMe_3. The exchange appears to proceed much more slowly, requiring 100 hours to decrease to 2H/Cp*. No absolute comparisons can be made between the two NMR tube experiments, as the ratio of **4**:D_2 was not held constant. The difference is great enough, however, to state that PMe_3 does decrease the rate of exchange of the $Nb^*(PMe_3)_2H_4$ hydride ligands with deuterium gas.[38]

When the standard stability/exchange tests were performed with $Nb^{*}(PMe_2Ph)_2H_4$, some surprising and remarkable reactions occurred. These are presented in a later chapter.

One of the standard tests for the "hydridic" character of hydride ligands is reaction with acetone to give isopropoxides.[39] Some compounds that do so, such as

$$Cp_2NbH(CO) + Me_2CO \longrightarrow Cp_2Nb(OCHMe_2)(CO)$$

are stable to alcohols and water, however.[39a] A more rigorous test for hydridic character may be whether the "H^{-1}" ligands can be protonated by weak acids such as methanol. Such reactions have been done with the Cp*Ta tetrahydrides, which yield $Ta^{*}(OMe_3)_4 + 2L + 2H_2$ with methanol, as well as $Ta^{*}(OCHMe_2)_4 + 2L$ with acetone.[1,2]

The niobium polyhydride complexes also react with methanol and acetone, although the results are not as clear as for the tantalum system. $Nb^{*}(dmpe)H_4$ reacts with methanol at room temperature over a period of 12 days to give, through several intermediates, one major product and free dmpe. The corresponding $Ta^{*}(dmpe)H_4$ also reacted with methanol at RT, contrary to the reactions with acetone, CO, D_2, and ethylene, each of which required heating for reactions to occur. This is taken to indicate that the methanol is capable of protonating the hydride and forming H_2 without prior coordination to the metal. This is why it is a better indicator of absolute hydridic character of a ligand, as the reaction does not depend on prior opening of a coordination site, often the rate determining step.[2]

The final spectrum of the reaction of Nb*(dmpe)H_4 with methanol shows a large Cp* resonance with a small downfield shoulder, and a very broad peak which contains methyl resonances from rapidly exchanging (on the NMR timescale) free and bound methoxy groups (figure 5). When the excess MeOH is pumped away, the spectrum sharpens into just two peaks: Cp* (including the shoulder) at δ 1.88 and OMe at δ 4.17, ratio 15:12 (figure 6). The integration, along with comparison to the analogous Ta*$(OMe)_4$ data (Cp* δ 2.00, OMe δ 4.22),[2] allows formulation of the reaction product as Nb*$(OMe)_4$. It is interesting that the phosphine is totally lost in these compounds; if the alkoxide is counted as a negative, one-electron donor the complexes are formally only 14-electron. Steric crowding probably prevents the phosphine from binding, and lone-pair donations from some of the methoxy ligands can augment the electron count.

Similarly, within four days at room temperature, Nb*$(PMe_3)_2H_4$ reacts with excess methanol to give a new Cp* resonance, a broad methoxy peak, and free phosphine. There is an unexplained singlet, ca. 1/4 the height of the Cp*, at δ 1.17, which disappears when the excess methanol and phosphine are pumped off. The final spectrum again shows a small peak appearing as a downfield spike on the Cp* resonance. The Cp* peak, intensity 15, appears at δ 1.88, the OMe, intensity 12.8, at δ 4.18, showing the product to be Nb*$(OMe)_4$ also.

Nb*$(PMe_2Ph)_2H_4$ also reacts in four days to give Nb*$(OMe)_4$

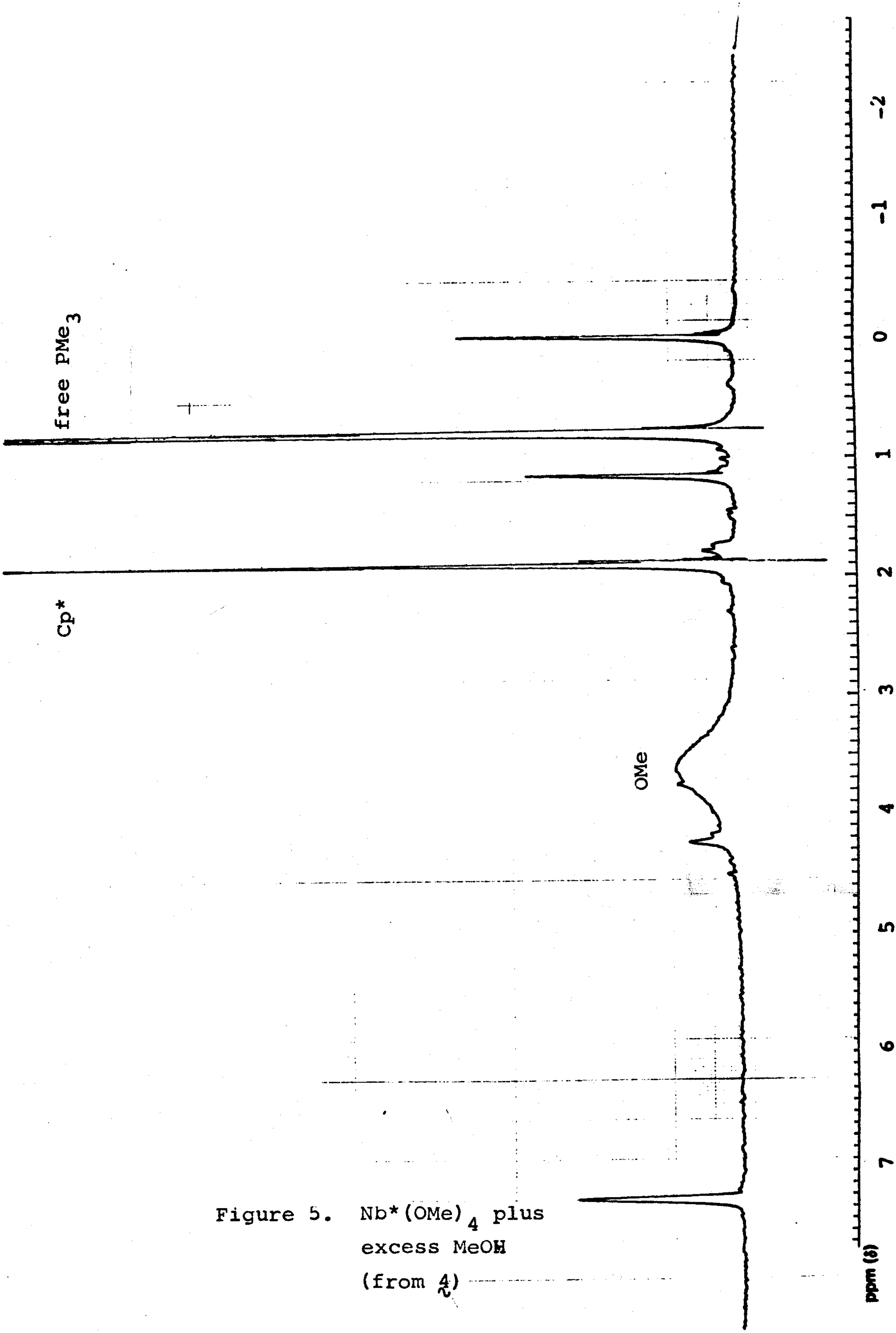


Figure 5. Nb*$(OMe)_4$ plus excess MeOH (from 4)

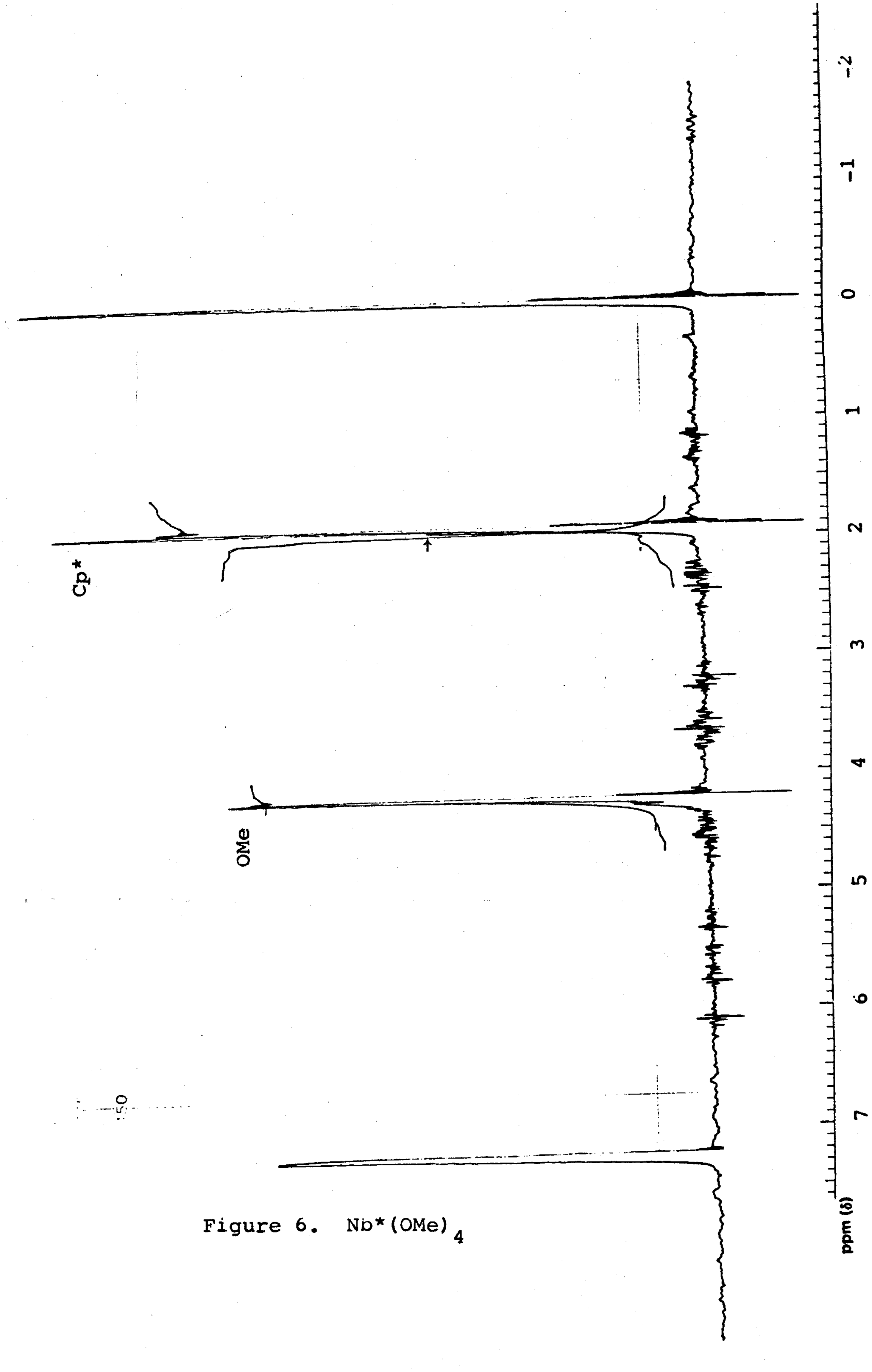


Figure 6. Nb*$(OMe)_4$

with the same feature on the Cp*.

Reactions of the niobium polyhydrides with acetone are not clean in any of the cases. $Nb^*(dmpe)H_4$ (3) shows no reaction after eight days at room temperature. Within one and a half hours at 80°, however, small bumps indicative of the isopropoxide C<u>H</u> hydrogens are seen around δ 5, along with free dmpe and other new peaks in the NMR spectrum. After 36 hours at 80°, there are two septets near δ 5, several peaks in the Cp* region, a mess at δ 1, much free dmpe, and no starting material (figure 7).

There appear to be a number of products formed: at least four major Cp* resonances are distinguishable; there are two different isopropoxide resonances (the C<u>H</u> spetets are visible, but the doublets for the methyl groups are not resolvable due to many peaks in the methyl region). Though the reaction is far from clean and simple, it does contribute several pieces of information. The necessity of heating the solution for the reaction to occur indicates that the dmpe must be lost and acetone coordinated to an open site on the niobium center to react, consistent with the tantalum findings.[2] The appearance of septets in the proper region[40] of the proton NMR spectrum, however messy that spectrum is, does show that 3 can reduce Me_2CO to $Me_2C(H)O^-$.

The reaction of $Nb^*(PMe_3)_2H_4$ (4) with acetone is also complicated. In an NMR tube containing 4 and ca. two equivalents of acetone, the reaction proceeds at room temperature to yield, after 11 hours, an NMR spectrum showing three septets, a large amount of starting material,

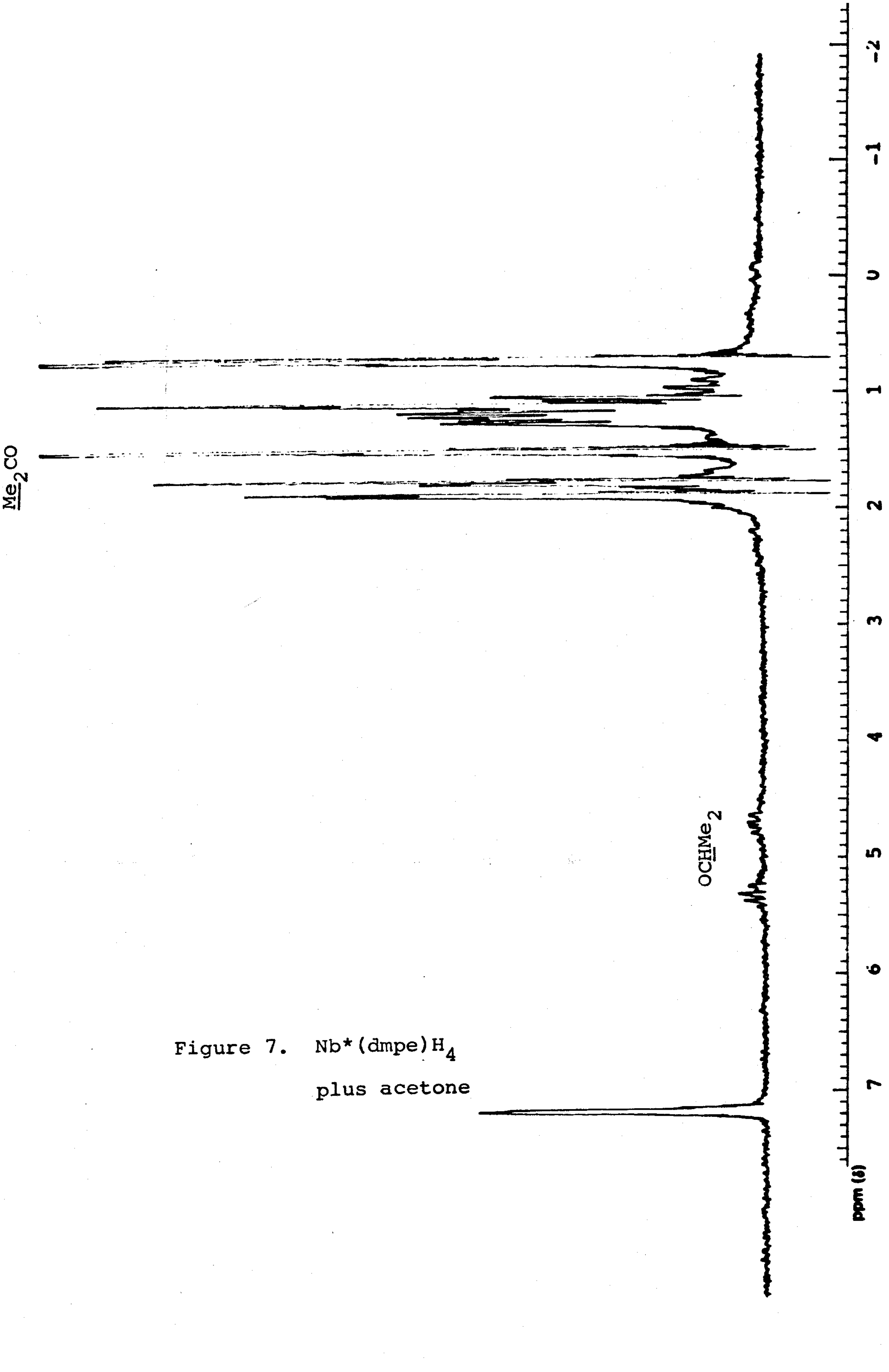


Figure 7. Nb*(dmpe)H_4 plus acetone

acetone, free phosphine, and what appears to be a doublet or inequivalent rings of a dimer in the Cp* region, as well as numerous other peaks (figure 8). The spectrum does not improve appreciably with time; the two peaks of the "doublet" in the Cp* region remain equal heights, and the phosphine methyl region is messy enough to obscure isopropoxide methyl resonances among various free and bound PMe_3 peaks. Further reactions occur, but there remains much starting material; apparently the reactions consume more than two acetone molecules per niobium, and do so rapidly enough that much of the hydride is left unreacted. Heating the solution destroys the starting material but does not simplify the spectrum.

Since the reactions did not consume only two acetone molecules per niobium anyway, a tube was prepared with an excess of four equivalents of acetone. The NMR spectrum after one day shows the three septets, but the rest of the spectrum is more complicated than before. After a week, the intensity of the septets has decreases somewhat, and there seems to be one major Cp*, and a major singlet at δ 1.2. The doublets with the appropriate coupling constants to go with the septets are not visible in the methyl region. After 25 days one septet is gone, another nearly so, and a new multiplet and a singlet have grown in nearby (figure 9). There are two major Cp* resonances. The methyl and phosphine-methyl regions are complicated. No attempts have been made to isolate of further characterize any of the products.

The reaction of **4** with acetone is obviously complex, with a number of pathways open. Part of this is due to the ability

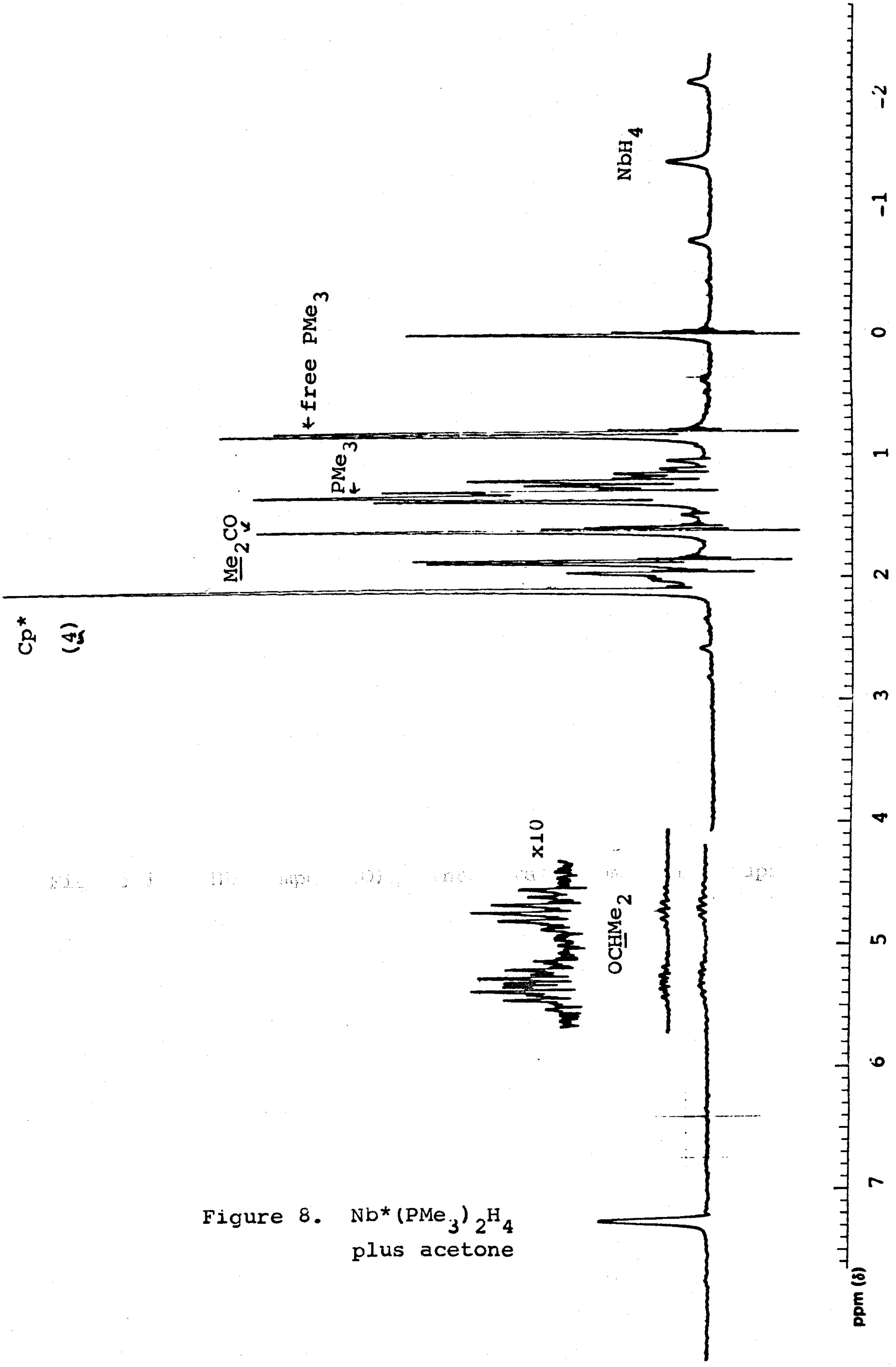


Figure 8. Nb*$(PMe_3)_2H_4$
plus acetone

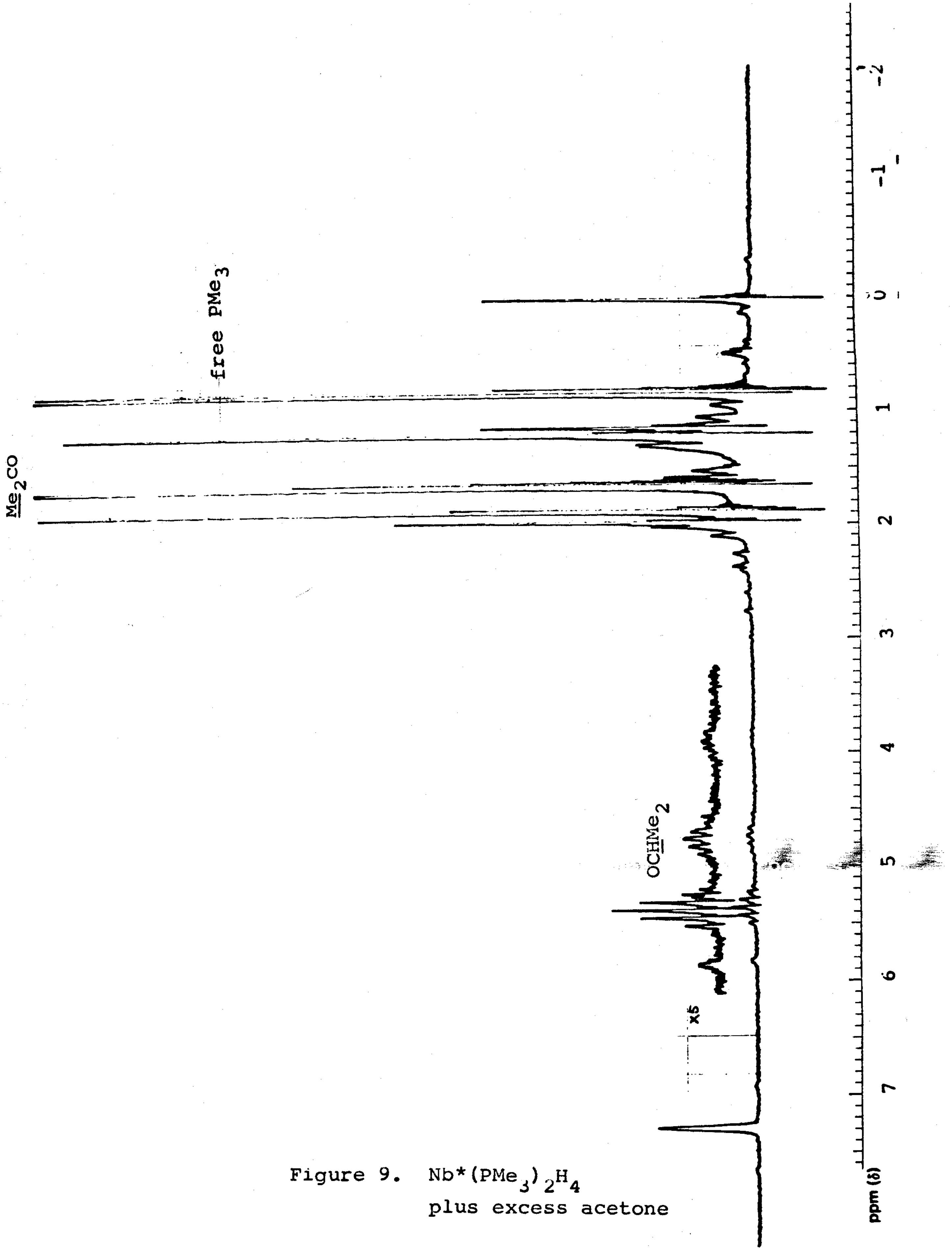


Figure 9. $Nb^*(PMe_3)_2H_4$ plus excess acetone

of **4** to reductively eliminate H_2 and the willingness of the niobium center to assume other oxidation states: not only Nb(V) but Nb(III) and Nb(I) are accessible. A variety of mixed alkoxide and phosphine complexes are then possible, as well as the possibility of coupled alkoxide products. It suffices for the moment to say that **4** also reduces acetone to isopropoxides.

With $Nb^{*}(PMe_2Ph)_2H_4$ and over four equivalents of acetone, the spectrum is a complicated mess after four hours at room temperature, but simplifies somewhat with time, and shows the same three septets after two days. Further results are qualitatively similar to the $Nb^{*}(PMe_3)_2H_4$ case.

Though the reactions with methanol and acetone are not simple and well-characterized, they do serve to show that these niobium polyhydrides react with such species, and demonstrate their hydridic character. They also point out the rate differences when phosphine loss is and is not required for reactions to occur. Data for niobium and tantalum alkoxides are found in Table II.

The Reactions of $\mathrm{Nb^*L_2H_4}$ with Carbon Monoxide

The reactions of the niobium polyhydrides with CO have, so far, yielded reduced metal carbonyls rather than reduced CO fragments. $\mathrm{Nb^*(dmpe)H_4}$ gives a single product, $\mathrm{Nb^*(dmpe)(CO)_2}$, whereas $\mathrm{Nb^*(PMe_3)_2H_4}$ gives three carbonyl compounds, $\mathrm{Nb^*(PMe_3)(CO)_3}$ and two apparent isomers of $\mathrm{Nb^*(PMe_3)_2(CO)_2}$. These three compounds exist together in mobile equilibrium. $\mathrm{Nb^*(PMe_2Ph)_2H_4}$ and $\mathrm{Nb^*(PMe_2Cy)_2H_4}$ make primarily the monophosphine tricarbonyl complexes under similar conditions. The $\mathrm{Nb^*(PMe_3)_2H_4}$ (**4**) system has been studied in the most depth to try to first identify the products in solution, then to understand their equilibria, and finally to see what this indicates about the mechanism of the reaction of the polyhydrides with CO.

$\mathrm{Nb^*(dmpe)H_4}$ (**3**) sealed under CO in an NMR tube shows no reaction in 14 hours at room temperature. When the solution is heated to 80°, however, a new Cp* peak is clearly visible in the NMR spectrum in 30 minutes. **3** goes cleanly and without visible intermediates to $\mathrm{Nb^*(dmpe)(CO)_2}$ (**9**) in 36 hours at 80° in toluene or benzene, with the uptake of two equivalents of CO and the release of two equivalents of H_2. The assignment of the product is made by NMR and IR data (Table III), elemental analysis and Toepler pump results (Experimental Section). The analogous compounds $\mathrm{Ta^*(dmpe)(CO)_2}$[1,2] and $\mathrm{CpNb(dmpe)(CO)_2}$[19] are known and the data consistent with them. Table III also lists IR and NMR data for a number of group V carbonyl compounds.

The ^1H NMR of **9** shows two non-first-order "filled in doublets" of equal intensity and a featureless lump, the total integrating to one dmpe unit per Cp* (figure 10). The two doublets are pairs of inequivalent methyls on the dmpe, one set pointing up into the ring, one away. This shows the dicarbonyl complex to be more rigid than the hydride complex, where the methyl groups were equivalent on the NMR time scale. It is assigned a structure as a "four-legged piano stool" with "*cis*" or more properly lateral CO groups, as seen in figure 11. This is the lowest energy configuration for compounds of the type $CpMX_4$.[41]

$Nb^*(PMe_3)_2H_4$ (**4**) sealed under CO reacts within hours at room temperature to give three new products and H_2, visible in the NMR spectrum of the reactions after less than an hour has elapsed. The starting material is gone in five days, but the relative intensities of the three products continue to shift for several months. Two of the Cp* resonances are superimposed, and two of the phosphine resonances overlap as well, making it difficult to decipher what is formed, and impossible to integrate cleanly.

To try to simplify the situation, excess phosphine was added, in the hopes that one or more of the products would be suppressed. Two samples were prepared at the same time, one simply **4** + CO (**A**), the other containing **4** + CO + 4 equivalents PMe_3 (**B**). Surprisingly, the two samples react at very nearly the same rate, and give about the same product distribution.

After 14 hours at RT, tube **A** shows ca. 26% reaction, the

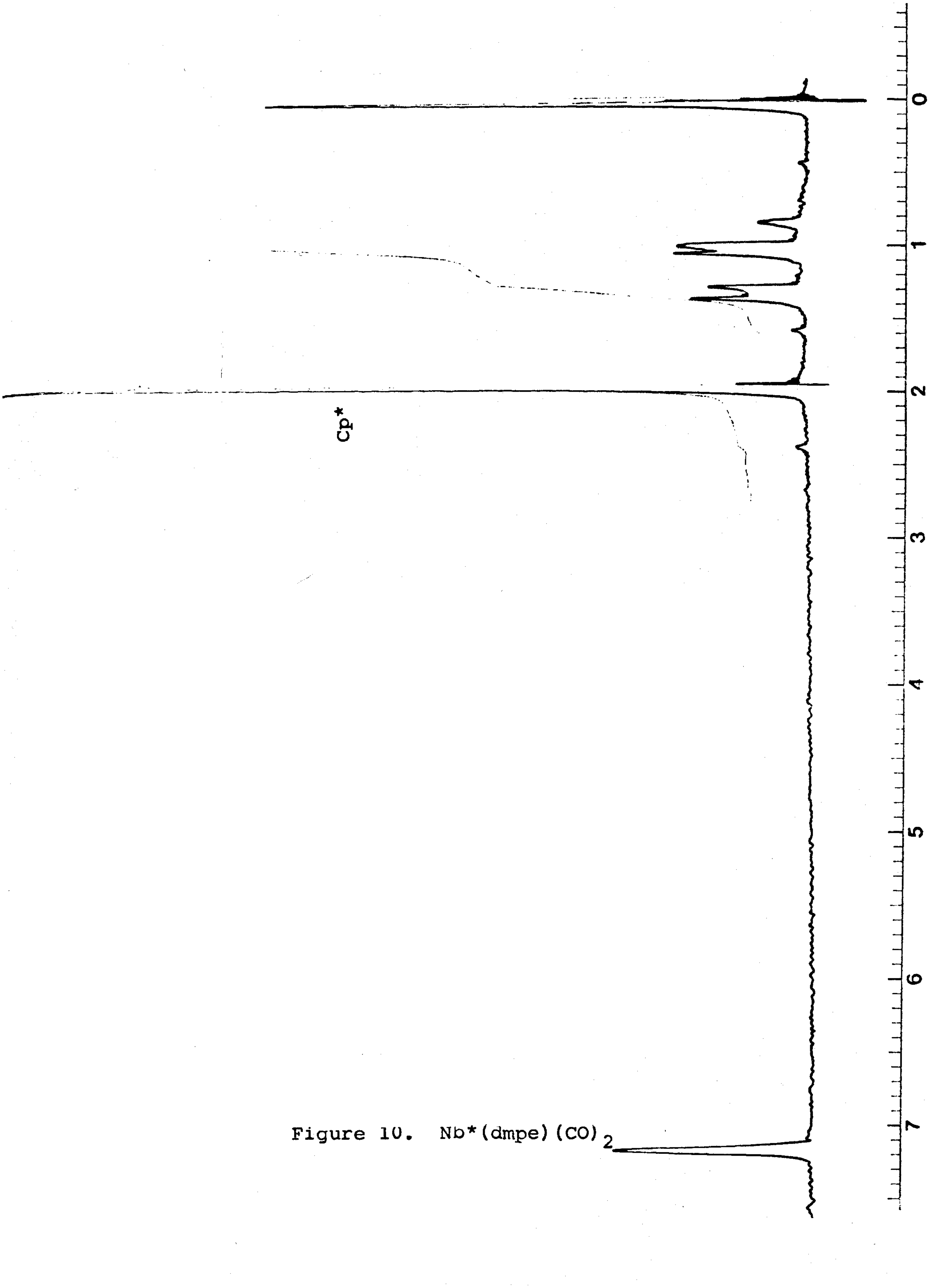


Figure 10. $Nb^*(dmpe)(CO)_2$

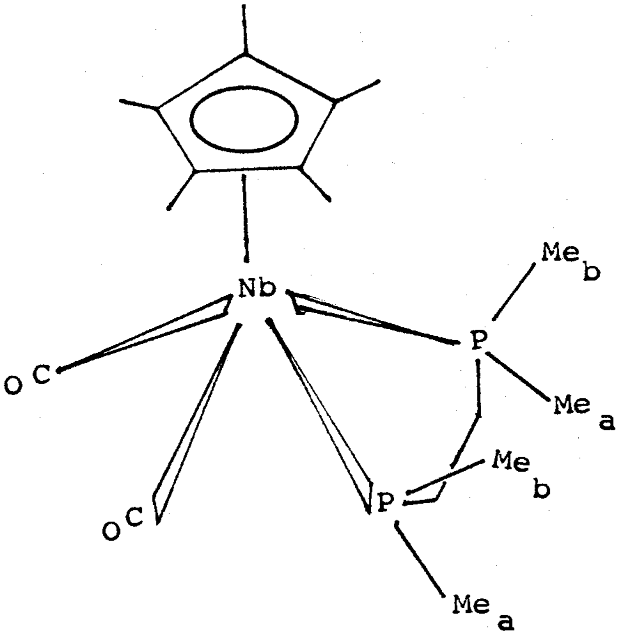


Figure 11. Nb*(dmpe)(CO)$_2$; inequivalent methyl groups

tube **B** ca. 21% reaction (based on peak heights of product Cp*'s versus the original). Both show peaks for H_2. By the fourth day, the starting material in each tube is essentially gone, and **A** shows phosphine resonances for two bisphosphine complexes (two "triplets" in the NMR), **10** and **11**, and one monophosphine complex (a "doublet") **12**, plus free phosphine. **B** shows **10** and **11** only (figures 12 and 13). After nine days, **10**>**11** in each tube, and **B** is showing some **12**. After a month, **11**>**10**, and **12** is larger in each tube, though still much larger in **A** than **B**. By two months, there is roughly twice as much **11** as **10** in each (figures 14 and 15). But when the samples are heated to 80°, **11** disappears. Upon standing at RT, **11** reappears in several days.

At this point, it is fairly clear that **12** contains only one phosphine (the phosphine methyls appear as a "doublet;" integration shows one Cp*/PMe_3; formation is greatly repressed by added phosphine), and is therefore formulated as $Nb^*(PMe_3)(CO)_3$ (three CO's to make it an 18-electron complex). Compounds **10** and **11** appear to be bisphosphine dicarbonyls: isomers or possibly a monomer/dimer pair. Separated compounds were needed for IR studies, though, before more could be said.

To try to obtain a single carbonyl product, 300 mg. of **4** were stirred under ca. three equivalents of CO and ca. four equivalents of PMe_3 in petroleum ether, in hopes that low CO plus high PMe_3 concentrations would prevent **12** from forming, and that a different solvent would favor either **10** or **11**. The product turns out to be over 95% **10**, with a very small amount

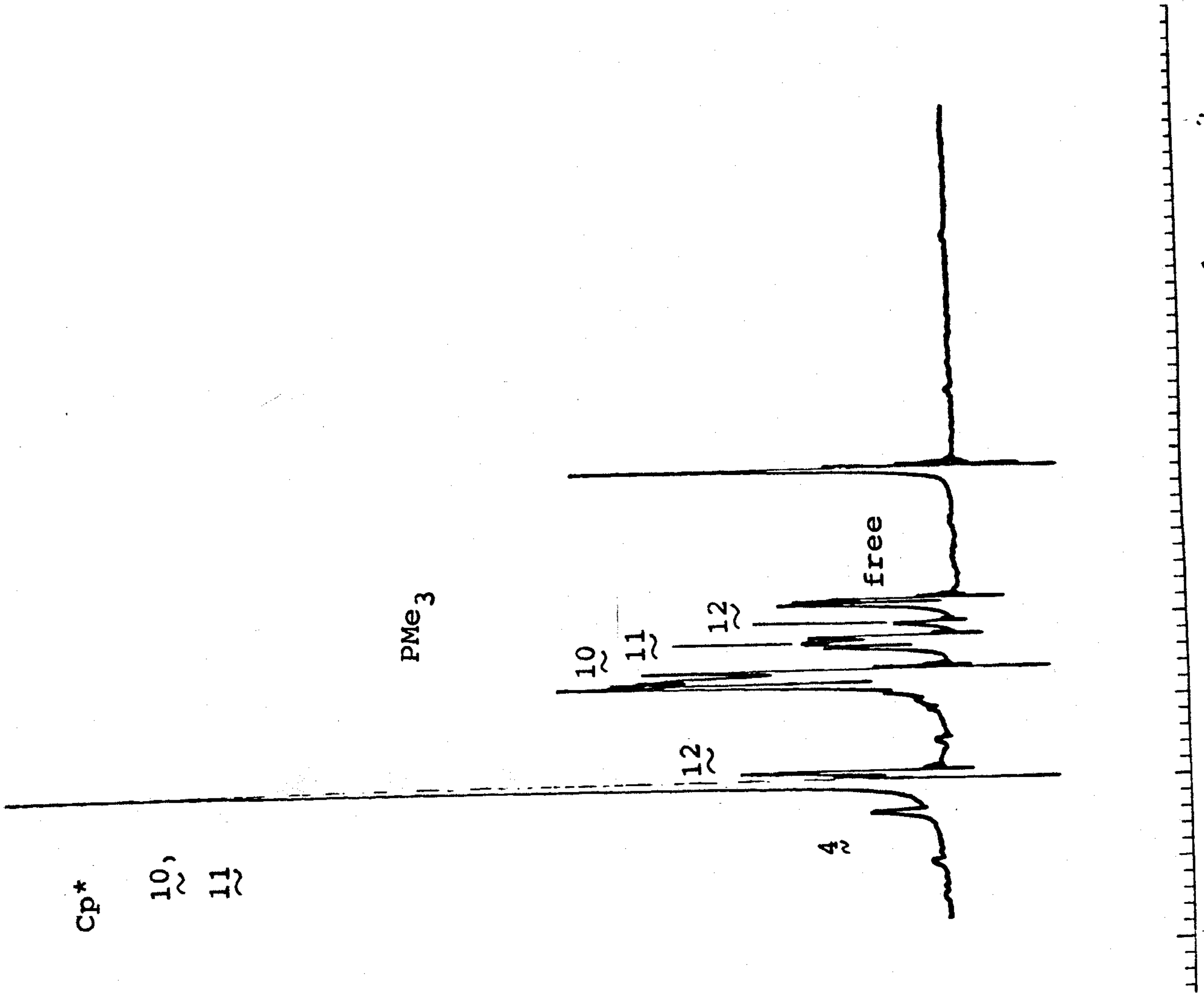


Figure 12. "A" $Nb^*(PMe_3)_2H_4 + CO$

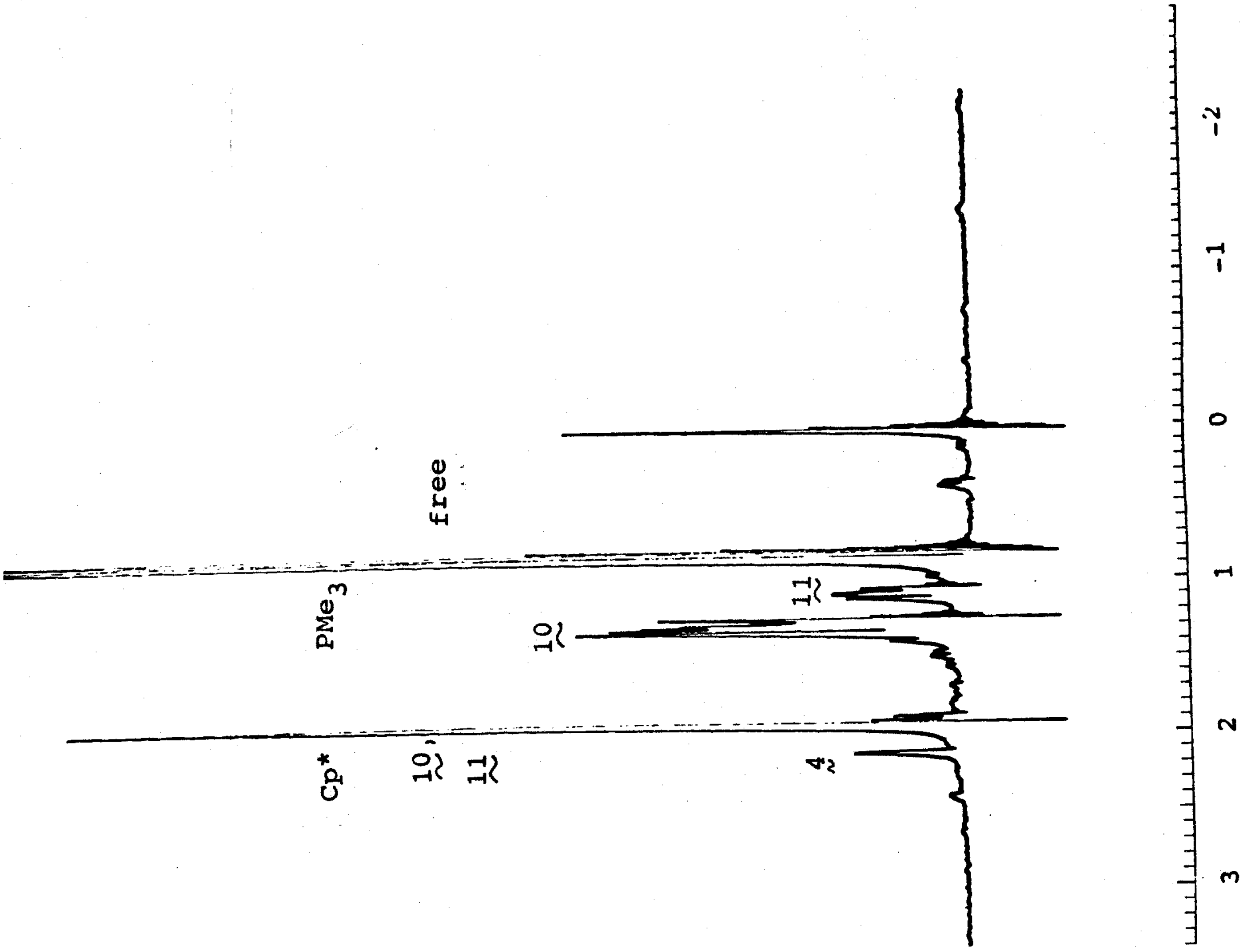


Figure 13. "B" $Nb^*(PMe_3)_2H_4 + CO + PMe_3$

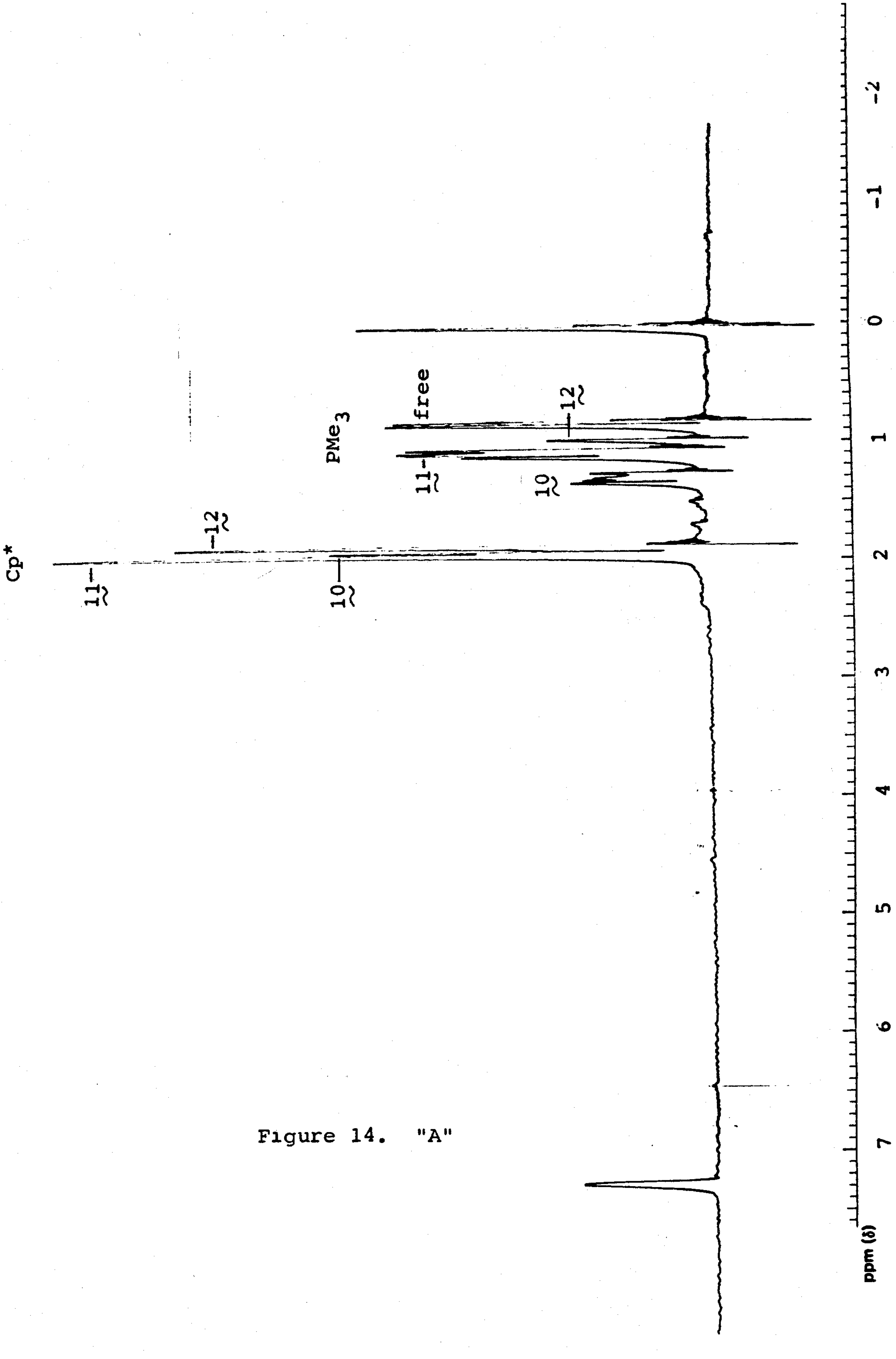


Figure 14. "A"

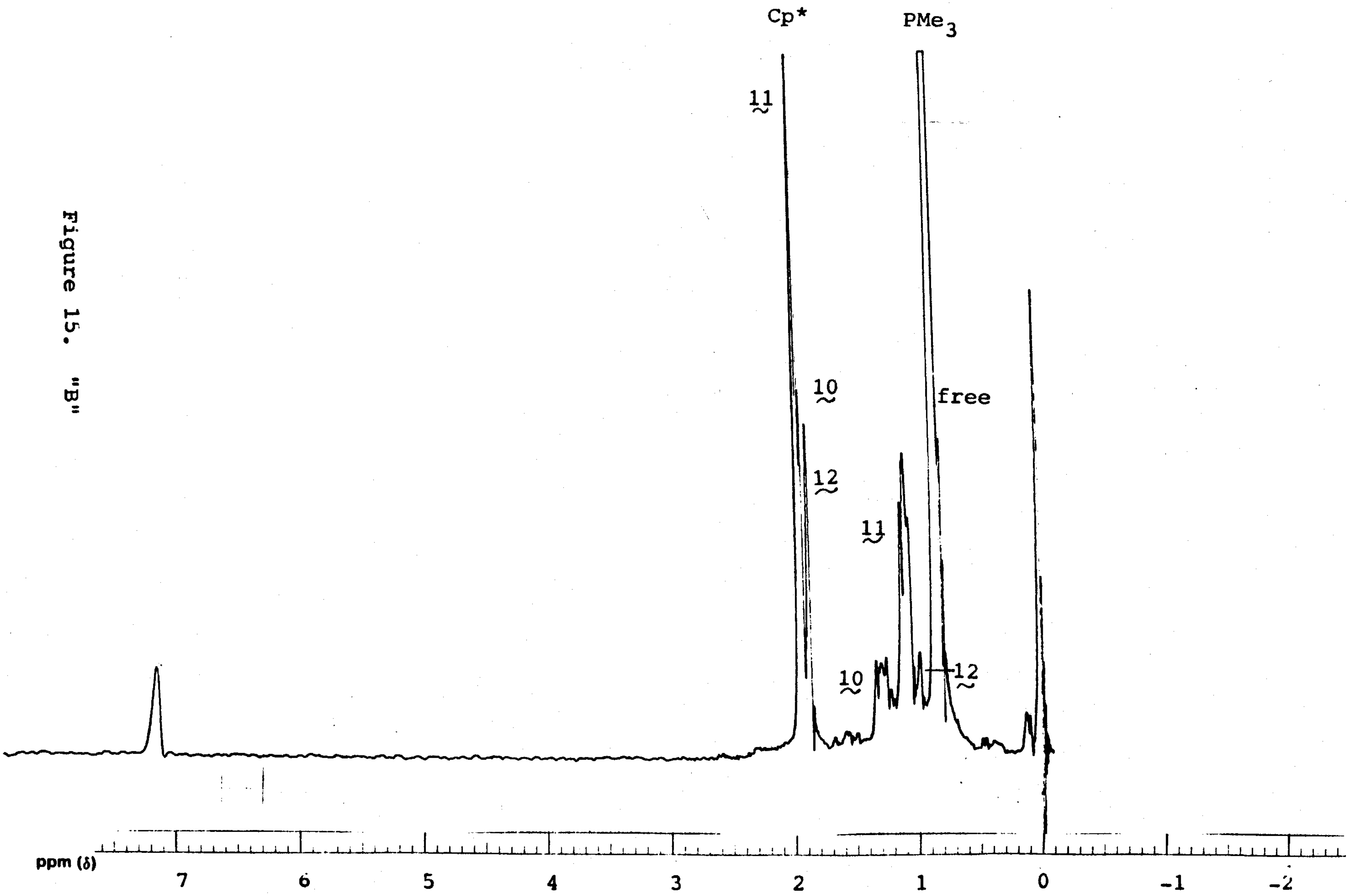


Figure 15. "B"

of 11 present. A solution of 10 in benzene transforms cleanly to ca. 75% 11, 25% 10 upon standing two weeks at RT, with no added CO. Another sample of 10, sealed under CO, reacts to form ca. 70% 12 in two weeks at RT. The solution of 75% 11, when sealed under CO, also goes to 12, although since 10 and 11 are always present together, it is not clear if 12 forms from both or from just 10, or just 11.

Accurate NMR and IR data on the three partially separated compounds were obtained from these reactions and are presented in Table III. Compound 10 is formulated as $Nb^{*}(PMe_3)_2(CO)_2$ by close analogy to the characterized $Ta^{*}(PMe_3)_2(CO)_2$. Although the Toepler pump experiments have not been done for Nb to prove it, it is strongly indicated that 11 forms from 10 with no addition of CO (in the sealed tube of just 10 going to 11, no decomposition products are seen, from which CO could have been scavenged), and no loss of CO (in the same tube, no 12 is seen, which should have formed from any CO released). Compound 11 is thus formulated as $Nb^{*}(PMe_3)_2(CO)_2$ also. IR data show no bridging CO's or other evidence for a dimer.

The most reasonable explanation for the pair of complexes 10, 11 appears to be "cis, trans" or lateral, diagonal isomerism, similar to that found for certain $CpM(CO)_2XY$ complexes (M=Re, Mo; X, Y= various combinations of halogens, alkyls, and phosphines).[41,42] The tantalum system also shows a pair of compounds with the stoichiometry of $Ta^{*}(PMe_3)_2(CO)_2$,[43] and the same explanation would appear to be in order there. There are some puzzling aspects to these pairs of compounds, however, and they are not completely understood.

In the rhenium systems, a number of compounds have been isolated in both lateral and diagonal isomers. The isomers may show differing solubility properties, NMR and IR data, and stability properties. For example, the diagonal isomer of $CpRe(CO)_2Br_2$ has higher IR CO stretching frequencies and a higher field Cp resonance in the NMR, and was considerably more soluble in organic solvents than the lateral isomer. The diagonal isomer was stable in solution to 110°, but the lateral form isomerized to the diagonal in solution when heated. Simple steric considerations account for all the observations about isomerization among the Re compounds presented: bulky groups preferred to be diagonal to each other.[42]

In the CpMo systems, a combination of steric and electronic effects appear to dictate the stereochemistry: where there are no severe steric interactions, strong _trans_ effect ligands appear to prefer to be "_cis_" or lateral. "_Cis_" and "_trans_" are used in a slightly different sense than for the square planar or octahedral complexes for which many of these properties were first defined.[41,44] Yet, it is reasonable that two strong pi acids such as CO would, if the circumstances would allow it, occupy lateral positions where they would not be competing for the same d orbitals for electron density.

In the $CpRe(CO)_2X_2$ cases, lateral and diagonal isomers were assigned on the basis of the relative strengths of the symmetric and antisymmetric CO stretches in the IR. The relationship[45] $\tan^2(\theta)=I_a/I_s$, where 2θ is the angle between the two C-O bonds, and $I_{a,s}$ is the relative intensity of the antisymmetric and symmetric bands respectively, was used. For $CpRe(CO)_2Br_2$, angles of 120° and 78° were obtained for the diagonal and lateral isomers.[42] The ranges expected for such compounds are 100-120° and 70-80°.[41] Very rough (i.e. using weighed cutouts from IR spectra for intensity data, and not extrapolating to infinite dilution) calculations for the niobium system reveal: $Nb^*(dmpe)(CO)_2$, constrained to be lateral by the chelating phosphine, gives a CO-CO angle of 95°. Compound **10** gives an angle of 116°, and compound **11**, 94°. While the values for the lateral isomers are somewhat high, they demonstrate the proper trend, and by analogy to the known lateral geometry of the dmpe complex, **11** is assumed to be lat-$Nb^*(PMe_3)_2(CO)_2$; **10** is diag-$Nb^*(PMe_3)_2(CO)_2$.

In the tantalum system, one bisphosphine dicarbonyl complex is made preferentially in benzene solution, and by the relative strengths of the CO stretching frequencies, it is the diagonal isomer.[1,2] In petroleum ether, however, the second, lateral isomer is quantitatively made because it is not very soluble in that solvent and precipitates, preventing further reaction or isomerization. The lateral isomer of Ta goes to the diagonal upon heating, with no loss or uptake of CO (Toepler pump results). Interestingly, the diagonal isomer does not react with CO to give the monophosphine tricarbonyl, but the lateral isomer does.[43] The reasons behind the isomers and their interconversions will be speculated upon in the discussion section.

The investigation of the reaction of Nb*$(PMe_2Ph)_2H_4$ (**5**) with CO has just been started, and only initial results are available. The polyhydride reacts rapidly and cleanly with CO to give initially a bisphosphine complex, then a monophosphine complex. It is not yet known if the addition of excess dimethylphenylphosphine has any effect on the rate of the reaction.

The rapid loss of H_2 from **5** is indicated by the presence in the initial spectrum (ten minutes after bringing to room temperature) of a small, ringing singlet at δ 4.5, assigned as H_2. Free PMe_2Ph is seen at the same time. This singlet is seen in the other polyhydrides, but not as clearly. After four hours, signs of both mono- and bisphosphine complexes are seen. All the starting material is consumed within ten days, and the monophosphine forms ca. 70% of the reaction mixture, bisphosphine 30%. This slowly reacts further, and the mixture was 90:10 when the experiment was halted. There appears to be no sign of a second bisphosphine complex. Unfortunately, an IR spectrum was not obtained when there was a significant amount of the bisphosphine complex remaining in solution. It is assumed, due to the larger bulk of PMe_2Ph over PMe_3, that the diagonal isomer is being formed. NMR and IR data are found in Table III.

The reaction of CO with a solution of Nb*$(PMe_2Cy)_2H_4$ proceeds much more quickly than for the other polyhydrides, even **5**.[46] A large, ringing singlet at δ 4.5 (large for H_2 in solution) and much free phosphine are seen in the initial NMR spectrum (figure 16). Within 15 minutes the intense red

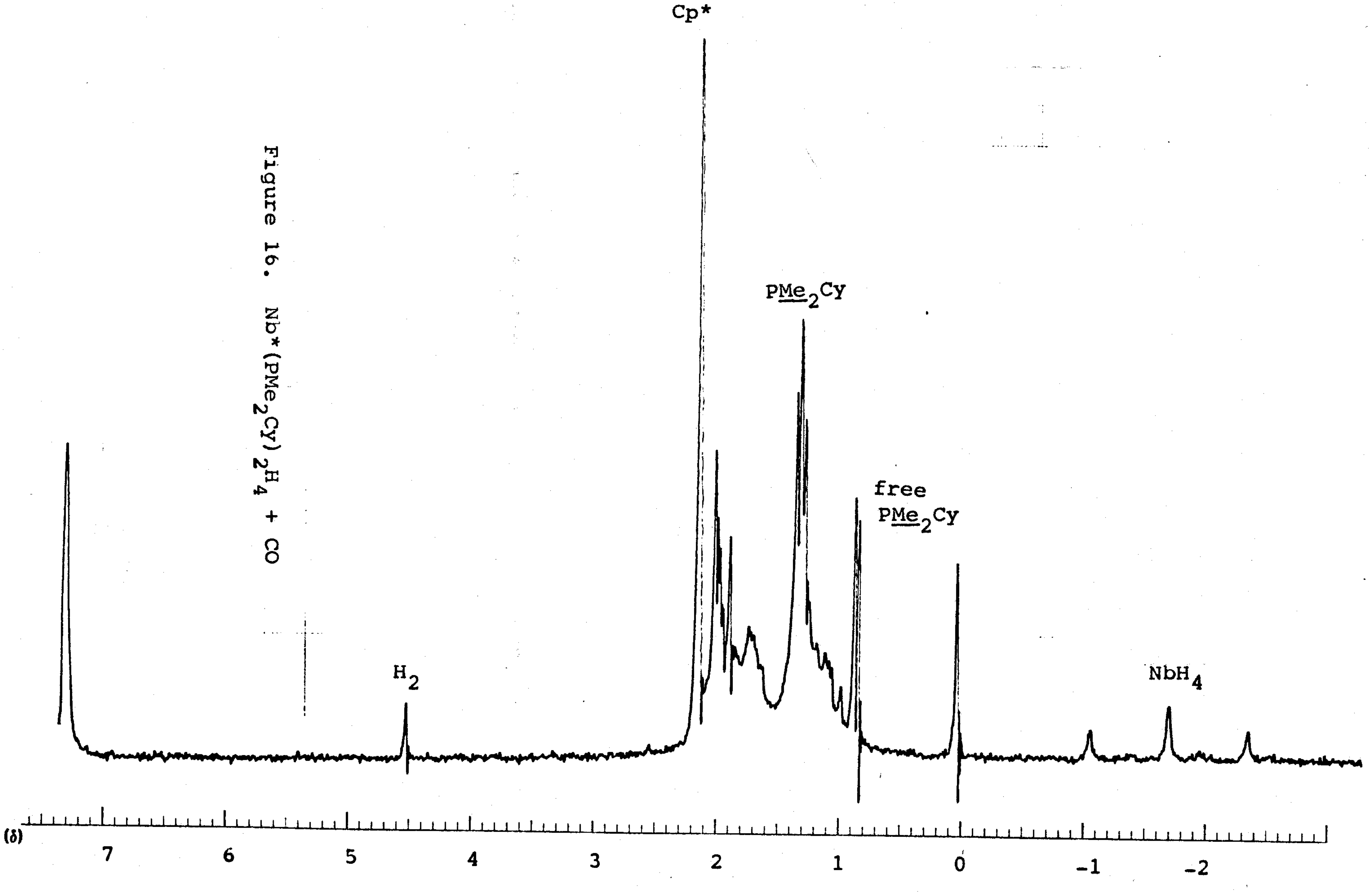


Figure 16. $\mathrm{Nb^*(PMe_2Cy)_2H_4}$ + CO

color characteristic of the solutions of these niobium carbonyl complexes is clearly visible. The starting material is ca. 80% gone in an hour at room temperature. As with the previous compound, the spectrum appears to contain resonances for a mono- and a bisphosphine complex, and free phosphine when the starting material has disappeared. The monophosphine tricarbonyl is the major product of this reaction. Spectral data are in Table III.

Table III

	Compound	IR (cm^{-1}) [a] (ν CO)	^1H NMR Data Assignment	Chemical Shift (δ)	Coupling (Hz)	(Reference)
9	Nb*(dmpe)$(CO)_2$	1835 str 1845 sh 1750 str	Cp*	2.00 s		
			$\underline{Me}_2PCH_2CH_2P\underline{Me}_2$	1.30 m, 10.7 m		
			$Me_2PC\underline{H}_2C\underline{H}_2PMe_2$	0.88 m		
10	Nb*$(PMe_3)_2(CO)_2$ (diag)	1840 med[b] 1745 str	Cp*	1.87 s		
			$P\underline{Me}_3$	1.25 "t"		
11	Nb*$(PMe_3)_2(CO)_2$ (lat)	1845 str[b] 1755 str	Cp*	1.88 s		
			$P\underline{Me}_3$	1.03 "t"		
12	Nb*$(PMe_3)(CO)_3$	1945 str[b] 1905 w 1830 str 1745 med	Cp*	1.83 s		
			$P\underline{Me}_3$	1.00 d	$J_{PH}=9$	
13	Nb*$(PMe_2Ph)_2(CO)_2$		Cp*	1.93 s		
			$P\underline{Me}_2Ph$	1.18 "t"		
14	Nb*(PMe Ph)$(CO)_3$	1945 str 1905 w 1825 str 1755 med	Cp*	1.72 s		
			$P\underline{Me}_2Ph$	1.32 d	$J_{PH}=7.5$	
	Nb*$(PMe_2Cy)_2(CO)_2$		Cp*	1.90 s		
			$P\underline{Me}_2Cy$	1.32 "t"		

a. Nujol mull b. Benzene solution

Table III

Compound	IR (cm^{-1}) a	^1H NMR Data			
		Assignment	Chemical Shift (δ)	Coupling (Hz)	(Reference)
$Nb^*(PMe_2Cy)(CO)_3$		Cp^*	1.83 s		
		$P\underline{Me}_2Cy$	0.98 d	$J_{PH}=7.5$	
$CpNb(dmpe)(CO)_2$	1840 1760	Cp	5.06 s		(19)
		$\underline{Me}_2PCH_2CH_2P\underline{Me}_2$	1.14, 0.91 d	$J_{PH}=8.3$, 6.4	
		$Me_2PC\underline{H}_2C\underline{H}_2PMe_2$	0.88 d	$J_{PH}=16.5$	
$Ta^*(dmpe)(CO)_2$	1830 1750	Cp^*	1.97 s		(2)
		$\underline{Me}_2PCH_2CH_2P\underline{Me}$	1.45, 0.99 d	$J_{PH}=7.5$, 6	
		$Me_2PC\underline{H}_2C\underline{H}_2PMe_2$	0.85 m		
$Ta^*(PMe_3)_2(CO)_2$	1842 1750	Cp^*	1.90 s		(2)
		$P\underline{Me}_3$	1.35 m		

Miscellaneous Reactions of $Nb^*L_2H_4$

Two additional types of experiments have been carried out with $Nb^*(dmpe)H_4$ (**3**) and $Nb^*(PMe_3)_2H_4$ (**4**) to explore their chemistry: reaction with group VI metal carbonyls, and reaction with ethylene.

The group V polyhydrides were exposed to group VI carbonyls to investigate the possibility of forming "metoxycarbene" species, as occurs with group IV hydrides. For example, $Cp^*_2ZrH_2$ reacts smoothly at -80° C with one equivalent of $Cp_2W(CO)$ to yield $Cp_2W{=}CHOZr(H)Cp^*_2$;[5a] and with $Cp_2Nb(CO)R$ to yield $Cp_2(R)Nb{=}CHOZr(H)Cp^*_2$ (R=H, alkyl).[5b] This is similar to the reactions of boron hydrides with organic carbonyls,[47] and important to the understanding of the mechanism of CO reduction by H_2 at metal centers.[4a]

When **3** is sealed in benzene with one equivalent of $Cp_2W(CO)$, however, no reaction is observed after three days at room temperature. After three hours at 80°, some decomposition of both **3** and the $Cp_2W(CO)$ are seen, but no resonances appear in the expected carbene region, δ 11-13 (based on data for Nb, W, Mo, and Cr "zirconoxy" carbenes[5,48]).

The reaction of **4** with $Cp_2Mo(CO)$ is complicated and not fully investigated yet. A sample of **4** sealed in an NMR tube with $Cp_2Mo(CO)$ (which contains a small amount of Cp_2MoH_2), shows a number of peaks in the NMR spectrum after 15 minutes at 80°. Most of **4** is left unreacted, but there is an increase in the amount of Cp_2MoH_2 visible; there is a large amount of free PMe_3, and there are several new Cp and Cp* resonances.

A small, broad peak appears very far upfield: the hydrides of 4 appear at -1.53, the Cp_2MoH_2 hydrides at -8.9, and the broad peak at -12.7. Further heating, and allowing to sit at room temperature for several weeks, produce minor changes in the spectrum, and general decomposition, but no signals are ever seen in the carbene region to indicate species such as $Cp^*(H)_x(L)_yNb{-}OCH{=}MoCp_2$. The reaction is clean enough in the early stages that further investigation to determine the reaction products is warranted.

Preliminary investigations of the reactions of 3 and 4 with ethylene have also been done. In the tantalum system, the reactions with C_2H_4 are complicated. $Ta^*(dmpe)H_4$ requires heating to 120° for any reaction with ethylene to ensue. The products are ethane, 1-butene, and a small amount of a new Cp* species, with much starting material left after all the ethylene in the sealed NMR tube is consumed. It is thought that a small part of the starting material hydrogenates the olefin, and the resulting reduced Ta species catalyzes the dimerization of C_2H_4 to 1-butene. When photolyzed in the presence of excess C_2H_4, $Ta^*(dmpe)H_4$ makes $Ta^*(dmpe)H_2(C_2H_4)$. $Ta^*(PMe_3)_2H_4$ appears to be a precursor for a ethylene dimerization catalyst; one isolated reaction product has been characterized as a metallacyclopentane butadiene complex, $Cp^*\overline{TaCH_2CH_2CH_2C}H_2(C_4H_6)$.[1,2]

For $Nb^*(dmpe)H_4$, results are also complicated, though somewhat different. Heating the reaction mixture to 80° is required for reaction, and a great deal of ethane is evolved from a solution of 3 plus excess ethylene. A new Cp* resonance appears concurrently with the ethane, and the starting material Cp* and dmpe signals decay. After four hours at 80° there remains much ethylene, but the starting material is nearly gone, and the NMR spectrum between δ 1-3 is quite complicated. There is a very large peak for ethane at 0.8. Very small peaks due to 1-butene may be seen near the ethylene resonance (δ 5.3). Apparently 3 is much more reactive towards ethylene than the Ta analogue, and hydrogenation of the olefin to ethane is the major reaction. The reduced Nb fragments may react further with the ethylene in various ways to give small amounts of 1-butene and the complicated mixture seen after the disappearance of all the starting material. The reaction to hydrogenate ethylene could probably be made catalytic under hydrogen.[2]

The reaction of 4 with excess ethylene in a sealed NMR tube proceeds at room temperature. After 16 hours a new Cp* peak has grown in to about the same intensity as the starting material peak in the NMR spectrum. There is a large, slightly broad doublet at δ 0.9, which contains two equivalents of free PMe_3 from the new Cp*, and ethane. There are resonances in the alkyl region which could be from a metallacycle or bound olefin. 1-butene is seen also. The reaction slows down as ethylene is consumed. After 39 hours there is still a small amount of 4, very little ethylene, and much 1-butene. After six days, much of the 1-butene is gone, and a second major Cp*, which appears to have a pair of doublets, centered at 1.07, associated with it, is gaining on the first. A preparative scale reaction, with ten equivalents of ethylene, yielded the two major products in a ratio of 2:1. The NMR spectrum of the isolated solid shows the two Cp* resonances, the pair of doublets, some faint vinylic resonances, and other broad resonances in the alkyl region (figure 17). These products have not been separated or further characterized yet.

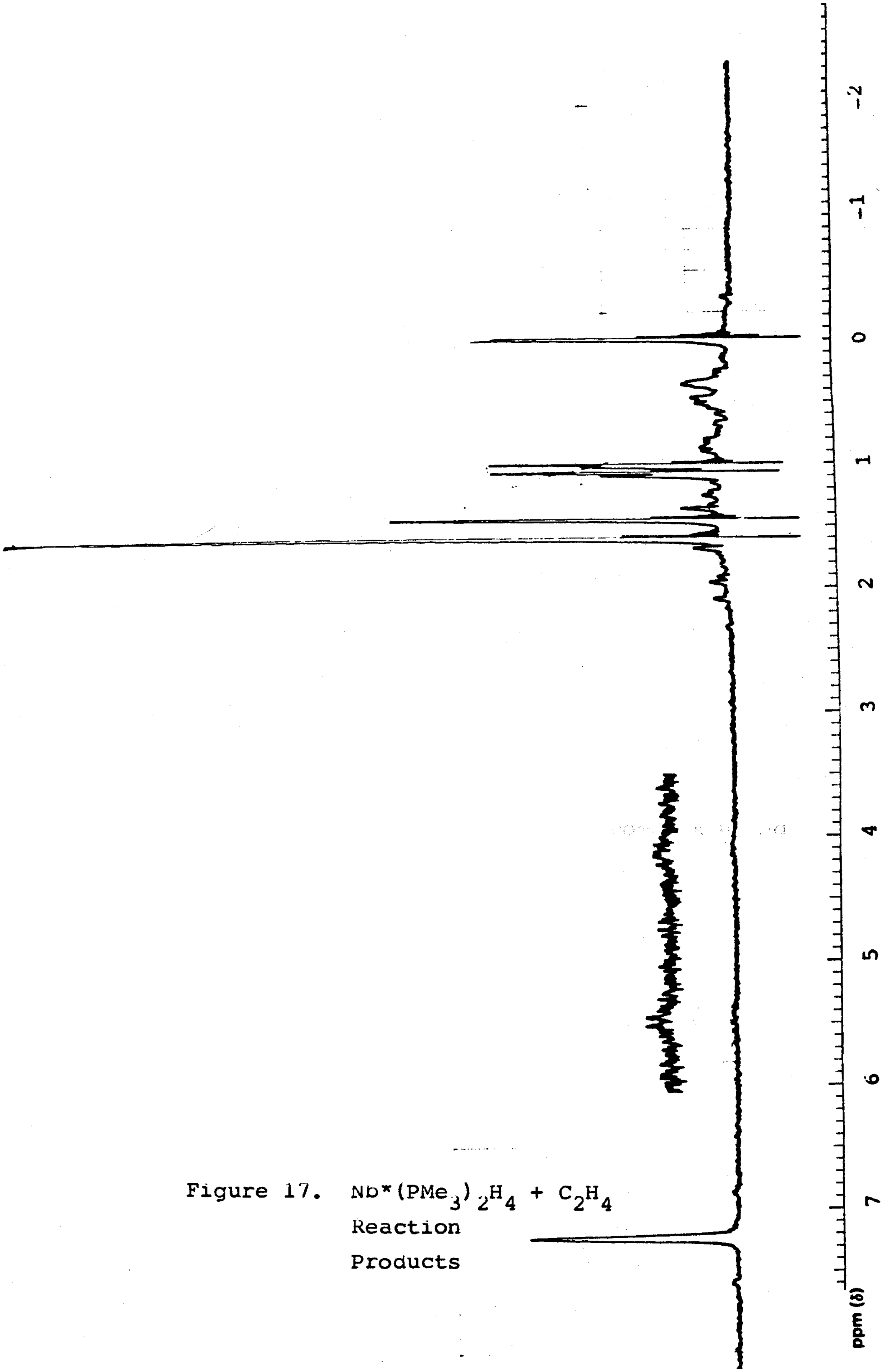


Figure 17. $Nb^{*}(PMe_3)_2H_4 + C_2H_4$ Reaction Products

The Novel Reactivity of Nb*$(PMe_2Ph)_2H_4$

A surprising and potentially important type of reaction was serendipitously discovered for Nb*$(PMe_2Ph)_2H_4$ (**5**): in the presence of H_2, the compound hydrogenates the phenyl groups on the phosphines to give first Nb*(PMe_2Ph)-$(PMe_2Cy)H_4$ (**7**), then Nb*$(PMe_2Cy)_2H_4$ (**6**). It also appears that **5** may be able to hydrogenate external activated aryls such as triphenylphosphine.

When a benzene solution of **5** is sealed under H_2 in an NMR tube (figure 18) it reacts at room temperature. Approximately 40% of the starting material reacts in 24 hours to give a new downfield Cp* resonance, two "filled in doublets" in the phosphine methyl region, and a new binomial triplet hydride resonance upfield of TMS. Another Cp* is visible as a small resonance at this point also (figure 19). This second Cp* grows until it equals--after four days--then overtakes the first. This second product has a "triplet" in the phosphine methyl region, and a different triplet hydride resonance associated with it (figure 20). During the reaction to give the two new products, the phenyl resonances slowly decrease, and a two-humped mound of proton intensity rises between δ 1-2½. First free PMe_2Ph, then free PMe_2Cy[49] are seen from 12 hours onward. The reaction slows as the amount of hydrogen decreases, but after three weeks at room temperature, the solution is almost all the second product (figure 21). This second product is deduced to be Nb*$(PMe_2Cy)_2H_4$ from the NMR data and the reaction conditions:

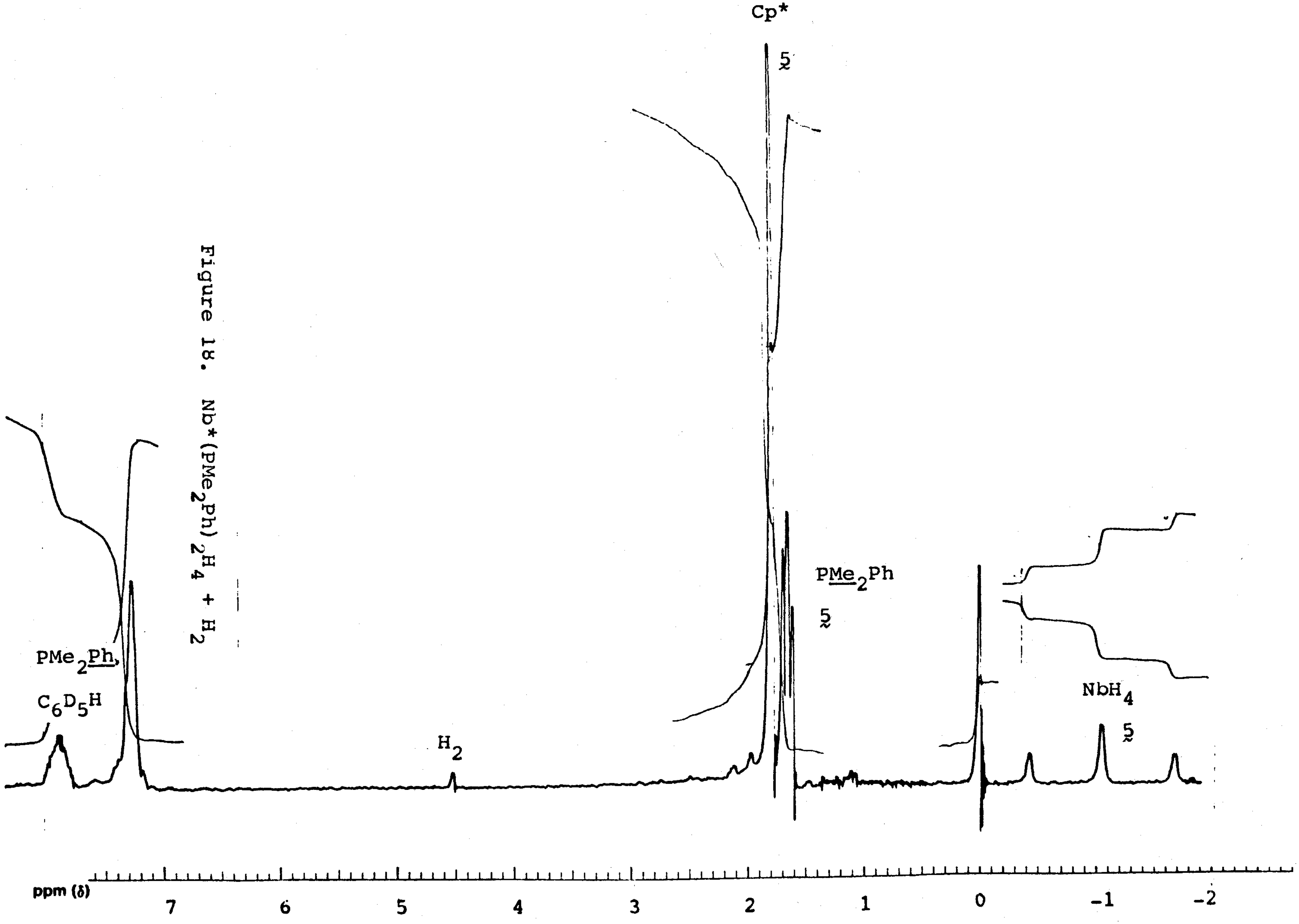


Figure 18. $Nb^*(PMe_2Ph)_2H_4 + H_2$

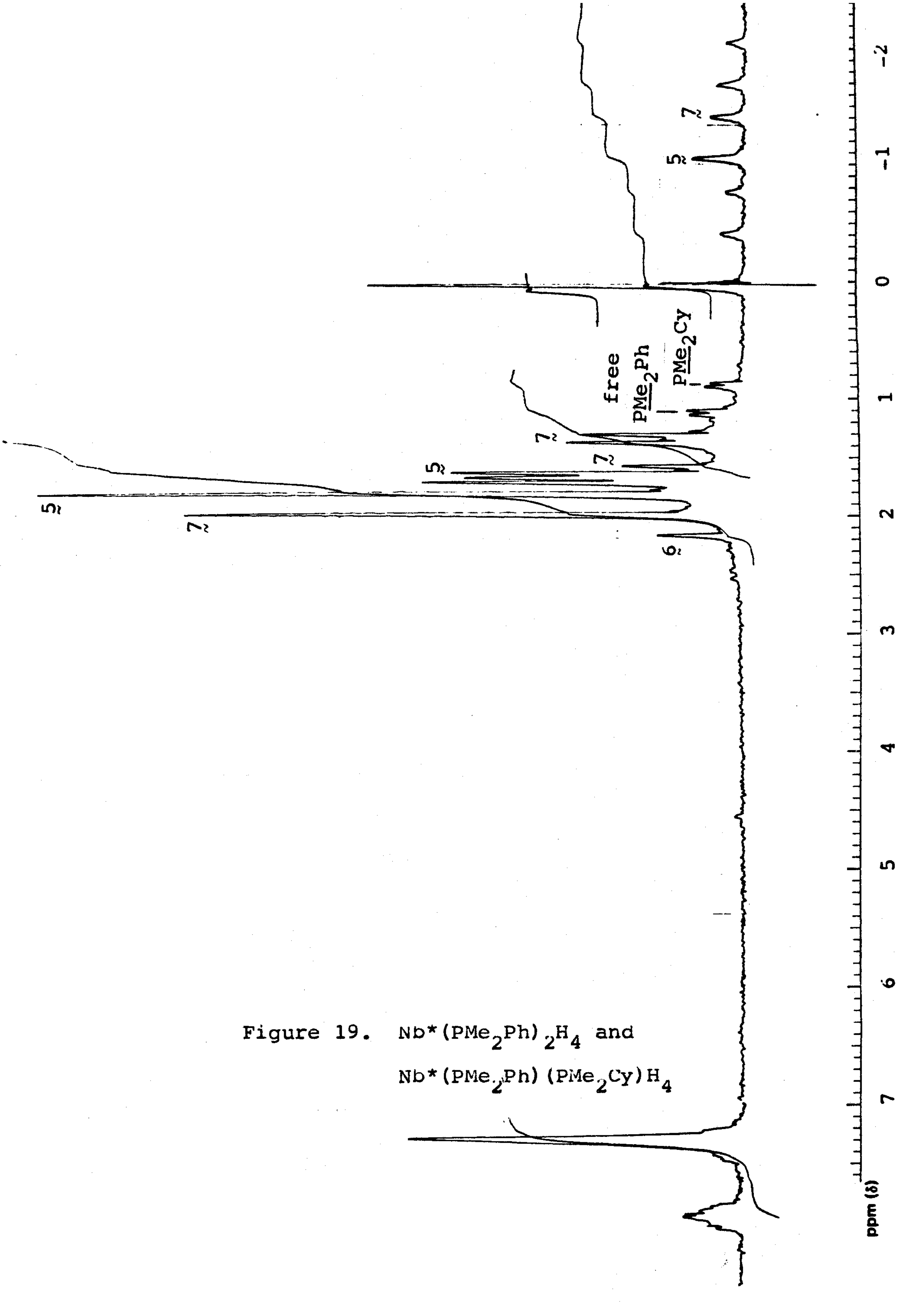


Figure 19. $Nb^*(PMe_2Ph)_2H_4$ and $Nb^*(PMe_2Ph)(PMe_2Cy)H_4$

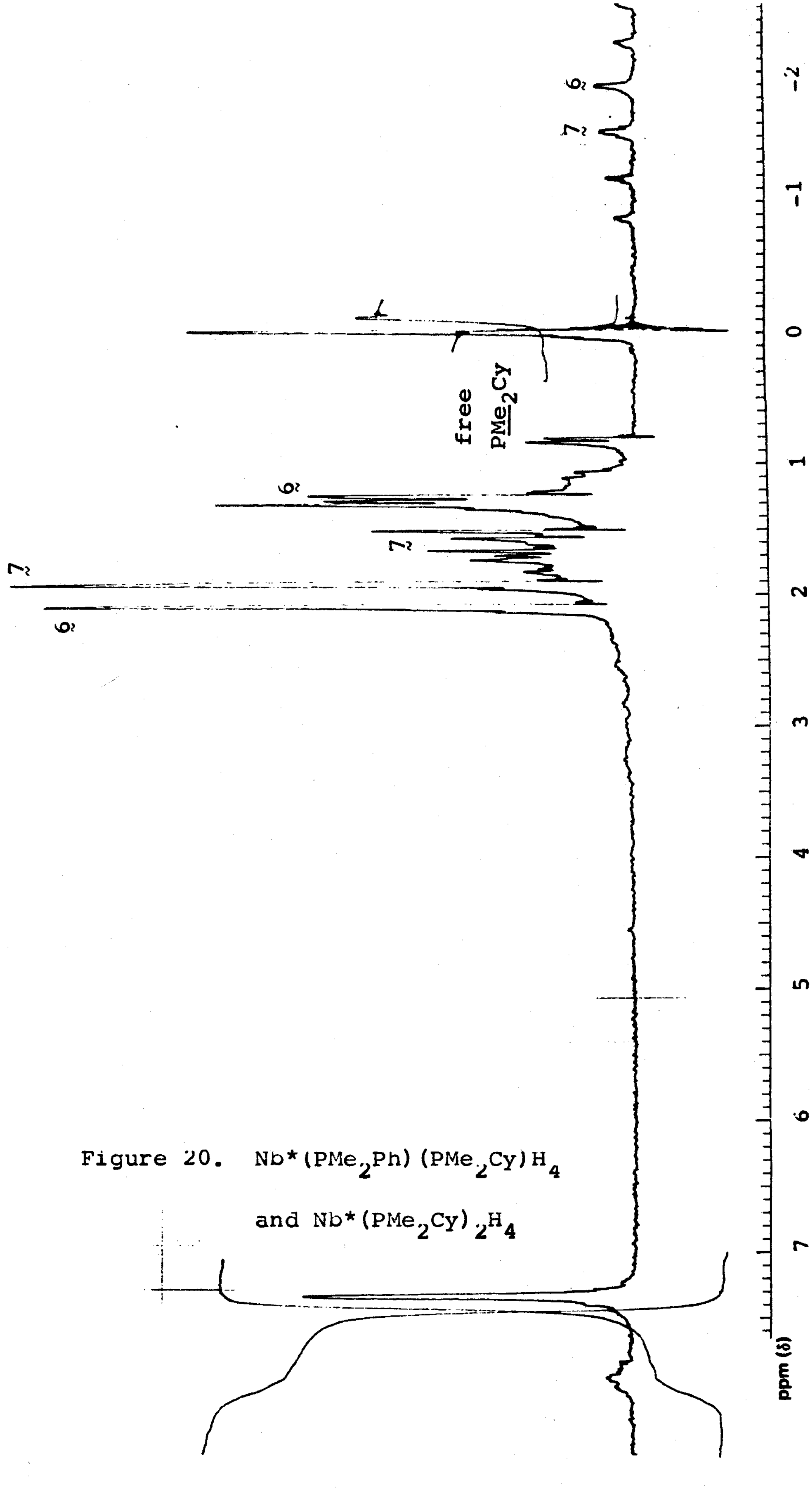


Figure 20. $Nb^*(PMe_2Ph)(PMe_2Cy)H_4$

and $Nb^*(PMe_2Cy)_2H_4$

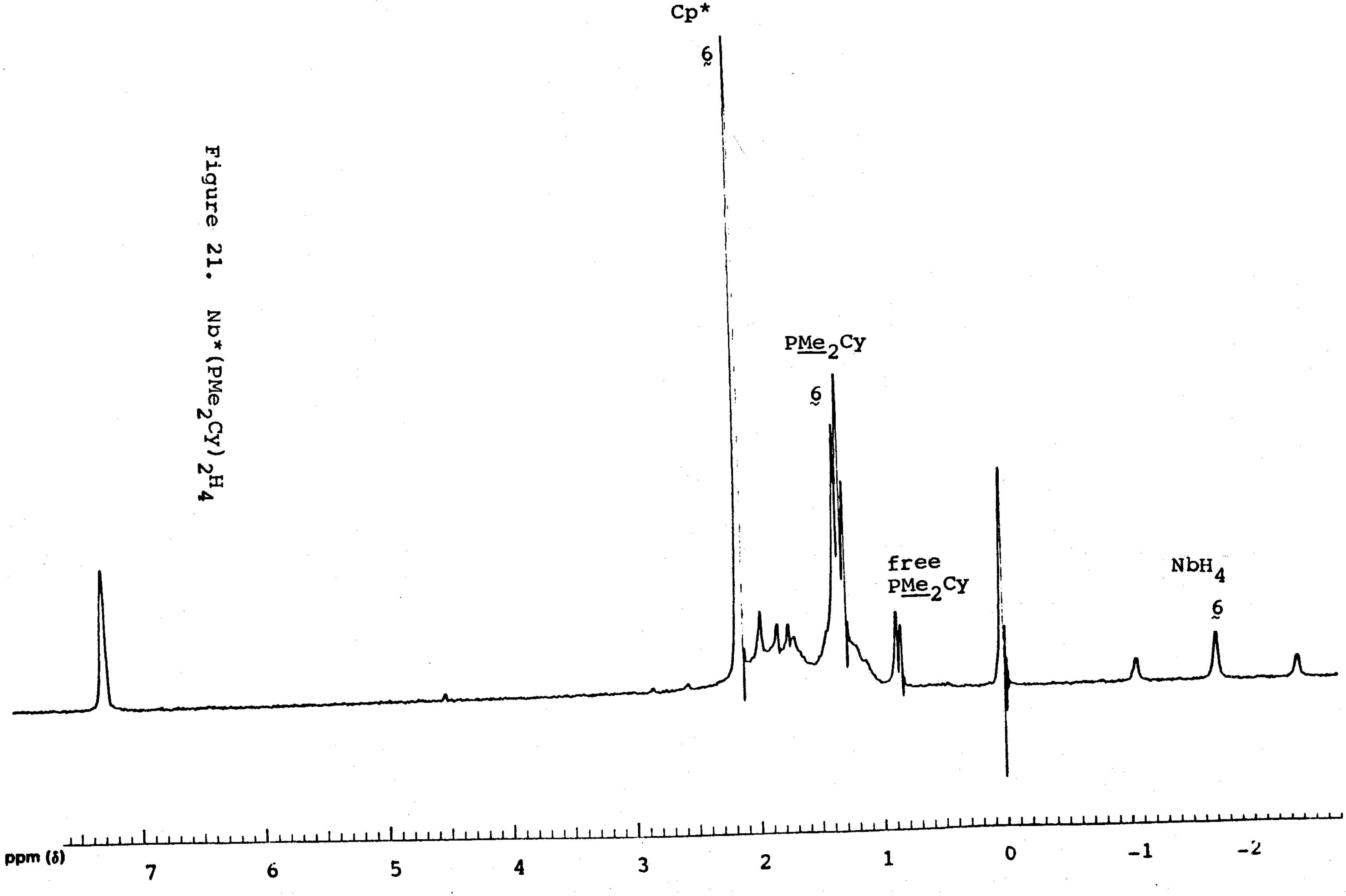


Figure 21. Nb*(PMe$_2$Cy)$_2$H$_4$

Clean conversion of 5 to 6 occurs only in the presence of H_2; the phosphine methyl resonances shift upfield from 1.65 to 1.30, closer to the trialkylphosphine value of 1.33 for PMe_3; the phosphine phenyl resonances disappear completely, replaced by a rise in the alkyl region, replaced in fact by two broad peaks very close in position and shape to the alkyl resonances seen for tricyclohexylphosphine (figure 22); and, despite all these changes, there remain hydride resonances of relative intensity 4H/Cp*, shifted upfield but still split by two equivalent phosphorus atoms.

The intermediate product is then assumed to be $Nb^*(PMe_2Ph)(PMe_2Cy)H_4$ (7): the Cp* and the NbH_4 resonances for 7 are between those for 5 and 6; and two distinct "doublets" are seen in the phosphine methyl region of the ^1H NMR, one close to the value for $P\underline{Me}_2Ph$ in 5, the other close to the value for $P\underline{Me}_2Cy$ in 6 (see data in Table IV).

This reactivity was first discovered during the standard NMR tube experiment to determine the rate of exchange of deuterium into the hydride positions of the complex using D_2. The original hydride signals certainly decreased, but there appeared the two new sets of hydride resonances, as well as the rise of the cyclohexyl peaks. The amount of proton intensity for the methyls and cyclohexyls in the final NMR spectrum of H,D-6 is greater than can be accounted for by the protons in the original PMe_2Ph alone and it appears, not surprisingly, that the hydrogenation of the phenyl groups involves the hydride ligands.

It may seem strange that 5 is hydrogenated so easily at

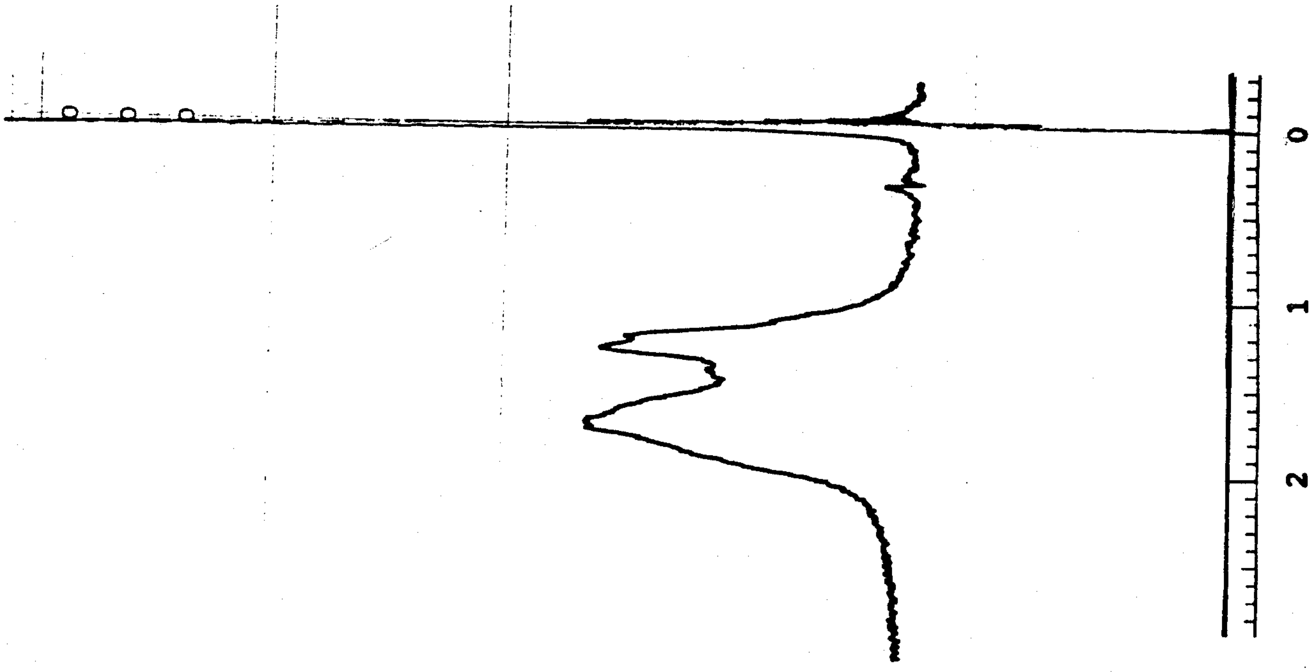


Figure 22. Tricyclohexylphosphine

Table IV

Compound	^{1}H NMR Resonances			
	Cp*	$P\underline{Me}_2Ph$	$P\underline{Me}_2Cy$	$Nb\underline{H}_4$
$Nb^*(PMe_2Ph)_2H_4$	1.80 s	1.65 't'	--	-1.05 t
$Nb^*(PMe_2Ph)(PMe_2Cy)H_4$	1.93 s	1.57 'd'	1.27 'd'	-1.43 t
$Nb^*(PMe_2Cy)_2H_4$	2.13 s	--	1.30 't'	-1.73 t

very low concentrations of H_2 when it was isolated originally from a reaction mixture which was vigorously stirred for four days under 100 atmospheres of H_2. A quirk of solubility allows the isolation of $\underset{\sim}{5}$: it alone of the hydrides synthesized is not extremely soluble in petroleum ether and apparently precipitates as it forms. Also, the hydrogenation of the phenyl rings may be inhibited by high pressures of H_2.

It is not yet known if the hydrogenation of the phenyl rings occurs inter- or intramolecularly, on free or bound phosphine. In one attempt to answer this, a small amount of $\underset{\sim}{5}$ and a very small amount of triphenylphosphine were sealed under H_2 in an NMR tube. This type of experiment is clearly limited by the amount of H_2 present, and the results of the reaction are not conclusive, yet very hopeful. Integrations of the spectra are not clear, since there are many overlapping resonances in the phenyl and alkyl regions of the NMR. But after three weeks at room temperature, the proton NMR spectrum shows less intensity in the phenyl region, and more in the alkyl region, than can be accounted for by the hydrogenation of the PMe_2Ph groups alone.[50] Further experiments are in progress.

In hopes that the hydrogenation may be a general feature of these niobium polyhydrides, with the PMe_2Ph simply providing the activated aryl, a sample was prepared with $Nb^*(PMe_3)_2H_4$ and PPh_3 sealed under H_2. However, no reaction is observed in two weeks at room temperature, and only slight changes after seven weeks.[51] The difference in reactivity may be due to steric differences and phosphine lability.

When a sample of 5 is sealed in benzene under vacuum, decomposition to several products is apparent after several hours at room temperature. After 17 hours, methyl resonances for two free phosphines, PMe_2Ph and PMe_2Cy are large, and the peaks of 7 are visible, along with much of the starting material. The largest new peak, however, is upfield of the original Cp* (not downfield as the Cp* resonances of 6 and 7 are). After 30 hours, this peak is the largest left in the spectrum, and there are no hydrides visible. Many large crystals begin forming after 12 hours. After three days the solution was decanted and spectra of the final solution and of the crystals were taken. The solution spectrum shows a jumble of decomposition products and much free phosphine. The sample with the crystals shows virtually nothing due to the very low solubility of the crystals; at amplitude 6000 a single peak at δ 1.8 is seen (not the same resonance as the major solution product). The solid has not been further characterized.

A sample of 6, isolated from a glass bomb preparation (ca. 85% 6, 15% 7) was allowed to stand in solution without added hydrogen. After six days at room temperature approximately half of it has decomposed to give another product, with a Cp* resonance at δ 1.93, and free PMe_2Cy. No other features are immediately apparent. This has not been further investigated.

Discussion

Although much work remains to be done on the Nb*L_2H_4 systems, some information has been gathered which, though occasionally confusing and seemingly contradictory, does allow speculation on the nature of these hydrides and of their reactions. The chemistry of Nb*$(PMe_3)_2H_4$ (4) has been investigated in the greatest detail, and the first part of the discussion will deal primarily with the reaction of the niobium polyhydrides based on the behavior of 4. The second part will deal with the hydrogenation of Nb*$(PMe_2Ph)_2H_4$.

The lability of the trimethylphosphine ligands on 4 has been noted. Though the exchange of ligands is not fast enough to merge or broaden the free and bound phosphine methyl resonances in the ^{1}H NMR, there is free phosphine in most of the NMR tube experiments. This PMe_3 lability of 4 seems to go along with its reactivity at room temperature, and, when compared to the analogous dmpe systems, implicates phosphine loss as an early step in the reactions of the polyhydrides. In all cases (except reaction with methanol), Nb*(dmpe)H_4 (3) requires heating to 80° C for any reactions to occur. Even after weeks at RT no new species are seen from 3 in the presence of D_2 or CO. Since the chelating bisphosphine is expected to dissociate with difficulty--or, perhaps more accurately, to re-attach the free end very rapidly--the necessity of heating 3 also speaks for phosphine loss as a necessary and rate-determining step for further reaction.[1,2,52] The niobium and tantalum polyhydrides are 18-electron, coordinately saturated compounds, and the opening of a coordination site by dissociation of a phosphine is strongly indicated in the tantalum system.

There are, however, several problems with this idea in the niobium system. First, it is odd that loss of phosphine should be the rate-determining step for reaction with D_2. "Simple" reductive elimination of H_2, followed by oxidative addition of D_2, would be the most obvious mechanism of deuterium exchange:

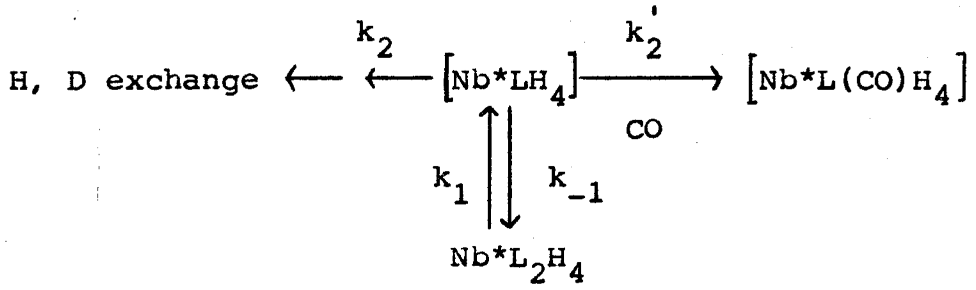
$$\mathrm{Nb^*(PMe_3)_2H_4} \xrightarrow{-H_2} \mathrm{Nb^*(PMe_3)_2H_2} \xrightarrow{D_2} \mathrm{Nb^*(PMe_3)_2H_2D_2}$$

Yet **3** has to be heated to do H/D exchange, and the reaction of **4** with D_2 is substantially slowed by the presence of excess phosphine.

3 also has to be heated to effect a reaction with CO, ethylene, or acetone, suggesting again a necessary dissociation of one or both ends of the dmpe ligand to open up a coordination site and allow reaction. But a second problem arises: the reaction of **4** with CO proceeds at room temperature at very nearly the same rate with and without a large excess of PMe_3. This indicates that phosphine loss is not involved in the rate determining step. Moreover, in the reaction of **4** and, more markedly of $\mathrm{Nb^*(PMe_2Ph)_2H_4}$ and $\mathrm{Nb^*(PMe_2Cy)_2H_4}$, H_2 is seen in solution in the ^1H NMR in the beginning stages of the reaction, suggesting that reductive elimination of H_2 occurs as an early step.

A mechanism for the reactions of the niobium polyhydrides can be sketched which explains all the data, if one is allowed to juggle with rate constants in the absence of kinetic data. Given Scheme I, where $k_2' >> k_2 \gtrsim k_{-1}$, the results obtained so far for all the systems can be rationalized.

Scheme I



1. Reactions of **3** with CO, acetone, ethylene, and D_2 are slow because the effective concentration of L is enormous when L is the dangling end of a chelating ligand. Therefore $k_{-1}\{L\}$ is always large, even though k_{-1} may be small. Forcing conditions, such as heating, which increase the rate constants without increasing {L}, are needed for k_2 and k_2' to compete.

2. The rate of deuterium exchange in **4** decreases with excess L because the rate determining step involves loss of L. k_2 may be the same or slightly larger than k_{-1}, but with L present $k_{-1}\{L\}$ becomes larger.

3. Excess L will have little effect on the CO reactions of **4** if k_2' is much, much greater than k_{-1}. k_2' must be so large that, when multiplied by {CO}, which is not large in solution, it still swamps out $k_{-1}\{L\}$.

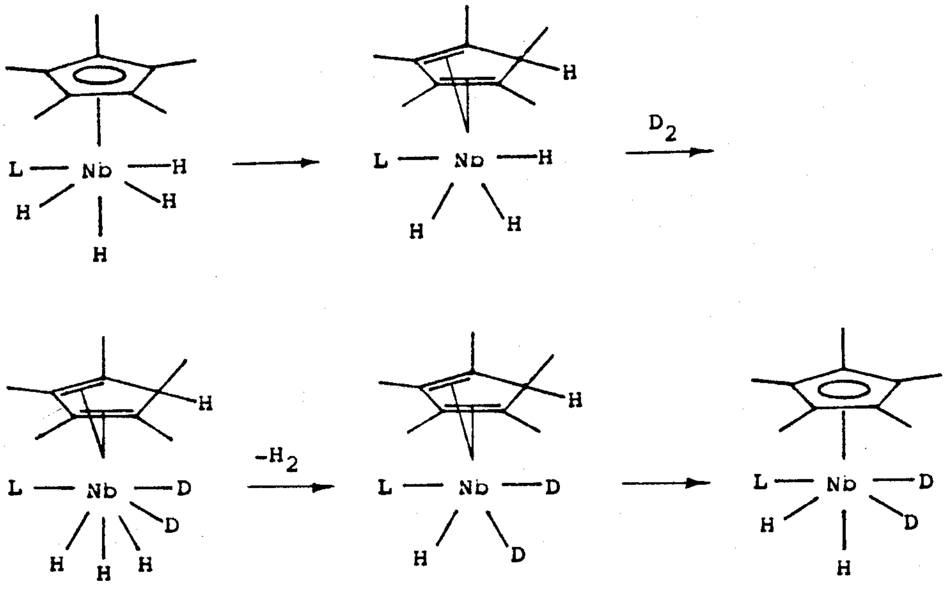
Point 3 is one of the weakest points in the scheme, yet it is supported to a degree by steric arguments. The small, rodlike CO molecule should be able to interact better with the niobium center which, though it has lost a phosphine, is still eight-coordinate and expected to be somewhat crowded. Furthermore, the rates of reaction of $Nb^*(PMe_2Ph)_2H_4$ and especially $Nb^*(PMe_2Cy)_2H_4$ with CO are greater than for $Nb^*(PMe_3)_2H_4$. These larger phosphines might be expected to be crowded off the molecule more easily (larger k_1) and to "get back in" with greater difficulty, giving a smaller k_{-1} and competing less with the addition of CO.[53]

Scheme I is not inconsistent with rapid evolution of H_2 during the reaction with CO, which could be a very fast third step. Reductive elimination might be expected to be more rapid from the species formed from the addition of CO than from the bisphosphine complex, due to the ability of CO to stabilize the d^2 Nb(III) formed by the loss of H_2. The d^0 carbonyl, with no backbonding electrons available for the CO, should be unstable with respect to reductive elimination: $Cp_2NbH_2(CO)^+$ eliminates H_2 above -30°;[16] $Cp^*{}_2MH_2(CO)$ (M=Zr, Hf) loses H_2 above -10° in the presence of excess CO.[54]

The scheme rationalizes the deuterium exchange results for **3** and **4**, but does not indicate *why* loss of L occurs first for this process. For, when phosphine loss occurs first, the exchange of H_2 must occur either through reductive elimination from a 16-electron species, as

$$Nb^*LH_4 \xrightarrow{-H_2} Nb^*LH_2$$

or through some other interaction of the 16-electron, d^o compound with D_2. This can be visualized in a manner analogous to that proposed for group IV complexes with D_2:[55]



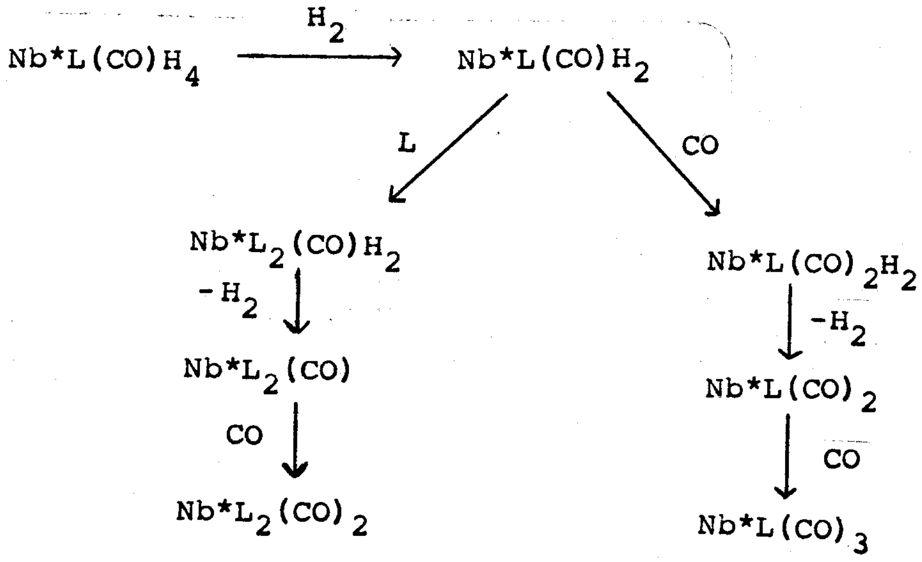
This also involves 14-electron species (albeit less "naked-looking" ones). It is not clear why loss of L seems to precede this, as both reductive elimination mechanisms can accomodate another two-electron ligand.

Such processes are possible, however. One of the criteria for reductive elimination is reasonable stability of the resulting reduced metal fragment.[56] The similar $Nb^{*}Me_3Cl$ is a 14-electron species and it is stable on the time scale of these chemical reactions. This makes the proposition of such 14-electron species as in the schemes not unprecedented.

There may be other explanations for the necessity of phosphine loss. In the late metal system $Os(CO)_4H_2$, for example, the rate of reductive elimination of H_2 is controlled by CO loss as the rate determining step. In this case it is because the product from the simple reductive elimination, $Os(CO)_4$, is very unstable, and the reaction actually proceeds by a binuclear mechanism. The ligand loss opens up a coordination site and allows the insertion of an Os-H bond of another molecule.[57] Something of that sort may be operative in the niobium system.

The proposed mechanism in Scheme I will accomodate a further mechanism for the reactions with CO, as shown in Scheme II. This is analogous to the mechanism proposed for the reactions of $Ta^*L_2H_4$ with CO[1,2] and supported by the dicarbonyl/tricarbonyl product distributions among the different systems.

Scheme II



In cases where there is much excess phosphine available, the lefthand branch of the scheme would be favored, leading to $Nb^*L_2(CO)_2$. In other cases, either branch would be followed, forming $Nb^*L_2(CO)_2$ and $Nb^*L(CO)_3$

In the tantalum system, the intermediate $Ta^*L_2(CO)H_2$ can can be detected.[1,2] No dihydrides, however, are seen in the niobium system.

Over extended periods of time, the concentration of $Nb^*L(CO)_3$ rises quite high in the sealed NMR tubes, despite the low solubility of CO in benzene and the limited amounts available (generally 6-8 equivalents). Apparently the tricarbonyl is a stable species and its formation is not easily reversed. This is reasonable in view of the stabilizing effect that the CO's have on the Nb(I) species. Sterically, also, the tricarbonyl may be favored significantly enough to make it the preferred form. This is supported by the formation of large amounts of the tricarbonyl monophosphine products in the reactions of the PMe_2Ph and PMe_2Cy tetrahydrides. Their steric crowding is shown by their not forming the two isomeric dicarbonyls, but apparently the diagonal one only. Only PMe_3 is small enough to form both the lateral and diagonal dicarbonyls.

The isomerization of the diagonal and lateral dicarbonyls is not fully understood. In both the niobium and tantalum systems, the lateral isomer transforms to the diagonal upon heating. This is seen for $CpRe(CO)_2Br_2$ also.[42] Apparently at higher temperatures the diagonal forms are the most stable, possibly because greater thermal motions of the ligands increases their steric requirements. For $Nb^*(PMe_3)_2(CO)_2$, at room temperature the favored form seems to be the lateral, as solutions slowly transform to this isomer. This can be explained on electronic grounds, as the two pi-acidic carbonyls will prefer--all else being equal--to be lateral and thus not directly compete for the same d electrons. Phosphines are not strong pi acids and will not compete with a CO to the degree that another CO will.[42,44] Such electronic effects are visible in the CpMo systems.[44] This balance between steric and electronic requirements for niobium indicates a high degree of sensitivity to the size of the phosphine on the part of the complex, as seen also in the results for $Nb^*(PMe_2Ph)_2(CO)_2$. Though the size of PMe_2Ph relative to PMe_3 as determined by cone angles is not much larger (122° versus 118° [33]), only the diagonal isomer is seen for the slightly larger phosphine complex.

The pi-acid character of the carbonyl may also explain the observation that only lateral-$Ta^*(PMe_3)_2(CO)_2$ goes on to the tricarbonyl in the presence of excess CO: CO's are better <u>trans</u>-labilizing ligands than phosphines,[44] and only in the lateral isomer is there a phosphine "<u>trans</u>" to a CO. Thus loss of a ligand "<u>trans</u>" to a CO and replacement of that ligand by a CO results in a net change only for the lateral isomer.

The data are consistent with a reaction sequence such as Scheme II. It is still puzzling, however, that the reaction of 4 with CO is not appreciably slowed by excess PMe_3. The tantalum system is.[1,2] It remains to be seen if the reaction of Nb*$(PMe_2Ph)_2H_4$ with CO is inhibited by excess phosphine or not. However, other reactions have, for the moment, eclipsed such "routine" experiments.

Nb*$(PMe_2Ph)_2H_4$ (5) hydrogenates the phenyl groups on the phosphine when sealed under H_2. This may be unique. It also appears to hydrogenate PPh_3 under similar conditions. These are very recent results, and even elementary experiments have not yet been carried out. This discussion must therefore be highly speculative, consisting of comparisons to literature examples of arene hydrogenation and propositions of reaction mechanisms.

There are still few homogeneous arene hydrogenation catalysts, although heterogeneous ones have been known since the turn of the century.[58] Homogeneous catalysts offer, as always, the possibilities of chemo- and stereoselectivity.[59] Of the homogeneous systems now known, the best documented is the catalyst precursor $(\eta^3C_3H_5)Co\{P(OMe)_3\}_3$, studied by Muetterties and co-workers.[60] This organocobalt compound was found to form a catalyst for the hydrogenation of a number of aromatic hydrocarbons and olefins in solution. It is a remarkable catalyst, in that it works at room temperature under one atmosphere of H_2, on a wide variety of substrates, including olefins, dienes, and arenes, with a range of substituents. Furthermore, addition of D_2 to C_6H_6 gives >95% all-cis-$C_6D_6H_6$, and this stereospecificity is seen for all the arenes. This indicates that all the bonds are hydrogenated before the substrate is released back into solution. Olefins are hydrogenated at roughly the same rates as arenes (given similar steric requirements), unusual for arene hydrogenation systems.

The system is thought to have the unsaturated complex $HCo\{P(OMe)_3\}_2$ as the active species, to bind arenes as η^4 species, and to proceed through a series of η^4-η^3 steps around the ring, adding H_2 to the Co when necessary. A reaction mechanism has been proposed which can explain all the products, isotope studies, etc. The major drawback for the catalyst is that it is not stable, and becomes inactive after 20-40 turnovers.[60]

Other systems which are claimed to catalyze hydrogenation of arenes, such as $(\eta^6C_6H_5Me)M(C_6F_6)$, M=Ni, Co; $(Cp^*RhCl_2)_2$; $RuHCl(\eta^6C_6Me_6)(PPh_3)$; and $\{(\eta^6C_6Me_6)Ru(\mu H)_2(\mu Cl)Ru(\eta^6C_6Me_6)\}Cl$,[61] are not as well studied, and for solid state catalysts, no molecular details have been defined at all,[60a] leaving much to be investigated in the area of arene hydrogenation. It is very interesting to note that in the allylcobalt system, triphenylphosphine was found not to react after 336 hours.[60b] This was assumed to be because the nucleophilicity of the "substituent" on the benzene--the phosphorus--bound preferentially to the catalyst, leaving the π system of the arene nothing to interact with. Indeed, phosphines are frequently considered poisons in catalyst systems because of the tenacity with which they bind to the metals.[62] No mention has been found in any other systems of reduction of a phenyl on a phosphorus, and it is seen that several olefin and arene hydrogenation catalysts have PPh_3 and even PMe_2Ph

itself as ligands.[63] The complex $WH_6(PMePh_2)_3$ is known, but shows no tendency to hydrogenate the phosphine phenyls.[64] It appears, then, that the case of **5** is unique.

It is not clear yet that the system is catalytic, but even if not, it is interesting and worthy of further study. Questions of the mechanism and of the scope of the reaction remain to be answered. Data is meager at this point:

1. Reduction of PMe_2Ph to PMe_2Cy occurs at RT under ca. three atomospheres of hydrogen.

2. Free PMe_2Ph is seen at the beginning, PMe_2Ph and PMe_2Cy in the middle, and free PMe_2Cy at the end of the reaction.

3. No vinylic resonances are seen.

4. All peaks are of normal sharpness in the NMR at RT.

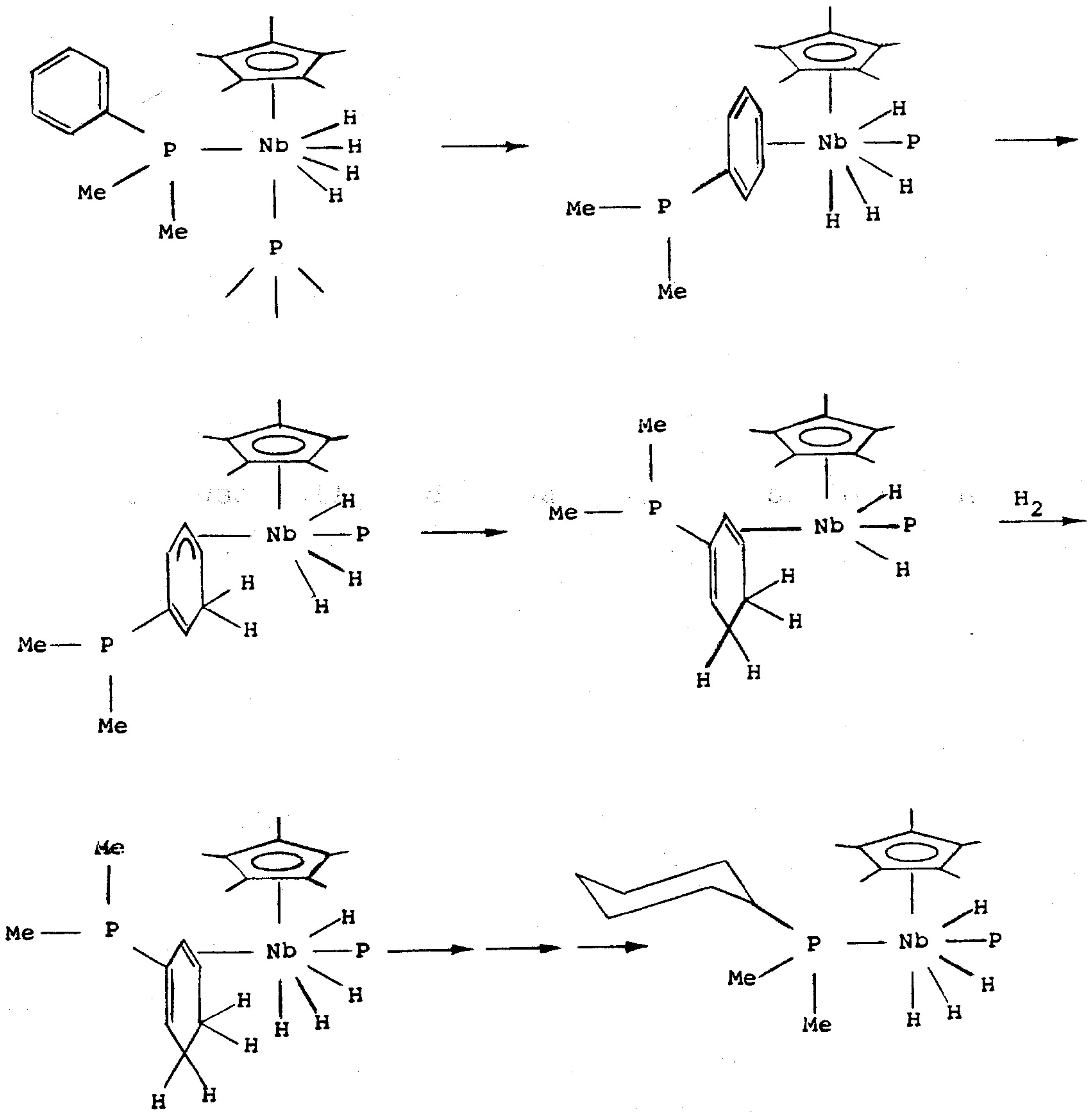
5. In the absence of H_2, decomposition to a number of products is seen, one of the initial ones identified as $Nb^*(PMe_2Ph)(PMe_2Cy)H_4$ in the NMR.

6. Benzene is not reduced to cyclohexane. PPh_3 may be reduced to PCy_3.

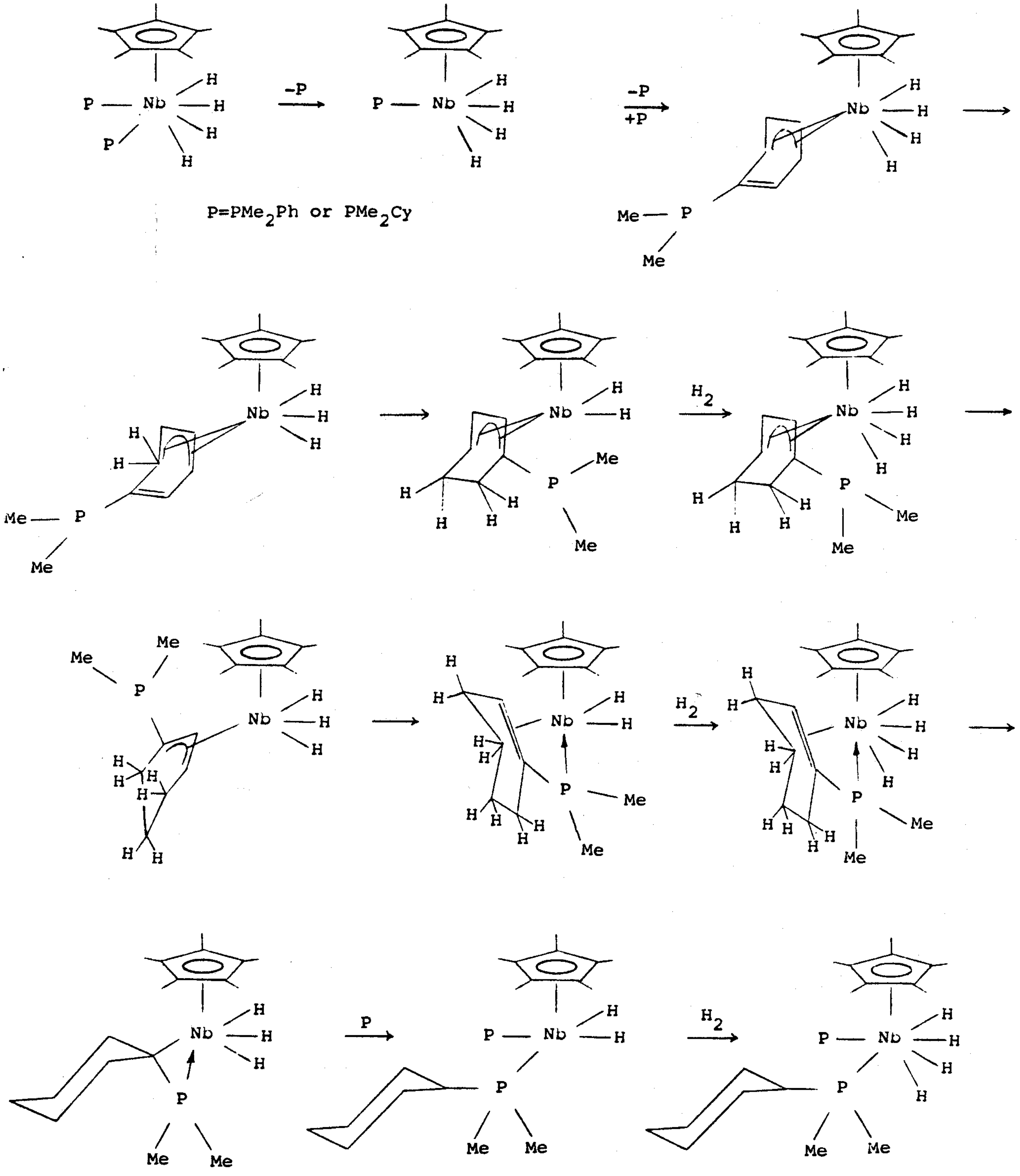
It seems clear that once the hydrogenation of a phenyl ring is started, it goes completely to the cyclohexyl, as no double-bond-containing intermediates are seen. There seems to be no preference to the hydrogenation of only one phosphine on all niobium centers before the second is attacked--the concentration of $Nb^*(PMe_2Ph)(PMe_2Cy)H_4$ builds up to ca. 50% of the mixture with starting material, then $Nb^*(PMe_2Cy)_2H_4$ is seen and gradually rises until the reaction mixture is again an equal mixture of two species, this time the mixed phosphine hydride and the final product, $Nb^*(PMe_2Cy)_2H_4$, then continues to all Nb*$(PMe_2Cy)_2H_4$.

At least two types of mechanism for intramolecular reduction can be drawn, one with η^2-η^3 slips along the phenyl ring (Scheme III), and the other, like that proposed for the allylcobalt complex, with η^4-η^3 slips (Scheme IV). Bonding of PMe_2Ph to a metal center through the phenyl ring, in an η^6 manner at least, has been seen in the system $(\eta^1PMe_2Ph)_3$-$Mo(\eta^6PMe_2Ph)$.[65]

Scheme III



Scheme IV



P=PMe$_2$Ph or PMe$_2$Cy

Scheme III does not explain well the amounts of free phosphine seen in the reaction mixtures, and it looks sterically crowded to have a phenyl ring facing the niobium center, plus all the other ligands, one of them another moderately bulky phosphine. Loss of the second phosphine would give 14-electron species at several points in the reaction.

The η^4-η^3 mechanism in Scheme IV allows 16- and 18-electron intermediates with a sterically less-crowded niobium center, and explains the free phosphine seen at all stages of the reaction. Such a mechanism is also proposed for the allylcobalt system, and one of the more compelling reasons given in that case was that an η^4-arene should be easier to reduce--an η^4-arene requires a noncoplanar carbon skeleton, perturbing the aromatic system, and supposedly rendering it more susceptible to hydrogenation.[60c]

The list of questions to be answered, experiments to be done, is long. Is it catalytic: will $Nb^*(PMe_2Cy)_2H_4$ also hydrogenate arenes--that is, is having labile, bulky phosphines on the Nb^*H_4 center the key, or is there something about the PMe_2Ph ligand that allows stoichiometric reduction to PMe_2Cy only? If it is catalytic, what arenes will it attack? What olefins? With what chemo-, stereoselectivity? What can be learned of the mechanism, and how does it contribute to the knowledge of catalytic arene hydrogenations? Are there synthetic organic applications--besides the production of PMe_2Cy, which is not now sold by specialty houses? (Catalytic production of PCy_3 from PPh_3

would be nice for a start.) What will PPh_2Me do--can $Nb^*(PPh_2Me)_2H_4$ be made from Nb^*Me_4, and if so, will it hydrogenate? Perhaps it will hydrogenate one phenyl per phosphine more rapidly than the other (expected for steric reasons) allowing the production of a phosphine with three different substituents, capable of forming an asymmetric center upon coordination.

Experimental Section

General Considerations: All of the manipulations were carried out using high-vacuum line and glove box techniques. Solvents were purified by vacuum transfer first from $LiAlH_4$, then from "titanocene," except for acetone, which was vacuum transferred from 4A molecular sieves, and dioxane and THF, from sodium-benzophenone ketyl. Benzene-d_6 (Stohler, Inc.) was vacuum transferred from titanocene. Hydrogen and deuterium gases (MCB) were purified by passage over 4A molecular sieves and MnO on vermiculite. Carbon monoxide (MCB) was used directly from the cylinder. Ethylene (Union Carbide) was condensed at 77 K and then evaporated at -78^{o} C. Reactions at high pressure of hydrogen were performed in a Parr stirred "mini" reactor, #4561, with a 2000 psi pressure gauge, using UHP hydrogen (Matheson) of minimum purity 99.999%.

Proton NMR spectra were recorded using a Varian EM390 spectrometer, with benzene-d_6 as the solvent. ^{31}P spectra were obtained using a JEOL FX90Q spectrometer; high field proton NMR using the Bruker WM500 from the NSF Southern California Regional NMR Facility. Infrared spectra were measured on a Beckman 4240 spectrophotometer, as nujol mulls on KBr plates, or as benzene solutions.

Note: Many reactions were carried out in sealed NMR tubes and monitered by NMR spectroscopy as the most feasible way of surveying the chemistry of the new polyhydrides, which were obtained in low yields from multistep syntheses. These "NMR tube reactions" require only 20-30 mg of compound, are adaptable to added solids, liquids, or gases as reagents, and can be subjected to varying conditions of heat or cold over long periods of time and can be monitered at any stage by NMR. For promising reactions, and those that have to be prepared on a large scale for absolute characterization or further reactions, the NMR tube experiments performed initially give information on the optimum conditions for the preparative scale reactions.

A typical example of an NMR tube experiment is the reaction of $Nb^*(PMe_3)_2H_4$ with D_2 and excess PMe_3: ca. 20 mg. (0.05 mmol) $Nb^*(PMe_3)_2H_4$ were transferred into an NMR tube sealed to a ground glass joint and fitted to a 19.8 ml gas volume with a glass joint to fit to the vacuum line. Benzene-d_6 (ca. 0.3 ml) was added. The tube was placed on the vacuum line, the solution frozen, and the assembly evacuated. Ca. 3 equivalent (0.16 mmol) PMe_3 were measured into the gas bulb and condensed into the NMR tube with liquid nitrogen. The tube was then immersed in liquid nitrogen to a point several cm below the joint, and and slightly less than one atm D_2 admitted. The tube was sealed with a torch. When warmed to RT the D_2 pressure was ca 3½ atm in ca. 2 ml volume, or about 6 equivalents of D_2/Nb. An initial NMR spectrum was taken, with careful integrations of all peaks, including TMS and the residual protons on benzene. The tube was left at RT and spectra taken at several hour to several day intervals for ten days. The hydride resonances decreased during that time until it was only one-fourth what it had been, relative to the Cp* peak. The Cp*, phosphine methyls, and benzene resonances all stayed the same relative to TMS. When the hydride resonances ceased changing and the system appeared to be in equilibrium, the tube was opened in the glove box and a solution IR spectrum taken to show the absorptions due to M-H and M-D bonds.

Procedures

$NbMe_3Cl_2$, Nb^*Me_3Cl, and Nb^*Me_4 10 g (37 mmol) $NbCl_5$ (sublimed one time) were placed in a large flask on one side of a swivel frit, and an empty two-necked flask fitted with a rubber septum on the other. Ca. 10 ml Et_2O were distilled onto the $NbCl_5$. $ZnMe_2$, prepared in a separate flask by the reaction of 8.83 g (64.8 mmol) dry $ZnCl_2$ with 104 ml 1.3M (135 mmol) LiMe in Et_2O, was vacuum transferred onto the $NbCl_5$ at -78°. The flask was warmed to RT with stirring. The reaction was judged complete when all the insoluble $NbCl_5$ chunks were gone and the solution was yellow-green. 5.5 ml (64.5 mmol) dioxane were transferred into the solution, the mixture filtered and washed. The frit assembly was filled with Ar and the solution transferred via cannula to a second frit assembly containing 6.77 g (38.8 mmol) KCp*[31] and ca. 10 ml Et_2O, at -78°. The KCp* reacted on contact to form red Nb^*Me_3Cl and KCl. The solution was warmed to RT and stirred for 15-20 minutes, then filtered and washed 3-6x. The solution was concentrated to ca. 50 ml, cooled, and the solid collected cold. 5.39 g (17.5 mmol) of red-maroon, microcrystaliine Nb^*Me_3Cl, pure by NMR, were collected, for 47% yield, based on $NbCl_5$.

3 g (9.72 mmol) Nb^*Me_3Cl were placed in a flask on a frit assembly, 30 ml Et_2O distilled on, and 8.16 ml 1.25M (10.2 mmol)

LiMe syringed in against an Ar counterflow, at -78°. The reaction was warmed to RT with stirring, and the Et_2O removed. Ca. 50 ml petroleum ether were added and the LiCl filtered off. The solution was concentrated to a few ml and the solid collected very cold on the frit. 2.0 g (6.9 mmol) of red, microcrystalline Nb^*Me_4 (71% yield based on Nb^*Me_3Cl) were collected and used immediately.

<u>$Nb^*(dmpe)H_4$</u> 1.66 g (5.76 mmol) Nb^*Me_4, 1 ml (ca. 1.1 equivalent) dmpe, and 50 ml pet. ether were placed in the high pressure Parr reactor, pressured to 1400 psi H_2, and stirred at RT for 1½ days. The reaction mixture was decanted and placed into a flask on a frit and removed to the vacuum line. The yellow-black solution was filtered, then reduced in volume to ca. 20 ml and stirred at -78° for one hour. Solid formed, which was filtered cold and washed 1x. 650 mg of greenish-white microcrystalline solid was isolated for 29.5% yield.

<u>$Nb^*(PMe_3)_2H_4$</u> 1.78 g (6.17 mmol) Nb^*Me_4, 2.4 ml (ca. 5 eq.) PMe_3 and 60 ml pet. ether were placed in the Parr reactor, pressured to 1400 psi H_2, and stirred for 4 days. The dark brown solution was placed in a flask on a frit and degassed on the vacuum line. A great deal of gas evolved during this procedure. The solution was then filtered and reduced in volume, cooled and stirred at -78° for 15 minutes. Orange solid formed and was collected very cold on the frit. Well-washed solid on the walls was white and crystalline, but due to the extreme solubility of the product, the bulk was washed only 1x. 1.03 g of orange solid, pure by NMR, were collected, for 43% yield.

$\underline{\text{Nb*(PMe}_2\text{Ph)}_2\text{H}_4}$ 1.96 g (6.80 mmol) Nb*Me_4, 2 ml (ca. 2 eq.) PMe_2Ph, and 60 ml pet. ether were placed in the Parr reactor, pressured to 1400 psi H_2, and stirred for 4 days at RT. The red-brown solution and light colored solid formed were removed to a flask on a frit and degassed. Ca. 30 ml pet. ether were removed during degassing but the pressure remained at ca. 50 mtorr. The solution was filtered and very pale purple-pink microcrystalline solid collected on the frit and washed 2x. 1.1 g of pure (by NMR) Nb*$(PMe_2Ph)_2H_4$ were isolated, for a yield of 31.8%.

$\underline{\text{Nb*(PMe}_2\text{Cy)}_2\text{H}_4}$ 150 mg (0.295 mmol) Nb*$(PMe_2Ph)_2H_4$ and ca. 10 ml benzene were placed in a glass bomb under 4 atm H_2 and stirred for two weeks at RT. The solution was degassed and placed in a flask on a frit. It was filtered and the benzene removed, leaving a brown oil. 1-2 ml pet. ether were distilled in and the solution cooled. Some solid appeared at -78°, and was collected very cold on the frit. The filtration went slowly due to technical difficulties, and a very small amount of brownish solid was collected, unwashed. The solid which was on the walls was well washed and was seen to be white and crystalline. Enough solid was collected for an NMR, showing it to be roughly 85% Nb*$(PMe_2Cy)_2H_4$ and 15% Nb*$(PMe_2Cy)(PMe_2Ph)H_4$.

$\underline{\text{Nb*(dmpe)(CO)}_2}$ 380 mg (0.99 mmol) Nb*(dmpe)H_4 and 5 ml toluene were placed in a glass bomb and 3.73 mmol CO added. The solution was stirred at 80° for 1½ days, the brown-green initial solution turning intensely red during that time. The gases were removed by Toepler pump, measured (3.51 mmol) and burned, yielding 1.64 mmol CO_2 and H_2O. Calculations give 2.1

eq. CO taken up, 1.9 eq. H_2 given off, per Nb. The solution in the bomb was worked up on a frit, and 350 mg of orange-red solid recrystallized from pet. ether.. The isolated yield was 81.4% due to solubility problems, though the reaction was quantitative by NMR.

$Nb^*(PMe_3)_2(CO)_2$ and $Nb^*(PMe_3)(CO)_3$ 300 mg (0.781 mmol) $Nb^*(PMe_3)_2H_4$ and 8 ml pet. ether were placed in a glass bomb with ca. 4 eq. PMe_3 and 3 eq. CO. The reaction was stirred at RT for 70 hr, changing color from yellow-brown to intense red. The gases were pumped off and the solution placed in a flask on a frit. The pet. ether and excess phosphine were removed and fresh pet. ether distilled in. The solution was filtered, condensed to 1-2 ml, and the solid collected very cold, washed 1x. 96 mg of microcrystalline orange-red diag-$Nb^*(PMe_3)_2(CO)_2$ were collected, for 28% isolated yield.

Approximately 30 mg diag-$Nb^*(PMe_3)_2(CO)_2$ in benzene-d_6 were sealed into an NMR tube and heated to 80° for 5 hours with no observable change. After 2 weeks at RT, however, it had reacted to give ca. 90% lat-$Nb^*(PMe_3)_2(CO)_2$.

Approximately 30 mg diag-$Nb^*(PMe_3)_2(CO)_2$ were sealed into another NMR tube under 3 atm CO. After 2 weeks at RT the NMR spectrum shows primarily $Nb^*(PMe_3)(CO)_3$ with small amounts of both bisphosphine dicarbonyls.

$Nb^*(PMe_2Ph)(CO)_3$ and $Nb^*(PMe_2Cy)(CO)_3$ Ca. 20 mg $Nb^*(PMe_2Ph)_2H_4$ were sealed in benzene-d_6 under 3 atm CO. After 2 weeks the NMR spectrum shows 90% $Nb^*(PMe_2Ph)(CO)_3$, 10% $Nb^*(PMe_2Ph)_2(CO)_2$. Ca. 20 mg.$Nb^*(PMe_2Cy)_2H_4$ were sealed in benzene-d_6 under ca. 3 atm CO. After 1 day the NMR shows 90% $Nb^*(PMe_2Cy)(CO)_3$, 10% Nb*$(PMe_2Cy)_2(CO)_2$.

<u>Nb*$(PMe_3)_2H_4$ plus Ethylene</u> 504 mg Nb*$(PMe_3)_2H_4$ were placed in a glass bomb with ca. 5 ml pet. ether and 11 eq. C_2H_4, let react 22 hours. The solution turned black. Excess ethylene, pet. ether, PMe_3 and any product gases were pumped away, leaving a black oil, which was recrystallized from a small amount of pet. ether, yielding a brilliant blue-purple solid, which shows a mixture of two products by NMR.

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35. P-Ta-P angles of 74-78° only have been found in five crystal structures (ref. 3).

36. For these bisphosphine complexes, the phsophine methyl resonances are non-first-order, due to virtual coupling between the phosphoruses. When describing the multiplicities of such resonances, quotation marks are used to indicate this.

37. Using approximate figures for the reactants in the NMR tube experiments: There are ca. 15 mg, 0.04 mmol 4, which releases 0.16 mmol H upon loss of hydride ligands; 3½ atm D_2 in 2 ml, ca. 0.30 mmol D_2 or 0.60 mmol D. $H:(H,D) = 0.16/(0.16+0.60) = 21\%$. It is reasonable that final equilibrium shows about one in four of the hydrides is H, 3 are D.

38. Another puzzling result of this reaction is that a relatively rapid buildup to ca. 15% (of the total Cp* intensity) of the primary decay product is seen in the sample which contained excess phosphine, but none is seen in the other sample. In all other cases, this decomposition is accompanied by loss of phosphine.

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	Phenyl	Cp*+Phosphine alkyls	TMS	Hydride
t=0	162	143	37	17
t=500 hr	68	348	37	16

Numbers confirm that the differences are due to the hydrogenation of phenyls to cyclohexyls: At t=500 hr, total phenyl + Cp* + alkyl = 416. This includes hydrogen from the hydrogenation of phenyls, (162-68)x6/5, not found in the initial spectrum, where total phenyl + Cp* + alkyl = 305. But 305 + (162-86)x6/5=418, very close to what is actually observed.

51. Results are not as clear as for the previous case. Integration of spectra show:

	Phenyl	Cp* (+ cyclohexyl under it)	TMS	Hydride
t=0	145	136	35	35
t=1100 hr	135	152	35	38

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