

**Synthesis, Characterization, and Reactivity of
New Hydride Compounds of Tantalum (V)**

**Thesis by
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**In Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy**

**California Institute of Technology
Pasadena, California
1983**

(Submitted July 6, 1982)

to my mother

ACKNOWLEDGMENTS

I would like to thank the members of the Bercaw group, both past and present, for creating a scientifically stimulating and challenging environment, and for putting up with me. I am especially grateful to Pete Wolczanski for his advice and criticism, to Bernie Santarsiero for his careful editing, and to Mike Fryzuk who taught me to use a vacuum line by example and the Socratic method. I am also indebted to Pete and Bernie for the crystallographic work described in chapter II. The National Science Foundation is acknowledged for financial support. Finally, I would like to thank John Bercaw for his support, personal and scientific as well as financial, and for his patience, insight, and good sense.

ABSTRACT

A series of (pentamethylcyclopentadienyl)tantalum bis(phosphine) polyhydride complexes, $\text{Cp}^*\text{TaL}_2\text{H}_4$ ($\text{L} = \text{PMe}_3, \text{PMe}_2(\text{C}_6\text{H}_5), \text{P}(\text{OMe})_3$, and $\text{L}_2 = \text{dmpe}$; $\text{Cp}^* = \eta^5\text{-C}_5(\text{CH}_3)_5$) and $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_3\text{Cl}$, have been prepared by high pressure hydrogenation of Cp^*TaMe_4 or $\text{Cp}^*\text{TaMe}_3\text{Cl}$ in the presence of L . The hydride ligands are more hydridic than protic in character. All of the compounds react with acetone and methanol to afford isopropoxide and methoxide complexes, respectively. Reactions with carbon monoxide yield carbonyl hydride and dicarbonyl compounds resulting from sequential reductive elimination of dihydrogen. Hydrogenation of ethylene is observed, as well as catalytic dimerization of ethylene to 1-butene. Most reactions of these eighteen-electron polyhydride complexes are thought to involve rate-determining loss of a phosphine ligand. Evidence is presented in support of coordination of acetone to tantalum prior to its reduction to isopropoxide. By contrast, methanol can react directly with the coordinatively saturated tantalum hydride species to generate H_2 .

Low temperature and high field NMR spectroscopy has been used to investigate the coordination geometries of these polyhydride complexes and some niobium analogues. Using symmetry arguments, the spectra indicate a C_s structure with equivalent phosphorus atoms for complexes with monodentate phosphine ligands. This is consistent with an X-ray crystal structure of $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_4$, in which the hydride ligands were not located. A different C_s structure, with inequivalent phosphorus atoms, is indicated for compounds with the bidentate dmpe ligand.

The reactions of $\text{Cp}^*\text{TaMe}_3\text{Cl}$ (1) with a variety of alkali metal alkoxide, alkylamide, and alkyl reagents have been examined. Reaction with LiNMe_2 produces $\text{Cp}^*\text{Ta}(\text{NMe}_2)\text{Me}_3$, but this decomposes at 25°C to an imine (or metallaazirane) complex, $\text{Cp}^*\text{Ta}(\text{CH}_2\text{NMe})\text{Me}_2$. The decomposition is a first-order, unimolecular process with a large kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} = 9.7$). Monoalkylamides (LiNHR) react with 1 to form imido complexes $\text{Cp}^*\text{Ta}(\text{NR})\text{Me}_2$. Reaction of 1 with lithium diisopropylamide forms a bridging methylene complex, $\text{Cp}^*\text{Me}_2\text{Ta}(\mu\text{CH}_2)(\mu\text{H})_2\text{TaMe}_2\text{Cp}^*$. The alkoxide compounds $\text{Cp}^*\text{Ta}(\text{OR})\text{Me}_3$ ($\text{R} = \text{Me}, \text{CHMe}_2, \text{CMe}_3$) are very stable and decompose only over 100°C . Alkyl complexes are stable only if the alkyl group does not have β -hydrogens. The rates of hydrogen abstraction or elimination processes in this system correlate with the nature of the atom bound to tantalum: for reactions involving a β -hydrogen the order is $\text{C} > \text{N} > \text{O}$ while α -hydrogen abstraction reactions appear to vary in the reverse order, $\text{N} > \text{C}$. These rates seem to reflect the thermodynamic preferences in these compounds.

Hydrogenation of the imido compounds ($\text{Cp}^*\text{Ta}(\text{NR})\text{Me}_2$) in the presence of phosphine ligands yield the first examples of imido-hydride complexes, $\text{Cp}^*\text{Ta}(\text{NR})\text{H}_2(\text{L})$ ($\text{L} = \text{PMe}_3, \text{PMe}_2(\text{C}_6\text{H}_5)$, $\text{R} = \text{CMe}_3, \text{CH}_2\text{CMe}_3$). An alkyl-hydride complex, $\text{Cp}^*\text{Ta}(\text{CH}_2\text{NMe})\text{Me}(\text{PMe}_3)\text{H}$, has also been prepared. The reaction of $\text{Cp}^*\text{TaMe}_3(\text{OCMe}_3)$ with hydrogen forms an unusual asymmetric dimer, $\text{Cp}^*(\text{Me}_3\text{CO})_2\text{HTa}(\mu\text{H})_2\text{TaH}_3\text{Cp}^*$, which has been characterized by NMR and IR spectroscopies.

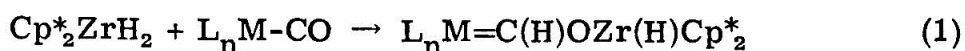
The tantalum hetero-olefin complexes $\text{Cp}^*\text{Ta}(\text{CH}_2\text{NMe})\text{Me}_2$ and $\text{Cp}^*\text{Ta}(\text{OCMe}_2)\text{Me}_2$ react readily with olefins, aldehydes, and nitriles. A number of five- and seven-atom metallacycles have been prepared.

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INTRODUCTION

Hydride complexes of the early transition metals have not been extensively explored, especially those in which the metal center has a formal d^0 configuration.¹⁻³ Of the compounds that have been examined, decamethylzirconocene dihydride, $\text{Cp}^*_2\text{ZrH}_2$ 1 ($\text{Cp}^* = \eta^5\text{-C}_5(\text{CH}_3)_5$), and the hafnium analogue have received the most attention.^{1,2} Interest in hydride compounds has been sparked by the discovery that 1 will stoichiometrically reduce carbon monoxide to methoxide, enolate, or pinacolate complexes, depending on the reaction conditions.² This type of reaction is extremely important because of its relationship to the Fischer-Tropsch reaction and the ability to use coal instead of petroleum as a source of liquid fuels and chemical feedstocks.⁴ The mechanism of the reduction of carbon monoxide by 1 is complicated and not fully understood.² A related and more straightforward reaction is the reduction of the CO ligands of other metal compounds (eq 1).⁵ The

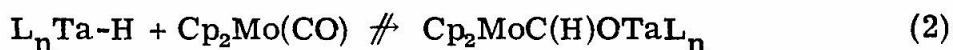


exceptional reactivity of 1 appears to be due to a number of properties: (i) the hydride ligands are extremely "hydridic" and resemble alkali metal hydrides,^{1,6} (ii) the zirconium center is coordinatively unsaturated (16 electron), (iii) reductive elimination of H_2 is not a facile process, and (iv) zirconium-oxygen bonds are extremely strong.⁷ The last point is the major reason why the zirconium activation of CO is a stoichiometric and not a catalytic process, since compounds with Zr-O bonds are thermodynamically very stable and not easily converted back to 1.

The goal of the present study has been to build a molecule that would mimic the reactions of Cp^*ZrH_2 (1), especially the carbon monoxide reduction chemistry. This would clarify which properties of 1 are most important and increase our understanding of the mechanism of CO reduction. In addition, if the reagent formed weaker metal-oxygen bonds, the reaction would be one step closer to a catalytic process. Tantalum was chosen as the metal because suitable starting materials were available and because tantalum(V)-oxygen bonds are expected to be weaker than Zr(IV)-O bonds.⁷ The synthesis and reactivity of a series of tantalum hydride complexes, $\text{Cp}^*\text{TaL}_2\text{H}_4$ and $\text{Cp}^*\text{TaL}_2\text{H}_3\text{Cl}$ ($\text{L}=\text{PR}_3$), is described in chapter I. These compounds have some of the properties of 1, but they are coordinatively saturated and do not reduce either free or bound carbon monoxide. 1 is coordinatively unsaturated because of the steric bulk of the two Cp^* groups which prevent both oligomerization and the binding of large neutral ligands.¹ There are three basic approaches to making $\text{Cp}^*\text{TaL}_2\text{H}_4$ type compounds that are unsaturated: increasing the size of the cyclopentadienyl ring,⁸ increasing the size of the phosphine ligand(s),⁹ or substituting one or more of the hydride ligands for other anionic ligands like alkoxide or dialkylamide groups. The last path was chosen because it offered an opportunity for electronic as well as steric variations at the metal center and because the properties of alkoxide and amide ligands in organometallic coordination environments have received little attention. The first synthetic attempts at these compounds involved metathesis of the chloride ligand in $\text{Cp}^*\text{TaL}_2\text{H}_3\text{Cl}$, but this met with little success as described in chapter III. A more fruitful approach

has been substitution of the chloride in the starting material, $\text{Cp}^*\text{Ta}(\text{CH}_3)_3\text{Cl}$, which has led into a number of interesting areas (chapters IV and V).

A variety of tantalum hydride compounds have been prepared; however, none of them are active in the reduction of carbon monoxide. It is not surprising that they do not cleanly reduce free CO, since even the reaction of $\underline{1}$ with CO is very sensitive to reaction conditions. However the lack of reaction of tantalum hydride compounds with metal carbonyl complexes (e.g., $\text{Cp}_2\text{Mo}(\text{CO})$, $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, eq 2) indicates that there is a more fundamental problem. Reaction 2 seems to be



thermodynamically unfavorable for the tantalum hydride complexes that have been prepared. The kinetic barriers to hydrogen transfer reactions like eq. 2 appear to be small, since the hydride compounds all readily reduce acetone to isopropoxide complexes. The thermodynamics may not be enormously favorable even in the zirconium system, since there are examples of reaction 1 where the zirconoxy-carbene product is in equilibrium with $\underline{1}$ and the metal carbonyl complex.^{5c} The difference in the thermodynamics is probably due to the weaker Ta-O bonds, compared to zirconium.⁷ Thus the strength of the Zr-O bond — the one property we have not been trying to mimic in the tantalum hydride compounds — appears to play a critical role in the CO reduction chemistry.¹⁰ We must re-evaluate the implicit

assumption that a compound with all of the characteristics of $\text{Cp}^*_2\text{ZrH}_2$ except the ability to form exceptionally strong metal-oxygen bonds would be able to reduce carbon monoxide.¹¹ Fortunately, the goal of carbon monoxide reduction has led us into a fruitful area of research which has touched on a number of important areas in organometallic and inorganic chemistry.

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- (6) For example, $\text{Cp}^*\text{ZrH}_2 + \text{LiR} \rightarrow \text{Cp}^*\text{ZrH(R)} + \text{LiH}$
 (R = CH₂CMe₃): Roddick, D. M.; Bercaw, J. E. manuscript in preparation.
- (7) Connor, J. A. Top. Curr. Chem. 1977, 71, 71.
- (8) This attack is presently being explored by Allen Van Asselt and Eric J. Moore.
- (9) A few attempts were made in this direction as described in chapter I.

(10) Both of the likely mechanisms for the reduction of CO by 1, the formyl and carbene mechanisms, depend on strong Zr-O bonds.^{2b} The formation of a stable thorium formyl complex from CO is thought to be due to an extremely strong thorium-oxygen interaction: Fagan, P.J.; Moloy, K. G.; Marks, T. J. J. Am. Chem. Soc. 1981, 103, 6959-6962.

(11) Of course there are many possible mechanisms for the reduction of carbon monoxide, and these thermodynamic considerations apply to only a small number of them. If the reduction proceeds by an unusual mechanism, it is difficult to predict what properties will be important. For example, an unusual dimeric tantalum (IV) hydride complex reacts with CO to form a bridging formyl compound by a pathway that involves paramagnetic intermediates.¹²

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CHAPTER I

Synthesis and Reactivity of New Phosphine
Polyhydride Compounds of Tantalum (V).¹

INTRODUCTION

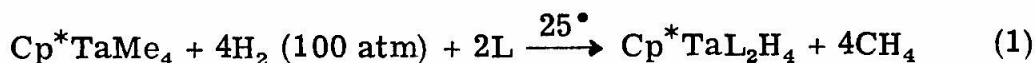
Polyhydride complexes have been isolated for most of the transition metals, often with phosphines as the only other ligands.² The primary focus of this research has been the definition of the solid state structures and the fluxional processes that are very common for these molecules.^{2,3} Polyhydride compounds have high coordination numbers (six to nine) and are among the least sterically crowded examples of these coordination geometries. The formal oxidation states for the metal center in early and middle transition metal polyhydrides are often high, with d^2 and d^0 configurations quite common. The chemistry of transition metal polyhydride complexes, especially those with formal d^0 configurations, has not yet been systematically examined. This may be due to the fact that these compounds are nearly always coordinatively saturated and thus relatively inert.⁴ Lower valent "hydrides" are generally chemically more protic than hydridic: they are stable to alcohols, can often be deprotonated with strong bases, and can usually be protonated by strong acids without loss of dihydrogen.

Our interest in d^0 transition metal hydride complexes was stimulated by the wealth of chemistry we found for bis(pentamethylcyclopentadienyl)zirconium dihydride, $Cp_2^*ZrH_2$ (1) ($Cp^* = \eta^5-C_5(CH_3)_5$).⁵ 1 is unusual both because its zirconium-hydride bonds are chemically like those of boron, aluminum or alkali metal hydrides and because it is coordinatively unsaturated. Both of these properties are thought to be important in its stoichiometric reduction of carbon monoxide.⁶ In this light we set out to prepare some new d^0 hydride complexes of

tantalum. The following is a report on the synthesis, characterization and reaction chemistry of a series of tantalum(V) polyhydrides of the general formula $\text{Cp}^*\text{TaL}_2\text{H}_{4-n}\text{Cl}_n$.

RESULTS

1. Synthesis and Characterization. The general synthetic strategy for the hydrides reported here is based on hydrogenation of a corresponding alkyl compound. High yield synthetic routes to (pentamethylcyclopentadienyl)tantalumtrimethylchloride, $\text{Cp}^*\text{TaMe}_3\text{Cl}$ (2), and (pentamethylcyclopentadienyl)tantalumtetramethyl, Cp^*TaMe_4 (3), have been described by Schrock and co-workers.⁷ Treatment of these alkyls with hydrogen under normal conditions yields intractable mixtures; even in the presence of added phosphines, hydrogenation at one atmosphere does not give identifiable products. We find that under 100 atm H_2 in the presence of phosphorus donor ligands, however, polyhydride complexes are formed in high yields. Thus $\text{Cp}^*\text{TaL}_2\text{H}_4$ ($\text{L} = \text{PMe}_3$ (4), $\text{PMe}_2(\text{C}_6\text{H}_5)$ (5), $\text{P}(\text{OMe})_3$ (6), and $\text{L}_2 = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$, ($\equiv \text{dmpe}$) (7)) were obtained by treatment of 3 with 100 atmospheres of H_2 and 2 - 3 equivalents of L in petroleum ether for a day at room temperature (eq 1). $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_3\text{Cl}$ (8)



3

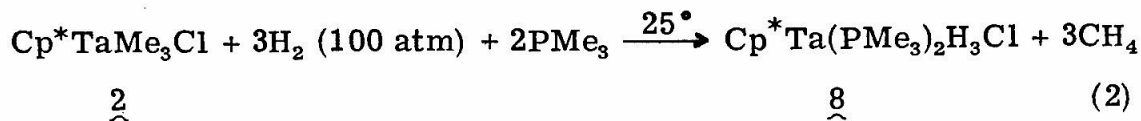
4 $\text{L} = \text{PMe}_3$

5 $\text{L} = \text{PMe}_2(\text{C}_6\text{H}_5)$

6 $\text{L} = \text{P}(\text{OMe})_3$

7 $\text{L}_2 = \text{dmpe}$

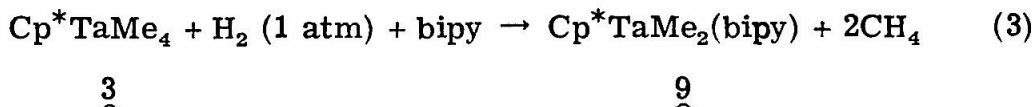
can be prepared similarly by hydrogenation of 2 in the presence of PMe_3 (eq 2). In all cases white crystalline materials can be obtained,



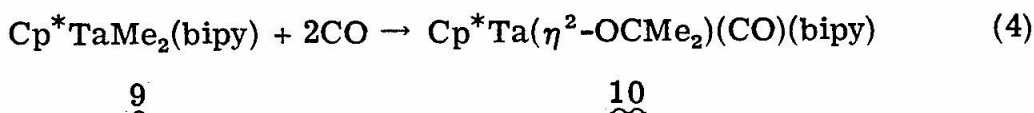
although the very high solubility of these compounds in hydrocarbon solvents does present some difficulty in their isolation.

Thus far the success of the method has been restricted to the use of phosphorus donors as auxiliary ligands. With trimethylamine, pyridine, tetrahydrofuran, ethylenediamine and dimethoxyethane intractable mixtures have been obtained. In the absence of an added ligand a black solid is obtained which is difficult to purify and has yet to be identified. The procedure also fails to give a clean product with phosphine ligands that are sterically demanding, like tri-t-butylphosphine⁸ or tricyclohexylphosphine. The reaction of 2 with dimethylphenylphosphine and hydrogen forms an unidentified rust colored solid along with a mixture of soluble products, one of which appears to be a monophosphine hydride complex (evidenced by a doublet resonance in the ¹H NMR spectrum, 11.97 δ , ²J_{PH} = 49 Hz). Presumably the greater size of $\text{PMe}_2(\text{C}_6\text{H}_5)$ compared to PMe_3 prevents the formation of a product analogous to 8, which itself is quite crowded (see below).

Hydrogenation of 3 in the presence of bipyridine (bipy) affords a black crystalline solid, 9, in high yield (eq 3). This reaction, unlike



those above, proceeds smoothly at one atmosphere of hydrogen. The stoichiometry of eq 3 has been confirmed by Toepler pump measurements of the hydrogen absorbed and the methane produced. In addition spectroscopic, analytical and molecular weight data support the formulation of 9 as $\text{Cp}^*\text{TaMe}_2(\text{bipy})$. Treatment of 3 with deuterium gas and bipy produced 9 and a mixture of methanes, roughly 80% CH_3D and 20% CH_4 . Surprisingly 9 can be treated with 100 atm hydrogen at room temperature for a week without change. Reaction does occur at 80° but a mixture of products is obtained. 9 reacts rapidly with two equivalents of carbon monoxide to give a bright blue compound, $\text{Cp}^*\text{Ta}(\eta^2\text{-OCMe}_2)(\text{CO})(\text{bipy})$, 10 (eq 4). The reaction of 3



with CO has also been reported to yield an η^2 -acetone or metalla-oxirane complex.⁷

The four tetrahydride complexes 4, 5, 6, and 7 are fluxional on the NMR timescale at ambient temperatures. Thus the hydrides appear as binomial triplets in the proton NMR spectra (fig. 1a) and in each case the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum exhibits only a singlet (NMR and IR data in Table I). The hydride count was established for 7 by integration and by observation of a quintet in the ^{31}P NMR spectrum on selective decoupling of dmpe protons. By contrast, the ^1H NMR spectrum of 8 at ambient temperatures indicates that the hydrides are not equivalent (fig. 1b). The 500 MHz proton spectrum⁹ exhibits two broad (30 and 50 Hz FWHM) hydride resonances which unlike 4 show

Figure 1. 90 MHz ^1H NMR spectra of (a) $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_4$ (4), (b) $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_3\text{Cl}$ (8), and (c) $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_3\text{Cl}$ (8) with one equivalent of added PMe_3 . Spectra obtained in benzene- d_6 with TMS; asterisks denote impurity resonances or spinning side bands.

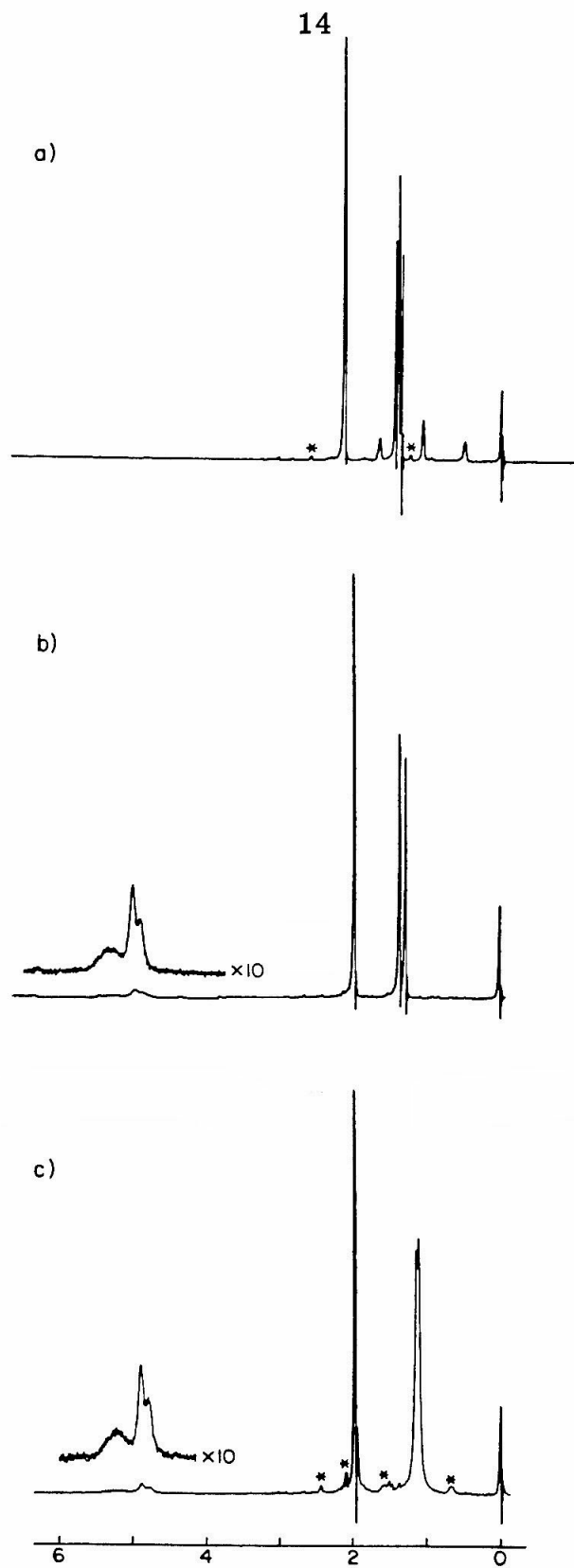
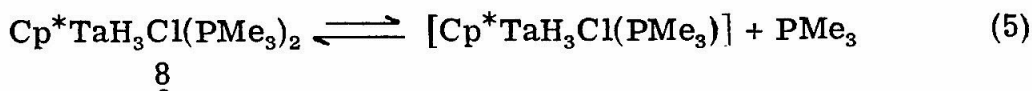


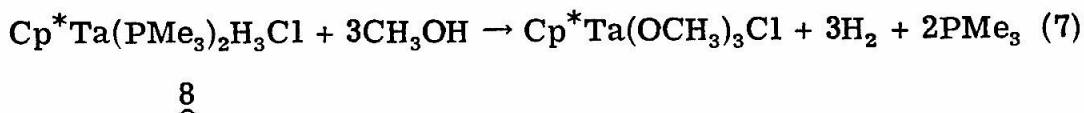
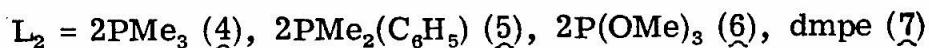
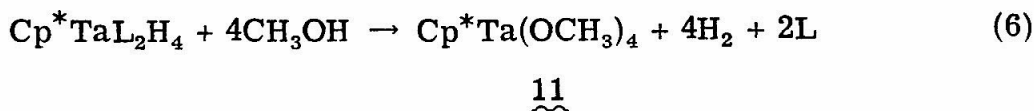
Fig. 1.

no resolvable P-H coupling. Moreover the hydrogens of the trimethylphosphine ligands appear as a triplet for 4 but as a doublet for 8. These observations suggest that the PMe_3 ligands in 8 are labile, undergoing a rapid, reversible dissociation (eq 5). In support of



this suggestion a solution of 8 with excess trimethylphosphine shows only one signal for PMe_3 in the ^1H NMR spectrum, intermediate between the positions of coordinated and free ligand (fig. 1c). This type of NMR behavior for phosphine complexes has been examined in detail by Tolman.¹⁰ The phosphine dissociation from 8 can be slowed sufficiently at low temperatures such that the expected strong P-H coupling may be observed. The low temperature NMR spectra of these hydride complexes are discussed in Chapter II.¹¹

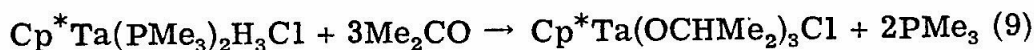
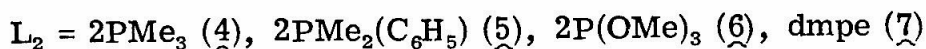
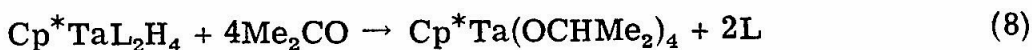
2. Reactions Involving Hydride Donation. These new hydride complexes react even with weak acids such as methanol to afford H_2 and the corresponding methoxytantalum species (eqs 6 and 7). The



molecular weights of these alkoxide complexes have not been determined; fluxional, oligomeric structures are entirely possible. Loss

of the phosphorus donor ligands accompanies these reactions, presumably due both to the greater steric crowding in the products and to the reduced Lewis acidity of the metal center because of π donation from the methoxy ligands. The π donor ability of methoxide undoubtedly also contributes to the stability of the (formally) coordinatively unsaturated $\text{Cp}^*\text{Ta}(\text{OCH}_3)_4$ and $\text{Cp}^*\text{Ta}(\text{OCH}_3)_3\text{Cl}$. The reaction of 4 with less than four equivalents of CH_3OH yields only the commensurate amounts of $\text{Cp}^*\text{Ta}(\text{OCH}_3)_4$ (11) and unreacted $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_4$, suggesting that the intermediate methoxy hydride complexes are more reactive toward methanol than 4. The reactivity of the hydride complexes varies over a fairly wide range: 8 reacts with methanol rapidly at 25°C , 4, 5, and 7 over a few hours at 25°C , and 6 requires hours at 80°C .

The facile reduction of acetone to the corresponding isopropoxide derivatives provides further evidence for the hydridic character of these compounds (eqs 8 and 9). The rates of these reactions also vary

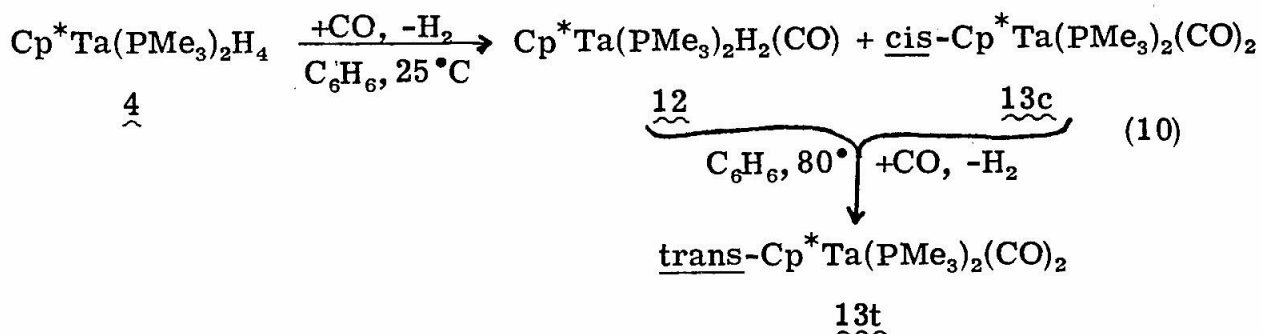


8

considerably, in the order 8 (seconds at 25°) $>$ 5 (hours at 25°) $>$ 4 (a day at 25°) $>$ 6 (hours at 80°) $>$ 7 (a week at 80°). This order of reactivity, 8 \gg 4 \gg 7, is also the expected order for the rate of phosphine loss (see Discussion). The phosphine ligands for 8 are very

labile (as described above, eq 5) and loss of PMe_3 from 4 should be much more facile than dissociation of one end of the dmpe ligand from 7. This suggests that the reduction of acetone is proceeding via an initial substitution of Me_2CO for phosphine. In agreement with this hypothesis, added trimethylphosphine was found to greatly inhibit the conversion of $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_4$ to $\text{Cp}^*\text{Ta}(\text{OCHMe}_2)_4$.

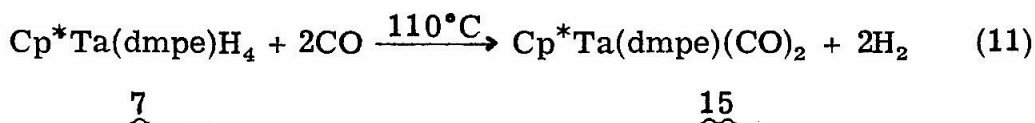
3. Reactions with Carbon Monoxide. Compounds 4, 5, 6, 7, and 8 react with carbon monoxide to form lower valent carbonyl complexes in which CO displaces two hydride ligands. These reactions proceed cleanly with stoichiometric evolution of dihydrogen. In each case the reaction with CO proceeds at a rate similar to that with acetone. The reaction of 4 with CO at ambient temperatures gives $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_2(\text{CO})$ (12) and a small amount of the cis isomer of $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2(\text{CO})_2$ (13c); heating this mixture to 80°C under a CO atmosphere causes complete conversion to trans- $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2(\text{CO})_2$ (13t) (eq 10).¹² These reactions



are inhibited by added trimethylphosphine, especially the formation of the Ta(I) products. Thus pure 12 is obtained in the presence of excess PMe_3 . 13c is prepared using petroleum ether as the solvent because it

precipitates from the reaction mixture, leaving the much more soluble 12 and 13t.¹³ A large difference in solubility between cis and trans isomers of "four-legged-piano-stool" complexes has been previously observed for a number of rhenium compounds.¹⁴ The assignment of cis and trans stereochemistry is made primarily on the basis of the relative intensities of the carbonyl bands in the IR spectrum, and by comparison with $\text{Cp}^*\text{Ta}(\text{dmpe})(\text{CO})_2$ (15, see below) which is constrained to have a cis geometry.¹⁵ 13c slowly isomerizes to 13t at 80°C indicating that the barrier to interconversion is quite large; this contrasts with isoelectronic molybdenum and tungsten complexes which often interconvert on the NMR timescale.¹⁶

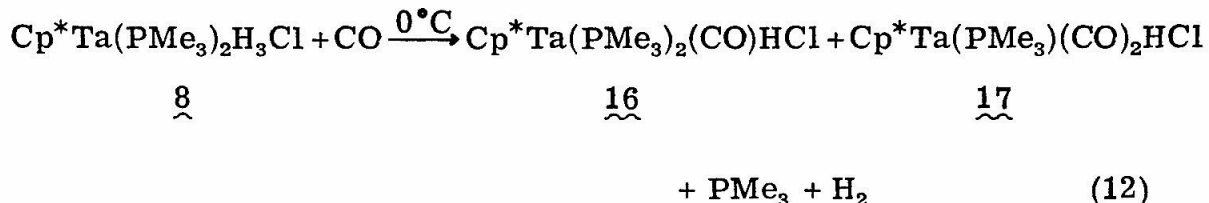
The reaction of 7 with carbon monoxide shows no evidence for a Ta(III) intermediate; the only detectable species during the reaction is the final product, $\text{Cp}^*\text{Ta}(\text{dmpe})(\text{CO})_2$ (15) (eq 11). Despite the vigorous



conditions, the reaction proceeds cleanly so that only 7 and 15 are observed by NMR even after 24 hrs at 110°C. Equation 11 is analogous to the reaction of $\text{Ta}(\text{dmpe})_2\text{H}_5$ with 1500 psi of CO at 80°C, reported to give $\text{Ta}(\text{dmpe})_2(\text{CO})_2\text{H}$; no tantalum(III) species were observed in this reaction either.¹⁷ Compounds 13c, 13t, 15, and $\text{Ta}(\text{dmpe})_2(\text{CO})_2\text{H}$ have extremely low CO stretching frequencies (1840 - 1730 cm^{-1}) that are among the lowest values reported for neutral monomeric carbonyl complexes. Similarly the carbonyl resonances in the ^{13}C NMR spectra are observed extremely downfield (271 - 278 δ). These data indicate

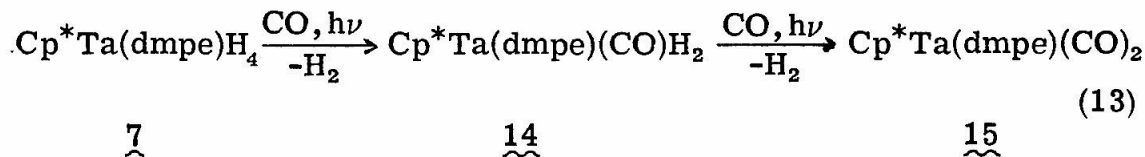
that the Ta(I) compounds are extremely electron rich and that there is a great deal of π back-bonding to the CO ligands.

$\underline{8}$ reacts rapidly with CO at 0°C to afford a mixture of $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2(\text{CO})\text{HCl}$ ($\underline{16}$) and $\text{Cp}^*\text{Ta}(\text{PMe}_3)(\text{CO})_2\text{HCl}$ ($\underline{17}$) (eq 12).



Free phosphine inhibits this reaction and increases the yield of $\underline{16}$ at the expense of $\underline{17}$. $\underline{17}$ is favored in more dilute solutions under higher pressures of CO. The reactions of $\underline{4}$ and $\underline{8}$ with $\text{Cp}_2\text{Mo}(\text{CO})$ ($\text{Cp} \equiv \eta^5\text{-C}_5\text{H}_5$) have also been examined: there is no reaction at ambient temperatures and at 80°C the tantalum compounds decompose to a number of products. A small amount of $\text{Cp}_2\text{Mo}(\text{CO})$ is converted to Cp_2MoH_2 and $\text{Cp}_2\text{Mo}(\text{PMe}_3)$.

4. Photochemistry. Irradiation of a benzene- \underline{d}_6 solution of $\underline{7}$ in an NMR tube under two atmospheres of carbon monoxide proceeds in a manner analogous to the thermal reaction of $\underline{4}$ with CO (eq 13). Since

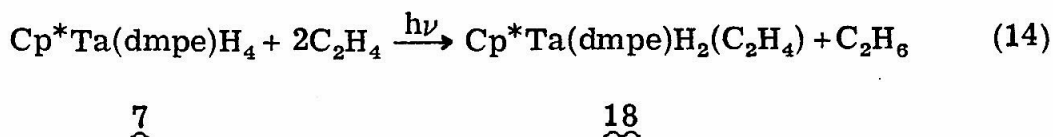


$\text{Cp}^*\text{Ta}(\text{dmpe})(\text{CO})\text{H}_2$ ($\underline{14}$) is as photosensitive as $\underline{7}$, it has been obtained only in mixtures with $\underline{7}$ and/or $\underline{15}$. Irradiation under vacuum leaves $\underline{7}$ unchanged except for a small amount of decomposition. No hydrogen/

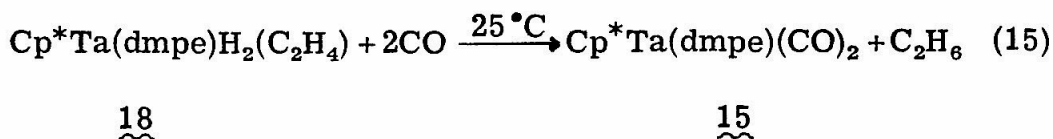
deuterium exchange is observed between solvent C_6D_6 and the hydride ligands of 7, in contrast to the photolysis of $CpMo(dmpe)H_3$.¹⁸ However, when irradiated under three atmospheres of D_2 exchange is observed with Ta-H ligands.

The absorption spectrum of 7 in petroleum ether shows no bands in the visible region with a strong absorption centered below 250 nm. Since the tail of this band barely extends past 300 nm, a low pressure mercury lamp that emits primarily at 254 nm has been used as a light source. While we realize benzene is an unusual solvent for photolyses in the ultraviolet region because it absorbs strongly below 280 nm, irradiation of 7 in a non-absorbing solvent such as petroleum ether does not accelerate the reaction. Furthermore, in contrast with the nearly quantitative conversions observed in benzene or toluene, photolyses in petroleum ether generate a number of side products.

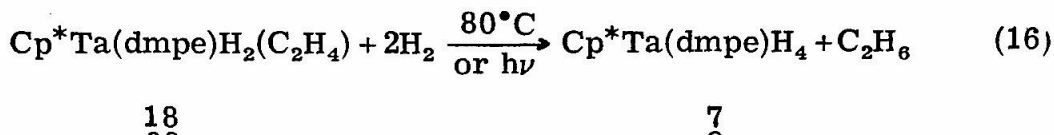
Photolysis of a benzene solution of 7 under two atmospheres of ethylene produces $Cp^*Ta(dmpe)H_2(C_2H_4)$ (18) and a stoichiometric amount of ethane (eq 14). 18 reacts at 25°C with two equivalents of



carbon monoxide to yield 15 and ethane (eq 15). The reaction of 18 with hydrogen at 80°C or under irradiation also releases ethane and



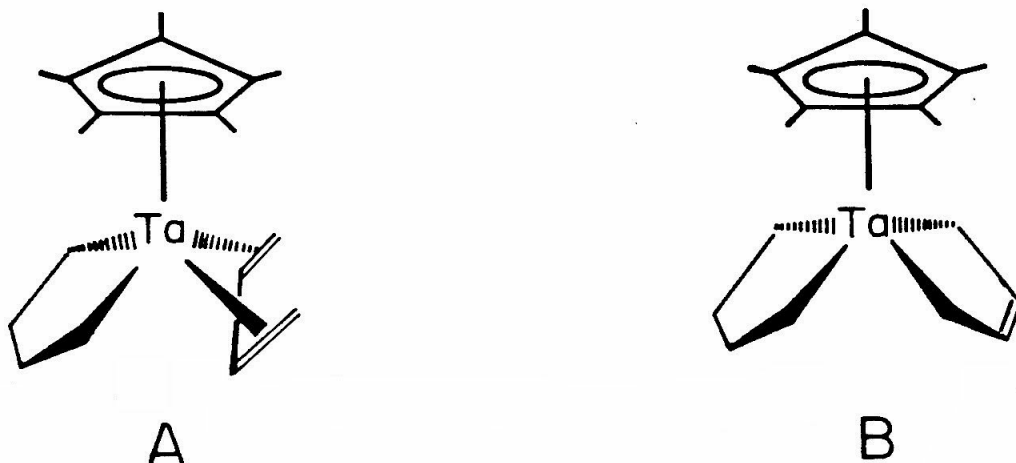
regenerates 7 (eq 16). The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 18 has eight



groups of lines all coupled to one or both phosphorus nuclei. The $^{13}\text{P}\{^1\text{H}\}$ NMR spectrum is a pair of doublets. An unsymmetrical static structure is thus implicated such that the six carbons of the dmpe ligand and the two carbons of the ethylene ligand are inequivalent. In contrast, the isoelectronic $\text{Cp}^*\text{Ta}(\text{dmpe})\text{H}_2(\text{CO})$ (14) is either fluxional or symmetrical, since both the hydride ligands and the carbon of the carbonyl appear as triplets in their respective NMR spectra.

5. Thermal Reactions with Ethylene. The reaction of 4, 5, 6, 7, or 8 with ethylene produces a mixture of tantalum containing products together with ethane, free phosphine, and 1-butene. These reactions proceed at roughly the same rate as the analogous thermal reactions with carbon monoxide or acetone. 7 and ethylene do not yield 18, the photolytic product. However, 18 is unstable at the high temperatures required for reaction, so that the intermediacy of 18 in these reactions is uncertain. 4 appears to be a precursor for a fairly active ethylene dimerization catalyst: under an atmosphere of ethylene the initial turnover rate of 1-butene is approximately one per hour. Since 4 is mostly unreacted after an hour the turnover per active catalyst is probably much higher, however. Added PMe_3 inhibits the reaction.

One of the products of the reaction of 4 with ethylene has been isolated and characterized as a metallacyclopentane butadiene complex, $\text{Cp}^*\text{TaCH}_2\text{CH}_2\text{CH}_2\text{CH}_2(\text{C}_4\text{H}_6)$, 19. 19 is also formed in the reactions of ethylene with 5 and 6. The 500 MHz ^1H NMR spectrum of 19 is shown in Figure 2; Table I contains tentative assignments based on selective decoupling experiments. The disparity in the ^{13}C -H coupling constants for the butadiene ligand ($^1J_{\text{C}_\alpha\text{H}} = 147 \text{ Hz}$, $^1J_{\text{C}_\beta\text{H}} = 160 \text{ Hz}$) suggests some contribution of the canonical form B shown below.



In light of the observation that solutions of 19 do not react with ethylene, the catalytic dimerization was not pursued further. Schrock and co-workers have examined several systems that are olefin dimerization catalysts.^{19,20} One based on a $\text{Cp}^*\text{TaCl}_2(\text{olefin})-\text{Cp}^*\text{TaCl}_2$ - (metallacyclopentane) cycle²⁰ appears to be similar to the system reported here.

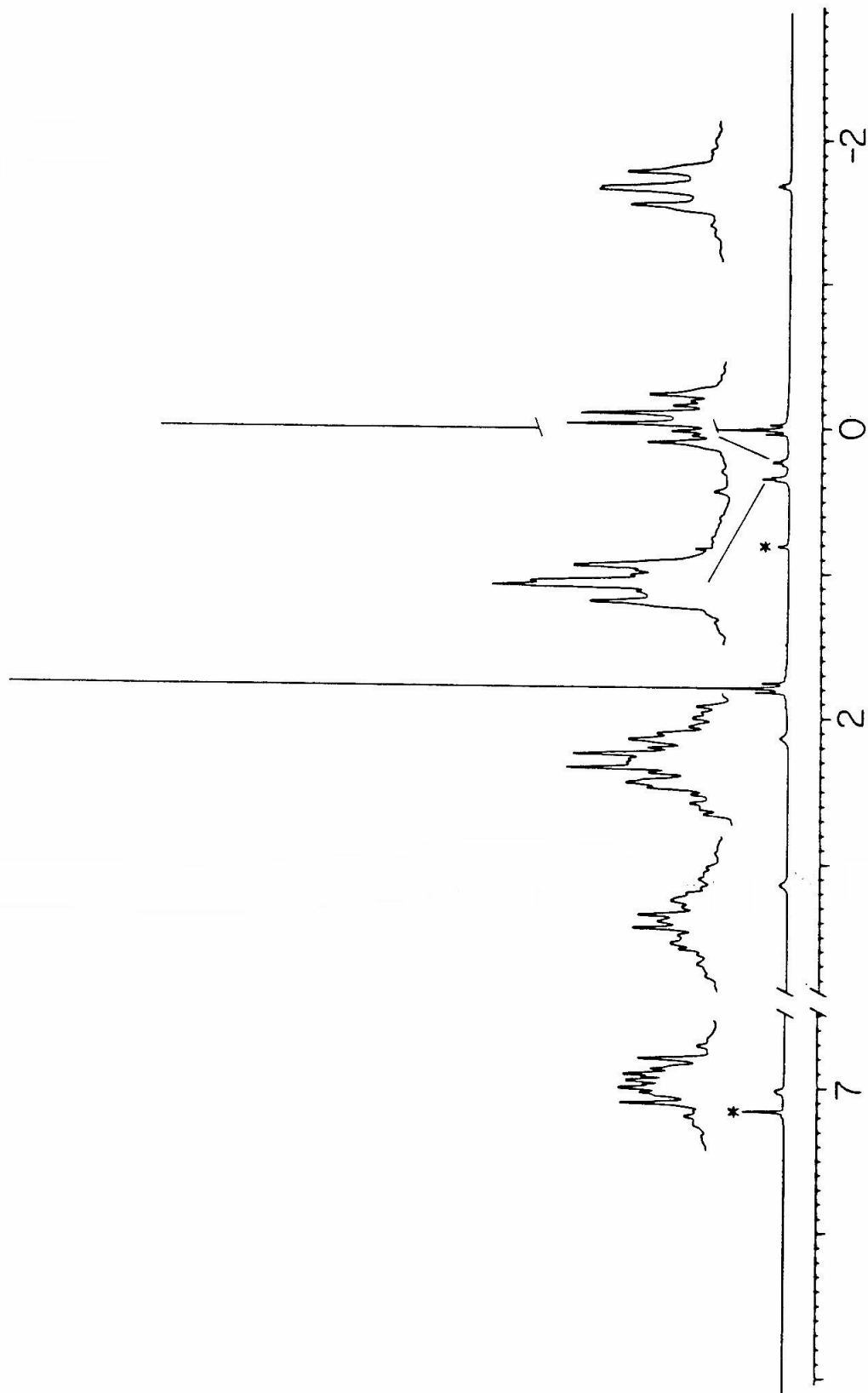


Figure 2. 500 MHz ^1H NMR spectrum of $\text{Cp}^*\text{TaCH}_2\text{CH}_2\text{CH}_2\text{CH}_2(\text{C}_4\text{H}_8)$ (19), benzene- d_6 solvent, TMS internal standard. Inserts are expanded by a factor of ten. Asterisks denote solvent and impurity resonances.

DISCUSSION

Hydrogenation of alkyl complexes has proven to be a powerful synthetic route to polyhydride compounds, especially for the early transition metals. In addition to the syntheses described above, other examples include the reaction of hexamethyltungsten with high pressures of hydrogen in the presence of phosphine to give WH_6L_3 , WH_4L_4 , or WH_2L_5 depending on the size of the ligand L,²¹ and the preparation of $\text{Ta}(\text{dmpe})_2\text{H}_5$ from $\text{TaMe}_5(\text{dmpe})$ ²² or $\text{Ta}(\text{C}_6\text{H}_5)_6^-$ with dmpe and hydrogen.¹⁷ This procedure has a number of advantages over the more common synthetic routes using boron or aluminum hydride reagents: usually non-forcing conditions and nonpolar media are used, and the problems of the boron or aluminum complexing with the transition metal hydride are avoided. The mechanism of the reaction is a matter of debate,²³ since the alkyl starting materials used are often formally d^0 (as are 2 and 3), and therefore cannot react with dihydrogen by a conventional oxidative addition/reductive elimination pathway. High pressures are usually required when the product is a polyhydride, presumably because a high concentration of dihydrogen is required to trap reactive, coordinatively unsaturated intermediates.

It is not clear why the hydrogenation of 3 is successful only in the presence of phosphine or phosphite ligands and not with oxygen or nitrogen donors. The sole exception occurs with bipyridine as the added ligand. In this case the reaction proceeds smoothly even at only one atmosphere of hydrogen to yield $\text{Cp}^*\text{TaMe}_2(\text{bipy})$ (9). Curiously, the reaction stops at 9, a d^2 , sixteen-electron complex that seems ideally suited to oxidatively add H_2 .

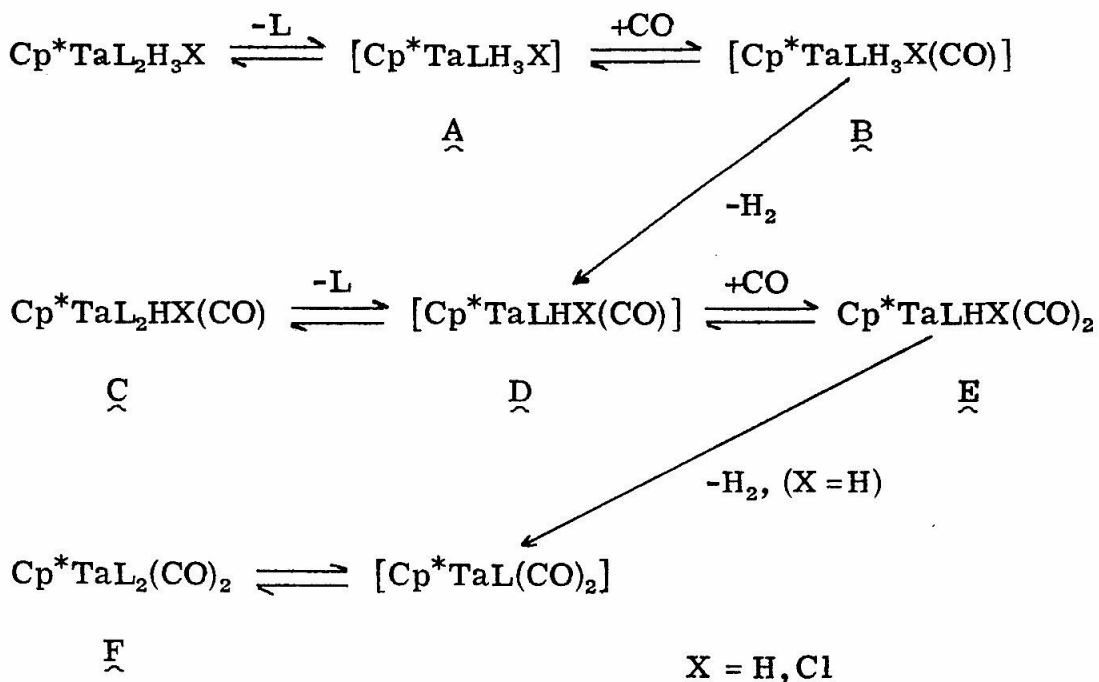
The five new polyhydride complexes reported here are formally eighteen-electron compounds and thus coordinatively saturated. Each compound reacts with carbon monoxide, acetone and ethylene at roughly similar rates, suggesting a common pathway. The strong inhibition of these reactions by excess phosphine suggests that dissociation of a phosphine ligand is a prerequisite for reaction with these substrates. This conclusion is also consistent with the relative reactivities of the polyhydride complexes. $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_3\text{Cl}$ (8) is the most reactive of the group--reactions with the above substrates are rapid at 0° . Furthermore, 8 is the only compound for which phosphine dissociation is rapid at room temperature on the NMR time-scale. 4 and 7 should be electronically quite similar, but the reactions of 4 proceed at room temperature while 7 requires heating to 100° to achieve comparable rates. Dissociation of one end of the bidentate dmpe ligand is expected to be more difficult than loss of one of two PMe_3 ligands. This anticipated difference in phosphine dissociation rate has also been observed for the reaction of $\text{Ta}(\text{CHCMe}_3)_2\text{Cl}_3$ ($\text{L}_2 = 2\text{PMe}_3, \text{dmpe}$) with ethylene. Displacement of the phosphine occurs rapidly at room temperature for the bis(trimethylphosphine) derivative; the dmpe complex requires heating to $80\text{-}100^\circ\text{C}$ for several hours.²⁴

The variation in the rate of phosphine loss from the bis(phosphine) compounds appears to be due to both electronic and steric factors. These complexes are formally nine coordinate, if the bulky $\eta^5\text{-C}_5\text{Me}_5$ ligand is considered to occupy three sites, and thus sterically quite crowded. Since a chloride ligand is larger than a hydride 8 is more

crowded than 4; phosphine dissociation should therefore be more favored in 8 than in 4 on steric grounds. Chloride can also act as a weak π donor and hence can serve as a potential three-electron donor. As such Cl^- is expected to better stabilize the product of ligand loss relative to H^- . A similar trend has been reported in the dissociation of triphenylphosphine from $\text{RuCl}_2(\text{PPh}_3)_3$ and $\text{RuHCl}(\text{PPh}_3)_3$.²⁵ 5 is slightly more reactive than 4, presumably because PMe_2Ph is larger than PMe_3 .²⁶ The low reactivity of 6 indicates that trimethylphosphite dissociates much more slowly than the ligands in 4 and 5, probably due to the small size of $\text{P}(\text{OMe})_3$.²⁶ Other workers have noted that, at least for later transition metal complexes, phosphite ligands are less labile than phosphine ligands. Tolman observed that phosphite ligands dissociate from $\text{Ni}(0)$ much more slowly than phosphine of similar size.¹⁰ Reactions of the iron and ruthenium hydrides H_2ML_4 ($\text{L} = \text{PR}_3$, $\text{P}(\text{OR})_3$) require conditions where ligand dissociation is facile. $\text{H}_2\text{M}(\text{PPh}_2\text{Me})_4$ ($\text{M} = \text{Fe}, \text{Ru}$) substitute CO or benzonitrile for phosphine at 30-60°C while the phosphite derivatives $\text{H}_2\text{M}[\text{P}(\text{OC}_2\text{H}_5)_3]_4$ do not react with CO at temperatures exceeding 100°C and at pressures up to 100 atm.²⁷

The reactions of the polyhydride compounds with carbon monoxide can be accommodated by the mechanism shown in Scheme I. For 4 and 7 the compounds C and F ($\text{X} = \text{H}$) have been isolated; for 8 the reaction produces a mixture of C and E ($\text{X} = \text{Cl}$). Dissociation of a phosphine ligand generates coordinatively unsaturated species A. A can add a CO ligand, which is expected to better stabilize the incipient $\text{Ta}(\text{III})$, d^2 species accompanying reductive elimination of H_2 .

Scheme I



Indeed, d^0 carbonyl complexes such as intermediate $\underline{\text{B}}$ are unstable because the metal has no filled nonbonding orbitals available for π bonding with the CO. The complexes $\text{Cp}^*_2\text{MH}_2(\text{CO})$ ($\text{M} = \text{Zr}, \text{Hf}$)²⁸ are unstable above -10° ; under most conditions these compounds form products based on the reduction of carbon monoxide.⁵ In the presence of excess CO, however, the predominant pathway can be reductive elimination of dihydrogen.²⁹ Similarly, $\text{Cp}_2\text{NbH}_2(\text{CO})^+$, proposed as an intermediate in the protonation of $\text{Cp}_2\text{Nb}(\text{H})\text{CO}$, eliminates H_2 above -30° .³⁰ Thus it is not surprising to find that for these tantalum systems reductive elimination of H_2 is a very facile process. It is interesting that the reduction from Ta(III) to Ta(I) is finely tuned: $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_2(\text{CO})$ ($\underline{\text{12}}$) is stable while $\text{Cp}^*\text{Ta}(\text{PMe}_3)\text{H}_2(\text{CO})_2$ is not

observed. $\text{Cp}^*\text{Ta}(\text{PMe}_3)\text{H}_2(\text{CO})_2$ would be analogous to 17 and presumably is an intermediate on the path from 12 to 13 (see Scheme I). Reductive elimination of H_2 from $\text{Cp}^*\text{Ta}(\text{PMe}_3)\text{H}_2(\text{CO})_2$ generates $\text{Cp}^*\text{Ta}(\text{PMe}_3)(\text{CO})_2$ which is trapped by PMe_3 to give specifically the cis isomer of 13. The same specificity has been observed in the photochemical reactions of $\text{CpMo}(\text{CO})_3\text{X}$, which involve trapping of a very similar intermediate, $\text{CpMo}(\text{CO})_2\text{X}$.^{16b}

These new tantalum polyhydride complexes are clearly hydridic rather than protic, that is, they behave formally as sources of H^- like boron or aluminum hydride reagents. In contrast, most transition metal hydrides are either acidic or radical precursors-- the hydrogen ligands react either as H^+ or in an increasing number of examples as sources of $\text{H}\cdot$.³¹ There is a rough correlation of chemical properties with position in the periodic table; the most acidic compounds are found for the later transition metals and the hydridic complexes on the far left.² Although this general trend is clear, obtaining a measure of the hydridic character of a specific transition metal hydride is difficult. There have been some attempts to construct a scale of hydridic character based on certain test reactions with common substrates; however, these reactions may require an open coordination site, so that a comparison of a series of hydrides may be dominated by the accessibility of a coordinatively unsaturated intermediate. One study has compared a number of cyclopentadienyl metal hydride complexes in their reactions with acetone and trifluoroacetone.³² While compounds 4, 5, 6, 7, and 8 react with acetone to yield isopropoxide complexes, the available evidence indicates that

phosphine dissociation is required for this process. Thus the relative reactivity of the hydride complexes is dominated by the rate of phosphine loss, not the hydridic character of the hydride ligands.

Presumably acetone, like ethylene, must coordinate before a hydrogen is transferred to the unsaturated carbon. It is also conceivable that this process closely resembles borane reductions of ketones and aldehydes, where coordination of the carbonyl oxygen accelerates H^- transfer.³³

The hydride compounds all react at $-80^\circ C$ with anhydrous HCl to generate a stoichiometric amount of dihydrogen. Since phosphine dissociation is very slow at low temperature, this reaction does not appear to require an open coordination site. Here the mechanism probably involves direct protonation of a metal hydride bond. A weak acid such as methanol can react either by direct protonation, if the hydride ligands are sufficiently reactive, or by coordinating to the metal prior to elimination of H_2 . The latter is probably the more facile process if an open site is available in view of the enhanced acidity of ligated MeOH. The tantalum oxygen interaction should also stabilize the transition state for hydrogen production by this mechanism. Compounds 4, 5, 6, and 8 react with methanol at roughly the same rate as they react with acetone or CO, consistent with phosphine loss and prior coordination of MeOH for these reactions. The reaction of 7 with MeOH, however, is three or four orders of magnitude faster than its reactions with acetone, CO, or ethylene (hours at room temperature vs. days at $100^\circ C$), implicating a direct, electrophilic attack of methanol at the Ta-H bonds of coordinatively saturated 7.

Under conditions where a coordination site is not available the rate of reaction with weak protic acids could thus be used as a rough measure of the hydridic character of a transition metal hydride. The rates of reaction of the series of tantalum hydrides reported herein with CH_3OH compare qualitatively as follows: $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_3\text{Cl}$, 8 (seconds, 25°C) $>$ $\text{Cp}^*\text{Ta}(\text{PMe}_2\text{Ph})_2\text{H}_4$, 5 \sim $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_4$, 4 \sim $\text{Cp}^*\text{Ta}(\text{dmpe})\text{H}_4$, 7 $>$ $\text{Cp}^*\text{Ta}[\text{P}(\text{OMe})_3]_2\text{H}_4$, 6 (hours, 80°C). Since 6 reacts (regardless of mechanism) with methanol more slowly than 7, 7 is more hydridic than 6 by this criterion. This order could reasonably be attributed to the greater σ donation from a phosphine vs. a phosphite. Unfortunately, the situation is muddled for 4, 5, and 8, since the mechanism could involve prior loss of a phosphine ligand. 7 seems to fall on this scale between $\text{Ta}(\text{dmpe})_2\text{H}_5$, which rapidly reacts with ethanol at 25°C ,¹⁷ and Cp_2TaH_3 , which is decomposed only by aqueous acids.³⁴ By contrast, d^2 group VI hydrides show no hydridic character by the above criterion. Cp_2WH_2 , Cp_2MoH_2 , and $\text{CpMo}(\text{dmpe})\text{H}_3$, like the d^2 group V species $\text{Cp}_2\text{Nb}(\text{PR}_3)\text{H}$, are all protonated by aqueous acid to give stable cations.³⁴⁻³⁶ We tentatively conclude therefore that d^0 transition metal hydrides are more hydridic than d^2 species bearing the same auxiliary ligands.

Table I. NMR^a and IR^b Data

Compound	IR	Assignment	Chemical Shift	Coupling
Cp*Ta(PMe ₃) ₂ H ₄ 4	ν(Ta-H) 1725, 1640	[C ₅ (CH ₃) ₅]	2.16 s	
	ν(Ta-D) 1225, 1095	[P(CH ₃) ₃] ₂	1.42 t	J _{PH} = 4
		TaH ₄	1.08 t	J _{PH} = 52.5
Cp*Ta[PMe ₂ (C ₆ H ₅)] ₂ H ₄ 5	ν(Ta-H) 1730, 1700, 1655	[C ₅ (CH ₃) ₅]	1.94 s	
		[P(CH ₃) ₂ (C ₆ H ₅)] ₂	1.73 m ^c	J _{PH} = 4 ^c
		[P(CH ₃) ₂ (C ₆ H ₅)] ₂	7.11 m	
		[P(CH ₃) ₂ (C ₆ H ₅)] ₂	7.70 m	
		TaH ₄	1.44 t	² J _{PH} = 50
Cp*Ta[P(OMe) ₃] ₂ H ₄ 6	ν(Ta-H) 1755, 1715, 1690	[C ₅ (CH ₃) ₅]	2.28 s	
		[P(OCH ₃) ₃] ₂	3.47 m ^c	J _{PH} = 5 ^c
		TaH ₄	-1.38 t	² J _{PH} = 58
Cp*Ta(dmpe)H ₄ 7	ν(Ta-H) 1715, 1625	[C ₅ (CH ₃) ₅]	2.33 s	
	ν(Ta-D) ^d 1250, 1160	(CH ₃) ₂ PCH ₂ CH ₂ P(CH ₃) ₂	1.32 m	
		(CH ₃) ₂ PCH ₂ CH ₂ P(CH ₃) ₂	1.16 d	J _{PH} = 15
		TaH ₄	0.19 t	² J _{PH} = 37
Cp*Ta(PMe ₃) ₂ H ₃ Cl 8	ν(Ta-H) 1765, 1700	[C ₅ (CH ₃) ₅]	1.96 s	
	ν(Ta-D) ^d 1250, 1220	[P(CH ₃) ₃] ₂	1.33 d	² J _{PH} = 7.5
		TaH'H ₂ "	5.2 ^e broad	
		TaH'H ₂ "	4.8 ^e broad	

Table I (continued)

Compound	IR	Assignment	¹ H NMR	Chemical Shifts	Coupling
Cp*TaMe ₂ (bipy) 9		[C ₅ (CH ₃) ₅] Ta(CH ₃) ₂ bipy	¹ H NMR	1.57 s	J _{HH} = 7 J _{HH} = 9
				0.13 s	
				4 H 6.29 m 2 H 7.08 d 2 H 7.77 d	
Cp*Ta(η ² OCMe ₂)(CO)bipy 10	ν(C=O) 1775	[C ₅ (CH ₃) ₅] Ta(CH ₃) ₂ [C ₅ (CH ₃) ₅] and bipy	¹ H NMR	10.46	J _{HH} = 9 J _{HH} = 7 J _{HH} = 7
				60.30	
				113.01	
				115.07	
				118.43	
122.43					
137.87					
139.60					
Cp*Ta(η ² OCMe ₂)(CO)bipy 10	ν(C=O) 1775	[C ₅ (CH ₃) ₅] [η ² OC(CH ₃)(CH ₃)'] [η ² OC(CH ₃)(CH ₃)'] bipy	¹ H NMR	1.47 s	J _{HH} = 9 J _{HH} = 7 J _{HH} = 7
				2.15 s	
				1.34 s	
				4 H 6.30 m 2 H 7.50 d 1 H 9.00 d 1 H 9.53 d	

Table I. (continued)

Compound	IR	Assignment	^{13}C NMR ^h	Chemical Shifts	Coupling
		$[\text{C}_5(\underline{\text{C}}\text{H}_3)_5]$		9.86 s	
		$[\eta^2 \text{OC}(\underline{\text{C}}\text{H}_3)(\underline{\text{C}}\text{H}_3)]$		30.78 q	
		$[\eta^2 \text{OC}(\underline{\text{C}}\text{H}_3)(\underline{\text{C}}\text{H}_3)]$		30.10 q	
		$[\eta^2 \text{OC}(\underline{\text{C}}\text{H}_3)(\underline{\text{C}}\text{H}_3)]$		87.46 s	
		Ta(CO)		257.41 s	
				149.35 d	
				144.65 d	
				138.54 s	
				124.14	
				122.12	
				121.91	
				120.77	
				114.40	
				113.26	
				111.67	
		$[\underline{\text{C}}_5(\underline{\text{C}}\text{H}_3)_5]$ and bipy ^h			
$\text{Cp}^*\text{Ta}(\text{OCHMe}_2)_4$	$\nu(\text{Ta-O})$ 575	$[\text{C}_5(\underline{\text{C}}\text{H}_3)_5]$		1.91 s	
		$[\text{OCH}(\underline{\text{C}}\text{H}_3)_2]_4$		4.58 septet	${}^3J_{\text{HH}} = 6$
		$[\text{OCH}(\underline{\text{C}}\text{H}_3)_2]_4$		1.17 d	${}^3J_{\text{HH}} = 6$

Table I. (continued)

Compound	IR	Assignment	^1H NMR	Chemical Shift	Coupling
$\text{Cp}^*\text{Ta}(\text{OCHMe}_2)_3\text{Cl}$	$\nu(\text{Ta-O})$ 575	$[\text{C}_5(\text{CH}_3)_5]$ $[\text{OCH}(\text{CH}_3)_2]_3$ $[\text{OCH}(\text{CH}_3)_2]_3$	^1H NMR	2.03 s 4.89 septet 1.20 d	$^3J_{\text{HH}} = 6$ $^3J_{\text{HH}} = 6$
$\text{Cp}^*\text{Ta}(\text{OMe})_4$ <u>11</u>		$[\text{C}_5(\text{CH}_3)_5]$ $(\text{OCH}_3)_4$	^1H NMR	2.00 s 4.22 s	
$\text{Cp}^*\text{Ta}(\text{PMe}_2)_2\text{H}_2\text{CO}$ <u>12</u>	$\nu(\text{CO})$ 1840 $\nu(\text{Ta-H})$ 1750, 1590	$[\text{C}_5(\text{CH}_3)_5]$ $[\text{P}(\text{CH}_3)_2]_2$ TaH_2	^1H NMR	2.01 s <u>c</u> 1.36 m -0.50 t	$J_{\text{PH}} = 3.5$ <u>c</u> $^3J_{\text{PH}} = 47$
		$[\text{C}_5(\text{CH}_3)_5]$ $[\text{C}_5(\text{CH}_3)_5]$ $[\text{P}(\text{CH}_3)_2]_2$ $\text{Ta}(\text{CO})$	$^{13}\text{C}\{^1\text{H}\}$ NMR	100.52 s 12.06 s 25.49 t 261.04 t	$J_{\text{PC}} = 14$ <u>f</u> $^3J_{\text{PC}} = 6$
<u>cis-Cp*Ta(PMe₂)₂(CO)₂</u> <u>13c</u>	$\nu(\text{CO})$ 1820, 1730	$[\text{C}_5(\text{CH}_3)_5]$ $[\text{P}(\text{CH}_3)_2]_2$ $[\text{C}_5(\text{CH}_3)_5]$	^1H NMR	1.94 s 1.15 m <u>c</u> 104.44 s	$J_{\text{PH}} = 7$ <u>c</u>
		$[\text{C}_5(\text{CH}_3)_5]$ $[\text{P}(\text{CH}_3)_2]_2$ $\text{Ta}(\text{CO})_2$	$^{13}\text{C}\{^1\text{H}\}$ NMR	12.44 s 23.06 t 278.31 t	$J_{\text{PC}} = 14$ $J_{\text{PC}} = 12$
<u>trans-Cp*Ta(PMe₂)₂(CO)₂</u> <u>13t</u>	$\nu(\text{CO})$ 1842, 1750	$[\text{C}_5(\text{CH}_3)_5]$ $[\text{P}(\text{CH}_3)_2]_2$	^1H NMR	1.90 s 1.35 m <u>c</u>	$J_{\text{PH}} = 8$ <u>c</u>

Table I (continued)

Compound	IR	Assignment	$^{13}\text{C}\{^1\text{H}\}$ NMR	Chemical Shift	Coupling
Cp*Ta(dimpe)H ₂ (CO) <u>14</u>	$\nu(\text{CO})^{\text{d}}$ 1850	$[\underline{\text{C}}_5(\text{CH}_3)_5]$	104.31 s		
		$[\underline{\text{C}}_5(\underline{\text{C}}\text{H}_3)_5]$	12.44 s		
		$[\text{P}(\underline{\text{C}}\text{H}_3)_3]_2$	20.48 t		$J_{\text{PC}} = 14^{\text{f}}$
		Ta(CO) ₃	278.11 t		$J_{\text{PC}} = 19.5$
Cp*Ta(dimpe)H ₂ (CO) <u>14</u>	$\nu(\text{CO})^{\text{d}}$ 1850	$[\underline{\text{C}}_5(\underline{\text{C}}\text{H}_3)_5]$	2.09 s		
		$(\underline{\text{C}}\text{H}_3)_2\text{P}\underline{\text{C}}\text{H}_2\text{CH}_2\text{P}(\underline{\text{C}}\text{H}_3)_2$	overlap with 6 and 15		
		TaH ₂	-2.30 t		$^2J_{\text{PH}} = 40$
Cp*Ta(dimpe)(CO) ₂ <u>15</u>	$\nu(\text{CO})$ 1830, 1745	$[\underline{\text{C}}_5(\underline{\text{C}}\text{H}_3)_5]$	1.97 s		
		$(\text{CH}_3)(\underline{\text{C}}\text{H}_3)\text{PCH}_2\text{CH}_2\text{P}(\underline{\text{C}}\text{H}_3)(\underline{\text{C}}\text{H}_3)$	1.45 d		$J_{\text{PH}} = 7.5 \text{ Hz}$
		$(\text{CH}_3)(\underline{\text{C}}\text{H}_3)\text{PCH}_a\text{H}_b\text{CH}_a\text{H}_b\text{P}(\underline{\text{C}}\text{H}_3)(\underline{\text{C}}\text{H}_3)$	0.99 d		$J_{\text{PH}} = 6 \text{ Hz}$
		$(\text{CH}_3)(\underline{\text{C}}\text{H}_3)\text{PCH}_a\text{H}_b\text{CH}_a\text{H}_b\text{P}(\underline{\text{C}}\text{H}_3)(\underline{\text{C}}\text{H}_3)$	0.85 m		
Cp*Ta(dimpe)(CO) ₂ <u>15</u>	$\nu(\text{CO})$ 1830, 1745	$[\underline{\text{C}}_5(\underline{\text{C}}\text{H}_3)_5]$	104.16 s		
		$[\underline{\text{C}}_5(\underline{\text{C}}\text{H}_3)_5]$	12.66 s		
		$(\underline{\text{C}}_a\text{H}_3)(\underline{\text{C}}_b\text{H}_3)\text{PCH}_2\text{CH}_2\text{P}(\underline{\text{C}}_a\text{H}_3)(\underline{\text{C}}_b\text{H}_3)$	21.32 dd		$J_{\text{PC}} = 30 \text{ \& } 4$
		$(\underline{\text{C}}_a\text{H}_3)(\underline{\text{C}}_b\text{H}_3)\text{PCH}_a\text{CH}_b\text{P}(\underline{\text{C}}_a\text{H}_3)(\underline{\text{C}}_b\text{H}_3)$	19.60 d		$J_{\text{PC}} = 17$
		$(\text{CH}_3)(\underline{\text{C}}\text{H}_3)\text{PCH}_2\text{CH}_2\text{P}(\underline{\text{C}}\text{H}_3)(\underline{\text{C}}\text{H}_3)$	32.95 dd		$J_{\text{PC}} = 26 \text{ \& } 17.5$
Ta(CO) ₂		270.88 dd		$J_{\text{PC}} = 17 \text{ \& } 4$	

Table I (continued)

Compound	IR	Assignment	^1H NMR	Chemical Shift	Coupling
$\text{Cp}^*\text{Ta}(\text{PMe}_3)_2(\text{CO})\text{HCl}$ 16	$\nu(\text{CO})$ 1820	$[\text{C}_5(\text{CH}_3)_5]$	1.83 s		
		$[\text{P}(\text{CH}_3)_3]_2$ TaH	1.26 m ^c 5.64 t	$J_{\text{PH}} = 4^c$ $^2J_{\text{PH}} = 45$	
$\text{Cp}^*\text{Ta}(\text{PMe}_3)(\text{CO})_2\text{HCl}$ 17	$\nu(\text{CO})$ 1975, 1890 $\nu(\text{Ta-H})$ 1645	$[\text{C}_5(\text{CH}_3)_5]$	$^{13}\text{C}\{^1\text{H}\}$ NMR 102.10 s		
		$[\text{C}_5(\text{CH}_3)_5]$	11.70 s		
		$[\text{P}(\text{CH}_3)_3]_2$	18.20 t	$J_{\text{PC}} = 15^f$	
		$\text{Ta}(\text{CO})$	267.83 t	$^2J_{\text{PC}} = 6$	
$\text{Cp}^*\text{Ta}(\text{PMe}_3)(\text{CO})_2\text{HCl}$ 17	$\nu(\text{CO})$ 1975, 1890 $\nu(\text{Ta-H})$ 1645	$[\text{C}_5(\text{CH}_3)_5]$	^1H NMR 1.75 s		
		$[\text{P}(\text{CH}_3)_3]$	1.05 d	$^2J_{\text{PH}} = 8$	
		TaH	5.78 d	$^2J_{\text{PH}} = 36$	
		$[\text{C}_5(\text{CH}_3)_5]$	$^{13}\text{C}\{^1\text{H}\}$ NMR 103.57 s		
		$[\text{P}(\text{CH}_3)_3]$	10.91 s		
$\text{Cp}^*\text{Ta}(\text{dmpe})(\text{C}_2\text{H}_5)_2$ 18	$\nu(\text{Ta-H})$ 1695, 1590	$[\text{C}_5(\text{CH}_3)_5]$	^1H NMR 2.01 s		
		$(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2$	1.5 - 0.5 m		
		TaH_2	-0.4 broad		
		$[\text{C}_5(\text{CH}_3)_5]$	two doublets separated by 9.34 ppm	$^2J_{\text{PP}} = 21$	
		$[\text{C}_5(\text{CH}_3)_5]$	$^{13}\text{C}\{^1\text{H}\}$ NMR 102.6 s 13.4 s		

Table I (continued)

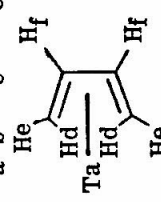
Compound	IR	Assignment	Chemical Shifts	Coupling
Cp*TaCH ₂ CH ₂ CH ₂ CH ₂ (C ₄ H ₉) 19		(CH ₃)(CH ₃)PCH ₂ CH ₂ P(CH ₃)(CH ₃) and CH ₂ CH ₂	J _{PC} = 23 & 27 J _{PC} = 13 & 20 J _{PC} = 7 & 50 J _{PC} = 13 J _{PC} = 4 & 11 J _{PC} = 4 J _{PC} = 21 J _{PC} = 3	
		each carbon gives rise to one set of resonances	33.4 dd 31.0 dd 27.7 dd 21.2 d 16.0 dd 14.5 d 12.4 d 9.0 d	
		[C ₅ (CH ₃) ₅] TaCH ₂ H _a C(H _c) ₂ C(H _e) ₂ CH ₂ H _b TaCH ₂ H _b C(H _c) ₂ C(H _e) ₂ CH ₂ H _a TaCH ₂ H _b C(H _c) ₂ C(H _e) ₂ CH ₂ H _b	¹ H NMR \bar{E} 1.77 s 2.15 m 3.10 m 0.33 m 0.24 m -1.64 m 7.00 m	J _{H_aH_b} = 6 J _{H_aH_c} = 5 J _{H_bH_c} = 7 J _{H_dH_e} = 6 J _{H_dH_f} = 10 J _{H_eH_f} = 5
				
		[C ₅ (CH ₃) ₅] [C ₅ (CH ₃) ₅] TaCH ₂ CH ₂ CH ₂ CH ₂ TaCH ₂ CH ₂ CH ₂ CH ₂ Ta(CH ₂ = CHCH = CH ₂) Ta(CH ₂ = CHCH = CH ₂)	¹³ C NMR 119.49 s 11.49 q 54.96 t 36.75 t 55.17 t 117.06 d	¹ J _{CH} = 127 ¹ J _{CH} = 118 ¹ J _{CH} = 124 ¹ J _{CH} = 147 ¹ J _{CH} = 160

Table I. (continued)

^aNMR spectra taken in benzene-d₆ solvent at ambient temperature.

Chemical shifts in δ measured from internal TMS; coupling constants reported in hertz. All phosphine complexes show one singlet in the ¹³P{¹H} NMR except 18 as noted.

^bIR spectra obtained as Nujol mulls except where indicated. Values given in cm⁻¹. The complete spectra are detailed in the experimental section.

^cNon-first-order NMR pattern intermediate between a doublet and triplet; coupling constants are those that best describe the pattern. See ref. 43.

^dIR spectrum taken in benzene-d₆ solvent.

^eSee ref. 9.

^fSee ref. 44.

^gSpectrum interpretable only at 500 MHz, see Fig. 2. Tentative assignments made by selective decoupling experiments and by analogy to refs. 45 and 46; coupling constant ± 3 Hz.

^hSee ref. 48.

EXPERIMENTAL

General Considerations. All manipulations were carried out using either high vacuum line or glove box techniques. Solvents were purified by vacuum transfer first from LiAlH_4 , then from titanocene prepared as described earlier.³⁷ Hydrogen and deuterium (Matheson) were purified by passage over MnO on vermiculite³⁸ and activated 4Å molecular sieves. Reactions at high pressure of hydrogen were performed in a Parr stirred "mini" reactor #4561 using UHP hydrogen (Matheson) of minimum purity 99.999%. Carbon monoxide (Matheson) was used directly from the cylinder. Ethylene (Matheson) was condensed at -196° and evaporated at -78° . Photolyses were performed using a low pressure mercury lamp. Elemental analyses and molecular weights were determined by Alfred Bernhardt Analytical Laboratory.

Trimethylphosphine (Strem) was stored under vacuum and vacuum transferred prior to use. Trimethyl phosphite was fractionally distilled and stored over 4Å molecular sieves, acetone was stored over 4Å molecular sieves, and methanol over freshly made sodium methoxide; all were vacuum transferred prior to use. Bipy (MCB) was sublimed prior to use.

^1H NMR spectra were recorded using Varian EM390, JEOL FX90Q, or Bruker WM500 spectrometers. ^{13}C and ^{31}P NMR spectra were obtained using a JEOL FX90Q spectrometer. Infrared spectra were measured on a Beckman 4240 spectrometer as nujol mulls and are reported in cm^{-1} .

Many reactions were carried out in sealed NMR tubes and monitored by NMR spectroscopy. Most of the information on rates of reactions has been obtained in this manner. A typical example is the reaction of $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_4$ (4) with CO: 30 mg (0.07 mmoles) of 4 was transferred to an NMR tube sealed to a ground glass joint and fitted with a Teflon needle valve adapter. Benzene- d_6 was vacuum transferred into the tube at -78° , 1 atm of CO introduced, the Teflon needle valve closed, the lower portion of the tube cooled to -196° and the tube sealed with a torch.

Procedures. $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_4$ (4). A high pressure reactor charged with 1.8 g Cp^*TaMe_4 (3), 60 ml petroleum ether, and 1.8 ml PMe_3 , was pressured to 1700 psi of hydrogen and stirred for five days. White $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_4$ (1.75 g, 77%) was crystallized from this solution, washed with petroleum ether, and dried in vacuo. Dec. 75° under vacuum. IR: 1725-1640, 1300, 1280, 1125, 1030, 955, 935, 905, 855, 720, 660. $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{D}_4$ was prepared by exchange of 4 with D_2 in C_6D_6 at room temperature for two days. Anal. Calcd for $\text{C}_{16}\text{H}_{37}\text{P}_2\text{Ta}$: C, 40.68; H, 7.90; Ta, 38.31. Found: C, 40.51; H, 7.74; Ta, 38.14.

$\text{Cp}^*\text{Ta}[\text{PMe}_2(\text{C}_6\text{H}_5)]_2\text{H}_4$ (5). A high pressure reactor, charged with 1.39 g 3, ⁷ 1.3 ml $\text{PMe}_2(\text{C}_6\text{H}_5)$ (Strem), and 100 ml petroleum ether, was pressured to 1560 psi of hydrogen and stirred for two days. White $\text{Cp}^*\text{Ta}[\text{PMe}_2(\text{C}_6\text{H}_5)]_2\text{H}_4$ (1.83 g, 88%) was crystallized from this solution, washed with petroleum ether and dried in vacuo. IR: 1730, 1700, 1655, 1270, 1290, 1110, 1025, 940, 915, 895, 740, 720, 700, 690, 490, 390.

Cp*Ta[P(OMe)₃]₂H₄ (6). A high pressure reactor, charged with 2.2 g of Cp*TaMe₄⁷ (3), 80 ml petroleum ether, and 1.5 ml of P(OMe)₃, was pressured to 1600 psi of hydrogen and stirred for one and a half days. White Cp*Ta[P(OMe)₃]₂H₄ (1.9 g, 57%) was crystallized from this solution, washed with petroleum ether and dried in vacuo. IR: 1755, 1715, 1690, 1180, 1070, 1030, 755, 740, 710, 510, 480. Anal. Calcd for C₁₆H₃₇O₆P₂Ta: C, 33.81; H, 6.56; Ta, 31.84. Found: C, 33.76; H, 6.47; Ta, 32.08.

Cp*Ta(dmpe)H₄ (7). A high pressure reactor, charged with 3.56 g of Cp*TaMe₄⁷ (3), 125 ml petroleum ether, and 1.8 ml dmpe,³⁹ was pressured to 1300 psi of hydrogen and stirred for a day. The solvent was removed and the product (3.35 g, 75%) recrystallized from petroleum ether. 7 sublimes with decomposition at 110°C. IR: 1715, 1625, 1295, 1280, 1035, 935, 895, 845, 805, 740, 725, 655.

Cp*Ta(dmpe)D₄ was prepared by photolysis of a C₆D₆ solution of 7 under D₂ for 36 hours. Anal. Calcd for C₁₆H₃₅P₂Ta: C, 40.86; H, 7.50; Ta, 38.47. Found: C, 40.71; H, 7.39; Ta, 38.21.

Cp*Ta(PMe₃)₂H₃Cl (8). A high pressure reactor, charged with 6.03 g of Cp*TaMe₃Cl^{20b} (2), 100 ml of petroleum ether, and 4 ml of PMe₃, was pressured to 1650 psi of hydrogen and stirred for five days. Blue-green 7 (5.73 g, 74%) was crystallized from this solution. 8 can be recrystallized from petroleum ether to give a white solid identical by NMR. IR: 1765, 1700, 1300, 1200, 950, 720, 340.

Cp*Ta(PMe₃)₂D₃Cl was prepared from a solution of 8 in C₆D₆ under D₂ for two days at 25°C. Anal. Calcd for C₁₆H₃₆ClP₂Ta: C, 37.92; H, 7.16; Ta, 35.70. Found: C, 37.88; H, 6.96; Ta, 35.82.

Cp*TaMe₂(bipy) (9). A solution of 1.15 g 3⁷ and 0.63 g bipy in 60 ml petroleum ether was stirred under an atmosphere of hydrogen for four days. Black solid (0.55 g, 36%) was crystallized from this solution, washed with cold petroleum ether and dried in vacuo. A separate reaction using D₂ was examined with a Toepler pump.⁴¹ 0.92 equivalents of D₂ were taken up and 1.75 equivalents of methane were produced, roughly 80% CH₃D and 20% CH₄ (by ¹H NMR). IR: 1575, 1560, 1300, 760, 725. UV/Vis spectrum (petroleum ether) 452, 545 nm, ε ~ 10⁴ M⁻¹ cm⁻¹. Cyclic voltametry in THF shows a reversible one-electron reduction at -2.2 V (vs. SCE, referenced to internal ferrocene). No oxidation wave was observed to +1.4 V. Anal. Calcd for C₂₂H₂₉N₂Ta: C, 52.29; H, 5.82; Ta, 36.01. Found: C, 52.33; H, 5.61; Ta, 36.25. Molecular weight (C₆H₆) calcd 502, found 491.

Cp*Ta(η²-OCMe₂)(CO) bipy (10). A solution of 0.16 g 9 in 10 ml benzene was stirred under an atmosphere of carbon monoxide for 20 min, the benzene and residual CO removed and the bright blue solid (0.06 g, 35%) washed with cold petroleum ether and dried in vacuo. A separate experiment using a Toepler pump indicated that 1.77 equivalents of CO were absorbed in this reaction. Treatment of 10 with anhydrous HCl produces no methane (by NMR). IR: 1775, 1580 (w, bipy), 1520 (w, bipy), 1160, 1080, 1030, 985, 720. Anal. Calcd for C₂₄H₂₉N₂O₂Ta: C, 51.62; H, 5.23; Ta, 32.40. Found: C, 51.48; H, 5.17; Ta, 32.33.

Cp*Ta(OCHMe₂)₄ 4 (0.49 g) was dissolved in 10 ml of toluene with 0.6 ml of acetone and stirred for two days at 25 °C. The solution was filtered, reduced to 5 ml and cooled to -78 ° yielding white crystalline solid, 0.15 g, 25%. The product is air sensitive and can be sublimed at room temperature at 10⁻⁴ mm Hg. IR: 1170, 1120, 980 (OCHMe₂), 1015 (Cp*), 575 (Ta-O).⁴⁰ Anal. Calcd for C₂₂H₄₃O₄Ta: C, 47.82; H, 7.94; Ta, 32.75. Found: C, 47.58; H, 7.60; Ta, 32.87.

Cp*Ta(OCHMe₂)₃Cl. Acetone (80 mm Hg in 108 ml, 8 equivalents) was condensed into a solution of 8 (30 mg) in 0.3 ml of C₆D₆; after an hour at 25 °C, solvent was removed to leave white Cp*Ta(OCHMe₂)₃Cl, 20 mg, 60%. IR: 1165, 1120, 995 (OCHMe₂), 1015 (Cp*), 575 (Ta-O).⁴⁰

Cp*Ta(OCH₃)₄ (11). Methanol (330 torr in 56.7 ml, 1.01 mmol) was condensed into a solution of 4 (0.1 g, 0.212 mmoles) in 10 ml petroleum ether. After stirring at 25 °C for 8 hr the solvent and residual gas were removed to leave a white solid (0.06 g, 65%). H₂ (0.840 mmole, 3.97 equivalents) was produced in the reaction, as measured by Toepler pump. IR: 1155, 1115, 655, 535, 480.

Cp*Ta(PMe₃)₂H₂(CO) (12). A thick walled glass reaction vessel with Teflon needle valve, charged with 0.51 g 4, 0.5 ml PMe₃, 10 ml toluene and 5 mmol carbon monoxide (2 atm.), was stirred at 25 °C for 24 days. The solvent and residual gas were removed and the light-brown solid (0.30 g, 56%) washed with cold petroleum ether and dried in vacuo. Toepler pump analysis of the residual gas⁴¹ showed 1.04 equivalents of dihydrogen produced. IR: 1840, 1750, 1690, 1300, 1280, 1030, 945, 845, 720, 710, 665. Anal. Calcd for C₁₇H₃₅OP₂Ta: C, 40.97; H, 7.08; Ta, 36.31. Found: C, 40.92; H, 6.98; Ta, 36.19.

cis-Cp*Ta(PMe₃)₂(CO)₂ (13c). A thick-walled glass reaction vessel with Teflon needle valve, charged with 1.0 g of 4, 0.6 mL PMe₃, 20 mL petroleum ether, and 6.25 atm. carbon monoxide (2.4 equivalents), was stirred for a day at 25 °C. After filtration, washing with petroleum ether and drying in vacuo, 0.09 g (8%) of red-brown 13c was obtained.¹³ 13c isomerizes to 13t in a day at 80 °C in benzene solution; no PMe₃ is produced in the reaction (by NMR) and no CO is liberated. IR: 1820, 1730 (ν CO), 1375, 1300, 1280, 1025, 950, 935, 710, 640.

trans-Cp*Ta(PMe₃)₂(CO)₂ (13t). A thick-walled glass reaction vessel with Teflon needle valve, charged with 0.49 g of 4, 0.4 ml PMe₃, 5 ml toluene, and 2.7 mmole carbon monoxide (loaded by Toepler pump), was stirred for two and one half days at 70°. The solvent and residual gas were removed and the red solid (0.15 g, 28%) recrystallized from petroleum ether. Toepler pump analysis of the gas present⁴¹ after reaction showed 1.92 equivalents of H₂ given off and 1.92 equivalents of CO taken up. IR: 1842, 1750, 1300, 1280, 1125, 1030, 940, 715, 660. Anal. Calcd for C₁₈H₃₃O₂P₂Ta: C, 41.23; H, 6.34; Ta, 34.51. Found: C, 41.41; H, 6.30; Ta, 34.38.

Cp*Ta(dmpe)H₂(CO) (14). 14 has only been prepared in a mixture with 7 and 15. In a typical reaction 40 mg of 7, 0.3 ml C₆D₆ and an atmosphere of CO were placed in an NMR tube which was then sealed with a torch. The solution was photolysed for 24 hrs. to give 50% 7, 40% 14 and 10% 15. IR of this solution showed a band at 1850 cm⁻¹ assignable to 14.

Cp*Ta(dmpe)(CO)₂ (15). A thick-walled glass reaction vessel with Teflon needle valve, charged with 0.90 g 7, 15 ml toluene, and 10 mmole CO (4 atm.), was stirred at 130° for a week. Bright red 15 (0.68 g, 68%) was crystallized from this solution, washed with cold petroleum ether and dried in vacuo. A separate experiment using a Toepler pump⁴¹ showed that 1.88 equivalents of CO were taken up and 1.88 equivalents of H₂ were given off. IR: 1830, 1750, 1300, 1280, 1090, 1030, 940, 920, 900, 635. Anal. Calcd for C₁₈H₃₁O₂P₂Ta: C, 41.39; H, 5.98; Ta, 34.64. Found: C, 41.17; H, 5.91; Ta, 34.78.

Cp*Ta(PMe₃)₂(CO)HCl (16). A solution of 8 (0.79 g), 2 ml PMe₃ and 20 ml petroleum ether was stirred under 150 torr of CO for 26 hrs. The CO was removed and pink-purple solid (0.24 g, 29%) was crystallized from the solution, washed, and dried in vacuo. IR: 1820, 1420, 1300, 1280, 1030, 950, 725, 665, 340. Anal. Calcd for C₁₇H₃₄ClOP₂Ta: C, 38.32; H, 6.43; Ta, 33.96. Found: C, 38.47; H, 6.28; Ta, 34.20.

Cp*Ta(PMe₃)(CO)₂HCl (17). A solution of 8 (0.50 g) in 60 ml petroleum ether was stirred under one atmosphere of carbon monoxide at -80° for one hour, then warmed to room temperature. The residual CO was removed, the solution filtered, reduced in volume and cooled to give a pink-purple solid, (0.115 g, 24%) which was washed and dried in vacuo. IR: 1975, 1890, 1645, 1030, 960, 750, 395. Anal. Calcd for C₁₅H₂₅ClO₂PTa: C, 27.17; H, 5.20; Ta, 37.33. Found: C, 26.97; H, 5.22; Ta, 37.50.

Cp*Ta(dmpe)H₂(C₂H₄) (18). A thick-walled quartz reaction vessel with Teflon needle valve, charged with 0.90g of 7, 15 ml of benzene, and 5 mmole ethylene (2 atm.), was photolysed while stirring for

three days. Light-yellow solid (0.50 g, 53%) was crystallized from benzene, washed with cold petroleum ether and dried in vacuo.

IR: 1695, 1590, 1290, 1280, 1090, 1030, 940, 925, 892, 840, 790, 740, 720, 695, 650. Anal. Calcd for $C_{18}H_{37}P_2Ta$: C, 43.55; H, 7.51; Ta, 36.45. Found: C, 43.34; H, 7.32; Ta, 36.74.

$Cp^*Ta\overline{CH_2CH_2CH_2CH_2}(C_4H_9)$ (19).⁴² A thick-walled glass reaction vessel with Teflon needle valve, charged with 0.83g 4, 30 ml petroleum ether, and 25 mmole ethylene, was stirred for six hrs. 17 (0.12 g, 16%) was crystallized from the solution and dried in vacuo. IR: 1040, 1030, 950, 845, 720.

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(48) ^{13}C NMR chemical shifts for 10 were obtained from a proton decoupled spectrum; only nine of the ten bipy carbons were observed. The multiplicities were obtained from an off-resonance decoupled spectrum; due to the complexity of the spectrum multiplicities could not be assigned to all peaks.

CHAPTER II

High Field NMR Studies of Tantalum and Niobium
Polyhydride Complexes.¹⁻⁴

INTRODUCTION

The structural characterization of molecules with high coordination numbers is of considerable interest, and transition metal complexes with a number of hydride ligands are among the most common and sterically least crowded examples of eight- and nine-coordinate complexes.⁵⁻⁷ The determination of these structures is complicated by the difficulties in locating hydrogen atoms by X-ray diffraction, principally owing to the low scattering efficiency of the hydrogen atom.^{7,8} The hydrogen atom positions of many structures have often been inferred from the orientation of the remaining ligands, but this is unreliable for polyhydride complexes lacking high crystallographic site symmetry.⁸ Neutron diffraction studies would, of course, be more useful, since the hydrogen atoms are precisely located, but at present experimental difficulties prevent routine use.⁷ NMR spectra have been used to establish stoichiometry, and occasionally coordination geometries,⁹ however, fluxional processes are common in these molecules, and static structures are rarely observed.⁹ In addition, the spectra often show complex overlapping patterns, particularly when ³¹P-¹H coupling is present. A very high field NMR spectrometer offers obvious advantages in these regards. Thus, we have utilized the 500 MHz NMR spectrometer at the NSF Southern California Regional NMR facility to obtain the NMR spectra of a series of niobium and tantalum hydride complexes Cp*ML₂H₃X (Cp* = η⁵-C₅Me₅; X = H, L = PMe₃, P(OMe)₃, L₂ = dmpe, M = Nb, Ta, and X = Cl, L = PMe₃, M = Ta).¹⁰ Starting from the heavy atom structure of Cp*Ta(PMe₃)₂H₄ (1) determined from single crystal X-ray diffraction data, we have

used NMR data to elucidate the structures of these compounds.

1. Description of Structure

Figure 1 depicts one of the two crystallographically independent molecules found in the structure of $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_4$ (1), along with the atom labeling scheme. There are no short intra- or intermolecular contacts. The hydride ligands were not located; their positions are discussed with the NMR spectra, below. The two independent molecules have very similar geometries (see fig 2), with statistically equivalent bond lengths and angles. The only exception is the pair of phosphorus-tantalum-phosphorus angles which are statistically although not substantially different, 116.0 and 112.3(1)°. In discussing the structure of 1, average values for all bond lengths and angles have been used.

The pentamethylcyclopentadienyl ring is coordinated in the conventional pentahapto manner with Ta-C bond lengths from 2.39 to 2.46 Å (Table I); the average (2.42 Å) is within the range found for other TaCp^* complexes.¹¹ The tantalum-phosphorus bond lengths are the same (average 2.532(3) Å) and within the range of Ta-PMe₃ distances previously observed (2.51 - 2.60 Å).¹² The two ring centroid-tantalum-phosphorus angles are essentially the same (119°), showing that the two phosphorus atoms are in very similar locations. There is a distinct asymmetry in the coordination geometry, however, since the point midway between the phosphorus nuclei is not directly opposite the Cp* ring: the ring centroid-tantalum-PP midpoint angle is 153°. Thus, the hydride ligands significantly influence the stereochemistry of the remaining ligands and appear to be somewhat asymmetrically disposed.

Figure 1. ORTEP drawing of $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_4$ (1), molecule 1).
The hydrogen atoms have been omitted for clarity; the hydride
ligands were not located.

Figure 2. Stereoscopic drawing of the unit cell of $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_4$ (1).

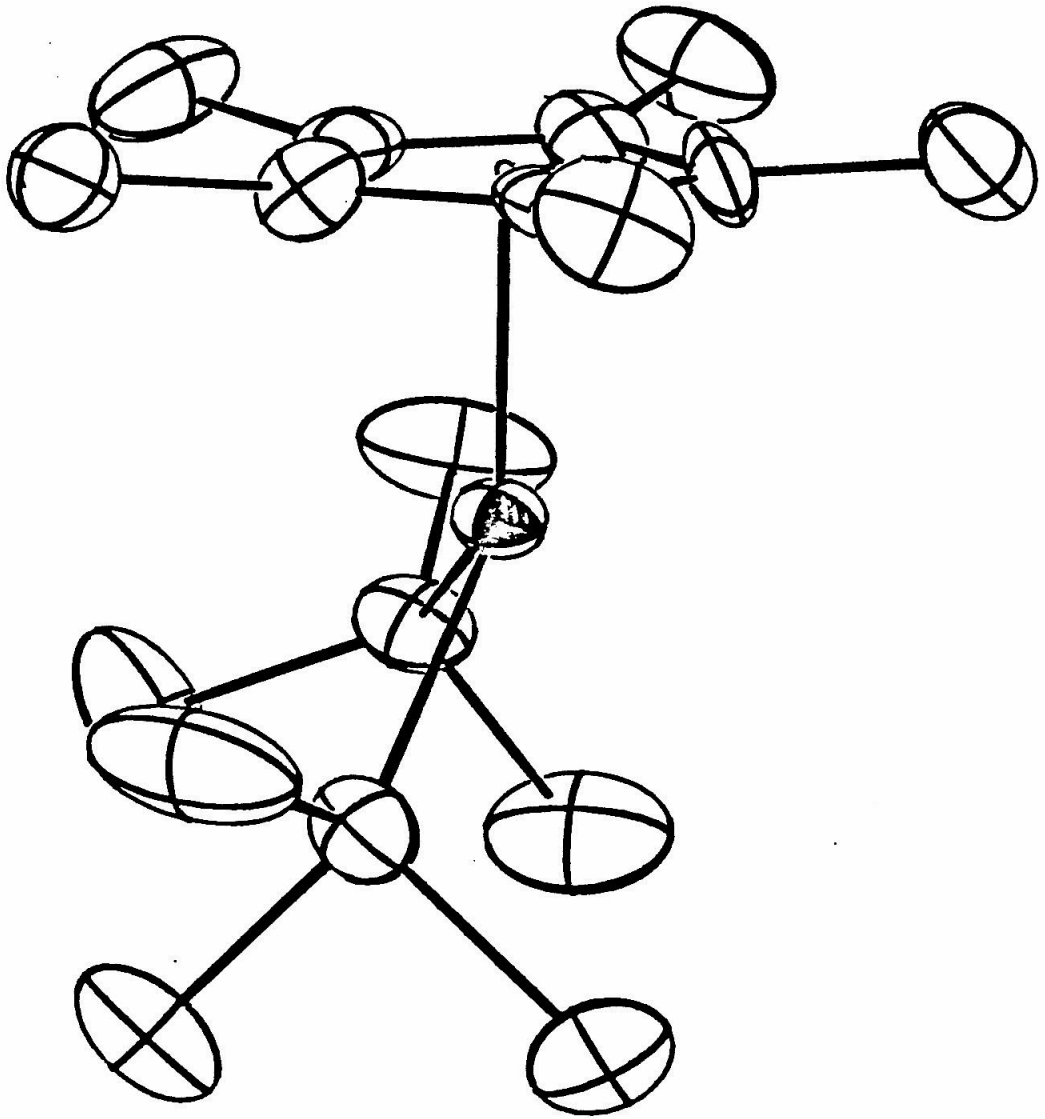


Fig. 1

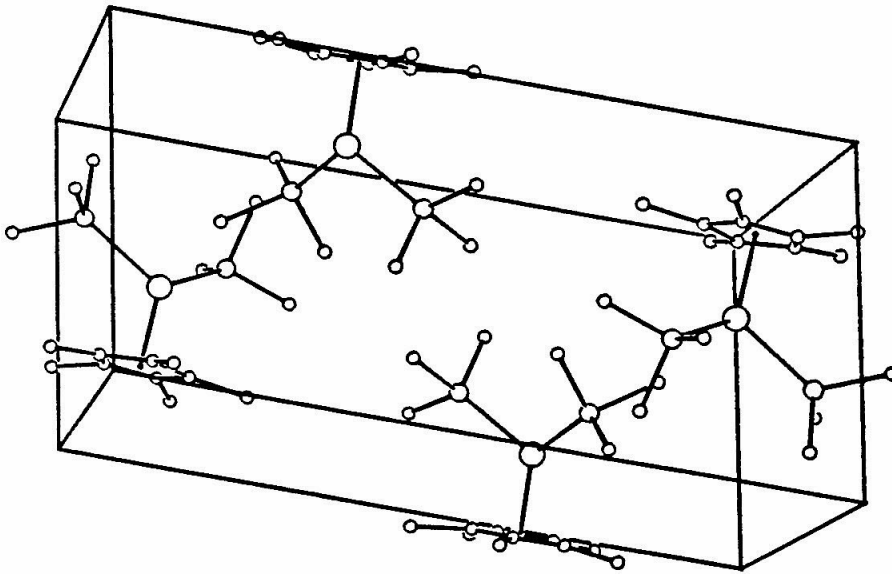
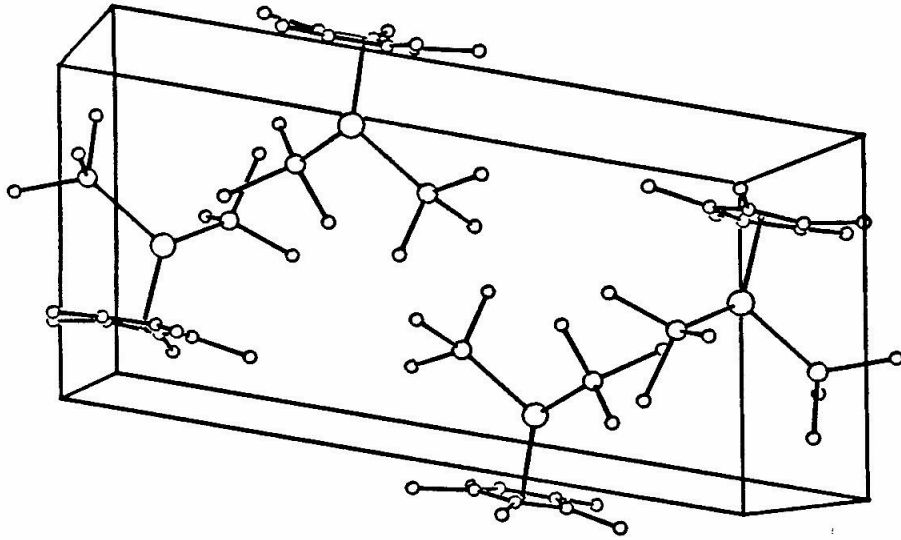


Fig. 2

Table I. Important Distances and Angles in the Structure of $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_4$.^a

	Molecule 1	Molecule 2	Average ^b
Ta-P	2.534(5) 2.529(5)	2.528(5) 2.535(5)	2.532(3)
P-Ta-P	116.01(14)	112.27(14)	114(3) [•]
Ta-C	2.387-2.455(17)	2.389-2.452(17)	2.42(3)
R-Ta-P ^c	117.5 117.2	119.3 121.0	119 [•]
P-C	1.78-1.85(2)	1.80-1.86(2)	1.82(2)
C-P-C	96.6-101.2(10)	96.1-100.6(10)	99.3(19) [•]
C-C (ring)	1.39-1.43(2)	1.39-1.45(2)	1.42(2)

^aDistances given in Å, and angles in degrees. Estimated standard deviations are indicated in parentheses. A more complete tabulation is given in ref. 1. ^bThe standard deviation of the average is estimated as $\{\sum^n(d_i - \bar{d})^2 / (n-1)\}^{\frac{1}{2}}$. ^cR = Cp* ring centroid.

2. NMR Studies: General Considerations

The determination of structures of inorganic complexes by NMR spectroscopy is in general not a straightforward procedure. Only for very well defined coordination geometries, like octahedral and square planar arrangements, can the stereochemistry be assigned simply from the number and multiplicity of the resonances.⁹ The NMR data have been interpreted without assuming any particular coordination geometry. In most cases the spectra provide sufficient information to determine the point group of the molecule and the disposition of the ligands with respect to the symmetry element(s). The NMR spectral analysis requires only the assumption that there are no accidental degeneracies in the spectra. Since the spectra are obtained at high field, degeneracies are particularly unlikely, especially for the resonances that are complex multiplets where fortuitous equivalence of both chemical shifts and coupling constants would be required.¹³

The compounds examined in this study are eight- or nine-coordinate, considering a cyclopentadienyl ring as formally occupying three sites. In view of the small energy differences between the various geometries for these coordination numbers and the low barriers for their interconversion,¹⁴ it is not surprising that the compounds are found to be highly fluxional at ambient temperatures. In addition, complexes with hydride ligands tend to have smaller barriers for rearrangement processes than those without.^{6,9,15} The use of low temperature, high field NMR spectroscopy provides favorable conditions for the observation of static structures.¹⁶ Relatively sharp spectra are observed and are taken as indicative of ground state

structures. Thus we assume that the degeneracies observed in the low temperature NMR spectra are indicative of a symmetry element of the molecule that requires the rigorous equivalence of the nuclei involved, not of a fluxional process with an extremely low energy barrier.

3. Compounds of the Type $\text{Cp}^*\text{ML}_2\text{H}_3\text{X}$

The ^1H NMR spectrum for each member of the series $\text{Cp}^*\text{ML}_2\text{H}_4$ ($\text{M} = \text{Ta}$, $\text{L} = \text{PMe}_3$, $\text{P}(\text{OMe})_3$, $\text{L}_2 = \text{dmpe}$, $\text{M} = \text{Nb}$, $\text{L} = \text{PMe}_3$, ($\text{L}_2 = \text{dmpe}$) exhibits a single binomial triplet for the four hydride ligands at ambient temperatures.¹⁰ As the temperature is lowered, the hydride signals broaden and give rise to more complex patterns. The spectra may be interpreted applying the assumptions above, without reference to the crystal structure of 1. In each case the geometry of the Cp^*ML_2 fragment is first determined and then the positions of the hydride ligands are considered. From a symmetry standpoint, there are only four possible arrangements for a Cp^*ML_2 group (fig 3): one with C_{2v} symmetry (A), two structures with C_s symmetry (B and C), and one with C_1 symmetry (D).¹⁷

The trimethylphosphite groups in $\text{Cp}^*\text{Ta}[\text{P}(\text{OMe})_3]_2\text{H}_4$ (2) are equivalent in the low temperature limit by both phosphorus and proton NMR spectroscopy, so that only structures A and B need to be considered as "frames" on which to place the hydride ligands. The hydride region of the low temperature proton NMR spectrum of 2 (fig 4) exhibits three multiplets in which the large splittings are due to phosphorus-hydrogen coupling and the small splittings are due to coupling between the hydride ligands; integration

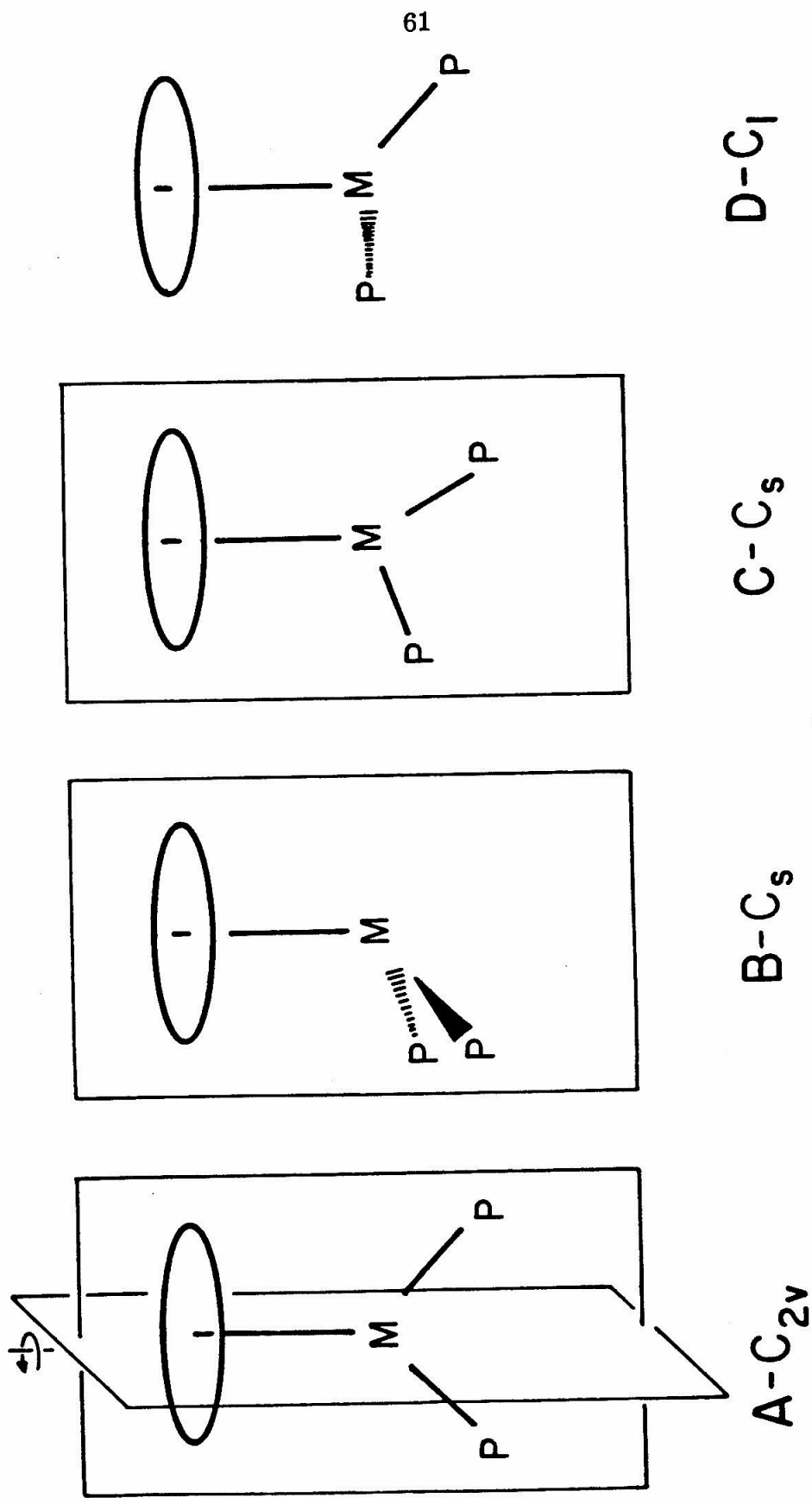


Figure 3. Possible geometries for a Cp*ML₂ fragment. The Cp* ligand is represented as an ellipse.

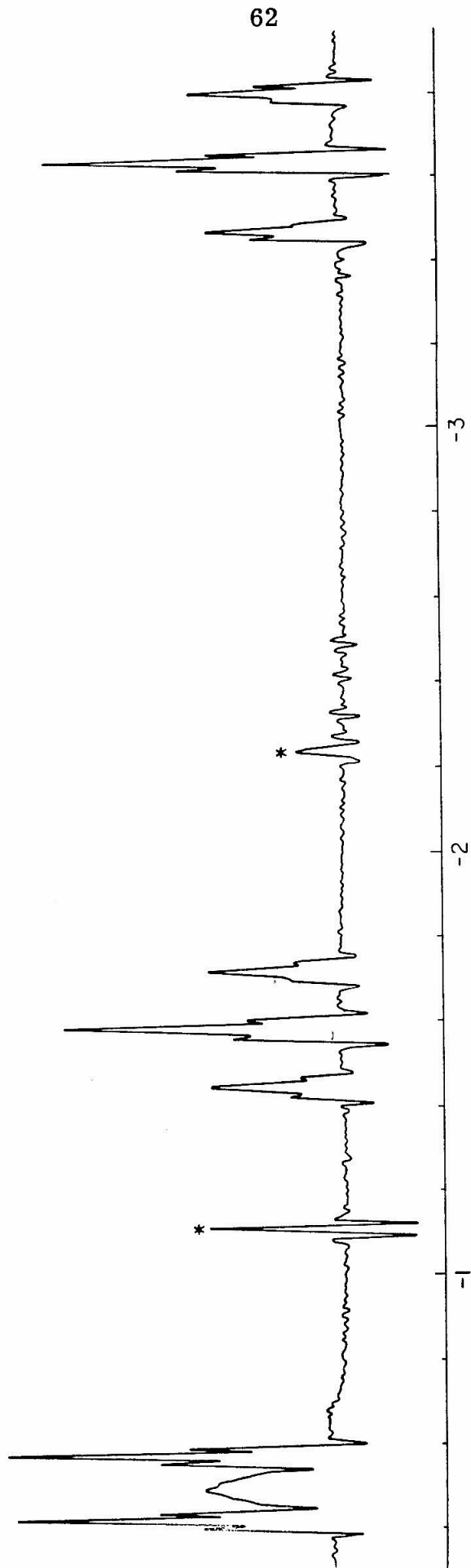


Figure 4. The hydride region of the 500 MHz ^1H NMR spectrum of $\text{Cp}^*\text{Ta}[\text{P}(\text{OMe})_3]_2\text{H}_4$ at -70°C . Asterisks denote impurity resonances. The spectrum is resolution enhanced.

yields a 2:1:1 ratio. A C_{2v} geometry (\underline{A}) for the complex is inconsistent with the integration because with this symmetry a ligand must lie on the twofold axis in order to be unique, i.e., in order not to have a symmetry generated partner, and in \underline{A} only one coordination site is available (trans to the Cp^*) for a unique hydride ligand. However, the C_s geometry of \underline{B} is consistent, if the two magnetically equivalent hydride ligands (H_a) are related to each other by the mirror plane and the two unique hydrides (H_b and H_c) are in the mirror plane. Furthermore, as a result of this geometry H_b and H_c each form an AX_2 pattern (a binomial triplet), and the two H_a ligands form a more complex $AA'XX'$ pattern, as observed in the spectrum.

Ideally, this structure can be envisioned as a tricapped trigonal prism (fig. 5, I), with the Cp^* ring at one triangular face, and the two phosphite ligands and one hydride ligand generating the opposite face. The remaining hydride ligands would occupy the three capping sites. This idealized geometry is the most common arrangement observed for nine-coordinate complexes,¹⁴ e.g., ReH_9^2 .¹⁸ The actual structure of $\underline{2}$ is expected to be significantly distorted from the idealized geometry, however, considering the variety of ligands involved.¹⁹

The structures of $Cp^*Ta(PMe_3)_2H_4$ ($\underline{1}$) and $Cp^*Nb(PMe_3)_2H_4$ ($\underline{3}$) are similar to the one described above, as indicated by the analysis of the low temperature NMR spectra. For both $\underline{1}$ and $\underline{3}$ the phosphine ligands are magnetically equivalent and the hydride resonances appear in a 2:1:1 ratio, although they are not well resolved. If only the coordination sphere is considered, the NMR analysis is consistent with the crystal structure of $\underline{1}$. Whereas the trimethylphosphine ligands are not

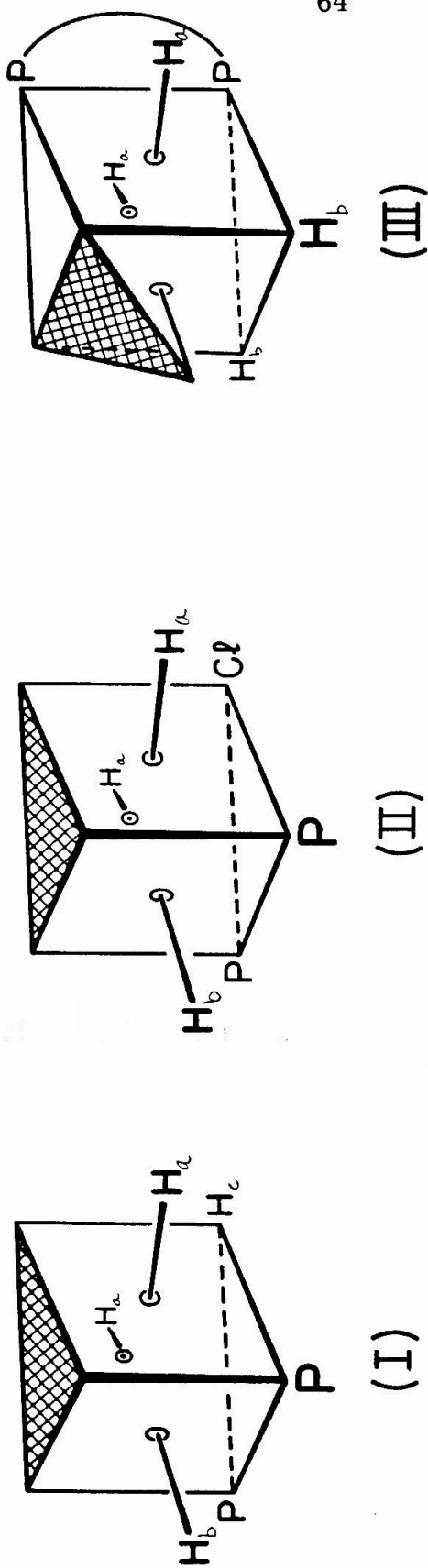


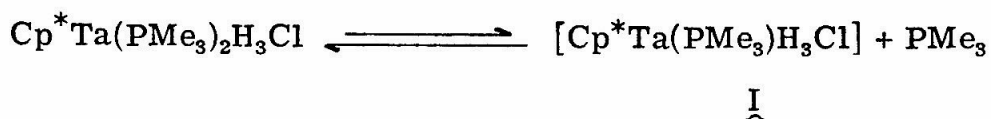
Figure 5.

- (I) Structure proposed for $\text{Cp}^*\text{Ta}[\text{P}(\text{OMe})_3]_2\text{H}_4$ (2), $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_4$ (1), and $\text{Cp}^*\text{Nb}(\text{PMe}_3)_2\text{H}_4$ (3).
 (II) Structure proposed for $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_3\text{Cl}$ (4).
 (III) Structure proposed for $\text{Cp}^*\text{Ta}(\text{dmpe})\text{H}_4$ (5) and $\text{Cp}^*\text{Nb}(\text{dmpe})\text{H}_4$ (6).

The Cp^* ligand is represented as a shaded triangle in these tricapped trigonal prism structures.

crystallographically equivalent in the solid state structure, the Cp* ring, Ta and P atoms do closely approach the idealized geometry B. Once again, the structure can be based on a trigonal prism, although the phosphorus-tantalum-phosphorus angle (114°) is considerably larger than that predicted for the (square-faced) idealized geometry (82°). The tricapped trigonal prism geometry (fig. 5, I), derived from the NMR analysis, places H_b in the cavity created by the Cp* ring and the methyl groups of the PMe₃ ligands (see fig. 1), and places H_c also in the pseudo-mirror plane, on the opposite side of the phosphorus atoms.

Cp*Ta(PMe₃)₂H₃Cl (4) seems to have the same basic geometry (fig. 5, II). The NMR spectra again indicate equivalent phosphine ligands in the low temperature limit and exhibit two multiplets of intensity 1 : 2 for the hydride ligands (fig. 6). The proposed structure is consistent with the resonance for the single hydrogen (H_b) being a first-order triplet of triplets, and the pair of equivalent hydrogen atoms (H_a) being a complex AA'MXX' pattern. In contrast to the highly fluxional tetrahydride compounds 1-3, the hydride ligands in 4 are inequivalent at room temperature on the NMR timescale¹⁰ a very rare occurrence for polyhydride complexes of non-octahedral geometry.⁹ Furthermore, the phosphine ligands in 4 are labile, undergoing a rapid reversible dissociation at ambient temperatures. Hence, the resultant



sixteen electron species I must also be static on the NMR timescale.

A different type of structure is adopted by the two complexes with

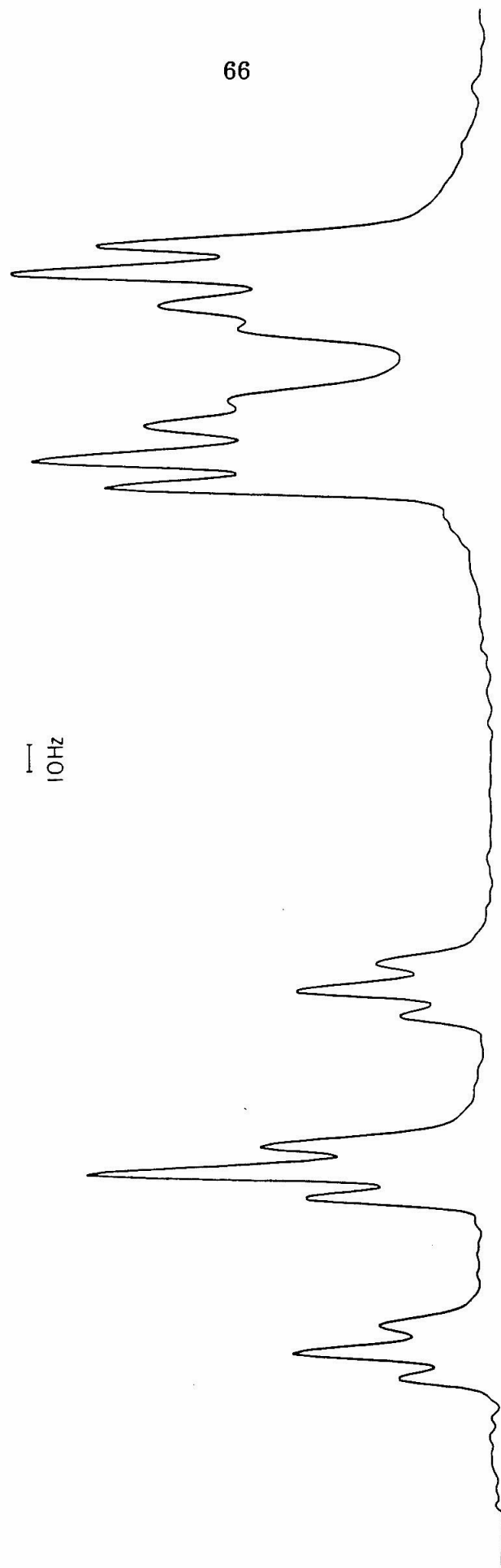
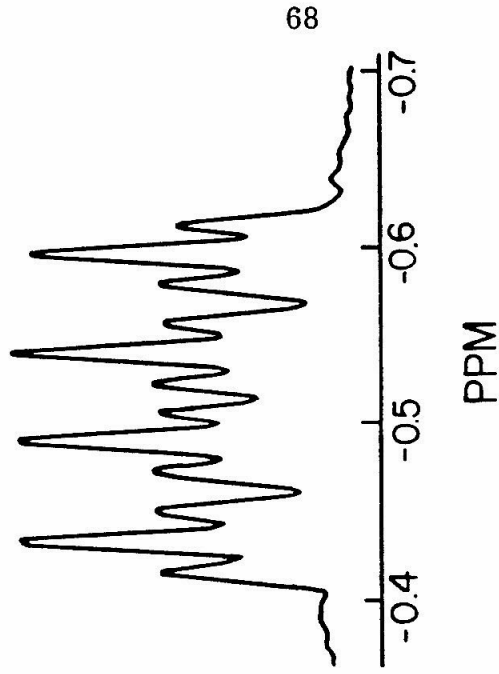
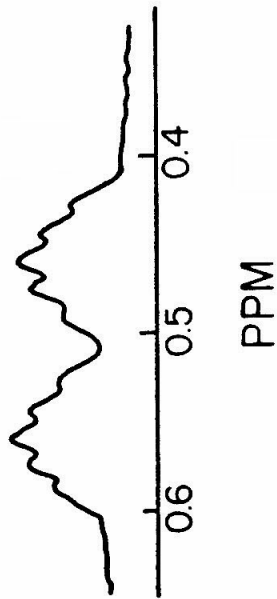


Figure 6. The hydride region of the 500 MHz ^1H NMR spectrum of $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_3\text{Cl}$ (4) at -70°C . The spectrum is resolution enhanced.

the bidentate dmpe ligand, $\text{Cp}^*\text{Ta}(\text{dmpe})\text{H}_4$ (5) and $\text{Cp}^*\text{Nb}(\text{dmpe})\text{H}_4$ (6). The low temperature $^{31}\text{P}\{^1\text{H}\}$ spectra for these compounds exhibit AB patterns, and the hydride ligands appear in the low temperature proton spectra as two multiplets (fig. 7), each integrating as two hydrogen atoms. The inequivalence of the phosphorus atoms rules out skeletal geometries A and B, and the pairwise equivalence of the hydride ligands implies a plane of symmetry. The C_s skeletal geometry C is indicated, with the two phosphorus nuclei in the mirror plane and each pair of hydride ligands related by the mirror plane. This geometry can also be derived from a tricapped-trigonal prism, with the Cp^* group spanning two corners of the prism and one capping site (fig. 5, III).

It should be emphasized that the NMR data are not consistent with a structure for 5 and 6 that resembles the one found for the complexes of monodentate phosphine ligands. The reasons for this structural difference are not obvious. Electronically, the complexes are very similar and the d_0 metal center could be expected to have small intrinsic geometrical preferences. An argument based on overall steric crowding is unlikely, since the cone angle of dmpe is roughly the same as two $\text{P}(\text{OMe})_3$ groups.²⁰ Further, $\text{Cp}^*\text{Ta}[\text{P}(\text{OMe})_3]_2\text{H}_4$ adopts the same basic geometry as $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_3\text{Cl}$, the most sterically crowded molecule in the series. There are structures in which the dmpe ligand does adopt the geometry found here for the complexes of monodentate phosphines, e.g., $\text{Cp}^*\text{Ta}(\text{dmpe})(\text{CO})_2$, which has a 'four-legged-piano-stool' type of geometry (by NMR spectroscopy).¹⁰ The small bite angle of the dmpe ligand (75°),²¹ relative to that preferred in the case of PMe_3 (114°), is undoubtedly an important factor in determining the structure.



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Figure 7. The resonances due to the hydride ligands in the 500 MHz ^1H NMR spectrum of $\text{Cp}^*\text{Ta}(\text{dmpe})\text{H}_4$ (5) at -70°C . The two portions are not plotted on the same vertical scale. The spectrum is resolution enhanced.

CONCLUSIONS

High field proton NMR spectroscopy has permitted the assignment of the coordination geometries for polyhydride complexes in the series $\text{Cp}^*\text{ML}_2\text{H}_3\text{X}$ ($\text{M} = \text{Nb}, \text{Ta}$). The hydride ligands appear in the NMR spectra in a 2:1:1 ($\text{X} = \text{H}$) or 2:1 ($\text{X} = \text{Cl}$) ratio, and the phosphorus atoms are equivalent when L is a monodentate phosphine. These data imply a C_s symmetry for these molecules; the structures are viewed as derived from a tricapped trigonal prism geometry (fig. 5, I and II). The conclusions are consistent with, but not dependent on, an X-ray crystal structure determination for $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_4$, in which only the heavy atoms were located. The hydride complexes with a bidentate dmpe ligand — $\text{Cp}^*\text{M}(\text{dmpe})\text{H}_4$ — adopt a very different structure: a C_s geometry with inequivalent phosphorus atoms (fig. 5, III), presumably due to the constrained P-Ta-P angle.

Table II. NMR Data for Cp*ML₂H₃X Compounds^a

¹ H NMR: Compound	Chemical Shift	Phosphorus-Hydrogen Coupling	Hydrogen-Hydrogen Coupling
Cp*Ta(PMe) ₃ H ₄ (1)	1 H _a	t, J _{PH} = 64	b̄
	1 H _b	t, J _{PH} = 78	
	2 H _c	m	
Cp*Ta[P(OMe) ₃] ₂ H ₄ (2)	1 H _a	t, J _{PH} = 82	J _{H_aH_b} (<3) ^d J _{H_aH_c} = 9 J _{H_bH_c} = 12
	1 H _b	t, J _{PH} = 68	
	2 H _c	J _{PH} ≈ 38 ^c	
Cp*Nb(PMe) ₃ H ₄ (3)	1 H _a	t, J _{PH} = 78	b̄
	1 H _b	t, J _{PH} = 76	
	2 H _c	broad s ^e	
Cp*Ta(PMe) ₂ H ₃ Cl (4)	1 H _a	t, J _{PH} = 68	J _{HH} = 10
	2 H _b	dm, J _{PH} = 72, J _{P'H} ≈ 15 ^c	
Cp*Ta(dmpe)H ₄ (5)	2 H _a	dd, J _{PH} = 53, J _{P'H} = 28	J _{HH} = 9
	2 H _b	dd, J _{PH} = 49, J _{P'H} = 15	
Cp*Nb(dmpe)H ₄ (6)	2 H _a	t, J _{PH} = 47	b̄
	2 H _b	m ^f	

Table II. (continued)

³¹P NMR

Cp*Ta(PMe₃)₂H₄ (1), Cp*Ta[P(OMe)₃]₂H₄ (2), Cp*Nb(PMe₃)₂H₄ (3), and Cp*Ta(PMe₃)₂H₃Cl (4) each show one singlet over the range 25 to -90°C.

Cp*Ta(dmpe)H₄ (5) shows a singlet at 25°, a pair of doublets at -80°: $|\delta_P - \delta_{P'}| = 0.75$ ppm, $J_{PP'} = 18$ Hz. The coalescence temperature is -45°C.

Cp*Nb(dmpe)H₄ (6) shows a singlet at 25°, a pair of doublets at -90°: $|\delta_P - \delta_{P'}| = 0.52$ ppm, $J_{PP'} = 34$ Hz. The coalescence temperature is -80°C.

^aSpectra in toluene-d₆ solvent at -70°C except as noted. Proton NMR spectra were obtained at 500 MHz and were frequently resolution enhanced to observe small coupling constants; only the resonances due to hydride ligands are reported. Assignments are arbitrary except where determined by integration. Chemical shifts are reported in δ , referenced to signals due to residual protons in the solvent; coupling constants are in Hertz. Phosphorus spectra obtained at 36.21 MHz and are proton decoupled. Ambient temperature spectra of the tantalum compounds are given in ref. 10a. ^bHydrogen-hydrogen coupling not resolved due to broad resonances. ^cNon-first-order NMR pattern; coupling constants are those that best describe the pattern (see Fig. 4 or 6). ^dCoupling not observed. Limits given are based on estimates of the resolution in the spectrum. ^e150 Hz full width half height.

^fBroad complex pattern, 70 Hz width.

EXPERIMENTAL

All manipulations were carried out using either high vacuum or glove box techniques, as previously described.^{10a, b} ^1H NMR spectra were recorded on Bruker WM500 or JEOL FX90Q spectrometers; the spectra were frequently resolution enhanced²² to observe small coupling constants. ^{31}P spectra were obtained using a JEOL FX90Q spectrometer.

Procedures. $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_4$ (1), $\text{Cp}^*\text{Ta}[\text{P}(\text{OMe})_3]_2\text{H}_4$ (2), $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_3\text{Cl}$ (4) and $\text{Cp}^*\text{Ta}(\text{dmpe})\text{H}_4$ (5) have been previously reported.^{10a, b} $\text{Cp}^*\text{Nb}(\text{PMe}_3)_2\text{H}_4$ (3) and $\text{Cp}^*\text{Nb}(\text{dmpe})\text{H}_4$ (6) are prepared in a manner analogous to the tantalum compounds; full details will be published.^{10c}

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CHAPTER III

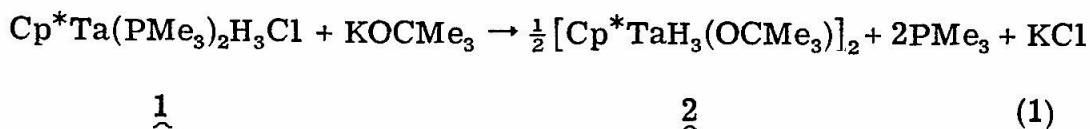
Reactions of $(\eta^5\text{-C}_5\text{Me}_5)\text{Ta}(\text{PMe}_3)_2\text{H}_3\text{Cl}$. Synthesis and
Characterization of $(\eta^5\text{-C}_5\text{Me}_5)(\text{Me}_3\text{O})_2\text{HTa}(\mu\text{H})_2\text{TaH}_3(\eta^5\text{-C}_5\text{Me}_5)^1$

INTRODUCTION

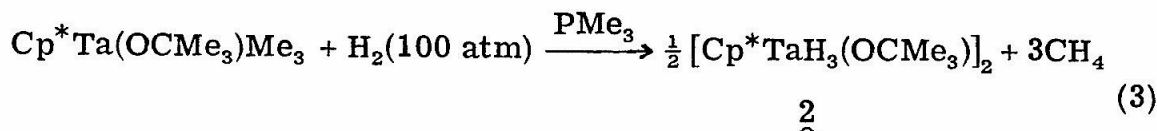
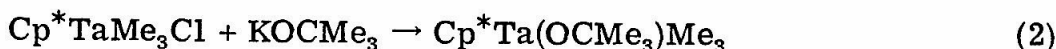
The vast majority of transition metal hydride compounds contain "soft", π acid ligands, either phosphine, carbonyl or hydrocarbon ligands.² Although hydrido-halide species are well known,² hydride complexes containing hydroxide,³ alkoxide,⁴ or amide ligands⁵ are rare and to our knowledge there are no reports of imido- or oxo-hydride compounds.⁶ These species may have chemical properties significantly different from their more common relatives. For example, they may be more resistant to deprotonation and reductive elimination because the hard ligands strongly stabilize high oxidation states. As a possible synthetic route to these compounds, we have examined the reactions of $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_3\text{Cl}$ (1)⁷ with a variety of reagents.

RESULTS AND DISCUSSION

Treatment of $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_3\text{Cl}$ (1) with one equivalent of potassium t-butoxide gives a new tantalum polyhydride complex, 2 (eq 1). 2 can also be prepared by high pressure hydrogenation of



$\text{Cp}^*\text{Ta}(\text{OCMe}_3)\text{Me}_3$, which is obtained from $\text{Cp}^*\text{TaMe}_3\text{Cl}$ and KOCMe_3 (eq 2, 3). Due to its extreme solubility in hydrocarbon solvents, 2 is



difficult to isolate. Although the hydrogenation reaction does not require trimethylphosphine, the product appears to be slightly cleaner if a stoichiometric amount of PMe_3 is added. An elemental analysis supports an empirical formula of $\text{Cp}^*\text{TaH}_3(\text{OCMe}_3)$, and the molecular weight indicates that 2 is dimeric in benzene solution (calcd. 785, found 760). The characterization of this unusual dimer has involved IR and high field NMR spectroscopies.

The 500 MHz proton NMR spectrum of 2 at 25° (fig. 1, Table I) shows three large singlets at 2.32, 2.12, and 1.42 δ , and integration gives a 5:5:6 ratio. The first two singlets are assigned to two inequivalent Cp^* ligands and the third resonance to two equivalent tert-butoxide groups. The inequivalence of the Cp^* rings indicates that the tantalum

Figure 1. 500 MHz ^1H NMR spectrum of $\text{Cp}^*(\text{Me}_3\text{CO})_2\text{HTa}(\mu\text{H})_2\text{TaH}_3\text{Cp}^*$.
The resonance at 7.15 δ is due to residual protons in the benzene- $\underline{\text{d}}_6$
solvent.

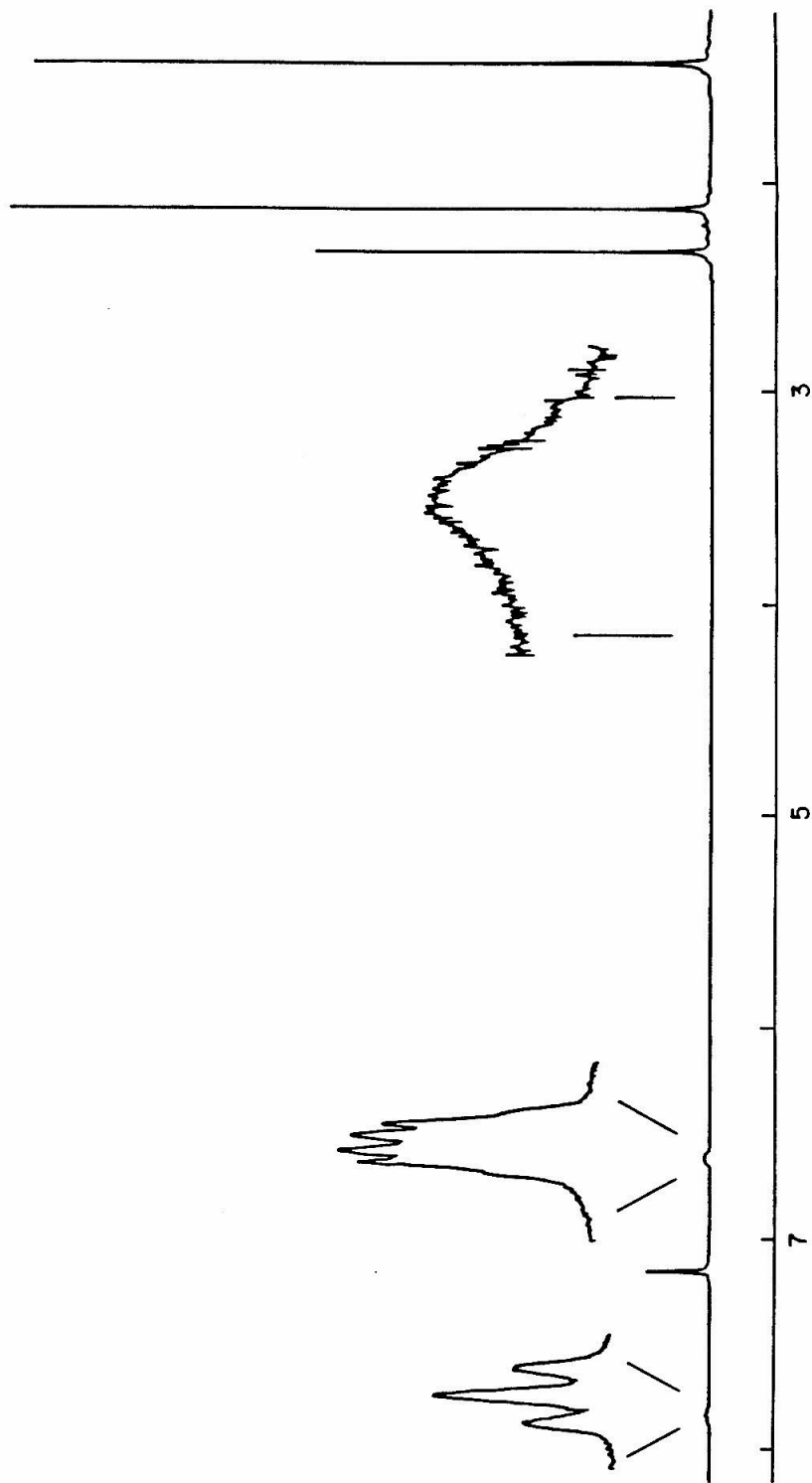


Fig. 1.

atoms are inequivalent, forcing the surprising conclusion that both alkoxide groups must be bound to one of the tantalum atoms. The spectrum also shows resonances assignable to hydride ligands: a triplet at 7.84 δ ($J_{\text{HH}} = 13$ Hz, 1H), a doublet of quartets at 6.62 δ ($J_{\text{HH}} = 13, 6$ Hz, 2H) and a very broad peak at 3.5 δ (250 Hz full width half height, 3H). The resonance at 6.62 δ collapses to a doublet ($J = 13$ Hz) on selective decoupling at 3.5 δ , but the triplet at 7.84 δ is unaffected. Since coupling is usually observed between inequivalent hydride ligands on the same metal center,⁸ the hydride at 7.84 δ and the group of three hydride ligands at 3.5 δ are expected to be bound to different tantalum atoms. The two hydrogen atoms at 6.62 δ appear to bridge the two tantalum atoms, since they couple to each of the other groups of hydride ligands. This arrangement of hydride ligands forces the same conclusion that both tert-butoxide groups are on the same tantalum atom: $\text{Cp}^*(\text{Me}_3\text{CO})_2\text{HTa}(\mu\text{H})_2\text{TaH}_3\text{Cp}^*$ (fig. 2).

The broad resonance at 3.5 δ separates into two sharp resonances as the sample is cooled from 25° to -70°, indicating that the fluxional process involving the three terminal hydride ligands is effectively frozen out. The equivalence of the t-butoxide ligands implies that there is a mirror plane in the molecule,⁹ containing the unique atoms or groups: the tantalum atoms, ring centroids, and unique hydride ligands. The structure has been drawn (fig. 2) with the bulky ligands (Cp* and OCMe₃) far apart, and with groups in the plane next to pairs of ligands, a reasonable configuration based on steric interactions.

The IR spectrum of 2 is completely consistent with this formulation. There are three absorptions due to tantalum-hydrogen

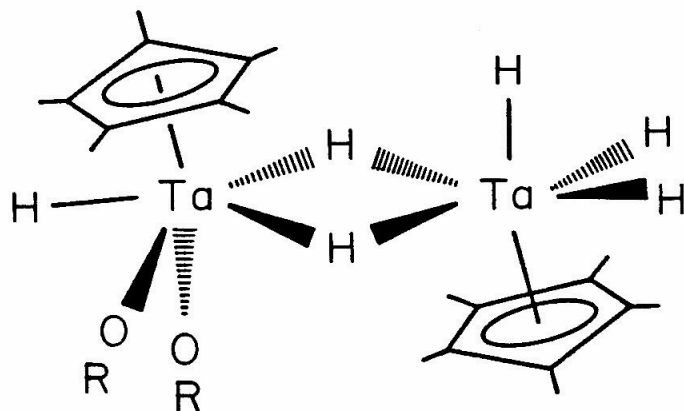


Figure 2. Structure proposed for compound 2.

stretching modes (1735, 1535, and 1280 cm^{-1}), which shift on deuteration (to 1250, 1110, and 860 cm^{-1}). The first two are terminal Ta-H stretches and the low energy band is in the region expected for hydride ligands bridging between early transition metal centers.¹⁰⁻¹⁴ The presence of both t-butoxide ligands on one tantalum atom is also supported by the IR spectrum of 2: while a carbon-oxygen-tantalum stretch in $\text{Cp}^*\text{Ta}(\text{OCMe}_3)\text{Me}_3$ is at 1020 cm^{-1} , 2 has two bands in this region (990 and 965 cm^{-1}).¹⁵ Similar splitting of the COTa stretching modes is also observed in monomeric dialkoxide complexes of tantalum.¹⁴

It is not clear why 2 adopts this geometry rather than the symmetrical alternative. This arrangement is probably the thermodynamically most stable configuration since there should be only a small kinetic barrier to scrambling ligands between metal centers.¹⁶ The fact that 2 is synthesized from equivalent monomers demonstrates the facility of this ligand exchange process. The asymmetric structure adopted by 2 is all the more surprising, considering the fact that a symmetric isomer with either bridging hydrides or bridging t-butoxides could be considered formally closed shell.

The hydride bridges in 2 are not cleaved by trimethylphosphine, in contrast with the hydrido-chloride and tetrahydride complexes (1 and $\text{Cp}^*\text{TaL}_2\text{H}_4$)⁷ which bind phosphine ligands in preference to oligomerizing. The reasons for this distinction are not fully understood, but we believe that they are due to the electronic properties of the alkoxide ligand and not simply to steric crowding about the metal center.¹⁷ The formation of 2 shows one of the difficulties in preparing coordinatively unsaturated hydride complexes of the early transition metals. These compounds

have a strong tendency to form oligomers with bridging hydrogen atoms, indicating that the hydrides in these complexes are good ligands for other metal centers (cf. BH_4^-). For example, Cp_2TaH_3 binds Lewis acids like AlEt_3 ,¹⁸ Cp_2ZrH_2 is polymeric,¹² and $(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{ZrH}_2$ is dimeric.¹¹

The reactions of $\underline{2}$ with carbon monoxide or ethylene are slow and require weeks at ambient temperatures or days at 80°C . In both cases two products are formed, indicated by two new Cp^* resonances in the NMR spectrum, one of which decomposes during prolonged heating at 80°C .¹⁹ Presumably these reagents cleave the dimer asymmetrically, but we have been unable to demonstrate this by isolating any of the products. $\underline{2}$ does not form an adduct with CO at -80°C , unlike $\text{Cp}^*_2\text{ZrH}_2$.²⁰ The reactions of $\underline{2}$ with $\text{Cp}_2\text{Mo}(\text{CO})$, $\text{Cp}_2\text{W}(\text{CO})$, and $\text{CpCo}(\text{CO})\text{PPh}_3$ are slow at 80°C and produce intractable mixtures. Deuterium gas exchanges with the hydride positions of $\underline{2}$ over a period of days at 80°C .

The reactions of $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_3\text{Cl}$ ($\underline{1}$) with reagents other than KOCMe_3 — alkyllithiums, benzylpotassium, lithium alkylamides, sodium amide, aluminum trichloride, cuprous chloride, or lithium chloride — give mixtures of products. Most of these reactions form a small amount of a hydride complex $\underline{3}$, identified by a characteristic hydride resonance in the proton NMR spectrum at 11.99δ ($d, {}^2J_{\text{PH}} = 49 \text{ Hz}$). $\underline{3}$ is also produced in the decomposition of $\underline{1}$ in etherial solvents. The best syntheses of $\underline{3}$ use one equivalent of CuCl or methyl chloride;²¹ although the latter route is cleaner, it does not go to completion because the liberated PMe_3 strongly inhibits the reaction. The best

formulation for $\underline{3}$ seems to be $\text{Cp}^*\text{Ta}(\text{PMe}_3)\text{H}_2\text{Cl}_2$, based both on the ^1H and ^{31}P NMR spectra, which indicate one phosphine and two hydride ligands, and the stoichiometric synthesis from $\underline{1}$ and CH_3Cl , an excellent hydride for chloride exchange reagent. Isolation of $\underline{3}$ is difficult because it is unstable in the absence of trimethylphosphine, and even the solid material decomposes in less than an hour under vacuum. In a benzene solution one molar in PMe_3 , however, it can be kept at 80°C for a day without significant decomposition.

In retrospect, it is not surprising that a variety of products are formed in the reactions of $\underline{1}$, since the phosphine, hydride, and chloride ligands are all expected to actively participate in the chemistry at the tantalum center. The formation of $\text{Cp}^*(\text{Me}_3\text{CO})_2\text{HTa}(\mu\text{H})_2\text{TaH}_3\text{Cp}^*$ ($\underline{2}$) from $\underline{1}$ indicates, more than anything else, the thermodynamic stability of $\underline{2}$.

Table I. ^1H NMR Data for $\text{Cp}^*(\text{Me}_3\text{CO})_2\text{HTa}(\mu\text{H})_2\text{TaH}_3\text{Cp}^* (2)^{\text{a}}$

Conditions	Chemical Shifts	Integral	Coupling	Assignment
C_6D_6 , 25°C	2.32	15	s	$\text{C}_5(\underline{\text{CH}}_3)_5$
	2.12	15	s	$\text{C}_5(\underline{\text{CH}}_3)_5$
	1.42	18	s	$[(\underline{\text{CH}}_3)_3\text{CO}]_2\text{Ta}$
	7.84	1	t, $^2J_{\text{HH}} = 13$ Hz	$\underline{\text{HTa}}(\mu\text{H})_2\text{TaH}_3$
	6.62	2	dq, $^2J_{\text{HH}} = 13$ and 6 Hz	$\text{HTa}(\mu\text{H})_2\text{TaH}_3$
	3.5	3	broad s ^b	$\text{HTa}(\mu\text{H})_2\text{TaH}_3$
C_7D_8 , -70°C	7.75	1	t, $^2J_{\text{HH}} = 13$ Hz	$\underline{\text{HTa}}(\mu\text{H})\text{Ta}(\text{H})(\text{H}')_2$
	6.61	2	m	$\text{HTa}(\mu\text{H})\text{Ta}(\text{H})(\text{H}')_2$
	5.51	1	t, $^2J_{\text{HH}} = 5$ Hz	$\text{HTa}(\mu\text{H})\text{Ta}(\underline{\text{H}})(\text{H}')_2$
	3.25	2	broad s ^c	$\text{HTa}(\mu\text{H})\text{Ta}(\text{H})(\underline{\text{H}}')_2$

^aSpectra obtained at 500 MHz. Chemical shifts are reported in δ , referenced to either TMS or the residual protons in the solvent. ^b250 Hz, full width, half height.

^c18 Hz full width, half height.

EXPERIMENTAL

All manipulations were carried out using either high vacuum or glove box techniques, as previously described.⁷ Potassium tert-butoxide (MCB) was sublimed and stored under nitrogen. ¹H NMR spectra were recorded on Bruker WM500 or JEOL FX90Q spectrometers; the spectra were occasionally resolution enhanced²² to observe small coupling constants. ³¹P and ¹³C NMR spectra were obtained using a JEOL FX90Q spectrometer. Infrared spectra were recorded on a Beckman 4240 spectrometer and are reported in cm⁻¹. Elemental analyses were determined by Alfred Bernhardt Analytical Laboratory. Molecular weights were determined either by osmometry (Bernhardt) or by isothermal distillation by the Singer method.²³

Cp*TaMe₃(OCMe₃). A solution of Cp*TaMe₃Cl²⁴ (3.1 g) and KOcMe₃ (0.88 g) in 75 ml diethyl ether was stirred at -80° for an hour and then warmed to room temperature. The diethyl ether was removed and 20 ml petroleum ether was added; the slurry was filtered into a sublimator and the solvent removed. Sublimation (10⁻³ torr) at 80° onto a probe at 0° yielded 2.4 g (71%) of yellow Cp*TaMe₃(OCMe₃). ¹H NMR (34°, C₆D₆) δ 1.75 (s, 15H, Cp*); 1.24 (s, 9H, OC(CH₃)₃); 0.43 (s, 9H, Ta(CH₃)₃). ¹³C NMR (34°, C₆D₆) δ 115.35 (s, C₅Me₅); 11.11 (q, J_{CH} = 127 Hz, C₅(CH₃)₅); 82.66 (s, OCMe₃); 52.51 (q, J_{CH} = 121 Hz, Ta(CH₃)CH₃'₂); 47.57 (q, J_{CH} = 118 Hz, Ta(CH₃)(CH₃)'₂); 30.61 (q, ¹J_{CH} = 126 Hz, OC(CH₃)₃, each peak of the quartet is split further into a septet, ³J_{CH} = 4 Hz). IR: 1360, 1240, 1185(st), 1020(st), 790, 460. Molecular weight (C₆H₆) calcd. 434; found 520 (Singer method).

$\text{Cp}^*(\text{Me}_3\text{CO})_2\text{HTa}(\mu\text{H})_2\text{TaH}_3\text{Cp}^*$ (2). A high pressure reactor, charged with 2.12 g $\text{Cp}^*\text{TaMe}_3(\text{OCMe}_3)$, 0.8 ml PMe_3 , and 120 ml petroleum ether was heated to 65° , pressurized to 1400 psi of hydrogen gas, and then stirred for a week. The solvent was removed, leaving a brown oil containing principally 2. After repeated additions and removals of petroleum ether, 0.9 g (43%) of white crystalline 2 was obtained. 2 is extremely soluble in hydrocarbon solvents, and it decomposes in vacuo at 135° . The ^1H NMR data are given in Table I. IR: 1735, 1535, 1280 (TaH; TaD: 1250, 1110, 860) 1360, 1240, 1185(st), 990(st), 965(st), 790, 540 (TaOCMe₃), 1030 (Cp^{*}). Anal. calcd for $\text{C}_{28}\text{H}_{54}\text{O}_2\text{Ta}_2$: C, 42.86; H, 6.94; Ta, 46.12. Found: C, 42.66; H, 6.70; Ta, 46.33. Molecular weight (C_6H_6) calcd, 785; found, 760 (Bernhardt). 2 can also be prepared by stirring a solution of $\text{Cp}^*\text{Ta}(\text{PMe}_3)_2\text{H}_3\text{Cl}$ (1) and KOCMe_3 in diethyl ether for 30 min.

$\text{Cp}^*\text{Ta}(\text{PMe}_3)\text{H}_2\text{Cl}_2$ (3). A good synthetic route to 3 has not been found;²¹ the following at least gives a relatively pure product. A suspension of 1 (0.52 g) and AlCl_3 (0.15 g) was stirred in 40 mL diethyl ether at -80°C for 1 hr and at 25°C for an hour. After removing the volatiles, recrystallization from petroleum ether/trimethylphosphine gave yellow 3 (0.02 g, 4%). ^1H NMR (C_6D_6): 2.11 (s, $\text{C}_5(\text{CH}_3)_5$), 1.43 (d, $^2J_{\text{PH}} = 9$ Hz, $\text{P}(\text{CH}_3)_3$), 11.99 (d, $^2J_{\text{PH}} = 40$ Hz, TaH_2). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum is a singlet; on selective proton decoupling at 1.43 δ , the ^{31}P spectrum is a triplet, $^2J_{\text{PH}} = 49$ Hz.

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(6) However, see chapter IV of this thesis. There is one report of a poorly characterized μ -oxo hydride complex.¹²

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(9) The other possible symmetry elements for $\text{Cp}_2^* \text{Ta}_2 \text{H}_6 (\text{OCMe}_3)_2$ can be ruled out as follows. An inversion center is clearly impossible because of the inequivalence of the Cp^* groups. A twofold rotation axis would require a linear ring centroid-tantalum-tantalum-ring centroid

arrangement which leaves no place for the two unique hydride ligands. A more complete discussion of the determination of structures from NMR spectra has been presented in Chapter II of this thesis.

(10) (i) $\nu(\text{Zr-H-Zr}) = 1330 \text{ cm}^{-1}$ in $(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{ZrH}_2$ ¹¹ and 1300 cm^{-1} in $(\text{Cp}_2\text{ZrH}_2)_x$.¹² There are additional examples in ref. 12. (ii) The IR spectrum of $[\text{Cp}^*\text{TaCl}_2\text{H}]_2$ has a band at 1580 cm^{-1} which is assigned to a bridging hydride stretch.¹³ In view of the normal range for terminal Ta-H stretching modes ($1625\text{-}1750 \text{ cm}^{-1}$),^{7, 14} we believe this band more likely is a terminal Ta-H mode.

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(15) (a) The IR spectrum is assigned following ref. 15b, pp 116-122. (b) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. "Metal Alkoxides", Academic Press: New York, N.Y. 1978.

(16) (a) Both alkoxide and hydride ligands are known to bridge metal centers readily.^{15b, 16b} (b) Teller, R. G.; Bau, R. Structure and Bonding 1981, 44, 1-82.

(17) The imido-hydride complexes $\text{Cp}^*\text{Ta}(\text{NCMe}_3)\text{H}_2(\text{L})$ are sterically similar (one less hydride ligand) to the hypothetical $\text{Cp}^*\text{Ta}(\text{OCMe}_3)\text{H}_3(\text{L})$ and they do not have very labile phosphine ligands

as might be expected for sterically crowded molecules.¹⁴

(18) Tebbe, F. N. J. Am. Chem. Soc. 1973, 95, 5412-5414.

(19) The products of $\underline{2} + \text{CO}$ contain carbonyl ligands:

$\nu(\text{CO}) = 1925, 1795 \text{ cm}^{-1}$.

(20) Marsella, J. A.; Curtis, C. J.; Bercaw, J. E.; Caulton, K. G. J. Am. Chem. Soc. 1980, 102, 7244-7246.

(21) $\text{Cp}^*\text{Ta}(\text{PMe}_3)\text{H}_2\text{Cl}_2$ (3) has recently been prepared by zinc reduction of Cp^*TaCl_4 in the presence of PMe_3 and H_2 . Sanner, R. D. and co-workers, personal communication, 1982. This synthesis is almost undoubtedly preferable to the one reported here.

(22) Ernst, R. R. Adv. Mag. Res. 1966, 2, 1.

(23) (a) Singer, R. Justus Liebigs Ann. Chem. 1930, 478, 246.

(b) Clark, E. P. Ind. Eng. Chem., Anal. Ed. 1941, 13, 820.

(24) McLain, S. J.; Wood, C. D.; Schrock, R. R. J. Am. Chem. Soc. 1979, 101, 4558-4570.

CHAPTER IV**Hydrogen Transfer and Hydrogenation Reactions of Tantalum
Compounds with Nitrogen Ligands. Comparison Among
Alkoxide, Amide, and Alkyl Complexes.¹**

INTRODUCTION

Research in organometallic chemistry has focused primarily on transformations of hydrocarbon ligands.² In contrast, the chemistry of groups bound to a metal center through nitrogen, oxygen, or other element has received little attention. For example, the reactions of metal-alkyl complexes with dihydrogen have been investigated for many years,³⁻⁶ but the first clear example of hydrogenolysis of a metal-alkoxide bond has only recently been reported.⁷ α - and β -hydrogen elimination processes have been extensively studied for alkyl ligands,^{8,9} but there are very few examples of hydrogen transfer reactions from dialkylamide or alkoxide ligands. This chapter describes the synthesis and reactivity of a series of alkyl, amide, and alkoxide complexes of tantalum. The properties of these compounds depend to a large extent on the presence of α - or β -hydrogen atoms and on the type of atom bound to tantalum.

RESULTS

The starting material for the compounds prepared in this study is (pentamethylcyclopentadienyl)tantalum trimethylchloride, $\text{Cp}^*\text{TaMe}_3\text{Cl}$, 1 ($\text{Me} \equiv \text{CH}_3$, $\text{Cp}^* \equiv \eta^5\text{-C}_5\text{Me}_5$).¹⁰ 1 reacts rapidly with lithium dimethylamide at 0°C in diethylether to give the expected metathesis product, $\text{Cp}^*\text{Ta}(\text{NMe}_2)\text{Me}_3$ (2), identified by its ¹H and ¹³C NMR spectra (see

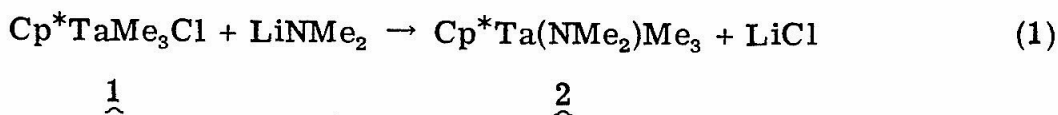
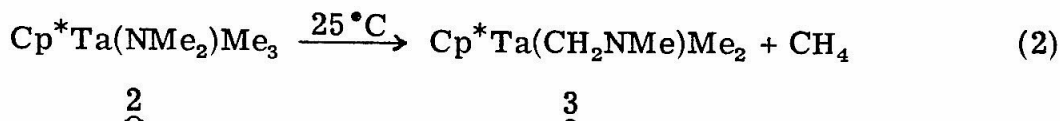
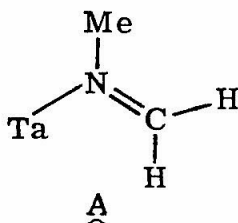


Table I). 2 can be isolated in good yield at 0°C or below, but at ambient temperatures it decomposes in solution or in the solid state to an imine complex, 3 (eq 2). The stoichiometry of eq 2 has been confirmed by

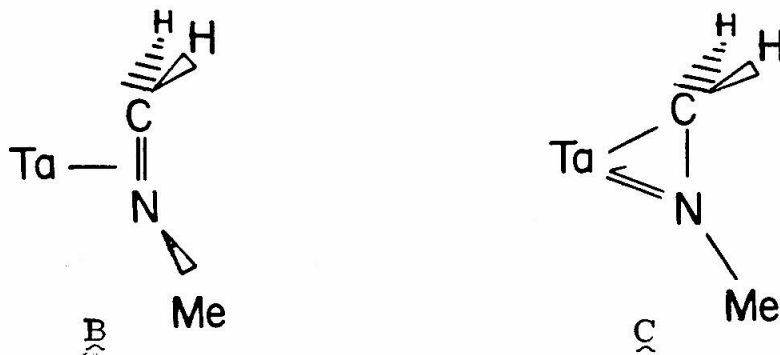


quantitatively collecting the methane formed, and identifying it by IR spectroscopy. 3 has been characterized by IR and NMR spectroscopies, elemental analysis, and molecular weight measurement (calcd: 389, found: 406). The ¹³C NMR spectrum of 3 indicates the presence of a methylene carbon (65.46δ, triplet, ¹J_{CH} = 155 Hz), in addition to the Cp* ligand and methyl groups on both tantalum and nitrogen. The high field chemical shift of the methylene carbon, the low energy C-N stretch (1265 cm⁻¹), and the equivalence of the methylene hydrogen atoms are all arguments against an η¹-structure (A), and strongly indicate that the imine ligand is bound to the tantalum through both the carbon and



nitrogen atoms.¹¹ A similar geometry has been found crystallographically for a tungsten imine complex,¹² and similar structures have been proposed for imine complexes of tantalum,¹³ zirconium,¹⁴ titanium,¹⁵ and group VIII metals.¹⁶ An analogous tantalum acetone complex, $\text{Cp}^*\text{Ta}(\text{OCMe}_2)\text{Me}_2$, is also thought to be bound through both the carbon and oxygen atoms.¹⁷

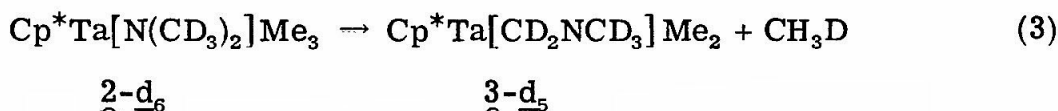
Two limiting resonance structures can be used to describe the bonding of the imine ligand (B and C); these resemble the structures



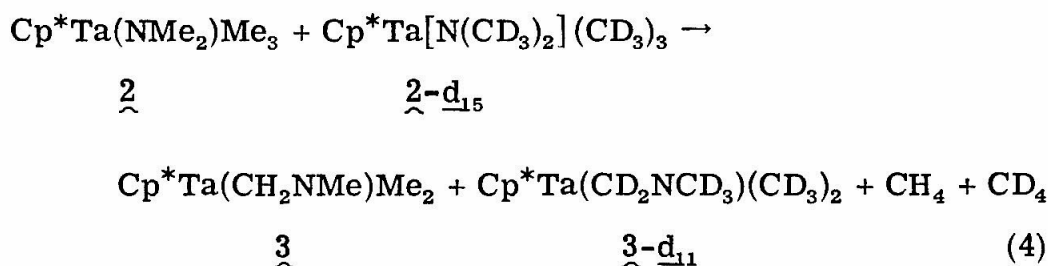
drawn for olefin binding to a transition metal center.¹⁸ Unlike olefin complexes, however, there is a distinct structural difference between the two bonding modes for an imine ligand. In the metallacycle form (C), the methyl substituent on the nitrogen is expected to be in the plane formed by the tantalum, nitrogen, and the methylene carbon,¹⁹ while in the π complex structure (B) the methyl group is significantly out of plane. This distinction is observable in the proton NMR spectrum

because the two methylene hydrogen atoms are expected to be inequivalent in the π complex form, as they are in uncoordinated methyleneimines ($\text{RN}=\text{CH}_2$).²⁰ The low temperature ^1H NMR spectrum of $\underline{3}$ is very similar to the spectrum at 25°C , which suggests that the observed equivalence of these hydrogen atoms is not due to a fluxional process. These data therefore indicate that $\underline{3}$ is best described not as a π complex, but as a three-atom metallacycle, or as a metallated dimethylamide (\underline{C}). The NMR data also suggest that this metallacycle is oriented perpendicular to the plane of the Cp^* ring (similar to an analogous benzyne complex²¹) and not in the "parallel" geometry found for related ethylene,²² acetylene,²³ and metallacyclopentane²⁴ derivatives.

The decomposition of $\underline{2}$ to $\underline{3}$ (eq 2) obeys first-order kinetics for greater than three half lives (fig 1), with $k = 5.6 \times 10^{-4} \text{ sec}^{-1}$ at 34°C . $\underline{2-d}_6$ forms only CH_3D (eq 3), and a mixture of $\underline{2}$ and $\underline{2-d}_{15}$ produces

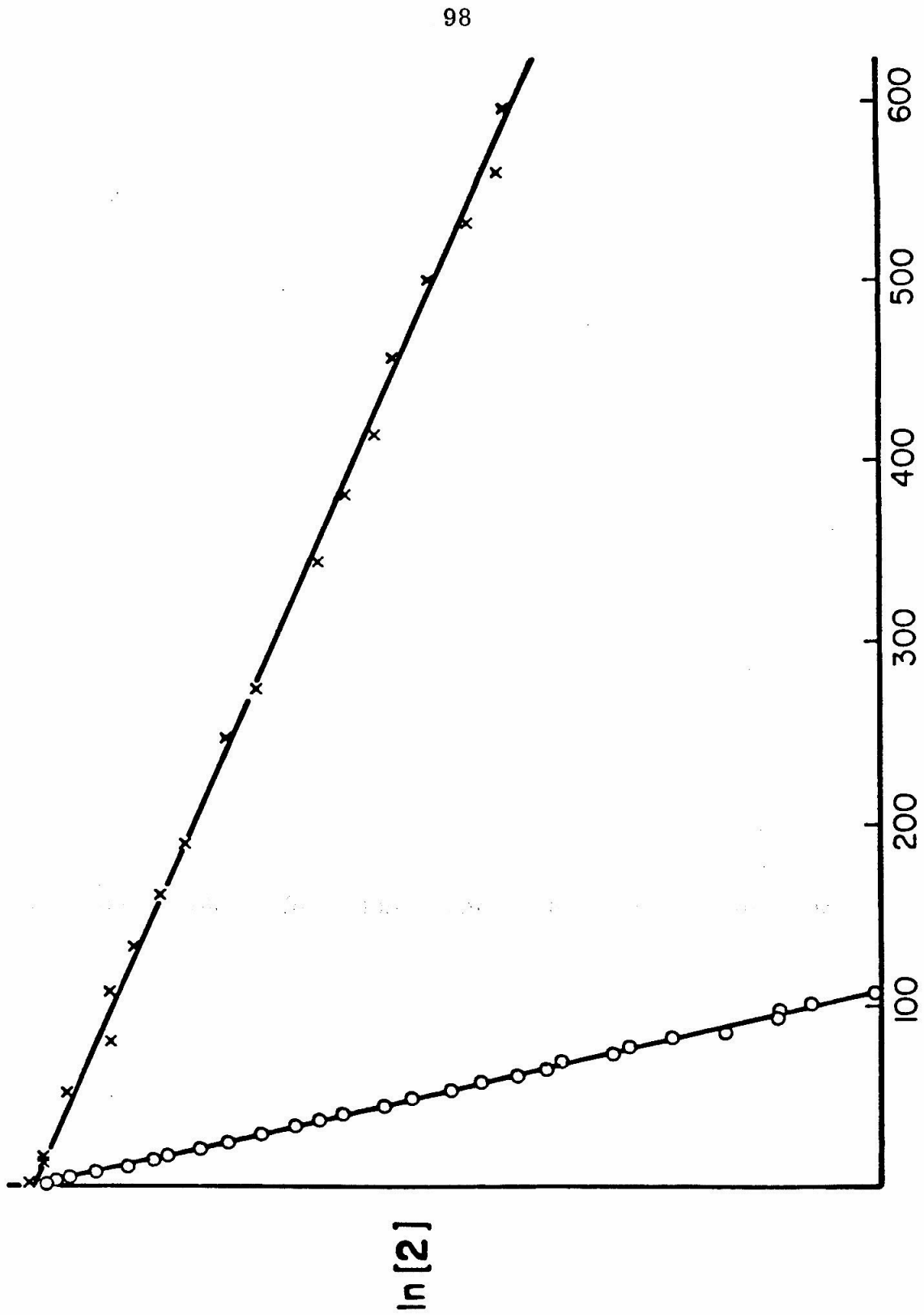


CH_4 and CD_4 with no observable crossover products ($<5\%$ CH_3D and CD_3H by NMR and IR spectroscopies, eq 4). The conversion of $\underline{2}$ to $\underline{3}$



is therefore a straightforward unimolecular process. The decay of $\underline{2-d}_6$ (eq 3) is much slower than the perprotio material (fig. 1): the

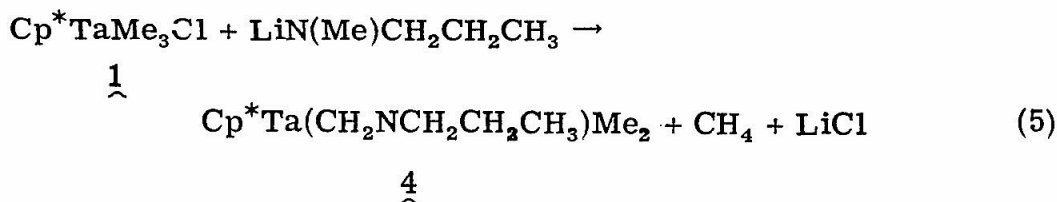
Figure 1. $\ln(\text{concentration})$ vs. time plots for the decomposition of $\text{Cp}^*\text{Ta}(\text{NMe}_2)\text{Me}_3$, $\underline{2}$ (circles), and $\text{Cp}^*\text{Ta}[\text{N}(\text{CD}_3)_2]\text{Me}_3$, $\underline{2-d_6}$ (crosses), at 34°C .



minutes
Fig. 1

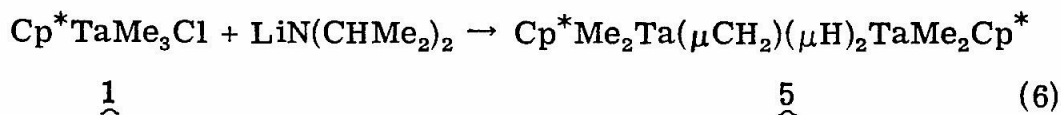
kinetic isotope effect (k_H/k_D) is 9.7 (± 1).

One other "imine" complex has been prepared, the N-propyl methyleneimine derivative (eq 5), but this reaction is not quantitative



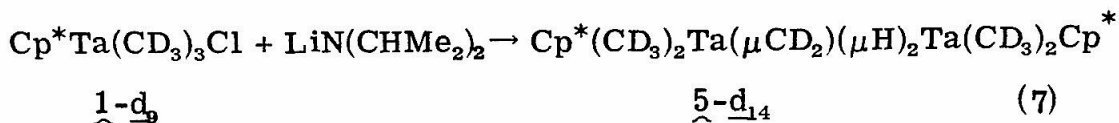
and a number of other products are formed. An intermediate amide complex analogous to $\underline{2}$ has not been observed.

The reaction of $\underline{1}$ with lithium diisopropylamide (LDA) gives a number of products but one ($\underline{5}$) can be cleanly isolated, albeit in only 10% yield, because of its limited solubility in petroleum ether (eq 6).

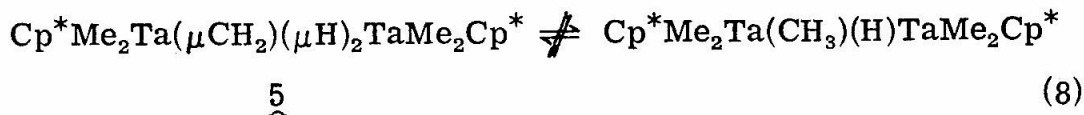


A small amount of methane (0.17 equivalents) is also formed in the reaction. $\underline{5}$ is stable in solution for only a few hours at ambient temperatures, but is sufficiently robust in the solid state to enable satisfactory elemental analyses to be obtained (see experimental section). The ^{13}C NMR spectrum of $\underline{5}$ indicates the presence of a methylene group (135.76 δ , triplet, $^1J_{\text{CH}} = 123$ Hz) in addition to tantalum methyl groups and the Cp^* ligand. The proton NMR spectrum has two triplets coupled to each other (0.54 and 9.72 δ , $J_{\text{HH}} = 6$ Hz), integrating as one hydrogen each (to $\text{Cp}^* = 15$). These triplets are assigned to a bridging methylene and two bridging hydride ligands.²⁵ Further evidence for the proposed

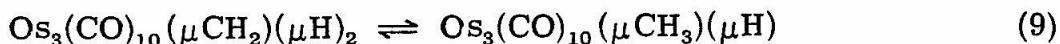
structure comes from the reaction of $\underline{1-d_9}$ with LDA which produces $\underline{5}$ deuterated at the methyl and methylene positions but not at the hydride ligands (eq 7). The hydride resonance in the ^1H NMR spectrum of



$\underline{5-d_{14}}$ is a singlet and the methylene signal at 0.54δ is absent.²⁶ This experiment also shows that the methylene group does not reversibly insert into the hydride ligands (eq 8), in contrast to the rapid scrambling



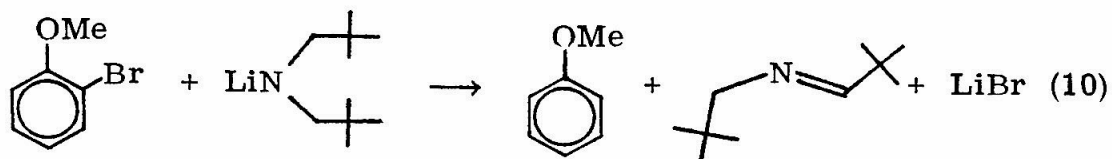
of hydride and methylene protons observed in a triosmium cluster (eq 9).^{25a} $\underline{5}$ does not appear to react with dihydrogen or ethylene



before it decomposes; reactions with carbon monoxide and methyl iodide are rapid but yield intractable mixtures.

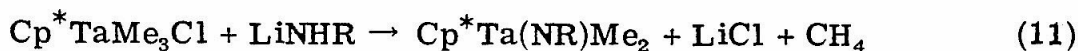
The mechanism of formation of $\underline{5}$ is not at all clear but various labeling experiments do indicate that the diisopropylamide is the source of the hydride ligands. $\underline{5}$ prepared in toluene- d_8 has no deuterium incorporation and pre-rinsing of glassware with D_2O has little effect. The synthesis using $\underline{1-d_9}$ (eq 7) shows that the hydrides are not derived from the tantalum methyl groups. Bulky lithium dialkylamides are known to donate hydride ions from the α -carbon to certain organic substrates, for example, the reduction of ortho-bromoanisole to anisole

(eq 10).²⁷ This seems to be a reasonable process in the tantalum



system also. The steric bulk of the diisopropylamide group appears to prevent the formation of a tantalum-nitrogen bond, and other pathways become competitive.

1 reacts with lithium monoalkylamides to give tantalum alkyl-imido complexes, not the expected amide compounds (eq 11). A formal



1

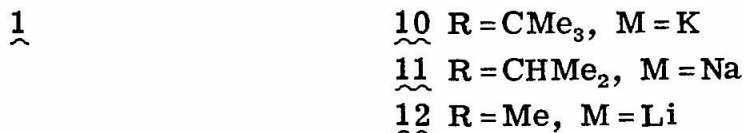
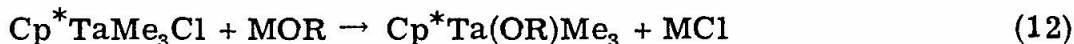
6, R = CMe₃

7, R = CH₂CMe₃

8, R = Me

α -abstraction occurs with the formation of methane, a product that has been quantitatively collected and identified. These compounds are extremely soluble in petroleum ether and sublime readily at 40°C, 10⁻⁴ torr. 6 melts at 30°C; when slightly impure it is a viscous liquid. Compounds 2 - 8 are all plagued with a persistent impurity, Cp*TaMe₄ (9),¹⁷ that is difficult to remove by either recrystallization or sublimation. Fortunately the amount of 9 formed is reduced in more dilute solutions. The problem is most severe in the synthesis of 8, which has not been obtained in pure form.

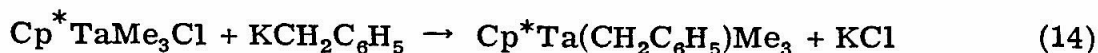
Alkali metal alkoxides react with 1 to give the corresponding tantalum alkoxide complexes (eq 12).²⁸ Compounds 10 - 12 are very soluble in hydrocarbon solvents and sublime readily. 10 melts at 40°C



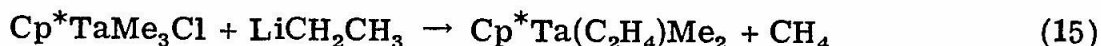
and is often isolated by short path distillation as a slightly impure liquid. Unlike the isoelectronic amide complexes, the alkoxide compounds are very stable: 12 decomposes only at 120°C and 10 and 11 are unchanged after a day at that temperature.

The ¹³C NMR spectra of 10 - 12 indicate that the methyl groups bound to the tantalum are not all equivalent at ambient temperatures, although the proton spectra show one broad resonance for the methyl ligands. Cp*Ta(X)Me₃ compounds most likely have 'four-legged-piano-stool' geometries in which the methyl groups are inequivalent if the molecule is not fluxional.²⁹ The ¹H and ¹³C NMR spectra of Cp*Ta(NMe₂)Me₃ (2) show inequivalent methyl groups at ambient temperature, while the alkyl complexes Cp*Ta(R)Me₃ (see below) have equivalent methyl groups. The alkoxide complexes are in an intermediate range: the methyl resonances for 12 in the ¹³C NMR spectrum coalesce at 45°C, equivalent to a 16.1 (±1) kcal/mole barrier to rearrangement.³⁰ For Cp*TaMe₃Cl (1), a ΔG[‡] of 13.6 (±1.4) kcal/mole has been derived for this fluxional process.¹⁰ The different behavior of these compounds is probably related to the π donor ability of the unique ligand (NR₂ > OR > Cl > R).³¹

A number of alkyl complexes of the Cp*TaMe₃ have been prepared (eq 13, 15); 9 has been previously reported.¹⁷ These compounds are

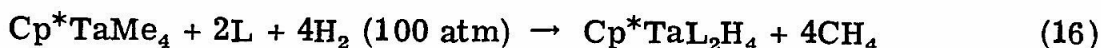
113 R = CH₂CMe₃9 R = Me114

thermally stable, decomposing only over a period of weeks at 80°C. Complexes of alkyl groups with β-hydrogen atoms, however, appear to be unstable, since treatment of 1 with ethyllithium is reported to give not an alkyl but an olefin complex (eq 15),³² presumably by

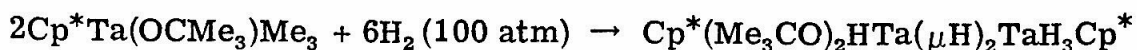


β-elimination from an intermediate ethyl derivative.

The reactions of the compounds described above with dihydrogen have also been examined. We have already observed that hydrogenation of tantalum alkyl compounds is a good synthetic route to hydride complexes.³³ Thus 9 reacts with hydrogen in the presence of phosphine ligands to give tetrahydride complexes (eq 16),³³ and the hydrogenation

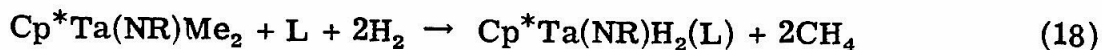
9

of 10 produces an unusual asymmetric dimer (eq 17).³⁴ The imido

10

(17)

compounds reported here (6 and 7) react cleanly with hydrogen in the presence of phosphine ligands to give dihydride complexes 15 - 18 (eq 18).



6, 7

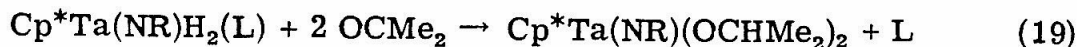
15 R = CMe₃, L = PMe₃

16 R = CMe₃, L = PMe₂(C₆H₅)

17 R = CH₂CMe₃, L = PMe₃

18 R = CH₂CMe₃, L = PMe₂(C₆H₅)

Unlike reactions 16 and 17 a high pressure of H₂ is not required, although the reactions are slow, requiring two weeks at 80°C under 3 atm of hydrogen. There is no evidence for the formation of amido ligands, even in the presence of H₂ and/or additional phosphine ligands. The trimethylphosphine complexes 15 and 17 are difficult to isolate because of their high solubility in hydrocarbon solvents, so the dimethylphenylphosphine derivatives have been examined in more detail. The hydrogen ligands in these compounds are "hydridic":³⁵ they reduce acetone to isopropoxide complexes (eq 19) and react with methanol to produce H₂.

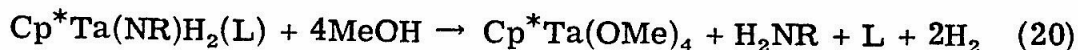


16, 18

19 R = CMe₃

20 R = CH₂CMe₃

Methanol also removes the imido ligand as the amine (eq 20), even if less

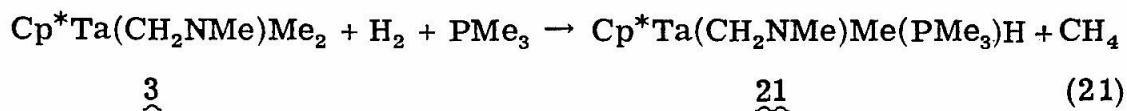


16, 18

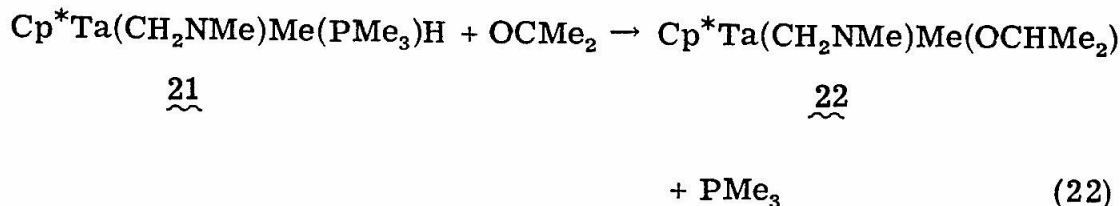
than a stoichiometric amount of MeOH is used. Cp*Ta(OMe)₄ can also be

prepared from $\text{Cp}^*\text{TaL}_2\text{H}_4$ complexes and methanol.³³ The reactions of 16 and 18 with carbon monoxide and ethylene give intractable mixtures of products.

Complex 3 reacts with hydrogen in the presence of trimethylphosphine to lose one equivalent of methane and form an imine-hydride complex, 21 (eq 21). 21 has been characterized by elemental analysis,

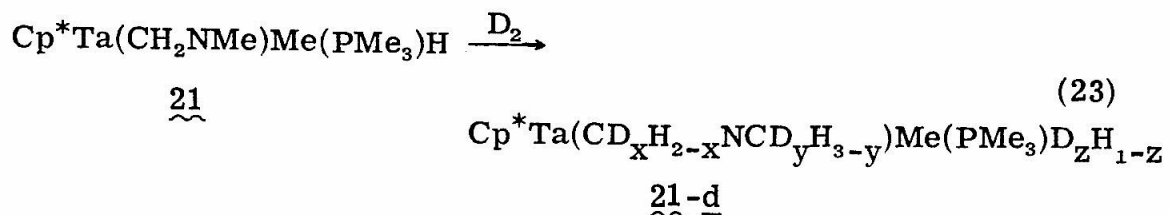


molecular weight measurement (calc. 451, found, 478), IR ($\nu\text{TaH} = 1680 \text{ cm}^{-1}$), and NMR spectroscopies. To our knowledge, 21 is the first isolable mononuclear tantalum alkyl hydride complex. The NMR spectra are particularly informative, since the phosphorus nucleus couples to the hydrogens of the tantalum methyl group and to the hydride ligand, and the two sets of hydrogens also couple to each other. It is interesting that 21 contains a phosphine ligand since 3 appears to be too sterically crowded to bind PMe_3 strongly.³⁶ 21 reacts with one equivalent of acetone with loss of PMe_3 to give an isopropoxide complex 22 (eq 22). 21 decomposes slowly under hydrogen although the

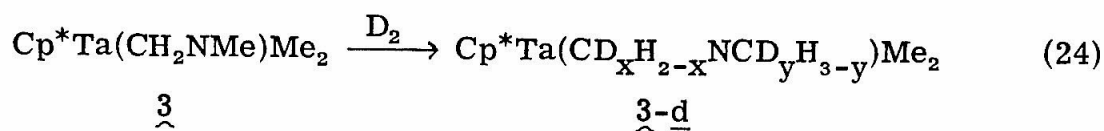


reaction is inhibited by excess PMe_3 . If 21 is stirred under D_2 , exchange is observed prior to decomposition, and deuterium is incor-

porated not only into the hydride position but also into the methylene and methyl groups of the imine ligand (eq 23). The protons of the imine



ligand in 3 will also exchange with D₂ (eq 24), although decomposition



does occur slowly under these conditions.

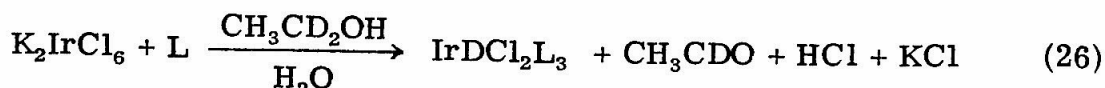
DISCUSSION

The decomposition of $\text{Cp}^*\text{Ta}(\text{NMe}_2)\text{Me}_3$ (2) to $\text{Cp}^*\text{Ta}(\text{CH}_2\text{NMe})\text{Me}_2$ (3) is a unimolecular β -hydrogen abstraction or elimination reaction, as evidenced by the kinetic and labeling experiments discussed above. This is not a common reaction of dialkylamide ligands, ^{19b, c} although an analogous decomposition of tantalum pentakis(diethylamide) to an "imine" complex has been observed (eq 25, $\text{Et} = \text{CH}_2\text{CH}_3$).¹³ There

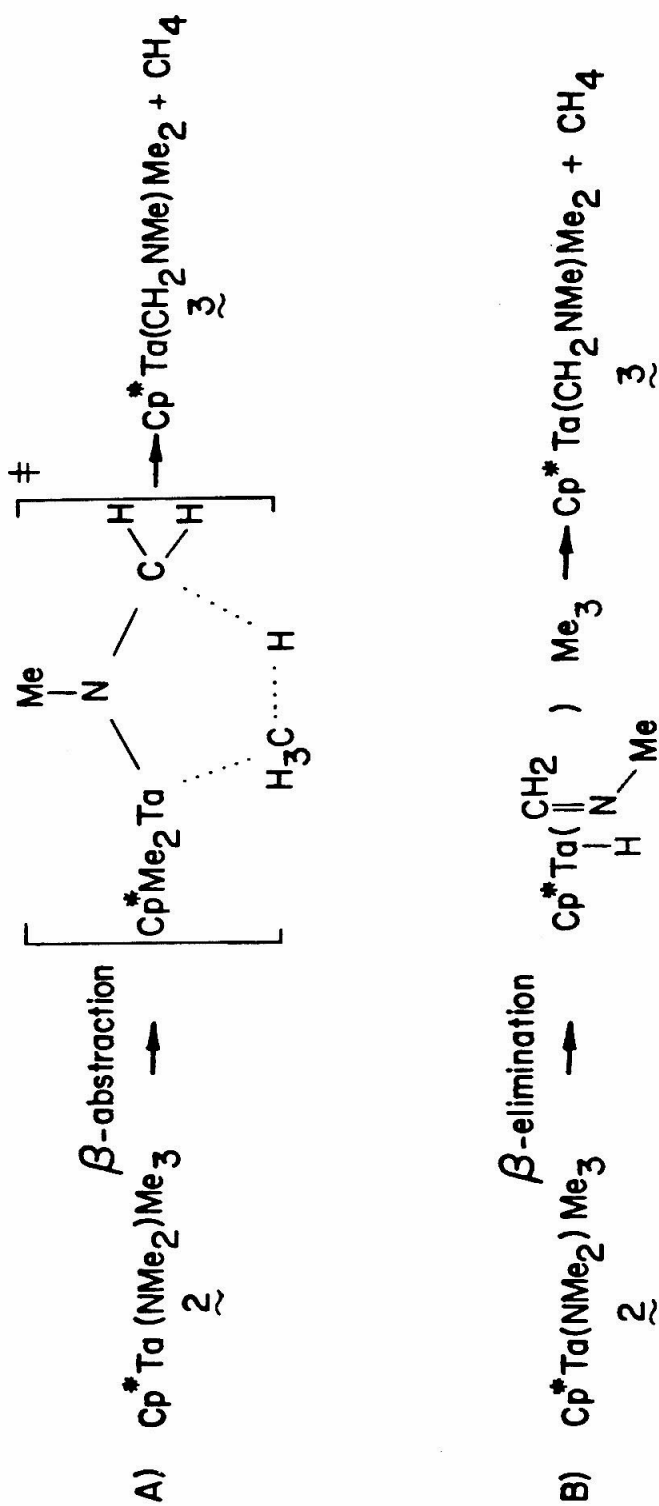


are two reasonable mechanisms for this transformation, (i) a direct hydrogen abstraction process and (ii) a β -hydrogen elimination pathway involving a tantalum hydride intermediate (see Scheme I). Mechanisms in between these two extremes can also be imagined.³⁷ The large kinetic isotope effect ($k(\underline{2})/k(\underline{2}-\underline{d}_6) = 9.7$) does not directly distinguish between the mechanisms, but it does indicate that the hydrogen atom that migrates is very loosely bound in the transition state. For comparison, abstraction of a hydrogen atom from CH_4 by a chlorine atom is ten times faster than deuterium abstraction from CD_4 .³⁸

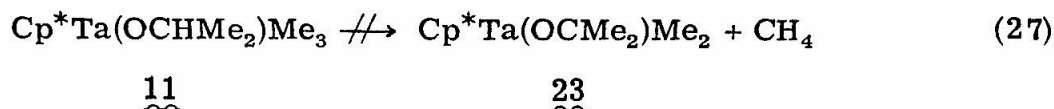
In view of the facile hydrogen migrations from amide ligands, the high thermal stability of the alkoxide compounds 10 - 12 is surprising. Although there are no unambiguous examples of alkoxide complexes that decompose by β -hydrogen transfer, this step is strongly suggested by the syntheses of metal hydride complexes in alcoholic solvents³⁹ (e.g., eq 26⁴⁰). This process does not occur in this tantalum system, even



SCHEME I

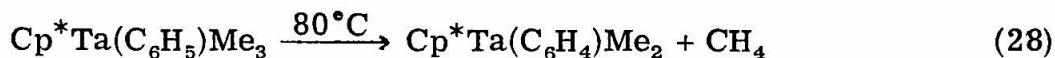


though the products should be stable. β -hydrogen transfer from the isopropoxide ligand of 11 would yield an η^2 -acetone complex (23, eq 27) that has been prepared by another route,¹⁷ and decomposition of 12

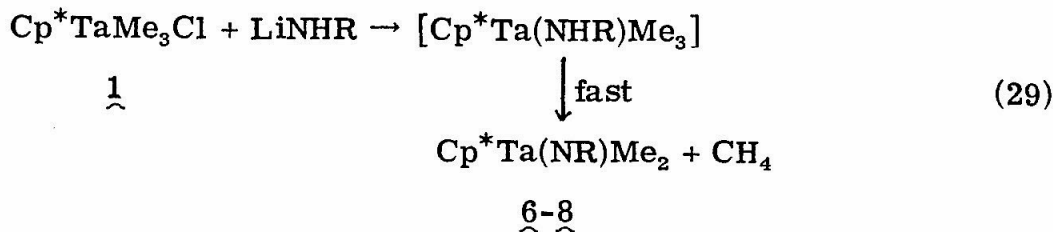


would give an η^2 -formaldehyde complex,⁴¹ completely analogous to the formation of the η^2 -imine complex 3.

In complexes of hydrocarbon ligands, however, β -hydrogen elimination processes appear to be very facile. Even the compound with a phenyl ligand, which is usually considered not to have β -hydrogens,⁴ is reported to decompose to a benzyne complex by this



pathway (eq 28).²¹ Alkyl groups without β -hydrogens form stable compounds with the Cp^*TaMe_3 fragment, and α -abstraction reactions have not been observed, even in the presence of PMe_3 . Schrock and co-workers have extensively investigated α -hydrogen transfer reactions in a variety of tantalum systems and they conclude that steric effects often play a dominant role.^{9, 42} The Cp^*TaMe_3 group does not appear to be bulky enough to induce these reactions. α -hydrogen transfer processes are observed, however, when 1 is treated with monoalkylamides. These reactions probably form an intermediate amide complex analogous to 2, but it is not observed because elimination of methane is rapid (eq 29).⁴³ The second step in eq 29 is best described as a hydrogen abstraction reaction and not an α elimination, because

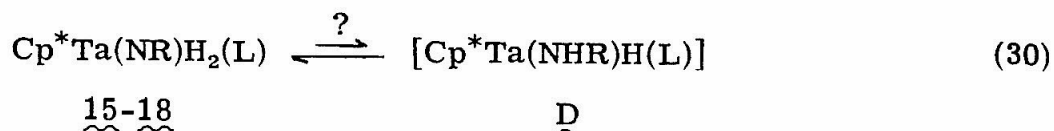


the elimination mechanism involves an unreasonable tantalum-hydride intermediate.^{37, 44, 45}

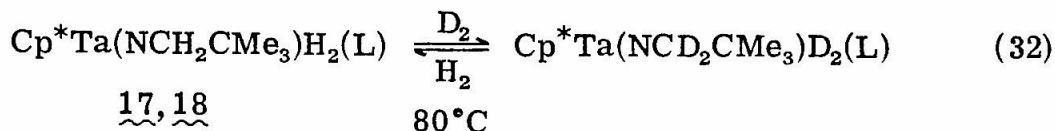
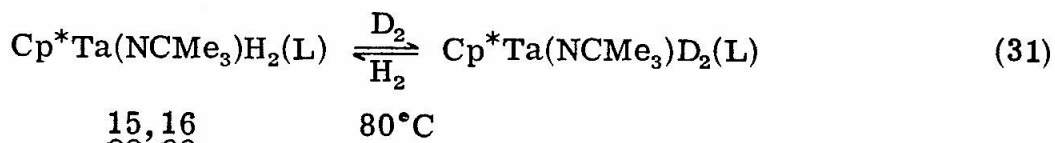
The rates of the hydrogen transfer processes correlate with the nature of the atom bound to the tantalum. For reactions involving a β -hydrogen, the observed order is $\text{C} > \text{N} > \text{O}$: hydrocarbon ligands undergo β -elimination readily while alkoxide complexes are stable. α -abstraction reactions appear to vary in the reverse order, $\text{N} > \text{C}$, since alkyl complexes are stable and imido compounds are rapidly formed. The reaction of 1 with LiOH gives methane and what appears to be an insoluble polymeric oxo complex,⁴⁶ so α -abstraction from oxygen ligands seems to be facile also. Given a choice, complexes of nitrogen ligands undergo α -abstraction reactions while hydrocarbon ligands β -eliminate. It should be emphasized that these comparisons are based on the reactivity of complexes of the Cp^*TaMe_3 fragment, and it is not clear that they will be valid for other metals or even tantalum complexes with different ligand arrays.⁴²

Additional insight is provided by the hydrogenation reactions, which complement the abstraction or elimination processes. Hydrogenation of the imido compounds 6 and 7 gives imido-hydride, not amide

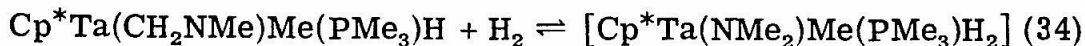
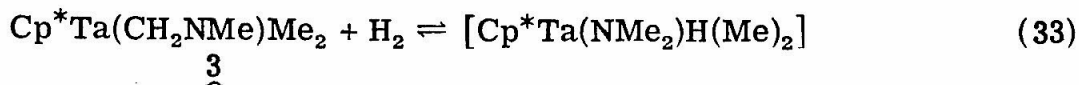
complexes; to our knowledge, these are the first reported imido-hydride compounds.⁴⁷ An amide complex like D (eq 30) does not seem to be easily accessible in the reactions of 15 - 18, since they exchange hydride



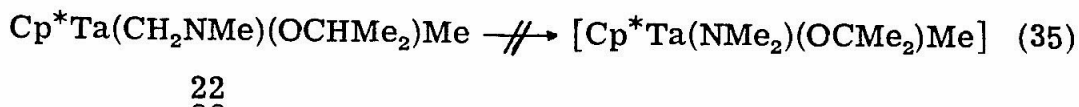
ligands slowly with D₂ even at 80°C (eq 31, 32). D would be expected to react rapidly with deuterium since it is a sixteen-electron tantalum



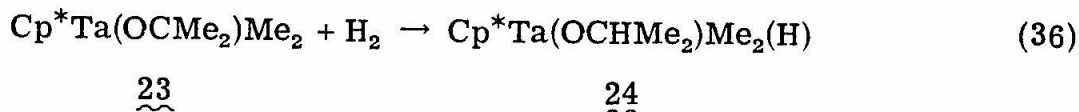
(III) species.⁴⁸ The neopentylimido compounds 17 and 18 exchange deuterium not only into the hydride positions, but also into the methylene group next to the nitrogen (eq 32).⁴⁹ Hydrogenation of the "imine" complex 3 does not yield an amide complex either, but labeling studies with D₂ indicate reversible formation of a dimethylamide intermediate (eq 33 and 34) since deuterium is found in both the methyl and methylene



positions of the imine ligands. The reaction of 21 with acetone gives an interesting product with both nitrogen and oxygen ligands, which does not appear to rearrange to a tautomer as in eq 35. Hydrogenation



of the tantalum acetone complex 23 has been reported to yield an isopropoxide derivative 24 (eq 36).¹⁷ In our hands this complex does not



decompose readily¹⁷ and complete spectroscopic data have been obtained,⁵⁰ including the location of the hydride resonance in the ¹H NMR spectrum at extremely low field, 16.77δ.

These various reactions indicate that the kinetic barriers to hydrogen transfer processes are small, and that the reaction rates reflect the thermodynamic preferences in this series of compounds. The absence of β-hydrogen elimination or abstraction reactions in the alkoxide compounds does not appear to be due to a kinetic problem, since facile reactions are observed between a tantalum acetone complex and hydrogen (eq 36) and between tantalum hydride complexes and acetone (eqs 19 and 22, and ref 33). Decomposition of the alkoxide compounds by this route seems to be thermodynamically unfavorable. The energetics of the β-hydrogen reactions correlate with the strength of the metal ligand bond (Ta-O > Ta-N > Ta-C),⁵¹ while the α-hydrogen reactions are more closely related to the stability of the multiple bond formed (Ta = NR > Ta = CR₂).⁴⁶

Table I. ^1H and ^{13}C NMR Data^a

Compound	Assignment	^{13}C NMR	
		^1H NMR	chemical shift multiplicity, coupling constant
$\text{Cp}^*\text{Ta}(\text{NMe}_2)\text{Me}_3$ (2) ^b	$\text{C}_5(\underline{\text{CH}}_3)_5$	1.62 s	10.95 q, $^1J_{\text{CH}} = 127$ Hz
	$\underline{\text{C}}_5(\text{CH}_3)_5$		113.12 s
	$\text{N}(\underline{\text{CH}}_3)_2$	2.37 s	40.90 q, $^1J_{\text{CH}} = 135$ Hz
	$\text{Ta}(\underline{\text{CH}}_2)(\underline{\text{CH}}'_3)_2$	0.67 s	51.30 ^c
	$\text{Ta}(\underline{\text{CH}}_3)(\underline{\text{CH}}'_3)_2$	0.17 s	45.67 q, $^1J_{\text{CH}} = 112$ Hz
$\text{Cp}^*\text{Ta}(\text{CH}_2\text{NMe})\text{Me}_3$ (3) ^d	$\text{C}_5(\underline{\text{CH}}_3)_5$	1.68 s	10.46 q, $^1J_{\text{CH}} = 127$ Hz
	$\underline{\text{C}}_5(\text{CH}_3)_5$		115.01 s
	$\text{Ta}(\underline{\text{CH}}_3)_2$	0.05 s	51.98 q, $^1J_{\text{CH}} = 118$ Hz
	$\text{Ta}(\underline{\text{CH}}_2\text{NMe})$	2.06 s	65.46 t, $^1J_{\text{CH}} = 155$ Hz
	$\text{Ta}(\text{CH}_2\text{N}\underline{\text{CH}}_3)$	3.91 s	47.20 q, $^1J_{\text{CH}} = 134$ Hz
$\text{Cp}^*\text{Ta}(\text{CH}_2\text{NCH}_2\text{CH}_2\text{CH}_3)\text{Me}_3$ (4)	$\text{C}_5(\underline{\text{CH}}_3)_5$	1.73 s	10.59 q, $^1J_{\text{CH}} = 127$ Hz
	$\underline{\text{C}}_5(\text{CH}_3)_5$		115.17 s
	$\text{Ta}(\underline{\text{CH}}_3)_2$	-0.09 s	51.07 q, $^1J_{\text{CH}} = 118$ Hz
	$\text{Ta}(\underline{\text{CH}}_2\text{NCH}_2\text{CH}_2\text{CH}_3)$	1.83 s	58.22 t, $^1J_{\text{CH}} = 153$ Hz
	$\text{Ta}(\text{CH}_2\text{N}\underline{\text{CH}}_2\text{CH}_2\text{CH}_3)$	4.09 t, $^3J_{\text{HH}} = 7$ Hz	59.96 tt, $^1J_{\text{CH}} = 134$ Hz, $^2J_{\text{CH}} = 5$ Hz
	$\text{Ta}(\text{CH}_2\text{NCH}_2\text{CH}_2\text{CH}_3)$	1.09 m	23.51 q, $^1J_{\text{CH}} = 123$ Hz
	$\text{Ta}(\text{CH}_2\text{NCH}_2\text{CH}_2\text{CH}_3)$	0.96 t, $^3J_{\text{HH}} = 7$ Hz	12.28 q, $^1J_{\text{CH}} \approx 130$ Hz

Table I₂ (continued)

Compound	Assignment	¹ H NMR	¹³ C NMR
Cp*Me ₂ Ta(μCH ₂)(μH) ₂ TaMe ₂ Cp* (5)	C ₅ (CH ₃) ₅	1.88 s	11.19 q, ¹ J _{CH} = 127Hz
	C ₅ (CH ₃) ₅		116.59 s
	Ta(CH ₃) ₂	0.17 s	44.15 q, ¹ J _{CH} = 120Hz
	Ta(μH) ₂ Ta	9.72 t, ³ J _{HH} = 6Hz	
	Ta(μCH ₂)Ta	0.54 t, ³ J _{HH} = 6Hz	135.76 t, ¹ J _{CH} = 123Hz
Cp*Ta(NCMe ₃)Me ₂ (6)	C ₅ (CH ₃) ₅	1.83 s	11.14 q, ¹ J _{CH} = 127Hz
	C ₅ (CH ₃) ₅		115.72 s
	Ta(CH ₃) ₂	0.13 s	43.12 q, ¹ J _{CH} = 118Hz
	Ta(NCMe ₃)		64.14 s
	Ta[NC(CH ₃) ₃]	1.42 s	33.81 q-septet, ¹ J _{CH} = 125Hz, ³ J _{CH} = 4Hz
Cp*Ta(NCH ₂ CMe ₃)Me ₂ (7)	C ₅ (CH ₃) ₅	1.76 s	10.62 q, ¹ J _{CH} = 127Hz
	C ₅ (CH ₃) ₅		114.94 s
	Ta(CH ₃) ₂	0.19 s	44.36 q, ¹ J _{CH} = 118Hz
	Ta(NCH ₂ CMe ₃)	3.91 s	70.94 tm, ¹ J _{CH} = 133Hz, ³ J _{CH} = 4Hz
	Ta(NCH ₂ CMe ₃)		35.53 s
	Ta[NCH ₂ C(CH ₃) ₃]	1.13 s	27.92 qm, ¹ J _{CH} = 125Hz, ³ J _{CH} = 4Hz

Table I. (continued)

Compound	Assignment	^1H NMR	^{13}C NMR
$\text{Cp}^*\text{Ta}(\text{NMe})\text{Me}_3$ (8)	$\text{C}_5(\underline{\text{CH}_3})_5$	1.78 s	10.46 q, $^1J_{\text{CH}} = 127\text{Hz}$
	$\underline{\text{C}}_5(\text{CH}_3)_5$		114.78 s
	$\text{Ta}(\underline{\text{CH}_3})_2$	0.14 s	43.96 q, $^1J_{\text{CH}} = 118\text{Hz}$
	$\text{Ta}(\underline{\text{NCH}_3})$	3.97 s	46.43 q, $^1J_{\text{CH}} = 133\text{Hz}$
$\text{Cp}^*\text{Ta}(\text{OCHMe}_2)\text{Me}_3$ (11)	$\text{C}_5(\underline{\text{CH}_3})_5$	1.75 s	11.05 q, $^1J_{\text{CH}} = 127\text{Hz}$
	$\underline{\text{C}}_5(\text{CH}_3)_5$		115.68 s
	$\text{Ta}(\underline{\text{CH}_3})_2(\text{CH}_3)'$	} 0.45 broad s	49.91 q, $^1J_{\text{CH}} = 119\text{Hz}$
	$\text{Ta}(\text{CH}_3)_2(\underline{\text{CH}_3})'$		53.94 q, $^1J_{\text{CH}} = 120\text{Hz}$
	$\text{Ta}(\text{OCHMe}_2)$	4.53 septet, $^3J_{\text{HH}} = 6\text{Hz}$	75.71 d-septet, $^1J_{\text{CH}} = 144\text{Hz}$, $^3J_{\text{CH}} = 4\text{Hz}$
	$\text{Ta}[\text{OCH}(\underline{\text{CH}_3})_2]$	1.14 d, $^3J_{\text{HH}} = 6\text{Hz}$	24.89 q, $^1J_{\text{CH}} = 126\text{Hz}$
$\text{Cp}^*\text{Ta}(\text{OMe})\text{Me}_3$ (12) ^e	$\text{C}_5(\underline{\text{CH}_3})_5$	1.72 s	10.98 q, $^1J_{\text{CH}} = 127\text{Hz}$
	$\underline{\text{C}}_5(\text{CH}_3)_5$		115.91 s
	$\text{Ta}(\underline{\text{CH}_3})_2(\text{CH}_3)'$	} 0.46 broad s	52.46 q, $^1J_{\text{CH}} = 119\text{Hz}$
	$\text{Ta}(\text{CH}_3)_2(\underline{\text{CH}_3})'$		54.97 q, $^1J_{\text{CH}} = 119\text{Hz}$
	$\text{Ta}(\text{OCH}_3)$	3.95 s	59.92 q, $^1J_{\text{CH}} = 143\text{Hz}$

Table I. (continued)

Compound	Assignment	^1H NMR	^{13}C NMR
$\text{Cp}^*\text{Ta}(\text{CH}_2\text{CMe}_3)_3\text{Me}_3$ (13)	$\text{C}_s(\underline{\text{CH}_3})_5$	1.67 s	11.36 q, $^1J_{\text{CH}} = 128\text{Hz}$
	$\underline{\text{C}}_s(\text{CH}_3)_5$		117.93 s
	$\text{Ta}(\underline{\text{CH}_3})_3$	0.71 broad s	71.90 q, $^1J_{\text{CH}} = 119\text{Hz}$
	$\text{Ta}(\underline{\text{CH}_2\text{CMe}_3})$	0.30 broad s	74.29 t, $^1J_{\text{CH}} = 118\text{Hz}$
	$\text{Ta}(\underline{\text{CH}_2\text{CMe}_3})$		35.19 s
	$\text{Ta}[\underline{\text{CH}_2\text{C}(\text{CH}_3)_2}]$	1.35 s	35.84 q-septet, $^1J_{\text{CH}} = 124\text{Hz}$, $^3J_{\text{CH}} = 5\text{Hz}$
$\text{Cp}^*\text{Ta}(\text{CH}_2\text{C}_6\text{H}_5)_3\text{Me}_3$ (14)	$\text{C}_s(\underline{\text{CH}_3})_5$	1.66 s	11.31 q, $^1J_{\text{CH}} = 128\text{Hz}$
	$\underline{\text{C}}_s(\text{CH}_3)_5$		118.99 s
	$\text{Ta}(\underline{\text{CH}_3})_3$	0.67 s	76.3 broad q, $^1J_{\text{CH}} = 120\text{Hz}$
	$\text{Ta}(\underline{\text{CH}_2\text{C}_6\text{H}_5})$	1.63 s	96.25 t, $^1J_{\text{CH}} = 120\text{Hz}$
			148.50 s
			127.51 dd, $^1J_{\text{CH}} = 157\text{Hz}$, $^3J_{\text{CH}} = 6\text{Hz}$ 122.89 d, $^1J_{\text{CH}} = 157\text{Hz}$ 101.58 d ^c
	$\text{Ta}(\underline{\text{CH}_2\text{C}_6\text{H}_5})$	7.3 m	

Table I_c (continued)

Compound	Assignment	¹ H NMR	¹³ C NMR
Cp*Ta(NCMe ₃)H ₂ (PMe ₃) (15)	C ₅ (CH ₃) ₅	2.18 s	12.71 q, ¹ J _{CH} = 126Hz
	C ₅ (CH ₃) ₅		110.10 s
	TaH ₂	6.00 d, ² J _{PH} = 61Hz	
	Ta[P(CH ₃) ₃]	1.25 d, ² J _{PH} = 6Hz	21.28 qd, ¹ J _{CH} = 128Hz, ¹ J _{PC} = 24Hz
	Ta(NCMe ₃)		64.34 s
	Ta[NC(CH ₃) ₃]	1.22 s	34.73 q-sept, ¹ J _{CH} = 125Hz, ³ J _{CH} = 4Hz
Cp*Ta(NCMe ₃)H ₂ (PMe ₃ C ₆ H ₅) (16)	C ₅ (CH ₃) ₅	2.06 s	12.46 q, ¹ J _{CH} = 126Hz
	C ₅ (CH ₃) ₅		110.32 s
	TaH ₂	6.38 d, ² J _{PH} = 59Hz	
	Ta[P(CH ₃) ₂ C ₆ H ₅]	1.63 d, ² J _{PH} = 7Hz	21.78 qd, ¹ J _{CH} = 130Hz, ¹ J _{PC} = 25Hz
	Ta(PMe ₂ C ₆ H ₅)	{ 7.51 m	{ 138.53 d, ¹ J _{PC} = 29Hz
		{ 7.05 m	{ 131.08 dd, ^c ¹ J _{PC} = 10Hz
			{ 128.76 ^c
			{ 128.1 ^c
	Ta(NCMe ₃)		64.47 s
	Ta[NC(CH ₃) ₃]	1.30 s	34.65 qd, ¹ J _{CH} = 126Hz, ⁴ J _{PC} = 2Hz

Table I. (continued)

Compound	Assignment	¹ H NMR	¹³ C NMR
Cp*Ta(NCH ₂ CMe ₃)H ₂ (PMe ₃) (17) ^f	C ₅ (CH ₃) ₅	2.17 s	
	TaH ₂	6.37 d, ² J _{PH} = 59Hz	
	Ta[P(CH ₃) ₃]	1.23 d, ² J _{PH} = 7Hz	
	Ta(NCH ₂ CMe ₃)	3.43 d, ⁴ J _{PH} = 5Hz	
	Ta[NCH ₂ C(CH ₃) ₃]	0.99 s	
Cp*Ta(NCH ₂ CMe ₃)H ₂ (PMe ₂ C ₆ H ₅) (18)	C ₅ (CH ₃) ₅	2.02 s	11.90 q, ¹ J _{CH} = 127Hz
	C ₅ (CH ₃) ₅		109.84 s
	TaH ₂	6.62 d, ² J _{PH} = 58Hz	
	Ta[P(CH ₃) ₂ C ₆ H ₅]	1.63 d, ² J _{PH} = 7Hz	21.06 qd, ¹ J _{CH} = 130Hz, ¹ J _{CP} = 24Hz
			138.40 d, ¹ J _{CP} = 29Hz
Ta(PMe ₂ C ₆ H ₅)		{ 7.48 m	{ 131.11 dd, ¹ J _{CH} = 155Hz, ¹ J _{CP} = 9Hz
		{ 7.03 m	{ 128.83 dd, ^c J _{CP} = 2Hz
Ta(NCH ₂ CMe ₃)		3.10 d, ⁴ J _{PH} = 5Hz	128.2 d, ¹ J _{CH} = 160Hz
			72.14 td, ¹ J _{CH} = 131Hz, ⁵ J _{CP} = 2Hz
Ta(NCH ₂ CMe ₃)		1.02 s	32.70 s
	Ta[NCH ₂ C(CH ₃) ₃]		27.63 q-septet, ¹ J _{CH} = 124Hz, ³ J _{CH} = 4Hz

Table I. (continued)

Compound	Assignment	^1H NMR	^{13}C NMR
$\text{Cp}^*\text{Ta}(\text{N}(\underline{\text{C}}\text{H}_3)_2)(\text{O}(\underline{\text{C}}\text{H}\text{Me}_2)_2)$ (19) ^f	$\text{C}_s(\underline{\text{C}}\text{H}_3)_5$	2.05 s	
	$\text{Ta}(\text{O}(\underline{\text{C}}\text{H}\text{Me}_2)_2)$	4.87 septet, $^3J_{\text{HH}}=6\text{Hz}$	
	$\text{Ta}[\text{O}(\underline{\text{C}}\text{H}(\underline{\text{C}}\text{H}_3)_2)_2]$	1.30 d, $^3J_{\text{HH}}=6\text{Hz}$	
	$\text{Ta}[\text{N}(\underline{\text{C}}\text{H}_3)_2]$	1.29 s	
$\text{Cp}^*\text{Ta}(\text{N}(\underline{\text{C}}\text{H}_2\text{CMe}_3)(\text{O}(\underline{\text{C}}\text{H}\text{Me}_2)_2)$ (20)	$\text{C}_s(\underline{\text{C}}\text{H}_3)_5$	2.00 s	10.75 q, $^1J_{\text{CH}}=127\text{Hz}$
	$\underline{\text{C}}_s(\underline{\text{C}}\text{H}_3)_5$		116.11 s
	$\text{Ta}(\text{O}(\underline{\text{C}}\text{H}\text{Me}_2)_2)$	4.86 septet, $^3J_{\text{HH}}=6\text{Hz}$	76.37 dm, $^1J_{\text{CH}}=142\text{Hz}$, $J_{\text{CH}}=4\text{Hz}$
	$\text{Ta}[\text{O}(\underline{\text{C}}\text{H}(\underline{\text{C}}\text{H}_3)(\underline{\text{C}}\text{H}_3)')_2]$	1.30 d, $^3J_{\text{HH}}=6\text{Hz}$	27.61 qm, $^1J_{\text{CH}}=125\text{Hz}$, $J_{\text{CH}}=5\text{Hz}$
	$\text{Ta}[\text{O}(\underline{\text{C}}\text{H}(\underline{\text{C}}\text{H}_3)(\underline{\text{C}}\text{H}_3)')_2]$	1.27 d, $^3J_{\text{HH}}=6\text{Hz}$	27.17 q, $^1J_{\text{CH}}=125\text{Hz}$
	$\text{Ta}(\text{N}(\underline{\text{C}}\text{H}_2\text{CMe}_3)$	3.93 s	69.91 t, $^1J_{\text{CH}}=129\text{Hz}$
	$\text{Ta}(\text{N}(\underline{\text{C}}\text{H}_2\text{CMe}_3)$		33.59 s
	$\text{Ta}[\text{N}(\underline{\text{C}}\text{H}_2\text{C}(\underline{\text{C}}\text{H}_3)_3)]$	1.02 s	27.61 qm, $^1J_{\text{CH}}=125\text{Hz}$, $J_{\text{CH}}=5\text{Hz}$

Table I. (continued)

Compound	Assignment	¹ H NMR	¹³ C NMR
Cp*Ta(CH ₂ NMe)Me(PMe ₃)H (21) ^E	C ₅ (CH ₃) ₅	1.93 s	11.66 q, ¹ J _{CH} = 127Hz
	C ₅ (CH ₃) ₅		111.00 s
	Ta(CH ₃)	-0.41 dd, ³ J _{PH} = 15Hz, ³ J _{HH} = 5Hz	18.66 qd, ^C ₂ ² J _{CP} = 11Hz
	Ta[P(CH ₃) ₃]	1.16 d, ² J _{PH} = 7Hz	17.92 qdm, ¹ J _{CH} = 128Hz, ¹ J _{CP} = 22Hz, ³ J _{CH} = 4Hz
	TaH	5.75 dq, ² J _{PH} = 60Hz, ³ J _{HH} = 5Hz	
	Ta(CHH'NMe)	{ 2.28 m 1.42 m	46.35 td, ¹ J _{CH} = 152Hz, ² J _{CP} = 17Hz
	Ta(CH ₂ NCH ₃)	3.62 s	46.60 qd, ¹ J _{CH} = 134Hz, ³ J _{CP} = 4Hz
	C ₅ (CH ₃) ₅	1.84 s	10.68 q, ¹ J _{CH} = 127Hz
	C ₅ (CH ₃) ₅		114.82 s
	Ta(CH ₃)	0.57 s	24.11 q, ¹ J _{CH} = 119Hz
Cp*Ta(CH ₂ NMe)Me(OCHMe ₂) (22)	Ta(OCHMe ₂)	4.23 septet, ³ J _{HH} = 6Hz	74.79 d-septet, ¹ J _{CH} = 144Hz, ² J _{CH} = 4Hz
	Ta[OCH(CH ₃)(CH ₃)']	0.93 ^h d, ³ J _{HH} = 6Hz	26.06 dq, ¹ J _{CH} = 126Hz, ³ J _{CH} = 5Hz
	Ta[OCH(CH ₃)(CH ₃)']	0.93 ^h d, ³ J _{HH} = 6Hz	25.89 dq, ¹ J _{CH} = 126Hz, ³ J _{CH} = 5Hz
	Ta(CHH'NMe)	{ 1.02 d, ² J _{HH} = 4Hz 1.44 d, ² J _{HH} = 4Hz	37.12 t, ¹ J _{CH} = 153Hz
	Ta(CH ₂ NCH ₃)	3.80 s	42.66 q, ¹ J _{CH} = 133Hz

Table I. (continued)

^aNMR spectra taken in benzene-d₆ solvent at 34° unless otherwise noted. Chemical shifts in δ measured from internal TMS. Long-range ¹³C-¹H coupling is reported only when a coupling constant could be determined from the pattern. For data on compounds 9 and 10, see refs. 17 and 34.

^bSpectra obtained at -40°C in toluene-d₈.

^cChemical shift determined from a proton decoupled spectrum. Coupling constant(s) could not be determined due to overlapping resonances or insufficient signal to noise in the gated decoupled spectrum.

^dSpectra obtained at 3°C.

^e¹³C NMR spectrum obtained at 0°C. The three tantalum-bound methyl groups are involved in a fluxional process with a coalescence temperature of 40°C in the ¹³C NMR.

^fA ¹³C NMR spectrum was not obtained for this compound.

^gThe ³¹P NMR spectrum with selective proton decoupling at 1.16 δ (P(CH₃)₃) is a doublet of quartets.

^hResonances separated by 0.003 ppm; resolved only at 500 MHz.

EXPERIMENTAL

All manipulations were carried out using either high vacuum line or glove box techniques, as previously described.³³ IR spectra were obtained on Nujol mulls unless indicated otherwise, and are reported in cm^{-1} . Molecular weights were determined either by osmometry (by Alfred Bernhardt Analytische Laboratorien) or by isothermal distillation using the Singer method.⁵² Methanol, isopropanol, acetone, dimethylamine (Eastman Kodak), methyl-n-propylamine (Pfaltz and Bauer), t-butylamine, and neopentylamine were stored over 4Å molecular sieves and vacuum transferred prior to use. Methylamine (Matheson) and dimethylamine-d₆ (Merck) were used without further purification. NaOCHMe_2 was prepared from sodium and isopropanol; lithium alkoxides and amides were prepared by the following procedure, described for LiNHMe . n-Butyllithium (1.55 M in hexane, 90 mL, 0.14 mole) was transferred via syringe to a frit apparatus and filtered. The solution was cooled to -80°C , 30 mL petroleum ether added, and H_2NMe (7 mL at -80°C , ~ 0.16 mole) added. After warming to 25°C , the white solid (LiNHMe) was isolated by filtration, washed once with petroleum ether/hexane, and dried in vacuo for 16 hr, 5.25 g (0.14 mole, 100%). Neopentyl-lithium was prepared from neopentylchloride and lithium and was re-crystallized from heptane. Benzylpotassium was prepared from toluene, butyllithium and potassium t-butoxide. $\text{Cp}^*\text{TaMe}_3\text{Cl}$ (1) was prepared by a published procedure.¹⁰ Many of the syntheses reported proceed quantitatively (by NMR) but the isolated yields are often low because the compounds are extremely soluble in hydrocarbon solvents.

Cp*Ta(NMe₂)Me₃ (2). Cp*TaMe₃Cl (1, 0.50 g) and LiNMe₂ (0.065 g) were stirred in 20 mL diethyl ether (Et₂O) at -80°C for one hour, warmed to 0°C for 5 min and the solvent removed. Recrystallization from petroleum ether, keeping the solution as cold as possible at all times, gave 0.275 g (50%) of a bright-yellow solid, 90% 2 and 10% 3 by NMR. 2 is completely decomposed after 24 hrs in the solid state at 25°C. IR 1310, 1290, 1020, 950, 715, 685, 495, 420.

Kinetic Measurements. The kinetics of decomposition of 2 and 2-d₆ were followed by ¹H NMR spectroscopy, monitoring the disappearance of the N(CH₃)₂ and/or Ta(CH₃)₂(CH₃)' resonances. All of the kinetic runs obeyed first-order kinetics for > 3 half lives (see fig. 1). The probe temperature was measured before and after each run using both MeOH and HOCH₂CH₂OH; values were 33.5°C (± 1). Two runs on samples from the same batch of 2-d₆ yielded rate constants of 5.57 and 5.65 × 10⁻⁴ sec⁻¹ and two runs on samples from different preparations of 2-d₆ gave k = 5.84 and 5.70 × 10⁻⁵ sec⁻¹.

Cp*Ta(CH₂NMe)Me₂ (3). Cp*TaMe₃Cl (1, 2.0 g) and LiNMe₂ (0.28 g) were stirred in 80 mL Et₂O at 25°C for 2 hr, the solvent removed, and recrystallization from petroleum ether gave yellow-orange 3 (1.37 g, 70%). IR 1265 (st, ν CN), 1150, 1030, 910, 490. Anal. Calcd for C₁₄H₂₆TaN: C, 43.19; H, 6.73; Ta, 46.48; N, 3.60. Found: C, 43.02; H, 6.57; Ta, 46.67; N, 3.75. Molecular weight (C₆H₆, Bernhardt) calcd: 389; found: 406.

Cp*Ta(CH₂NCH₂CH₂CH₃)Me₂ (4). Cp*TaMe₃Cl (1, 0.50 g) and LiN(Me)CH₂CH₂CH₃ (0.11 g) were stirred in 10 mL of benzene for a day.

The solvent was removed, petroleum ether added, the solution filtered and the petroleum ether removed, leaving an orange oil containing 4 (70% pure by NMR). IR (C_6D_6) 1245 (st, ν CN), 1155, 1030, 965, 920, 860.

$Cp^*Me_2Ta(\mu CH_2)(\mu H)_2TaMe_2Cp^*$ (5). Cp^*TaMe_3Cl (1, 0.50 g) and $LiN(CHMe_2)_2$ (0.14 g) were stirred in 20 mL of toluene for 2.5 hr at $0^\circ C$ and 10 min at 25° . After removal of the solvent, recrystallization from petroleum ether gave rust colored 5, 45 mg (10%). Methane (0.22 mmole, 0.17 equivalents) was evolved in this reaction (by Toepler pump). IR 1260, 1145, 1025, 800, 770, 480, 440. Anal. Calcd for $C_{25}H_{46}Ta_2$: C, 42.38; H, 6.54; Ta, 51.08. Found: C, 42.21; H, 6.36; Ta, 51.30. Molecular weight (C_6H_6 , Bernhardt) calcd: 709; found: 1390, 1420; in view of the instability of 5, this value may be questionable.

$Cp^*Ta(NCMe_3)Me_2$ (6). Cp^*TaMe_3Cl (1, 1.00 g) and $LiNHCMe_3$ (0.22 g) were stirred in 80 mL Et_2O for 15 min. The volatiles were removed, petroleum ether added, the solution filtered, and the solid obtained on removal of the petroleum ether was sublimed ($25^\circ C$, 10^{-4} torr) to give light yellow 6 (0.85 g, 81%). Melting point IR 1280 (st, ν TaNC), 1215, 1150, 1025, 800, 725, 525, 500. Anal. calcd for $C_{16}H_{30}NTa$: C, 46.04; H, 7.25; N, 3.36. Found: C, 45.94; H, 7.01; N, 3.22. Molecular weight (C_6H_6) calcd: 417; found, 1300 (Bernhardt), 520 (Singer method).

$Cp^*Ta(NCH_2CMe_3)Me_2$ (7). Cp^*TaMe_3Cl (1, 0.50 g) and $LiN(H)CH_2CMe_3$ (0.13 g) were stirred in 30 mL Et_2O at $25^\circ C$ for 30 min. After removing the volatiles, recrystallization from petroleum ether

yielded yellow 7 (0.20 g, 37%). 7 sublimes at 40°C, 10⁻⁴ torr. IR 1290 (st, ν TaNC), 1210, 1155, 1025, 800, 725, 525, 500. Anal. Calcd for C₁₇H₃₂NTa: C, 47.33; H, 7.48; N, 3.25. Found: C, 47.08; H, 7.30; N, 3.18. Molecular weight (C₆H₆) calcd: 431; found, 1377 (Bernhardt).

Cp*Ta(NMe)Me₂ (8). Cp*TaMe₃Cl (1, 170 mg) and LiNHMe (23 mg) were stirred in 20 mL Et₂O at 25°C for 10 min. The volatiles were removed, benzene added and the suspension filtered to give a yellow solution containing 70% 8 and 30% 9 (by NMR). IR (C₆D₆) 1295 (st, ν TaNC), 1160, 1030, 790.

Cp*Ta(OCMe₃)Me₃ (10) has been previously reported.³⁴

Cp*Ta(OCHMe₂)Me₃ (11). Cp*TaMe₃Cl (1, 0.50 g) and NaOCHMe₂ (0.12 g) were stirred in 40 mL Et₂O for 3 hr. After removing the solvent, recrystallization from petroleum ether gave 0.22 g of yellow 11 (42%). An additional 0.1 g of slightly impure 11 was obtained by sublimation of the recrystallization residue (50°C, 10⁻⁴ torr). IR 1190, 1120 (st), 1015 (st), 850, 580, 465. Anal. Calcd for C₁₆H₃₁OTa: C, 45.72; H, 7.43. Found: C, 45.64; H, 7.24.

Cp*Ta(OMe)Me₃ (12). Cp*TaMe₃Cl (1, 215 mg) and LiOMe (30 mg) were stirred in 70 mL Et₂O for 2 hr at 25°C. The solvent was removed, benzene added, and after filtration removal of the benzene left 12, >90% pure by NMR. IR (C₆D₆) 1190, 1120 (st), 1030, 790, 650.

Cp*Ta(CH₂CMe₃)Me₃ (13). Cp*TaMe₃Cl (1, 0.50 g) and LiCH₂CMe₃ (0.10 g) were stirred for 1½ hr in petroleum ether. After filtration, 0.07 g of yellow 13 (13%) was crystallized from this solution. IR (C₆D₆) 1250, 1160, 1025, 860, 680.

Cp*Ta(CH₂C₆H₅)Me₃ (14). A solution of Cp*TaMe₃Cl (1, 0.25 g) and KCH₂C₆H₅ (0.10 g) in 15 mL toluene was stirred at -80°C for an hour and at 0°C for an hour. After filtration, red-brown 14 (0.13 g, 43%) was crystallized from petroleum ether/toluene. 14 sublimes with decomposition (80°C, 10⁻⁴ torr). IR 1600, 1200, 1170, 1160, 1055, 1030, 800, 765, 750, 700.

Cp*Ta(NCMe₃)H₂(PMe₃) (15). A thick-walled glass reaction vessel with Teflon needle valve, charged with Cp*Ta(NCMe₃)Me₂ (6, 0.523 g, 1.25 mmole), PMe₃ (310 torr in 104.8 mL, 1.75 mmole), 10 mL benzene, and 4 atm H₂, was stirred at 80°C for 11 days. The volatiles were removed and recrystallization from petroleum ether gave 0.17 g of white solid, 15 (29%). IR 1700-1650 (ν TaH), 1270 (st, ν TaNC), 1210, 1030, 955, 935, 720.

Cp*Ta(NCMe₃)H₂(PMe₂C₆H₅) (16). A high pressure reactor, charged with 1.8 g of Cp*Ta(NCMe₃)Me₂ (6), 0.8 mL PMe₂C₆H₅, 40 mL benzene, and 700 psi H₂, was stirred for four days at 85°C. The solution was transferred to a fritted apparatus, filtered, and dried in vacuo for 24 hr. The residue was treated with 5 mL hexamethyl-disiloxane (Me₃SiOSiMe₃) and filtered to give 0.84 g of white 16 (37%). 16 can be recrystallized from benzene/petroleum ether. IR 1715, 1660 (ν TaH), 1270 (st, ν TaNC), 1210, 1030, 950, 930, 900, 795, 710, 690, 490. Anal. Calcd for C₂₂H₃₇NPTa: C, 50.10; H, 7.07; Ta, 34.30. Found: C, 49.95; H, 6.97; Ta, 34.52.

$\text{Cp}^*\text{Ta}(\text{NCH}_2\text{CMe}_3)\text{H}_2(\text{PMe}_3)$ (17). An NMR tube sealed to a ground glass joint was loaded with $\text{Cp}^*\text{Ta}(\text{NCH}_2\text{CMe}_3)\text{Me}_2$ (7, 15 mg, 0.035 mmole), PMe_3 (43 torr in 19.8 mL, 0.046 mmole) and 0.3 mL benzene- d_6 . The tube was cooled to 77°K, one atmosphere of H_2 introduced and the tube sealed with a torch. After two weeks at 80°C, the volatiles were removed leaving 17.

$\text{Cp}^*\text{Ta}(\text{NCH}_2\text{CMe}_3)\text{H}_2(\text{PMe}_2\text{C}_6\text{H}_5)$ (18). A high pressure reactor, charged with 2.1 g $\text{Cp}^*\text{Ta}(\text{NCH}_2\text{CMe}_3)\text{Me}_2$ (7), 0.99 mL $\text{PMe}_2\text{C}_6\text{H}_5$, 50 mL benzene, and 1200 psi H_2 , was stirred at 80°C for five days. After removing the volatiles and drying in vacuo for 36 hr, recrystallization of the residue yielded 1.20 g of white solid, 18 (46%). IR 1720-1650 (ν TaH), 1275 (st, ν TaNC), 1205, 1025, 940, 900, 835, 740, 715, 695, 490. Anal. Calcd for $\text{C}_{23}\text{H}_{39}\text{NPTa}$: C, 51.02; H, 7.26; Ta, 33.42. Found: C, 50.94; H, 7.08; Ta, 33.41. Molecular weight (C_6H_6 , Singer method) calcd: 542; found 550.

$\text{Cp}^*\text{Ta}(\text{NCMe}_3)(\text{OCHMe}_2)_2$ (19). An NMR tube sealed to a ground glass joint was loaded with $\text{Cp}^*\text{Ta}(\text{NCMe}_3)\text{H}_2(\text{PMe}_2\text{C}_6\text{H}_5)$ (16, 75 mg, 0.038 mmole), acetone (59 torr in 25.3 mL, 0.080 mmole), and 0.3 mL benzene- d_6 , and sealed with a torch. After three days at 25°C and an hour at 80°C, the volatiles were removed leaving 19. IR (C_6H_6) 1275 (st, ν TaNC), 1215, 1120, 1030, 995, 980, 845, 740.

$\text{Cp}^*\text{Ta}(\text{NCH}_2\text{CMe}_3)(\text{OCHMe}_2)_2$ (20). 20 was prepared from $\text{Cp}^*\text{Ta}(\text{NCH}_2\text{CMe}_3)\text{H}_2(\text{PMe}_2\text{C}_6\text{H}_5)$ (18, 75 mg, 0.14 mmole) and acetone (150 torr in 33 mL, 0.27 mmole) by a procedure analogous to the synthesis of 19. IR (C_6H_6) 1280 (st, ν TaNC), 1120, 995, 980, 860, 840, 585.

Cp*Ta(CH₂NMe)Me(PMe₃)H (21). A thick walled glass reaction vessel with Teflon needle valve, charged with 1.86 g Cp*Ta(CH₂NMe)Me₂ (3, 4.78 mmole), 5 mL benzene, PMe₃ (1100 torr in 104 mL, 6.15 mmole), and 4 atm of H₂, was stirred at 25°C for 24 hr. After removing the volatiles, recrystallization from petroleum ether gave 1.01 g of red 21 (39%). IR 1680 (ν TaH), 1490, 1280, 1240 (st), 1025, 955 (st), 935, 900, 720, 665, 480, 450. Anal. Calcd for C₁₈H₃₃NPTa: C, 42.58; H, 7.37; N, 3.10. Found: C, 42.35; H, 7.15; N, 2.91. Molecular weight (C₆H₆, Bernhardt) calcd: 451, found: 478.

Cp*Ta(CH₂NMe)Me(OCHMe₂) (22). A solution of Cp*Ta(CH₂NMe)Me(PMe₃)H (21, 25 mg, 0.046 mmole) and acetone (41 torr in 25.3 mL, 0.056 mmole) in 10 mL petroleum ether was stirred at -80°C for 30 min and at 25°C for 30 min. Removal of the volatiles left 22, 70% pure (by NMR). 22 is extremely soluble in hydrocarbon solvents. IR (C₆D₆) 1270, 1160, 1130 (st), 1000 (st), 970, 905, 850, 620.

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(36) 3 binds trimethylphosphine weakly since the resonances in the ^1H NMR spectrum of 3 are shifted up to 1 ppm on addition of one or two equivalents of PMe_3 , but the PMe_3 resonance is unshifted from free PMe_3 . Evaporation of the PMe_3 regenerates the spectrum of 3.

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(44) The decomposition of tantalum (V) alkyls to alkylidene complexes is also described as an α -elimination process.⁹

(45) Since the α -abstraction reactions are facile, it is tempting to view the β -hydrogen transfer reactions (e.g., eq 2) as proceeding by a similar mechanism.

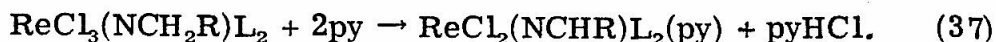
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CHAPTER V

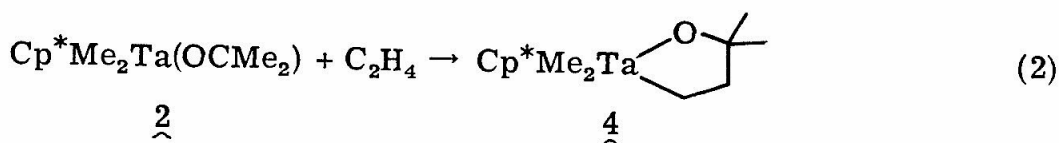
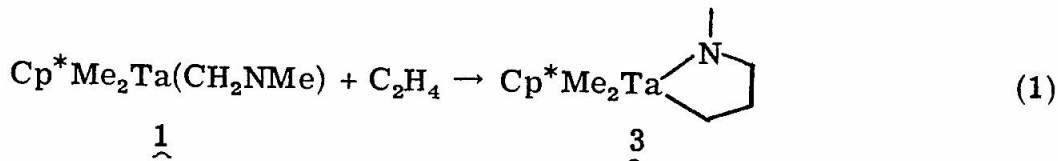
Metallacycle Forming Reactions of
Tantalum Imine and Acetone Complexes

INTRODUCTION

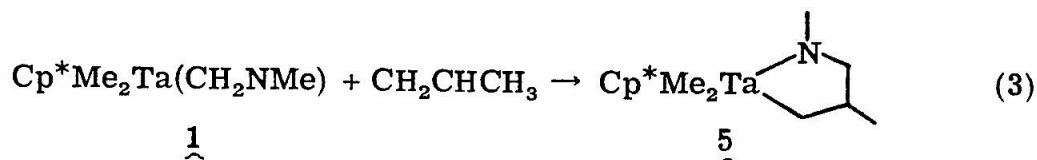
The coupling of two olefins by a transition metal center to form a metallacyclopentane has been studied in a number of systems.¹⁻⁶ In contrast, the analogous reaction of hetero-olefins (aldehydes, ketones, imines, etc.) remains largely unexplored.⁷⁻¹¹ In fact, the chemistry of π -bound hetero-olefin complexes has received little attention.⁹⁻¹² This chapter reports a number of metallacycle forming reactions of tantalum imine and acetone complexes.

RESULTS

$\text{Cp}^*\text{Me}_2\text{Ta}(\text{CH}_2\text{NMe})$ ¹³ (1) and $\text{Cp}^*\text{Me}_2\text{Ta}(\text{OCMe}_2)$ ¹⁴ (2) both react rapidly and quantitatively with ethylene at 25 °C to form hetero-metallacycle products 3 and 4 (eq. 1 and 2). $\text{Cp}^*\text{Me}_2\text{Ta}$ (metallacycle)

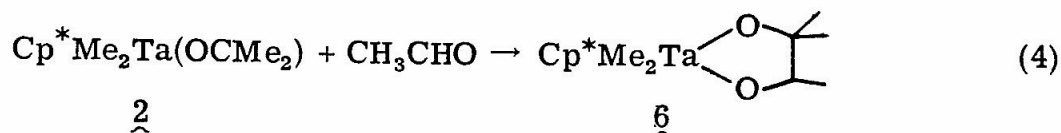


compounds undoubtedly have 'four-legged-piano-stool' geometries, similar to the structures of $\text{Cp}^*\text{Cl}_2\text{Ta}$ (metallacycle) derivatives determined by X-ray diffraction.¹⁵ Proton and carbon-13 NMR spectroscopies are the principal characterization of the metallacycle complexes (see Table I; IR spectra and analytical data are listed in the experimental section). For example, the ¹H NMR spectrum of 3 contains two triplet resonances each coupled to a triplet of triplets pattern. Together with the observation of three methylene groups in the ¹³C NMR spectrum, these data clearly indicate a CH₂CH₂CH₂ linkage and therefore the structure drawn in eq. 1. The NMR spectra for 3 and 4 also indicate that these molecules are highly fluxional at ambient temperatures, since, for example, the two methyl groups on the tantalum are equivalent in each case.¹⁶ The reactions of 1 with other olefins have also been examined: propylene slowly forms a metallacycle at 25 °C (5, eq 3), but isobutylene is unreactive after days at 80 °C.

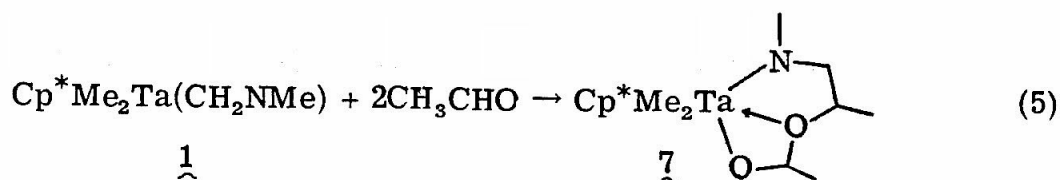


The ^{13}C NMR spectrum of 5 at ambient temperatures exhibits broad resonances due to a fluxional process, but at -60°C this is slowed sufficiently to allow observation of two isomers of 5, both of which appear to have the methyl substituent on the β carbon. Neither 1 nor 2 reacts with dimethylacetylene or *t*-butylacetylene, even at 80°C .

The reaction of 2 with acetaldehyde rapidly yields a pinacolate type complex 6 (eq 4). 1 reacts rapidly with two molecules of acetalde-

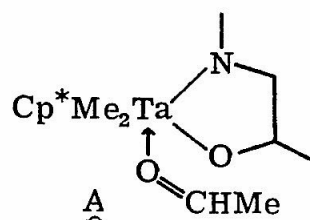


hyde and appears to form an unusual seven-membered metallacycle (7, eq 5).¹⁷ If only one equivalent of CH_3CHO is used, a mixture is

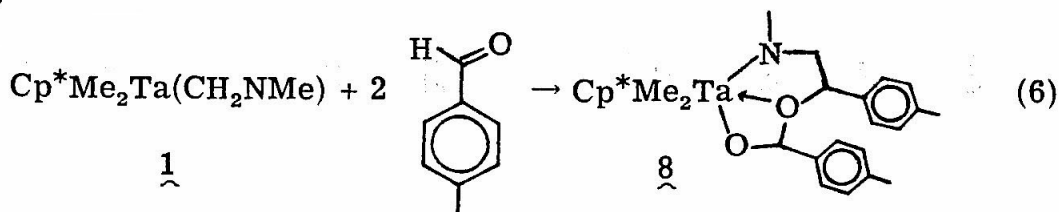


produced with comparable amounts of 1, 7, and what appears to be a mono-aldehyde complex analogous to 6. The ^1H and ^{13}C NMR spectra of 7 indicate that there are two different CH_3CHO groups present. The formation of the C-C bond in the metallacycle is clearly implied by the H-H coupling observed in the proton NMR spectrum, for example, the methylene hydrogens are each doublets of doublets. There is, however, no

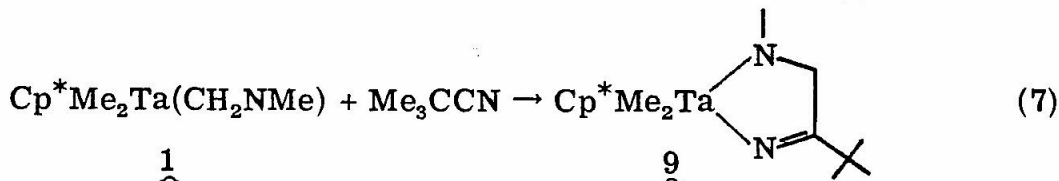
direct spectroscopic evidence for the formation of the C-O bond in the proposed structure. A simple O-bound aldehyde complex (A, below) is unlikely since the IR spectrum of 7 does not have a high energy C=O



stretch¹⁸ and acetaldehyde is not displaced from 7 by trimethylphosphine, water, methanol, or HCl. Thus the second CH₃CHO appears to be incorporated into the metallacycle. The chemical shifts in the NMR spectra also seem to be most consistent with this formulation.¹⁹ Other aldehydes appear to react similarly with 1 and a para-tolualdehyde derivative (8) has been isolated (eq 6).²⁰ 1 reacts readily with acetone, but a mixture of products is formed; 2 does not react with acetone at 80°C.²¹

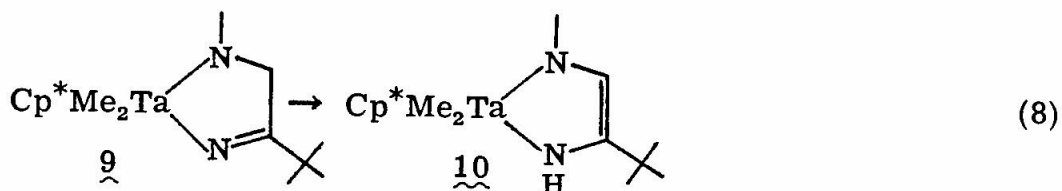


t-Butylnitrile slowly adds to 1 at ambient temperatures giving a metallacycle product with a carbon nitrogen double bond (9, eq 7), but

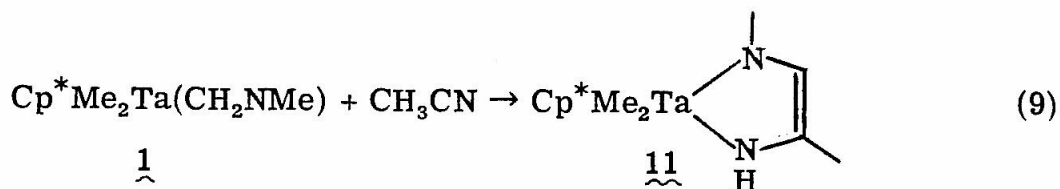


this is unstable and rearranges to a diamide metallacycle 10 by a

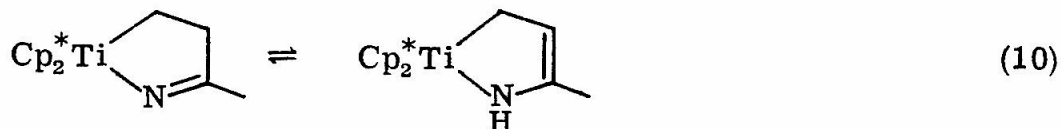
formal 1,3 hydrogen shift (eq 8). The reaction of 1 with acetonitrile



gives a rearranged product directly and an intermediate analogous to 9 is not observed (eq 9). A similar isomerization has been observed

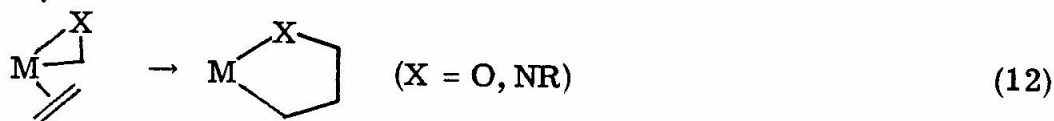


in a titanium system, as shown in eq. 10. Surprisingly, 2 does not react with acetonitrile.



DISCUSSION

Metal-olefin complexes are usually described by two limiting resonance structures, a π complex (I), or a metallacycle (II, fig. 1). Compounds 1 and 2 appear to be much better represented as three-atom metallacycles because they have low C-X stretching frequencies (1: $\nu_{CN} = 1265 \text{ cm}^{-1}$, 2: $\nu_{CO} = 1200 \text{ cm}^{-1}$), high field NMR chemical shifts for the carbon in the ring (1: 65δ , 2: 111δ),¹⁹ and 1 has a proton NMR spectrum inconsistent with resonance form I.^{13,14} Since the coupling of two olefins is normally visualized as drawn in eq. 11, it is not obvious that 1 and 2 will undergo a similar reaction (eq. 12).²²



However, 1 and 2 react readily with unsaturated organic molecules, and this chemistry is in many ways analogous to that of a titanium ethylene complex.³ Thus the better valence bond resonance structure for these compounds does not give a good indication of their reactivity.²³ On the other hand, thermodynamic considerations suggest that the complexes best described by resonance form II should be the most reactive since the factors that stabilize II over I will strongly stabilize the five-atom metallacycle products.

The reactions of 1 and 2 are clearly influenced by the formation of strong tantalum-nitrogen and tantalum-oxygen bonds,²⁴ since only metallacycles with the heteroatoms bound to the metal are produced.

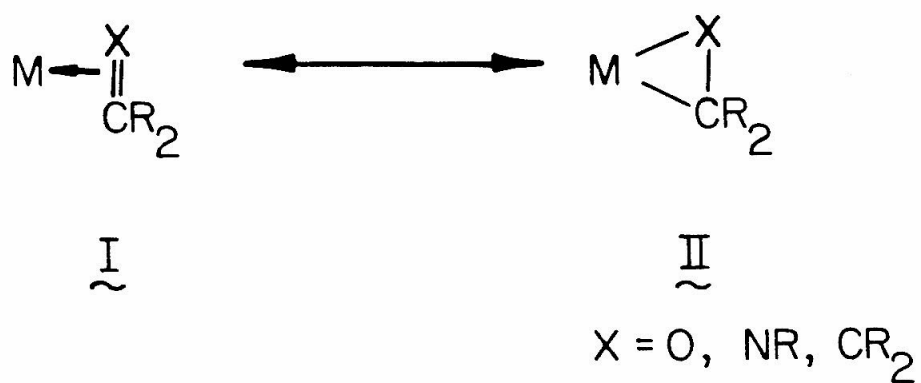
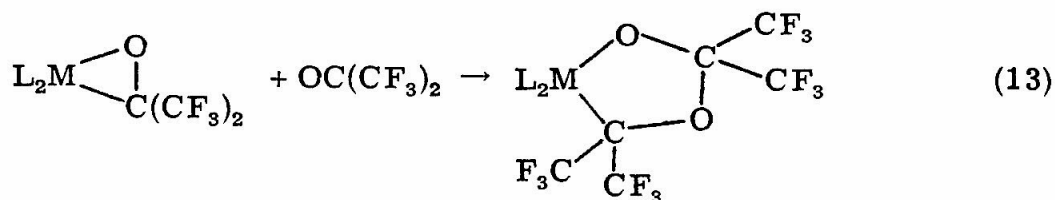


Figure 1. Resonance structures for transition metal olefin complexes.

In contrast, 'head-to-tail' metallacycles are formed by nickel, palladium, and platinum complexes (eq 13),⁹ presumably because the M-O and M-C bond strengths are more comparable for these



elements.^{24, 25} Steric effects are also important in this chemistry, as evidenced by the rapid reaction of 1 with ethylene while isobutylene is inert. On the other hand, there are still many aspects of the reactivity of these compounds that are not well understood, for example, the lack of reaction of 2 with acetonitrile.

Table I. ^1H and ^{13}C NMR Data^a

Compound	Assignment	^1H NMR chemical shift multiplicity, coupling constant	^{13}C NMR chemical shift multiplicity, coupling constant
$\text{Cp}^*\text{Me}_2\text{Ta}(\text{NMeCH}_2\text{CH}_2\text{CH}_2) \text{ (3)}$	$\text{C}_5(\underline{\text{CH}}_3)_5$	1.71 s	10.89 q, $^1J_{\text{CH}} = 127\text{Hz}$
	$\underline{\text{C}}_5(\text{CH}_3)_5$		115.98 s
	$\text{Ta}(\underline{\text{CH}}_3)_2$	0.41 s	57.62 q, $^1J_{\text{CH}} = 119\text{Hz}$
	$\text{Ta}[\text{N}(\underline{\text{CH}}_3)\text{CH}_2\text{CH}_2\text{CH}_2]$	2.53 s	42.15 q, $^1J_{\text{CH}} = 133\text{Hz}$
	$\text{Ta}(\text{NMe}\underline{\text{C}}\text{H}_2\text{CH}_2\text{CH}_2)$	3.58 t, $^3J_{\text{HH}} = 6\text{Hz}^b$	65.81 t, $^1J_{\text{CH}} = 140\text{Hz}$
	$\text{Ta}(\text{NMe}\underline{\text{C}}\text{H}_2\text{CH}_2\text{CH}_2)$	2.94 tt, $^3J_{\text{HH}} = 6 \text{ \& } 6\text{Hz}^b$	31.30 t, $^1J_{\text{CH}} = 127\text{Hz}$
	$\text{Ta}(\text{NMe}\underline{\text{C}}\text{H}_2\text{CH}_2\text{CH}_2)$	1.16 t, $^3J_{\text{HH}} = 6\text{Hz}^b$	69.90 t, $^1J_{\text{CH}} = 120\text{Hz}$
$\text{Cp}^*\text{Me}_2\text{Ta}(\text{OCMe}_2\text{CH}_2\text{CH}_2) \text{ (4)}^c$	$\text{C}_5(\underline{\text{CH}}_3)_5$	1.77 s	11.20 q, $^1J_{\text{CH}} = 127\text{Hz}$
	$\underline{\text{C}}_5(\text{CH}_3)_5$		116.90 s
	$\text{Ta}(\underline{\text{CH}}_3)_2$	0.41 s	59.44 q, $^1J_{\text{CH}} = 119\text{Hz}$
	$\text{Ta}[\text{OC}(\underline{\text{CH}}_3)_2\text{CH}_2\text{CH}_2]$		87.74 s
	$\text{Ta}[\text{OC}(\underline{\text{CH}}_3)_2\text{CH}_2\text{CH}_2]$	1.43 s	30.14 qq, $^1J_{\text{CH}} = 125\text{Hz}$, $^3J_{\text{CH}} = 4\text{Hz}$
	$\text{Ta}(\text{OCMe}_2\text{CH}_2\text{CH}_2)$	2.90 t, $^3J_{\text{HH}} = 7\text{Hz}^b$	51.63 t, $^1J_{\text{CH}} = 124\text{Hz}$
	$\text{Ta}(\text{OCMe}_2\text{CH}_2\text{CH}_2)$	1.29 t, $^3J_{\text{HH}} = 7\text{Hz}^b$	66.11 t, $^1J_{\text{CH}} = 122\text{Hz}$

Table I_x (continued)

Compound	Assignment	¹ H NMR	¹³ C NMR	
Cp [*] Me ₃ Ta(NMeCH ₂ CHMeCH ₂) (5) ^d	C ₅ (CH ₃) ₅	1.68 s	11.04 q, ¹ J _{CH} = 127Hz	
	C ₅ (CH ₃) ₅		115.40 s	
	Ta(CH ₃)(CH ₃)'	0.52 s	57.15 q, ¹ J _{CH} = 127Hz	
	Ta(CH ₃)(CH ₃)'	0.35 s	56.71 q, ¹ J _{CH} = 116Hz	
	Ta [N(CH ₃)CH ₂ CHMeCH ₂]	2.50 s	41.46 q, ¹ J _{CH} = 133Hz	
	Ta (NMeCH ₂ CHMeCH ₂)	f	72.19 ^e -t, ¹ J _{CH} = 120Hz	
	Ta (NMeCH ₂ CHMeCH ₂)	f	36.30 d, ¹ J _{CH} = 126Hz	
	Ta [NMeCH ₂ CH(CH ₃)CH ₂]	1.37 d, ³ J _{HH} = 4Hz	26.16 q, ¹ J _{CH} = 124Hz	
	Ta (NMeCH ₂ CHMeCH ₂)	f	77.43 ^e -t, ¹ J _{CH} = 120Hz	
	Cp [*] Me ₃ Ta(OCMe ₂ CHMeO) (6) ^e	C ₅ (CH ₃) ₅	1.81 s	10.97 q, ¹ J _{CH} = 128Hz
		C ₅ (CH ₃) ₅		119.14 s
Ta(CH ₃)(CH ₃)		0.46 q, ⁴ J _{HH} = 1Hz	61.33 q, ¹ J _{CH} = 119Hz	
Ta(CH ₃)(CH ₃)		0.28 q, ⁴ J _{HH} = 1Hz	53.22 q, ¹ J _{CH} = 120Hz	
Ta(OCMe ₂ CHMeO)			93.36 s	
Ta [OC(CH ₃)(CH ₃)CHMeO]		1.31 s	29.52 q-quintet, ¹ J _{CH} = 125Hz, ¹ J _{CH} = 4Hz	
Ta [OC(CH ₃)(CH ₃)CHMeO]		1.35 s	23.49 q-quintet, ¹ J _{CH} = 126Hz, ¹ J _{CH} = 4Hz	
Ta(OCMe ₂ CHMeO)		4.79 q, ³ J _{HH} = 6Hz	93.36 d, ¹ J _{CH} = 137Hz	
Ta [OCMe ₂ CH(CH ₃)O]		1.23 d, ³ J _{HH} = 6Hz	20.28 q, ¹ J _{CH} = 126Hz	

Table I₂ (continued)

Compound	Assignment	¹ H NMR	¹³ C NMR
Cp*Me ₃ Ta[NMeCH ₂ CHMeOCHMeO] (7)	C ₅ (CH ₃) ₅	1.91 s	10.99 q, ¹ J _{CH} = 127Hz
	C ₅ (CH ₃) ₅		118.82 s
	Ta(CH ₃)(CH ₃)	-0.19 s	43.67 q, ¹ J _{CH} = 117Hz
	Ta(CH ₃)(CH ₃)		38.88 q, ¹ J _{CH} = 115Hz
	Ta[N(CH ₃)CH ₂ CHMeOCHMeO]	2.33 s	43.11 q, ¹ J _{CH} = 136Hz
	Ta[NMeCHH'CHMeOCHMeO]	{ 2.58 dd, ³ J _{HH} = 12Hz, ² J _{HH} = 6Hz 2.30 dd, ³ J _{HH} = 4Hz, ² J _{HH} = 6Hz	62.26 t, ¹ J _{CH} = 134Hz
	Ta[NMeCH ₂ CHMeOCHMeO]		74.38 ^e -d, ¹ J _{CH} = 141Hz
	Ta[NMeCH ₂ CH(CH ₃)OCHMeO]	1.15 d, ³ J _{HH} = 6Hz	19.79 ^e -q, ¹ J _{CH} = 125Hz
	Ta[NMeCH ₂ CHMeOCHMeO]	5.43 q, ³ J _{HH} = 6Hz	96.00 ^e -d, ¹ J _{CH} = 154Hz
	Ta[NMeCH ₂ CHMeOCH(CH ₃)O]	1.04 d, ³ J _{HH} = 6Hz	23.03 ^e -qd, ¹ J _{CH} = 125Hz, ² J _{CH} = 4Hz
Cp*Me ₃ Ta[NMeCH ₂ CH(C ₆ H ₄ Me)OCH(C ₆ H ₄ Me)O] (8)	C ₅ (CH ₃) ₅	2.20 s	11.18 q, ¹ J _{CH} = 127Hz
	C ₅ (CH ₃) ₅		119.51 s
	Ta(CH ₃)(CH ₃)	0.05 s	45.30 q, ¹ J _{CH} = 117Hz
	Ta(CH ₃)(CH ₃)		39.45 q, ¹ J _{CH} = 115Hz
	Ta[N(CH ₃)CH ₂ CH(C ₆ H ₄ Me)OCH(C ₆ H ₄ Me)O]	2.68 s	45.10 q, ¹ J _{CH} = 134Hz
	Ta[NMeCHH'CH(C ₆ H ₄ Me)OCH(C ₆ H ₄ Me)O]	{ 2.69 dd, ³ J _{HH} = 4Hz, ² J _{HH} = 12Hz 2.50 t, ³ J _{HH} = 12Hz	63.43 t, ¹ J _{CH} = 137Hz

Table I. (continued)

Compound	Assignment	¹ H NMR	¹³ C NMR
Ta [NMeCH ₂ CH(C ₆ H ₄ Me)OCH(C ₆ H ₄ Me)O]	Ta [NMeCH ₂ CH(C ₆ H ₄ Me)OCH(C ₆ H ₄ Me)O]	5.26 dd, ³ J _{HH} = 4 & 11 Hz	80.58 ^d d, ¹ J _{CH} = 145 Hz
		6.56 s	100.73 ^d d, ¹ J _{CH} = 156 Hz
		2.17 s	21.25 q, ¹ J _{CH} = 126 Hz
Ta [NMeCH ₂ CH(C ₆ H ₄ CH ₃)OCH(C ₆ H ₄ CH ₃)O]	Ta [NMeCH ₂ CH(C ₆ H ₄ CH ₃)OCH(C ₆ H ₄ CH ₃)O]	2.09 s	21.06 q, ¹ J _{CH} = 126 Hz
			125.95 d, ¹ J _{CH} = 157 Hz
Cp*Me ₂ Ta [NMeCH ₂ C(CMe ₃)N] (9) ^h	Cp*Me ₂ Ta [NMeCH ₂ C(CMe ₃)N] (9) ^h	6.9-7.5 m	127.05 d, ¹ J _{CH} = 159 Hz
			128.30 d, ¹ J _{CH} = 158 Hz
			128.68 d(q), ¹ J _{CH} = 156 Hz, ¹ J _{CH} = 6 Hz
			136.21 s(q), ¹ J _{CH} = 7 Hz
			137.77 s(q), ¹ J _{CH} = 7 Hz
			139.79 s(t), ¹ J _{CH} = 8 Hz
			143.43 s
			10.85 q, ¹ J _{CH} = 127 Hz
			118.54 s
			55.76 q, ¹ J _{CH} = 118 Hz
44.65 q, ¹ J _{CH} = 133 Hz			
87.21 tq, ¹ J _{CH} = 130 Hz, ⁵ J _{CH} = -6 Hz			
182.03 s			
Cp*Me ₂ Ta [NMeCH ₂ C(CMe ₃)N] (9) ^h	Cp*Me ₂ Ta [NMeCH ₂ C(CMe ₃)N]	1.82 s	
		0.36 s	
		2.89 s	
		5.10 s	

Table I₂ (continued)

Compound	Assignment	¹ H NMR	¹³ C NMR
Cp*Me ₂ Ta[NMeCHC(CMe ₃)NH] (10)	Ta[NMeCH ₂ C(CMe ₃)N]		39.45 s
	Ta[NMeCH ₂ C{C(CH ₃) ₃ }N]	1.19 s	29.44 q-septet, ¹ J _{CH} = 126Hz, ³ J _{CH} = 5Hz
	C ₅ (CH ₃) ₅	1.71 s	10.81 q, ¹ J _{CH} = 127Hz
	C ₅ (CH ₃) ₅		117.17 s
	Ta(CH ₃) ₂		
	Ta[N(CH ₃)CHC(CMe ₃)NH]	0.19 s	54.80 q, ¹ J _{CH} = 118Hz
	Ta[NMeCHC(CMe ₃)NH]	3.43 s	44.83 qd, ¹ J _{CH} = 134Hz, ⁵ J _{CH} = 6Hz
	Ta[NMeCHC(CMe ₃)NH]	6.61 d, ⁴ J _{HH} = 3Hz	125.96 d, ¹ J _{CH} = 170Hz
	Ta[NMeCHC(CMe ₃)NH]		149.67 s
	Ta[NMeCHC(CMe ₃)NH]	1.27 s	39.45 s
Cp*Me ₂ Ta[NMeCHCMeNH] (11)		6.9 broad s	30.57 q-septet, ¹ J _{CH} = 125Hz, ³ J _{CH} = 5Hz
	C ₅ (CH ₃) ₅		
	C ₅ (CH ₃) ₅		
	Ta(CH ₃) ₂		
	Ta[N(CH ₃)CHCMeNH]	1.73 s	10.83 q, ¹ J _{CH} = 127Hz
	Ta(NMeCHCMeNH)	0.06 s	116.69 s
	Ta(NMeCHCMeNH)	3.36 s	51.14 q, ¹ J _{CH} = 118Hz
	Ta(NMeCHCMeNH)	6.24 s	43.83 qd, ¹ J _{CH} = 134Hz, ⁵ J _{CH} = 6Hz
	Ta[NMeCHC(CH ₃)NH]		123.46 d, ¹ J _{CH} = 176 Hz
	Ta(NMeCHCMeNH)	2.14 s	133.00 s
	6.4 broad s	18.53 qd, ¹ J _{CH} = 126Hz, ³ J _{HH} = 4Hz	

TABLE I (continued)

^aNMR spectra taken in benzene-d₆ at 34°C unless otherwise noted.

Chemical shifts in δ measured from internal TMS. ¹³C NMR assignments are made on the basis of multiplicity, chemical shift, comparisons with other compounds, and ¹J_{CH} coupling constants, using the rule of thumb that ¹J_{CH} is larger for carbon atoms bound to electronegative elements than for carbon atoms bound to electro-positive elements.²⁸ Long range ¹³C-¹H coupling is reported only when a coupling constant could be determined from the pattern.

^bNon-binomial triplet resonance (AA'XX' pattern).

^cAssignments confirmed by ¹³C labeling at the quaternary carbon.

See ref. 30.

^dSpectrum taken at -65°C in toluene-d₈. Only the resonances for the major isomer are listed. The spectrum of the minor isomer is given in reference 29.

^eAssignment uncertain.

^fNot observed.

^gAssignments confirmed by ¹³C labeling at the quaternary carbon.

See ref. 31.

^hSolution also contained 1 and Me₃CCN.

EXPERIMENTAL

All manipulations were carried out using either high vacuum line or glove box techniques, as previously described.²⁶ Molecular weights (in C₆H₆) were determined either by osmometry (by AlfredtBernhardt Analytische Labororien) or by isothermal distillation using the Singer method.²⁷ Cp*Me₂Ta(CH₂NMe) (1) and Cp*Me₂Ta(OCMe₂) (2) were prepared by literature methods.^{13, 14} Acetaldehyde was distilled and stored under vacuum, acetonitrile was stored over CaH₂ and t-butylnitrile was stored over 4Å molecular sieves; all were vacuum transferred prior to use. IR spectra were obtained as Nujol mulls unless indicated otherwise and are reported in cm⁻¹. Most of the syntheses reported proceed quantitatively (by NMR), but isolated yields are often low because the compounds are extremely soluble in hydrocarbon solvents.

Cp*Me₂Ta(NMeCH₂CH₂CH₂) (3). A solution of 1 (0.50 g) in petroleum ether (30 mL) was stirred at -78°C under one atmosphere of ethylene and slowly warmed to 25°C. Orange 3 (0.35 g, 67%) was crystallized from this solution. IR 1235, 1185, 1150, 1110, 1030, 960, 715, 460. Anal. Calcd for C₁₆H₃₀NTa: C, 46.05; H, 7.24; Ta, 43.35. Found: C, 45.85; H, 7.08; Ta, 43.31. Molecular weight: calcd, 417; found, 848 (osmometry, Bernhardt), 460 (±80, isothermal distillation by Singer method, complicated by slow decomposition to higher molecular weight materials).

Cp*Me₂Ta(OCMe₂CH₂CH₂) (4). A solution of 2 (0.50 g) in petroleum ether (20 mL) was stirred at -78°C under an atmosphere of ethylene and slowly warmed to 25°C. Filtration and removal of the

volatiles gave 4 as a light-orange oil. IR 1175, 1150 (st), 1030, 950 (st), 900, 890, 860, 780, 600.

Cp*Me₂Ta(NMeCH₂CHMeCH₂) (5). The synthesis of 5 is analogous to that of 3 except that the solution was stirred at 25°C for 16 hrs; 1.0 g of 1 yielded 0.18 g of orange 5 (16%). IR (C₆H₆) 1200, 1150, 1115, 1080, 1015, 980 (st), 780, 735. Anal. Calcd for C₁₇H₃₂NTa: C, 47.33; H, 7.48; N, 3.25. Found: C, 47.21; H, 7.48; N, 3.11. Molecular weight: calcd, 431; found, 400 (Singer method).

Cp*Me₂Ta(OCMe₂CHMeO) (6). A solution of 2 (95 mg) and acetaldehyde (90 torr in 56.4 mL, 1.16 equivalents) was stirred in 4 mL toluene at -80°C and allowed to warm to 25°C. Removal of the volatiles gave 6 as a yellow oil. IR (C₆D₆) 1195, 1155, 1130, 1090 (st), 1040, 1030, 960, 915, 785, 745, 655, 585.

Cp*Me₂Ta(NMeCH₂CHMeOCHMeO) (7). A solution of 1 (0.49 g, 1.29 mmole) and acetaldehyde (481 torr in 108.1 mL, 2.80 mmole) in petroleum ether (20 mL) was stirred at -78°C and warmed to 25°C. White solid (7, 0.29 g, 48%) was crystallized from this solution. IR 1340, 1325, 1205, 1170, 1140 (st), 1120, 1090, 1070, 1050, 990, 895, 770, 615, 560, 460, 450. Anal. Calcd for C₁₈H₃₄NO₂Ta: C, 45.28; H, 7.18; N, 2.93. Found: C, 45.20; H, 7.19; N, 3.04. Molecular weight: calcd, 477; found, 640 (Singer method).

Cp*Me₂Ta[NMeCH₂CH(C₆H₄Me)OCH(C₆H₄Me)O] (8). para-Tolualdehyde (0.30 mL, 0.31 g, 2.6 mmole) was added via syringe to a solution of 1 (0.50 g, 1.3 mmole) in 20 mL toluene at -78°C. The solution was allowed to warm and the volatiles were removed. Recrystallization from petroleum ether gave 0.27 g of white solid

(8, 33%). IR 1510, 1220, 1205, 1175, 1120 (st), 1095 (st), 1040, 1020, 990, 930, 875, 815, 795, 665, 630, 595. Anal. Calcd for $C_{30}H_{42}NO_2Ta$: C, 57.23; H, 6.72; N, 2.22. Found: C, 57.04; H, 6.73; N, 2.09.

Molecular weight: calcd, 630; found, 619 (Bernhardt).

$Cp^*Me_2Ta[NMeCH_2C(CMe_3)N]$ (9). 9 has not been isolated in pure form because its rearrangement to 10 is unpredictable and may be catalyzed by glass surfaces. The best procedure uses an NMR tube as the reaction vessel: an NMR tube sealed to a ground glass joint was loaded with 1 (64 mg, 0.16 mmole), *t*-butylnitrile (29 torr in 104.8 mL, 0.16 mmole), and 0.4 mL benzene- d_6 , and sealed with a torch. The reaction was monitored by NMR and by color (9 is red and 10 is green); the maximum concentration of 9 was reached after two days at 25°C. IR (C_6D_6) 1633 (ν C=N), 1120 (st), 1080, 1030, 980 (st), 865, 785, 640.

$Cp^*Me_2Ta[NMeCHC(CMe_3)NH]$ (10). A solution of 1 (0.45 g), *t*-butylnitrile (0.13 mL, 0.10 g), and benzene (10 mL) was stirred at 25°C for 15 hr and then the volatiles were removed. After repeated attempts to crystallize solid from petroleum ether and hexamethyldisiloxane (and repeated passage through a glass frit), the remaining green oil contained primarily 10. IR 3380 (ν NH), 1605 (ν C=C), 1255, 1145, 1125, 1025, 800, 750, 645, 570, 470.

$Cp^*Me_2Ta(NMeCHCMeNH)$ (11). A solution of 1 (0.50 g) and acetonitrile (0.15 mL) in 40 mL petroleum ether was stirred at 25°C for 13 hr. Dark-green solid (11, 0.26 g, 47%) was crystallized from this solution. IR 3370 (ν NH), 1620 (ν C=C), 1240, 1205, 1150, 1125, 1025, 740, 590, 490. Anal. Calcd for $C_{16}H_{29}N_2Ta$: C, 44.65; H, 6.79;

N, 6.51. Found: C, 44.52; H, 6.57; N, 6.64. Molecular weight:
calcd, 430; found, 885 (Bernhardt).

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(21) Coupling of two acetones to form a pinacolate complex has been reported.^{2a}

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(30) For $Cp^*Me_2\overline{TaO^{13}CMe_2CH_2CH_2}$, carbon-carbon coupling is observed in the ^{13}C NMR for the β -methylene carbon ($^1J_{CC} = 37$ Hz) and the two methyl carbons ($^1J_{CC} = 40$ Hz) consistent with a C-C single bond.²⁸ No two-bond coupling to the methylene bound to tantalum is observed.

(31) For $Cp^*Me_2\overline{TaO^{13}CMe_2CHMeO}$, carbon-carbon coupling is observed in the ^{13}C NMR for the methyl resonances at 29.52 and 23.49 (both $^1J_{CC} = 39$ Hz). The resonances due to the methyne carbon are obscured by the enriched carbon. Coupling to the methyne hydrogen is observed, however: $^2J_{CH} = 2$ Hz.