

α -Hydride Elimination: The First Observable Equilibria between Alkylidene Complexes and Alkylidyne Hydride Complexes

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Abstract: Ta(CHCMe₃)(dmpe)Cl₃ is reduced by sodium amalgam in the presence of dmpe to give Ta(CHCMe₃)(dmpe)₂Cl. The neopentylidene ligand is grossly distorted toward a neopentylidyne hydride system as evidenced by the low value for ν_{CH_α} (2200 cm⁻¹) and J_{CH_α} (57 Hz). Addition of AlMe_xCl_{3-x} reagents generates aluminum-stabilized neopentylidyne hydride complexes. The complex Ta(CCMe₃)(H)(dmpe)₂(ClAlMe₃) crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with $a = 9.8587$ (24) Å, $b = 22.2799$ (63) Å, $c = 14.7965$ (40) Å, $\beta = 103.479$ (20)°, and $Z = 4$. Diffraction data (Mo K α ; $2\theta = 4$ –45°) were collected with a Syntex P₂₁ diffractometer, and the structure was refined to $R_F = 3.6\%$ for all 4152 reflections ($R_F = 2.9\%$ for those 3693 data with $|F_o| > 3\sigma(|F_o|)$). The tantalum atom has a pentagonal bipyramidal coordination geometry with two dmpe ligands and the hydride ligand (Ta–H = 1.80 (5) Å) lying in the equatorial plane. The neopentylidyne ligand (Ta \equiv C = 1.850 (5) Å) and a Cl–AlMe₃ ligand (Ta–Cl = 2.768 (2) Å) occupy the two axial sites. Replacing the chloride in Ta(CHCMe₃)(dmpe)₂Cl with iodide produces a product which at 200 K is approximately a 9:1 mixture of Ta(CCMe₃)(H)(dmpe)₂I and Ta(CHCMe₃)(dmpe)₂I. At 335 K it is approximately a 1:1 mixture of the two, and they interconvert rapidly on the NMR time scale. Replacing the chloride with triflate produces a mixture which contains less than 50% Ta(CHCMe₃)(dmpe)₂(CF₃SO₃) at 355 K.

Niobium and tantalum complexes which contain alkylidene ligands with large M–C _{α} –C _{β} angles have been known for several years.^{1c-f} The recent discovery of a tungsten complex containing a similarly distorted methylene ligand suggests that this phenomenon is largely due to electronic rather than steric factors.² It appears that the metal is attempting to remove the α -hydrogen atom to give an alkylidyne hydride complex. In some cases, alkylidyne hydride complexes do form and can be isolated.³ We report in this paper examples of tantalum neopentylidene complexes which are in equilibrium with, and rapidly interconverting with, their neopentylidyne hydride tautomers. In one case neopentylidyne hydride complexes are generated by forming "adducts" with aluminum reagents. This "aluminum induced" α -elimination reaction may provide some new clues as to how aluminum reagents function, sometimes uniquely, in catalytic reactions involving organometallic reagents.

Results

Preparation of Ta(CHCMe₃)(dmpe)₂Cl and Its Aluminum Alkyl Adducts. Orange, crystalline Ta(CHCMe₃)(dmpe)₂Cl can be prepared in good yield by reducing Ta(CHCMe₃)(dmpe)Cl₃ with sodium amalgam under argon in the presence of dmpe. This method was used recently to prepare Ta(CHCMe₃)(PMe₃)₄Cl from Ta(CHCMe₃)(PMe₃)₂Cl₃.³ Ta(CHCMe₃)(dmpe)₂Cl and Ta(CHCMe₃)(PMe₃)₄Cl are members of the only class of "Ta(III)" neopentylidene complexes which do not also contain ethylene. We believe this is why the neopentylidene ligands are some of the strangest we have found so far.

Spectroscopic evidence suggests that in Ta(CHCMe₃)(dmpe)₂Cl the Ta=C _{α} –C _{β} angle in the neopentylidene ligand must be close to 180° and the α -hydrogen atom is in what could be called a bridging position between the neopentylidene α -carbon atom and tantalum. First, the IR spectrum shows an extraordinarily low

energy CH _{α} mode at 2200 cm⁻¹. Second, the CH _{α} coupling constant is only 57 Hz. Third, a quintet is found for the α -hydrogen atom in the ¹H NMR spectrum at –8.49 ppm. All are characteristic of a grossly distorted neopentylidene ligand^{1e} and, if we may use these values as a measure of that distortion, the most distorted we have seen so far. The fact that only one type of phosphine ligand and two types of dmpe methyl groups are observed suggests that the neopentylidene ligand is trans to the chloride ligand and that the complex is axially symmetric on the NMR time scale. The ³¹P NMR spectrum of Ta(CHCMe₃)(dmpe)₂Cl in pentane does not change upon cooling the sample to 150 K. Therefore the activation energy for "rotation" of the neopentylidene ligand which leads to equivalence of all phosphine ligands must be quite small. Perhaps it is best not to call this an alkylidene ligand rotation at all; migration of H _{α} about the TaP₂ faces in the upper half of the molecule may be a more accurate description.²

Ta(CHCMe₃)(dmpe)₂Cl reacts readily with 1 equiv of AlMe₃ to give a pale red complex which is still soluble in toluene. At 298 K the ¹³C NMR spectrum shows a signal at 280 ppm for a carbon atom which is not appreciably coupled to a proton. The proton resonance can be observed at 3.13 ppm in the ¹H NMR spectrum as a triple triplet due to coupling to two inequivalent pairs of phosphorus nuclei (Figure 1b). In the proton-coupled ³¹P NMR spectrum, the signal due to one of these pairs of phosphorous nuclei is split by 90 Hz (Figure 1a); the other is only broadened. Finally, the IR spectrum of this complex shows a peak at 1590 cm⁻¹. Taken together, these data suggest that this adduct is actually a neopentylidyne hydride complex. An adduct containing AlMe₂Cl is analogous. In each case the addition of 1 equiv or more of tetrahydrofuran results in formation of AlMe_xCl_{3-x}(THF) and Ta(CHCMe₃)(dmpe)₂Cl.

An important question is how the aluminum is bonded in these complexes. We thought it most likely the aluminum was interacting with the hydride or the chloride ligand, but we could not exclude the possibility that it was bound to the neopentylidyne α -carbon atom, a type of bonding which was found recently in the methylidyne complex, W(CH)(PMe₃)₃(Cl)(AlMe₂Cl).⁴

(1) (a) State University of New York at Buffalo. (b) Massachusetts Institute of Technology. (c) Schrock, R. R. *Acc. Chem. Res.* 1979, 12, 98–104. (d) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* 1979, 18, 1930–1935. (e) Schultz, A. J.; Brown, R. K.; Williams, J. M.; Schrock, R. R. *J. Am. Chem. Soc.* 1981, 103, 169–176. (f) Messerle, L. W.; Jennische, P.; Schrock, R. R.; Stucky, G. J. *Am. Chem. Soc.* 1980, 102, 6744–6752.

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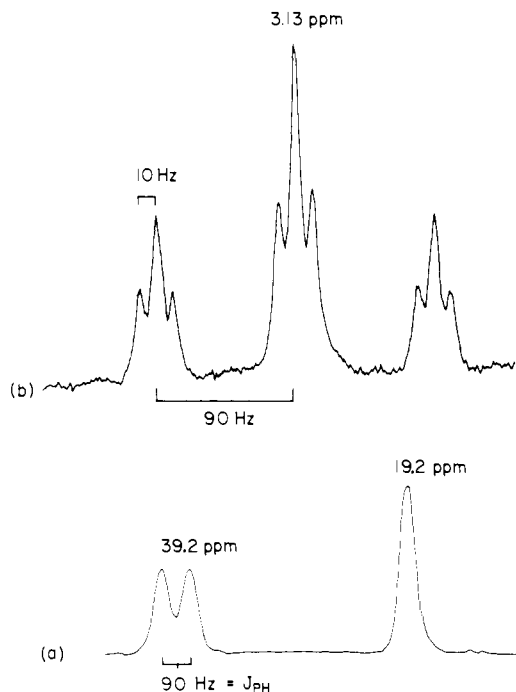


Figure 1. (a) ^{31}P NMR spectrum of $\text{Ta}(\text{CCMe}_3)(\text{H})(\text{dmpe})_2(\text{ClAlMe}_3)$ at 208 K (^1H coupled). (b) Hydride resonance in the 208 K ^1H NMR spectrum of $\text{Ta}(\text{CCMe}_3)(\text{H})(\text{dmpe})_2(\text{ClAlMe}_3)$.

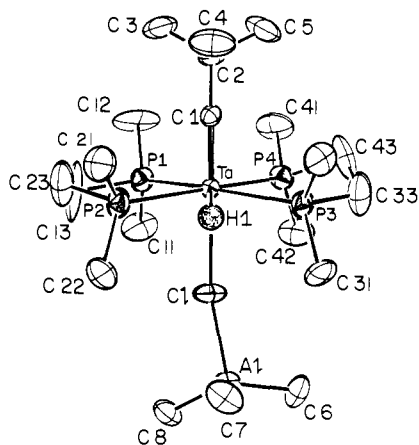


Figure 2. Labeling of atoms in the $\text{Ta}(\text{CCMe}_3)(\text{H})(\text{dmpe})_2(\text{ClAlMe}_3)$ molecule (ORTEP-II diagram; 30% ellipsoids).

Table I. Interatomic Distances (\AA) with Esd's for $\text{Ta}(\text{CCMe}_3)(\text{H})(\text{dmpe})_2(\text{ClAlMe}_3)$

atoms	dist	atoms	dist
(A) Distances from the Tantalum Atom			
Ta-P(1)	2.625 (2)	Ta-Cl	2.758 (2)
Ta-P(2)	2.522 (2)	Ta-C(1)	1.850 (5)
Ta-P(3)	2.527 (2)	Ta-H(1)	1.796 (49)
Ta-P(4)	2.602 (2)		
(B) Distances from the Aluminum Atom			
Al-Cl	2.310 (2)	Al-C(7)	1.955 (8)
Al-C(6)	1.957 (8)	Al-C(8)	1.960 (8)
(C) Distances within the Neopentylidene Ligand			
C(1)-C(2)	1.512 (8)	C(2)-C(4)	1.516 (11)
C(2)-C(3)	1.522 (10)	C(2)-C(5)	1.521 (11)
(D) Distances within the dmpe Ligands			
P(1)-C(11)	1.800 (10)	P(3)-C(31)	1.800 (8)
P(1)-C(12)	1.783 (12)	P(3)-C(32)	1.807 (8)
P(1)-C(13)	1.809 (13)	P(3)-C(33)	1.822 (9)
P(2)-C(21)	1.801 (9)	P(4)-C(41)	1.814 (10)
P(2)-C(22)	1.799 (9)	P(4)-C(42)	1.816 (9)
P(2)-C(23)	1.819 (12)	P(4)-C(43)	1.794 (10)
C(13)-C(23)	1.287 (16) ^a	C(33)-C(43)	1.472 (15)

^a The anomalously short distance for this $\text{C}(\text{sp}^3)\text{-C}(\text{sp}^3)$ linkage is clearly a result of conformational disorder in the chelate system $\text{P}(1)\text{-C}(13)\text{-C}(23)\text{-P}(2)$. See text.

The Structure of $\text{Ta}(\text{CCMe}_3)(\text{H})(\text{dmpe})_2(\text{ClAlMe}_3)$. An ORTEP-II drawing of the molecule is shown in Figure 2 and a stereoscopic view in Figure 3. Interatomic distances with estimated standard deviations (esd's) appear in Table I and interatomic angles (with esd's) in Table II.

The central tantalum(V) atom is seven-coordinate with a pentagonal-bipyramidal coordination environment. The distribution of the equatorial ligands is shown in Figure 4. The two chelate angles are close to equal, with $\text{P}(1)\text{-Ta-P}(2) = 75.40(6)^\circ$ and $\text{P}(3)\text{-Ta-P}(4) = 75.25(6)^\circ$. The interchelate angles are decidedly inequivalent, with $\text{P}(1)\text{-Ta-P}(4) = 85.53(6)^\circ$ and $\text{P}(2)\text{-Ta-P}(3) = 123.02(6)^\circ$; the hydride ligand acts as bisector for this last angle, with $\text{P}(2)\text{-Ta-H}(1) = 62.3(16)^\circ$ and $\text{P}(3)\text{-Ta-H}(1) = 60.9(16)^\circ$. Interestingly, the phosphorus atoms adjacent to the hydride ligand are associated with *shorter* Ta-P bond lengths than the other two phosphorus atoms ($\text{Ta-P}(2) = 2.522(2) \text{\AA}$ and $\text{Ta-P}(3) = 2.527(2) \text{\AA}$ vs. $\text{Ta-P}(1) = 2.625(2) \text{\AA}$ and $\text{Ta-P}(4) = 2.602(2) \text{\AA}$).

The equatorial tantalum-hydride linkage, $\text{Ta-H}(1) = 1.80(5) \text{\AA}$, is normal within the limits of experimental error. The hydride lies directly in the equatorial belt, the deviation from the least-

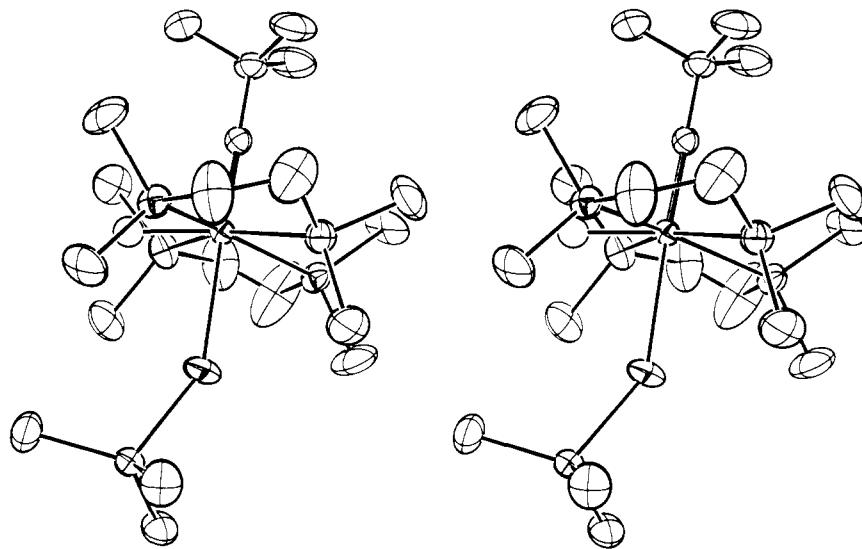


Figure 3. Stereoscopic view of the $\text{Ta}(\text{CCMe}_3)(\text{H})(\text{dmpe})_2(\text{ClAlMe}_3)$ molecule.

Table II. Interatomic Angles (Deg) and Esd's for Ta(CCMe₃)(H)(dmpe)₂(ClAlMe₃)

atoms	angle	atoms	angle
(A) Equatorial-Equatorial Angles about Tantalum			
P(1)-Ta-P(2)	75.40 (6)	P(2)-Ta-H(1)	62.3 (16)
P(1)-Ta-P(4)	85.53 (6)	P(3)-Ta-H(1)	60.9 (16)
P(3)-Ta-P(4)	75.25 (6)	P(2)-Ta-P(3)	123.02 (6)
(B) Axial-Axial Angle about Tantalum			
Cl-Ta-C(1)	177.39 (17)		
(C) Axial-Equatorial Angles about Tantalum			
Cl-Ta-P(1)	82.71 (5)	C(1)-Ta-P(1)	94.92 (17)
Cl-Ta-P(2)	87.56 (6)	C(1)-Ta-P(2)	92.91 (17)
Cl-Ta-P(3)	89.08 (5)	C(1)-Ta-P(3)	92.82 (17)
Cl-Ta-P(4)	85.61 (6)	C(1)-Ta-P(4)	93.13 (17)
Cl-Ta-H(1)	82.1 (16)	C(1)-Ta-H(1)	100.4 (16)
(D) Tantalum-Chlorine-Aluminum Angle			
Ta-Cl-Al	149.85 (9)		
(E) Angles about the Aluminum Atom			
Cl-Al-C(6)	102.2 (3)	C(6)-Al-C(7)	115.6 (4)
Cl-Al-C(7)	108.1 (3)	C(6)-Al-C(8)	114.5 (4)
Cl-Al-C(8)	100.5 (3)	C(7)-Al-C(8)	113.8 (4)
(F) Angles within the Neopentylidene Ligand			
Ta-C(1)-C(2)	178.7 (4)	C(1)-C(2)-C(4)	112.3 (6)
C(1)-C(2)-C(3)	109.9 (6)	C(1)-C(2)-C(5)	111.0 (6)
(G) Angles within the dmpe Ligands ^a			
Ta-P(1)-C(11)	122.0 (3)	Ta-P(3)-C(31)	119.4 (3)
Ta-P(1)-C(12)	122.1 (4)	Ta-P(3)-C(32)	116.7 (3)
Ta-P(1)-C(13)	107.9 (5)	Ta-P(3)-C(33)	113.9 (3)
Ta-P(2)-C(21)	117.3 (3)	Ta-P(4)-C(41)	121.6 (4)
Ta-P(2)-C(22)	118.2 (2)	Ta-P(4)-C(42)	120.7 (3)
Ta-P(2)-C(23)	113.2 (4)	Ta-P(4)-C(43)	108.3 (4)
C(11)-P(1)-C(12)	100.1 (5)	C(31)-P(3)-C(32)	101.3 (4)
C(11)-P(1)-C(13)	100.3 (6)	C(31)-P(3)-C(33)	101.5 (4)
C(12)-P(1)-C(13)	100.6 (6)	C(32)-P(3)-C(33)	101.5 (4)
C(21)-P(2)-C(22)	101.4 (4)	C(41)-P(4)-C(42)	99.7 (5)
C(21)-P(2)-C(23)	102.5 (5)	C(41)-P(4)-C(43)	99.2 (5)
C(22)-P(2)-C(23)	101.8 (5)	C(42)-P(4)-C(43)	104.3 (5)
P(1)-C(13)-C(23)	124.4 (11)	P(3)-C(33)-C(43)	113.2 (7)
P(2)-C(23)-C(13)	116.0 (10)	P(4)-C(43)-C(33)	114.1 (8)

^a Angles involving atoms C(13) and C(23) are subject to systematic errors of uncertain magnitude as a result of conformational disorder in the chelate system defined by P(1)-C(13)-C(23)-P(2). See text.

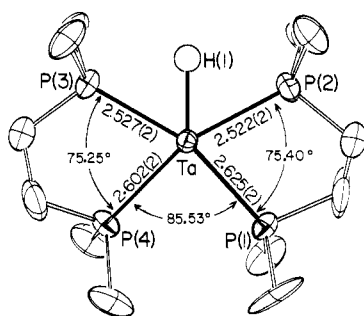


Figure 4. Geometry in the pentagonal equatorial plane of the Ta(CCMe₃)(H)(dmpe)₂(ClAlMe₃) molecule.

squares plane⁵ defined by P(1), P(2), P(3), P(4), and H(1) being +0.12 (5) Å.

The two axial ligands are bonded to the tantalum atom in grossly different ways. The tantalum-neopentylidene bond length and Ta-C(1)-C(2) angle (1.850 (5) Å and 177.39 (17)°) are characteristic of a Ta≡C triple bond and are close to the analogous values found for the benzylidene ligand in Ta(η⁵-C₅Me₅)(CPh)(PMe₃)₂Cl (1.849 (8) Å and 171.8 (6)°).⁶ In contrast, the "AlMe₃Cl" ligand is only weakly bonded to tantalum

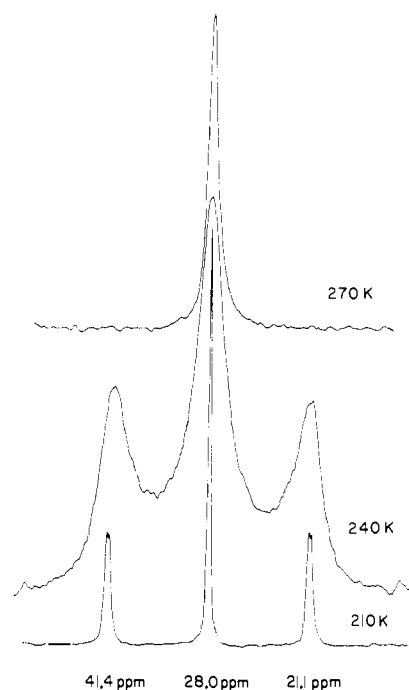


Figure 5. Variable-temperature ³¹P{¹H} NMR spectrum of a 1:1 mixture of Ta(CHCMe₃)(dmpe)₂Cl (28.0 ppm) and Ta(CCMe₃)(H)(dmpe)₂(ClAlMe₃) (21.1 and 41.4 ppm) in toluene-*d*₈.

(Ta-Cl = 2.758 (2) Å). This Ta-Cl bond length should be compared with normal Ta-Cl bond lengths of 2.366 (2) Å in Ta(η⁵-C₅Me₅)(C₄H₈)Cl₂⁷ (only one independent chlorine), 2.375 (2)-2.362 (2) Å in Ta(η⁵-C₅Me₅)(C₇H₁₂)Cl₂,⁷ 2.445 (4)-2.437 (2) Å in [(η⁵-C₅Me₄Et)TaCl₂]₂(H)(μ-CHPMe₃)(μ-O),⁸ 2.360 (4)-2.387 (4) Å in [(η⁵-C₅Me₄Et)TaCl₂]₂(μ-H)(μ-CHO),⁹ and 2.548 (2) Å in Ta(η⁵-C₅Me₅)(CPh)(PMe₃)₂Cl.⁶ It is also interesting and important to note that in the dinuclear complex, [Ta(CHCMe₃)(PMe₃)Cl]₂,¹⁰ one bridging chlorine ligand is trans to a distorted neopentylidene ligand; this neutron diffraction determined Ta-Cl distance is 2.815 (2) Å. The grossly different tantalum to axial ligand bond lengths in Ta(CCMe₃)(H)(dmpe)₂(ClAlMe₃) could explain why the tantalum atom is situated 0.1880 (2) Å above the plane defined by P(1), P(2), P(3), P(4), and H(1). The four independent C(1)-Ta-P angles range from 92.82 (17)° to 94.92 (17)° and the C(1)-Ta-H(1) angle is 100.4 (16)°.

The AlMe₃Cl ligand is understandably not symmetric. The Cl-Al distance of 2.310 (2) Å is longer than a typical terminal Cl-Al bond length such as that (2.152 (2) Å) found in W-(CH)(PMe₃)₃(Cl)(AlMe₂Cl).⁴ The AlMe₃ moiety is bent toward the equatorial hydride ligand with a Ta-Cl-Al angle of 149.85 (9)°. The geometry about the aluminum atom is a flattened tetrahedron with Cl-Al-C(Me) angles of 100.5 (3)-108.1 (3)° and C-Al-C angles of 113.8 (4)-115.6 (4)°. The three Al-Me distances are normal (1.955 (8) Å to 1.960 (8) Å).

NMR Studies. A variable-temperature proton-decoupled ³¹P NMR spectrum of a mixture of Ta(CHCMe₃)(dmpe)₂Cl and Ta(CCMe₃)(H)(dmpe)₂(ClAlMe₃) is shown in Figure 5. At 210 K signals for each are observed. By the time the temperature of the sample is raised to 270 K, however, the two complexes are interconverting rapidly on the NMR time scale. Cooling the sample regenerates the original spectrum.

A similar phenomenon can be observed by ¹³C NMR. At low temperatures α-carbon resonances for both species are observed while at 346 K in toluene only one signal is observed at 244 ppm for a sample consisting of a 1:1 mixture of the two complexes.

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(5) In the orthonormal coordinate system *x*, *y*, *z*, the plane is defined as -0.5546*x* - 0.8207*y* - 0.1373*z* = -3.3098.

(6) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 171.

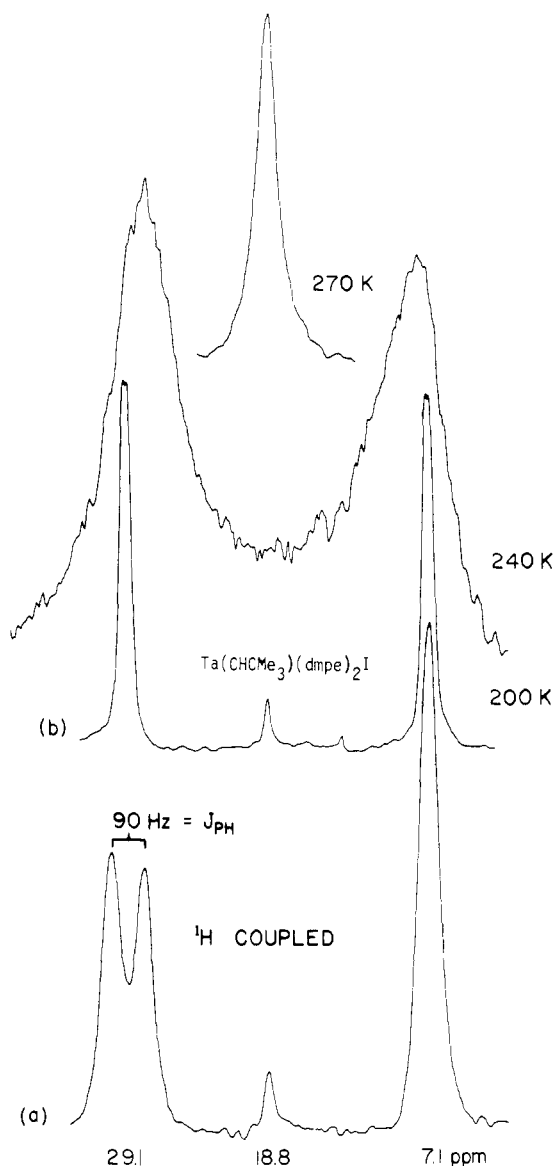


Figure 6. (a) ^{31}P NMR spectrum of a mixture of $\text{Ta}(\text{CHCMe}_3)(\text{dmpe})_2\text{I}$ (18.8 ppm) and $\text{Ta}(\text{CCMe}_3)(\text{H})(\text{dmpe})_2\text{I}$ (7.1 and 29.1 ppm) at 200 K in toluene- d_8 (^1H coupled). (b) Variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{Ta}(\text{CHCMe}_3)(\text{dmpe})_2\text{I}/\text{Ta}(\text{CCMe}_3)(\text{H})(\text{dmpe})_2\text{I}$ in toluene- d_8 .

One might then suspect that the CH_α coupling constant would be the average of what it is in $\text{Ta}(\text{CHCMe}_3)(\text{dmpe})_2\text{Cl}$ (57 Hz) and what it is in $\text{Ta}(\text{CCMe}_3)(\text{H})(\text{dmpe})_2(\text{ClAlMe}_3)$ (<5 Hz). A proton-coupled, phosphorus-decoupled ^{13}C NMR spectrum at 67.89 MHz of the 1:1 mixture showed that $J_{\text{CH}_\alpha} = 35$ Hz. Coupling of C_α to phosphorus prevented resolution of the signal in the gated proton-decoupled spectrum.

All of the above data suggest that the neopentylidene α -hydrogen atom is hopping from the α -carbon atom to the metal when AlMe_3 coordinates to the trans chloride ligand and back again when AlMe_3 leaves (eq 1). While we suspect that loss of the



AlMe_3Cl^- ion to give a 16-electron cationic complex might be an important feature of the chemistry of this complex if a donor ligand is available (to give an 18-electron cationic complex), we do not think it necessary to propose that loss of AlMe_3Cl^- is part of the process which averages the NMR signals for the two species in the absence of a donor ligand.

Preparation and NMR Study of $\text{Ta}(\text{CHCMe}_3)(\text{dmpe})_2\text{I}$. We thought it might be possible to duplicate the effect of adding

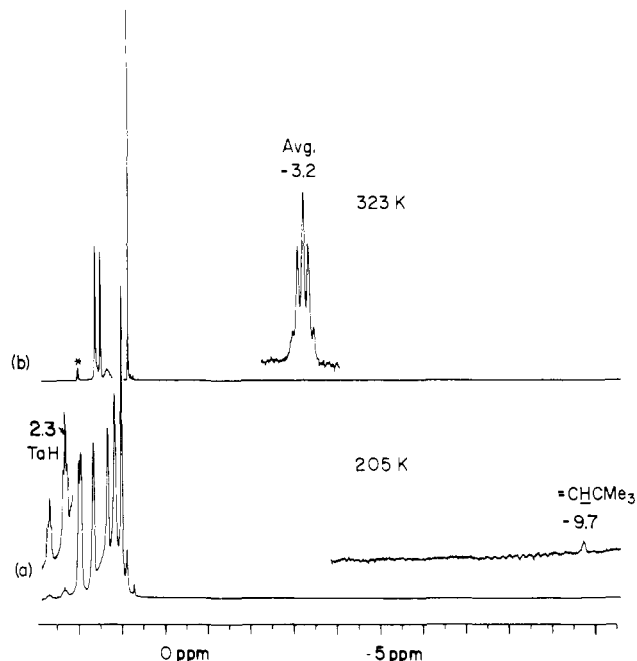


Figure 7. 250-MHz ^1H NMR spectrum of $\text{Ta}(\text{CHCMe}_3)(\text{dmpe})_2\text{I}/\text{Ta}(\text{CCMe}_3)(\text{H})(\text{dmpe})_2\text{I}$ in toluene- d_8 (* = $\text{C}_6\text{D}_5\text{CD}_2\text{H}$).

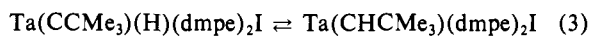
AlMe_3 to $\text{Ta}(\text{CHCMe}_3)(\text{dmpe})_2\text{Cl}$ by changing the chloride ligand to a more ionic, loosely bound halide ligand. The analogous iodide complex can be prepared smoothly and easily as shown in eq 2.



$\text{Ta}(\text{CHCMe}_3)(\text{dmpe})_2\text{I}$ is similar to $\text{Ta}(\text{CHCMe}_3)(\text{dmpe})_2\text{Cl}$ in its physical properties except that while it is red in solution at room temperature, it is pale yellow at 195 K.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{Ta}(\text{CHCMe}_3)(\text{dmpe})_2\text{I}$ at 200 K shows it actually to be $\sim 90\%$ $\text{Ta}(\text{CCMe}_3)(\text{H})(\text{dmpe})_2\text{I}$ (Figure 6b). In the ^1H -coupled spectrum, the lower field peak splits into a doublet due to coupling of that set of phosphorus nuclei to the hydride ligand (Figure 6a; cf. Figure 1a). As the temperature of the sample is raised, the ^{31}P signals for $\text{Ta}(\text{CCMe}_3)(\text{H})(\text{dmpe})_2\text{I}$ to give an average resonance at 270 K. Due to this averaging process, we cannot tell to what extent the equilibrium between $\text{Ta}(\text{CHCMe}_3)(\text{dmpe})_2\text{I}$ and $\text{Ta}(\text{CCMe}_3)(\text{H})(\text{dmpe})_2\text{I}$ changes at higher temperatures.

The ^1H NMR spectrum at 205 K shows part of the triple triplet resonance for the hydride ligand in $\text{Ta}(\text{CCMe}_3)(\text{H})(\text{dmpe})_2\text{I}$ at 2.30 ppm and a relatively small, broad resonance for the α -hydrogen atom in $\text{Ta}(\text{CHCMe}_3)(\text{dmpe})_2\text{I}$ at -9.7 ppm (Figure 7). These resonances broaden, collapse, and coalesce to give a quintet pattern ($J_{\text{HP}} = 15$ Hz) which at 323 K is located at -3.20 ppm. The quintet pattern suggests that the averaging process is strictly intramolecular. If we assume that the hydride and α -hydrogen resonances at this temperature would also be at 2.30 and -9.70 ppm, respectively, then the average signal for a 50:50 mixture of the two at 323 K should be found at -3.55 ppm. It is clear that at 323 K the amount of $\text{Ta}(\text{CCMe}_3)(\text{H})(\text{dmpe})_2\text{I}$ approximately equals the amount of $\text{Ta}(\text{CHCMe}_3)(\text{dmpe})_2\text{I}$ (eq 3). The actual



$$K_{\text{eq}} \approx 1 \text{ at } 323 \text{ K}$$

fraction of $\text{Ta}(\text{CCMe}_3)(\text{H})(\text{dmpe})_2\text{I}$ in the mixture is $(9.70 - 3.20)/(9.70 + 2.60) = 0.53$. In benzene- d_6 at the same temperature, the quintet is observed at -2.0 ppm. Either slightly more $\text{Ta}(\text{CCMe}_3)(\text{H})(\text{dmpe})_2\text{I}$ is present in benzene at this temperature or the TaH and TaCHCMe_3 resonances would not be found at 2.30 and -9.70 ppm, respectively, if it were possible to obtain the spectrum at 205 K in C_6D_6 .

The ^{13}C NMR spectrum of $[\text{Ta}(\text{CHCMe}_3)(\text{dmpe})_2\text{I}]^+$ is consistent with what we know so far. At 344 K a C_α resonance is observed at 248 ppm. The value for J_{CH_α} should be the weighted average of the estimates for J_{CH_α} in $\text{Ta}(\text{CHCMe}_3)(\text{dmpe})_2\text{I}$ (~ 55 Hz) and $\text{Ta}(\text{CCMe}_3)(\text{H})(\text{dmpe})_2\text{I}$ (≤ 5 Hz). (The former cannot be measured easily, since little $\text{Ta}(\text{CHCMe}_3)(\text{dmpe})_2\text{I}$ actually is present at temperatures where it is not interconverting with $\text{Ta}(\text{CCMe}_3)(\text{H})(\text{dmpe})_2\text{I}$.) We find that $J_{\text{CH}_\alpha} \approx 28$ Hz, as it should for approximately a 1:1 mixture of rapidly interconverting $\text{Ta}(\text{CCMe}_3)(\text{H})(\text{dmpe})_2\text{I}$ and $\text{Ta}(\text{CHCMe}_3)(\text{dmpe})_2\text{I}$.

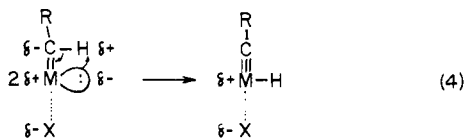
Preparation of $\text{Ta}(\text{CHCMe}_3)(\text{dmpe})_2(\text{CF}_3\text{SO}_3)$. $\text{Ta}(\text{CHCMe}_3)(\text{dmpe})_2\text{Cl}$ reacts with an excess of $\text{Me}_3\text{SiO}_3\text{SCF}_3$ to give yellow prisms of a triflate derivative in 89% yield. This product is solely $\text{Ta}(\text{CCMe}_3)(\text{H})(\text{dmpe})_2(\text{CF}_3\text{SO}_3)$ at low temperatures. At 355 K less than 50% $\text{Ta}(\text{CHCMe}_3)(\text{dmpe})_2(\text{CF}_3\text{SO}_3)$ must be present, since the quintet is observed at 0.08 ppm (cf. $\text{Ta}(\text{CCMe}_3)(\text{H})(\text{dmpe})_2\text{I}$, Figure 7).

We thought it reasonable to consider the possibility that the triflate came off the metal to form a cationic complex, at least in polar solvents. But a differential vapor pressure molecular weight determination in tetrahydrofuran was consistent with the complex being neutral, or at least a tight ion pair much like the situation in $\text{Ta}(\text{CCMe}_3)(\text{H})(\text{dmpe})_2(\text{ClAlMe}_3)$.

Discussion

The structure of $\text{Ta}(\text{CCMe}_3)(\text{H})(\text{dmpe})_2(\text{ClAlMe}_3)$ is one of a fairly large class of seven-coordinate transition-metal complexes of the form $\text{M}(\text{L-L})_2\text{L}_3$ where (L-L) represents a bidentate chelate ligand. The vast majority of these species exhibit pentagonal-bipyramidal (PB) geometry;¹⁰ the few capped octahedra or capped trigonal prisms are believed to be the result of increased steric interactions in the PB geometry between organic groups of the chelate ligands.^{10,11} An interesting exception is the structure of $\text{Ta}(\text{H})(\text{CO})_2(\text{dmpe})_2$ which, although badly hampered by disorder, was shown to be a capped octahedron.¹² Because the spectroscopic data for $\text{Ta}(\text{CCMe}_3)(\text{H})(\text{dmpe})_2\text{I}$ and $\text{Ta}(\text{CCMe}_3)(\text{H})(\text{dmpe})_2(\text{CF}_3\text{SO}_3)$ are so similar to those for $\text{Ta}(\text{CCMe}_3)(\text{H})(\text{dmpe})_2(\text{ClAlMe}_3)$, we believe their structures are also pentagonal bipyramids.

Distortion of an alkylidene ligand from a Y to a T shape is now well-documented.¹⁰⁻¹² Since one α -hydrogen atom in the T-shaped ligand is essentially bridging between C_α and the metal, actual transfer of H_α to the metal can be viewed as a continuation of this distortion. However, from our experience, H_α will not actually transfer to the metal unless the metal is formally d^2 (counting the alkylidene ligand as a dianion). If the metal is formally d^0 , H_α either remains in the bridging position, transfers to an alkyl group on the same metal to give alkane, or is removed by an external base.¹⁰ In an important theoretical study of model systems, Hoffmann concludes that α elimination from an alkylidene ligand can be described as an attraction of the CH_α electron pair into the metal-carbon double bond combined with an attraction of H_α to a relatively electron-rich metal orbital;¹³ the two operate concomitantly as the alkylidene pivots in the plane in which it lies. Therefore it seems most consistent to view the α -elimination reaction as a proton transfer from C_α (or, more accurately, the incipient $\text{M}\equiv\text{C}_\alpha$ triple bond) to a metal's lone pair (eq 4). If



X is changed from chloride to a more ionic, loosely bound ligand

with diminished π -electron-donor capabilities, then not only would the metal be more cationic and the system as a whole more polarized in the appropriate sense, but the second π orbital which is necessary to form the $\text{M}\equiv\text{C}$ triple bond would not be accepting much π -electron density from X. We contend that " ClAlMe_3 ", iodide, and triflate are all more ionic, loosely bound, poorer π -electron donors than chloride and that this is why the alkylidene hydride complexes are preferred over the "distorted alkylidene" complexes.

There is already much evidence that α elimination from an alkyl ligand (to give an alkylidene hydride complex) is related to α elimination from an alkylidene ligand. Therefore the phenomenon we describe here may prove relevant to understanding the role of aluminum reagents in transition-metal alkyl chemistry beyond their simplest function as alkylating agents. For example, it has been suggested that the reason why ethylene is polymerized so rapidly by certain catalysts is that intermediate alkyl complexes behave as alkylidene hydrides due to interaction of the α -hydrogen atom with the metal.¹⁴ Such an interaction could be induced by, and an incipient alkylidene hydride complex stabilized by, an aluminum reagent in a manner related to what we have observed here. In other circumstances an aluminum reagent could create an incipient "cationic" alkyl complex which could be deprotonated by excess aluminum alkyl to give an aluminum-stabilized alkylidene complex¹⁵ or one in which an intramolecular α -abstraction reaction¹⁶ might be more facile.

Finally, these results raise an interesting question. Is it possible that "soft" anions such as iodide or triflate can assume at least one of the important roles of an aluminum reagent elsewhere in early-transition-metal alkyl chemistry? An answer seems within reach since iodide and triflate could be substituted for chloride in other systems by using the trimethylsilyl reagents we have observed here.

Experimental Section

All experiments were done either under argon by standard Schlenk techniques or under nitrogen in a Vacuum Atmospheres HE43-2 drybox. Solvents were rigorously dried under nitrogen by standard techniques. $[\text{Ta}(\text{CHCMe}_3)(\text{dmpe})\text{Cl}_3]_x$ was prepared by the published method.¹⁶ NMR values are measured in parts per million.

Preparations. $\text{Ta}(\text{CHCMe}_3)(\text{dmpe})_2\text{Cl}$. Dmpe (1.63 g, 10.8 mmol) was added to $[\text{Ta}(\text{CHCMe}_3)(\text{dmpe})\text{Cl}_3]_x$ (5.0 g, 9.9 mmol) suspended in THF (100 mL). The nitrogen was removed by freeze-pump-thaw cycles, and the solution was placed under argon. Sodium amalgam (113 g, 0.41%) was added, and the mixture was stirred under argon at room temperature for 12 h. The red solution was decanted, and the amalgam was washed with 100 mL of ether. The decanted solution and the extracts were filtered through a pad of Celite, and the filtrate was evaporated to dryness. The crude product was recrystallized from ether; yield 4.7 g (81%).

^1H NMR (C_6D_6 , 250 MHz, 298 K) 1.52 (m, 12, $-\text{PMe}'\text{Me}$), 1.41 (m, 12, $-\text{PMe}'\text{Me}$), 1.35 (m, 8, $\text{PCH}_2\text{CH}_2\text{P}$), 0.87 (s, 9, CHCMe_3), -8.49 (quintet, 1, $J_{\text{HP}} = 6.7$ Hz, CHCMe_3); ^{13}C NMR (C_6D_6 , 22.53 MHz, 298 K, ^1H gated decoupled) 217.3 (doublet, $J_{\text{CP}} = 7.8$ Hz, $J_{\text{CH}} = 57$ Hz, CHCMe_3), 47.1 (s, CHCMe_3), 34.6 (q, $J_{\text{CH}} = 125$ Hz, CHCMe_3), 33.8 (triple quintet, $J_{\text{CP}} = 7.8$ Hz, $J_{\text{CH}} = 129$ Hz, $\text{PCH}_2\text{CH}_2\text{P}$), 23.2 (quartet of quintets, $J_{\text{CP}} = 5.9$ Hz, $J_{\text{CH}} = 125$ Hz, $-\text{PMe}'\text{Me}$), 18.8 (quartet of quintets, $J_{\text{CP}} = 5.9$ Hz, $J_{\text{CH}} = 126$ Hz, $-\text{PMe}'\text{Me}$); ^{31}P NMR (toluene, 298 K, 36.43 MHz) 28.00 (s) (the spectrum at 153 K in pentane was unchanged); IR (Nujol) 2200 cm^{-1} (ν_{CH_α}). Anal. Calcd for $\text{TaC}_{17}\text{H}_{42}\text{ClP}_4$: C, 34.79; H, 7.16. Found: C, 34.77; H, 7.31.

$\text{Ta}(\text{CCMe}_3)(\text{H})(\text{dmpe})_2(\text{ClAlMe}_3)$. AlMe_3 (0.15 g, 2.1 mmol) was added to $\text{Ta}(\text{CHCMe}_3)(\text{dmpe})_2\text{Cl}$ (1.2 g, 2.05 mmol) in pentane (50 mL) at -30°C . Tan microcrystals immediately precipitated and were filtered off; yield 1.15 g (85%). The crude product is pure by ^1H NMR spectroscopy but can be recrystallized easily from toluene-pentane solutions at -30°C .

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Table III. Experimental Data for the X-ray Diffraction Study of Ta(CCMe₃)(H)(dmpe)₂(ClAlMe₂)

(A) Crystal Parameters	
crystal system: monoclinic	space group: $P2_1/c$
$a = 9.8587$ (24) Å	$V = 3160.5$ (15) Å ³
$b = 22.2799$ (63) Å	$Z = 4$
$c = 14.7965$ (40) Å	mol wt = 658.50
$\beta = 103.479$ (20)°	ρ (calcd) = 1.38 g cm ⁻³
(B) Data Collection	
radiation: Mo K α (λ 0.71073 Å) from graphite monochromator	
2θ limits: 4.0°–45°	
scan width: [1.6 + $\Delta(K\alpha_1 - K\alpha_2)$]°	
scan speed: 2.55° min ⁻¹	
scan type: coupled $2\theta - \theta$	
bkgd measmt: stationary crystal and counter; 1/4 total scan time before and after scan	
reflections measd: $+h+k+l$	
reflections collected: 4495 total yielding 4152 unique data	
absorption coeff: 39.8 cm ⁻¹	
"ignorance" factor: 0.02	

¹H NMR (toluene-*d*₈, 250 MHz, 213 K) 3.13 (tt, 1, ²J_{HP} = 10 Hz; ²J_{HP} = 90 Hz, TaH), 1.58 (broad singlet, 12, PMe), 1.17 (broad singlet, 6, PMe), 1.09 (broad singlet, 6, PMe), 0.85 (s, 9, CMe₃), -0.1 (s, 9, AlMe₃) (the dmpe methylene resonances could not be assigned); ³¹P{¹H} NMR (toluene-*d*₈, 36.43 MHz, 298 K) 28.7 (broad singlet), ³¹P{¹H} NMR (213 K) 21.1 (broad doublet, ²J_{PP} ≈ 10 Hz), 41.4 (broad doublet, ²J_{PP} ≈ 10 Hz); ³¹P NMR (213 K) 21.4 (broad singlet), 41.4 (doublet, ²J_{HP} = 91 Hz); ¹³C NMR (C₆D₆, 22.53 MHz, 298 K, ¹H gated decoupled) 272.3 (broad singlet, CCMe₃), 49.2 (s, CCMe₃), 34.6 (q, ¹J_{CH} = 125 Hz, CMe₃), 30.7 (triplet of quintets, ¹J_{CP} = 12 Hz, ¹J_{CH} = 129 Hz, PCH₂CH₂P), 22.6 (q, ¹J_{CH} = 127 Hz, PMe), 16.5 (q, ¹J_{CH} = 125 Hz, PMe), -4.4 (q, ¹J_{CH} = 109 Hz, ClAlMe₂); IR (Nujol) 1590 cm⁻¹ (s, ν_{TaH}). Anal. Calcd for TaC₂₀H₃₁ClP₄Al: C, 36.46; H, 7.75. Found: C, 36.00; H, 7.31.

Ta(CCMe₃)(H)(dmpe)₂(ClAlMe₂Cl). AlMe₂Cl (0.8 mL, 1.8 M in hexane, 1.4 mmol) was added to Ta(CHCMe₃)(dmpe)₂Cl (0.75 g, 1.28 mmol) in pentane (50 mL) at -30 °C. White microcrystals precipitated immediately. The crystals were collected by filtration, washed with pentane (30 mL), and dried in vacuo; yield 0.75 g, (86%). Ta(CCMe₃)(H)(dmpe)₂(ClAlMe₂Cl) is not soluble in pentane and only sparingly soluble in toluene (ca. 1 g in 30 mL).

¹H NMR (toluene-*d*₈, 250 MHz, 213 K) 3.33 (triplet of multiplets, 1, J_{HP} = 89 Hz, TaH), 1.6 (broad singlet, 12, PMe), 1.2 (broad singlet, 12, PMe), 0.86 (s, 9, CCMe₃), 0.12 (s, 6, AlMe₂Cl₂); ³¹P{¹H} NMR (toluene-*d*₈, 36.43 MHz, 208 K) 19.2 (m, ²J_{PP} = 11 Hz), 39.2 (m, ²J_{PP} = 11 Hz); ³¹P NMR 19.2 (broad singlet), 39.2 (broad doublet, ²J_{HP} = 91 Hz); IR (Nujol) 1595 cm⁻¹ (s, ν_{TaH}). ¹H NMR signals for the dmpe methylene protons could not be located. Anal. Calcd for TaC₁₉H₄₈Cl₂P₄Al: C, 33.59; H, 7.07. Found: C, 33.39; H, 7.33.

Ta(CHCMe₃)(dmpe)₂I/Ta(CCMe₃)(H)(dmpe)₂I. Me₃SiI (1.4 g, 5.8 mmol) was added to 1.7 g (2.9 mmol) of Ta(CHCMe₃)(dmpe)₂Cl in 20 mL of toluene at room temperature. After 2 h the toluene was removed in vacuo and the orange crystalline solid, which was pure product by ¹H NMR spectroscopy, was recrystallized from a mixture of toluene and pentane; yield 1.8 g (92%).

¹H NMR (toluene-*d*₈, 206 K) 2.30 (tt, ²J_{HP} = 90 Hz, 10 Hz, TaH), 1.95, 1.69, 1.39, 1.26 (each a singlet, 6, PMe groups), 1.00 (s, 9, CMe₃), -9.7 (br s due to Ta(CHCMe₃)(dmpe)₂I) (see Figure 7); ¹³C{¹H} NMR (toluene-*d*₈, 62.83 MHz, 336K) 248.3 (m, av of Ta=CHCMe₃ and Ta=CCMe₃), 47.6 (s, CMe₃), 34.5 (s, CMe₃), 32.8 (m, PCH₂CH₂P), 23.9 (br s, PMe), 22.4 (br s, PMe'); ¹³C{³¹P} NMR (benzene-*d*₆, 67.89 MHz, 336 K) 249 (d, ¹J_{CH} = 28 Hz, avg Ta=CCMe₃ and Ta=CHCMe₃), 48 (s, CMe₃), 34.5 (q, ¹J_{CH} = 129 Hz, CMe₃), 33 (t, ¹J_{CH} = 126 Hz, PCH₂CH₂P), 23.9 (q, ¹J_{CH} = 121 Hz, PMe), 22.4 (q, ¹J_{CH} = 121 Hz, PMe'); ³¹P{¹H} NMR (see Figure 6) (J_{PP} ≈ 10 Hz in Ta(CCMe₃)(H)(dmpe)₂I). Anal. Calcd for TaC₁₇H₄₂I₂P₄: C, 30.10; H, 6.20. Found: C, 29.81; H, 6.06.

Ta(CCMe₃)(H)(dmpe)₂(CF₃SO₃). This compound was prepared with Me₃SiOSO₂CF₃ in a manner similar to that used to prepare Ta(CCMe₃)(H)(dmpe)₂I. The crude product was recrystallized from a mixture of THF and ether; yield 75%.

¹H NMR (toluene-*d*₈, 208 K) 3.45 (tt, 1, ²J_{HP} = 89 Hz, ²J_{HP} = 12 Hz, TaH), 1.64, 1.60, 1.32, 1.22 (each a singlet, 6, PMe), 0.85 (s, 9, CCMe₃); ¹H NMR (toluene-*d*₈, 355 K) 1.55 (br s, 12, PMe), 1.45 (br s, 12, PMe), 0.81 (s, 9, CCMe₃), 0.08 (br quintet, 1, ²J_{HP} = 38 Hz, TaH); ¹³C NMR (C₆D₆Br, 298 K) 279.3 (br s, CCMe₃), 120.8 (q, ¹J_{CF} = 318.6, CF₃SO₃), 50.1 (s, CCMe₃), 35.4 (q, ¹J_{CH} = 125 Hz, CCMe₃), 31.3 (t,

Table IV. Final Positional Parameters for Ta(CCMe₃)(H)(dmpe)₂(ClAlMe₂)

atom	x	y	z	B _{iso}
Ta	0.28991 (2)	0.10199 (1)	0.76645 (1)	
Cl	0.1162 (2)	0.00334 (8)	0.73614 (13)	
P(1)	0.0561 (2)	0.15990 (8)	0.69966 (12)	
P(2)	0.1945 (2)	0.12473 (9)	0.90674 (12)	
P(3)	0.4954 (2)	0.03311 (8)	0.77206 (12)	
P(4)	0.3024 (2)	0.08931 (8)	0.59377 (12)	
Al	0.0735 (2)	-0.09577 (7)	0.76600 (13)	
C(1)	0.4006 (5)	0.1700 (2)	0.7826 (4)	
C(2)	0.4938 (6)	0.2248 (3)	0.7970 (5)	
C(3)	0.4063 (9)	0.2812 (3)	0.7963 (7)	
C(4)	0.6027 (10)	0.2225 (4)	0.8881 (6)	
C(5)	0.5722 (9)	0.2303 (4)	0.7203 (6)	
C(6)	0.1235 (9)	-0.1374 (4)	0.6618 (6)	
C(7)	0.1863 (9)	-0.1161 (4)	0.8893 (5)	
C(8)	-0.1272 (8)	-0.0925 (3)	0.7594 (6)	
C(11)	-0.0942 (8)	0.1235 (5)	0.6282 (7)	
C(12)	0.0519 (10)	0.2292 (5)	0.6389 (10)	
C(13)	-0.0144 (12)	0.1831 (8)	0.7966 (9)	
C(21)	0.3117 (11)	0.1584 (4)	1.0054 (5)	
C(22)	0.1231 (10)	0.0638 (4)	0.9607 (6)	
C(23)	0.0496 (12)	0.1775 (5)	0.8826 (7)	
C(31)	0.4868 (9)	-0.0434 (4)	0.8093 (8)	
C(32)	0.6610 (7)	0.0568 (4)	0.8440 (6)	
C(33)	0.5393 (10)	0.0229 (5)	0.6601 (6)	
C(41)	0.2794 (13)	0.1525 (5)	0.5144 (6)	
C(42)	0.1947 (10)	0.0341 (4)	0.5198 (5)	
C(43)	0.4775 (10)	0.0688 (6)	0.5913 (6)	
H(1)	0.364 (5)	0.062 (2)	0.872 (3)	4.2 (12)
H(3A)	0.4654	0.3153	0.8053	7.0
H(3B)	0.3581	0.2789	0.8448	7.0
H(3C)	0.3407	0.2843	0.7381	7.0
H(4A)	0.6587	0.2576	0.8943	7.0
H(4B)	0.6599	0.1881	0.8888	7.0
H(4C)	0.5577	0.2203	0.9382	7.0
H(5A)	0.6299	0.2649	0.7307	7.0
H(5B)	0.5073	0.2337	0.6619	7.0
H(5C)	0.6284	0.1956	0.7202	7.0
H(6A)	0.1097	-0.1793	0.6671	7.0
H(6B)	0.2186	-0.1298	0.6627	7.0
H(6C)	0.0663	-0.1232	0.6050	7.0
H(7A)	0.1703	-0.1567	0.9030	7.0
H(7B)	0.1611	-0.0907	0.9343	7.0
H(7C)	0.2822	-0.1106	0.8903	7.0
H(8A)	-0.1595	-0.1313	0.7706	7.0
H(8B)	-0.1749	-0.0792	0.6993	7.0
H(8C)	-0.1443	-0.0653	0.8049	7.0
H(11A)	-0.1680	0.1516	0.6110	7.0
H(11B)	-0.1229	0.0915	0.6621	7.0
H(11C)	-0.0711	0.1079	0.5739	7.0
H(12A)	-0.0416	0.2430	0.6203	7.0
H(12B)	0.0883	0.2234	0.5855	7.0
H(12C)	0.1067	0.2581	0.6785	7.0
H(13A)	-0.0994	0.1616	0.7900	7.0
H(13B)	-0.0336	0.2247	0.7876	7.0
H(21A)	0.2640	0.1647	1.0535	7.0
H(21B)	0.3439	0.1957	0.9876	7.0
H(21C)	0.3888	0.1324	1.0272	7.0
H(22A)	0.0911	0.0785	1.0122	7.0
H(22B)	0.1931	0.0343	0.9812	7.0
H(22C)	0.0473	0.0463	0.9169	7.0
H(23A)	0.0848	0.2157	0.9044	7.0
H(23B)	-0.0165	0.1645	0.9159	7.0
H(31A)	0.5712	-0.0634	0.8077	7.0
H(31B)	0.4108	-0.0631	0.7690	7.0
H(31C)	0.4737	-0.0439	0.8709	7.0
H(32A)	0.7302	0.0277	0.8409	7.0
H(32B)	0.6530	0.0607	0.9065	7.0
H(32C)	0.6866	0.0942	0.8224	7.0
H(33A)	0.5064	-0.0153	0.6362	7.0
H(33B)	0.6378	0.0244	0.6692	7.0
H(41A)	0.2874	0.1392	0.4548	7.0
H(41B)	0.3490	0.1818	0.5371	7.0
H(41C)	0.1897	0.1696	0.5096	7.0
H(42A)	0.2124	0.0355	0.4594	7.0
H(42B)	0.0990	0.0426	0.5158	7.0
H(42C)	0.2162	-0.0048	0.5454	7.0
H(43A)	0.5339	0.1038	0.6030	7.0
H(43B)	0.4770	0.0539	0.5311	7.0

Table V. Anisotropic Thermal Parameters (in Å²)^a for Ta(CCMe₃)(H)(dmpe)₂(ClAlMe₃)

atom	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Ta	2.938 (13)	2.738 (13)	3.151 (14)	0.148 (7)	0.898 (9)	0.014 (7)
Cl	6.31 (9)	3.98 (8)	7.58 (10)	-1.56 (7)	1.33 (8)	0.63 (7)
P(1)	3.58 (7)	4.41 (8)	5.39 (8)	0.75 (6)	0.42 (6)	0.09 (6)
P(2)	6.89 (10)	5.34 (9)	4.09 (8)	1.01 (8)	2.68 (7)	0.11 (7)
P(3)	3.49 (7)	4.15 (8)	5.46 (9)	0.76 (6)	0.85 (6)	-0.16 (6)
P(4)	4.98 (8)	5.60 (9)	3.41 (7)	-0.42 (7)	1.07 (6)	-0.32 (6)
Al	4.32 (8)	3.56 (8)	4.29 (9)	-0.32 (6)	0.60 (7)	0.26 (6)
C(1)	3.5 (2)	3.3 (2)	3.7 (2)	0.5 (2)	0.9 (2)	-0.0 (2)
C(2)	4.2 (3)	3.4 (3)	5.9 (3)	-0.8 (2)	0.6 (2)	-0.4 (2)
C(3)	7.2 (5)	3.6 (3)	14.3 (7)	-1.4 (3)	2.0 (5)	-1.0 (4)
C(4)	8.8 (5)	7.3 (5)	8.1 (5)	-4.4 (4)	-1.9 (4)	0.8 (4)
C(5)	7.7 (5)	7.9 (5)	10.0 (6)	-4.8 (4)	3.5 (4)	-1.6 (4)
C(6)	8.2 (5)	6.1 (4)	7.4 (4)	2.0 (4)	1.7 (4)	-1.1 (3)
C(7)	6.8 (4)	8.3 (5)	5.6 (4)	-0.4 (4)	-0.3 (3)	2.0 (3)
C(8)	5.2 (4)	6.7 (4)	7.0 (4)	-0.5 (3)	1.5 (3)	1.2 (3)
C(11)	4.1 (4)	8.1 (5)	13.0 (7)	-0.0 (4)	-1.8 (4)	-0.4 (5)
C(12)	5.7 (5)	8.2 (6)	25.1 (13)	0.9 (4)	-0.2 (6)	8.6 (8)
C(13)	10.9 (8)	25.6 (16)	10.4 (7)	13.6 (10)	-0.7 (6)	-6.0 (9)
C(21)	11.9 (7)	8.1 (5)	5.4 (4)	-1.8 (5)	3.1 (4)	-1.8 (4)
C(22)	10.1 (6)	8.4 (5)	6.1 (4)	-0.7 (4)	5.0 (4)	0.3 (4)
C(23)	10.5 (7)	10.5 (7)	9.3 (6)	5.4 (6)	6.2 (6)	1.7 (5)
C(31)	6.3 (4)	4.3 (4)	16.0 (8)	2.1 (3)	3.4 (5)	1.8 (4)
C(32)	3.8 (3)	7.5 (5)	10.0 (5)	1.4 (3)	-1.4 (3)	-1.4 (4)
C(33)	8.1 (5)	12.3 (7)	7.6 (5)	5.3 (5)	3.7 (4)	0.6 (5)
C(41)	14.2 (8)	9.1 (6)	5.5 (4)	-3.6 (6)	2.9 (5)	0.6 (4)
C(42)	12.1 (7)	8.0 (5)	4.6 (4)	-3.6 (5)	2.0 (4)	-1.8 (3)
C(43)	7.2 (5)	16.5 (9)	5.6 (4)	2.5 (6)	3.1 (4)	-2.0 (5)

^a The anisotropic thermal parameters enter the expression for the calculated structure factor in the form $\exp[-1/4(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$.

¹J_{CH} = 129 Hz, PCH₂CH₂P, 23.4 (q, ¹J_{CH} = 126 Hz, PMe), 17.0 (q, ¹J_{CH} = 128 Hz, PMe); ³¹P{¹H} NMR (THF, 236 K) 41.6 (br s), 21.4 (br s); ³¹P NMR (THF, 236 K) 41.6 (d, ²J_{PH} = 88 Hz), 21.4 (br s); IR (Nujol) 1610 cm⁻¹ (TaH). Anal. Calcd for TaC₁₈H₄₂F₃O₃P₄S: C, 30.87; H, 6.00. Found: C, 30.56; H, 6.08.

Collection of X-ray Diffraction Data. A crystal measuring approximately 0.2 × 0.3 × 0.6 mm was used throughout the analysis. It was wedged into a thin-walled glass capillary which was purged with argon, flame sealed, inserted into a brass pin with beeswax, and placed into a eucentric goniometer.

The crystal was aligned, and data were collected on a Syntex P2₁ automated diffractometer with used of methods described previously.¹⁷ Crystal parameters and other details may be found in Table III. Final unit cell parameters are based on a least-squares refinement of the setting angles of the unresolved Mo Kα components of 25 reflections with 2θ between 27° and 33°.

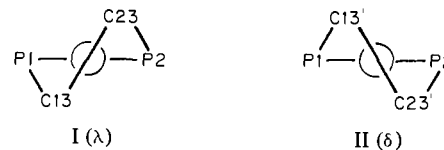
Crystallographic computations were carried out by using the SUN-YAB-modified Syntex XTL system as implemented on a NOVA 1200 computer.

Solution and Refinement of the Structure. An empirical absorption correction based on the ψ-scan method was applied to the raw intensity data. Seven curves were used, displaying transmission factors ranging from 0.752 to 0.820.

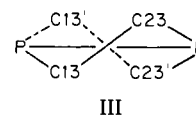
A Patterson synthesis was used to locate the tantalum atom; difference-Fourier calculations located all other nonhydrogen atoms. A further difference-Fourier synthesis, based only upon data with (sin θ)/λ < 0.30 Å⁻¹, provided the location of the terminal hydride ligand; the positional and isotropic thermal parameters of this atom were included in the model as variables. All other hydrogen atoms were included in fixed idealized positions [*d*(C-H) = 0.95 Å].¹⁸ Least-squares refinement proceeded smoothly to convergence, yielding the discrepancy indices *R*_F = 3.6%, *R*_{wF} = 4.5%, and GOF = 1.02¹⁹ for all 4152 unique data (none rejected). The corresponding indices based only on the 3693 reflections having |*F*_o| > 3σ(|*F*_o|) were *R*_F = 2.9%, *R*_{wF} = 3.5%, and GOF = 1.34. The final NO:NV ratio was 16.7:1. Positional and thermal parameters are listed in Tables IV and V.

The anomalously short C(13)-C(23) distance of 1.287 (16) Å [cf. the accepted C(sp³)-C(sp³) distance of ~1.54 Å] in conjunction with the large thermal ellipsoids of atom C(13) indicate the presence of a con-

formational disorder of this chelate ligand. The observed structure is, presumably, the composite of the λ and δ conformers of the P(1)-C(13)-C(23)-P(2) system (see I and II). Attempts to resolve the dis-



ordered components (via difference-Fourier syntheses) were not successful; the electron density of the C(13)-C(23) system in the resulting composite image (III) is thus



described by artificial thermal ellipsoids. (Note that there is no requirement for a 1:1 ratio of λ:δ conformer—indeed Figure 2 suggests that the λ component is more prevalent than the δ.) We note further that a number of other structures with dmpe ligands^{12,20} exhibit a disorder pattern similar to that found in the present complex.

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Registry No. Ta(CHCMe₃)(dmpe)₂Cl, 80559-92-8; Ta(CCMe₃)(H)(dmpe)₂(ClAlMe₃), 80559-93-9; Ta(CCMe₃)(H)(ClAlMe₂Cl), 80559-94-0; Ta(CHCMe₃)(dmpe)₂I, 80559-95-1; Ta(CCMe₃)(H)(dmpe)₂I, 80559-96-2; Ta(CCMe₃)(H)(dmpe)₂(CF₃SO₃), 80559-97-3; Ta(CHMe₃)(dmpe)Cl₃, 75299-05-7; AlMe₃, 75-24-1; AlMe₂Cl, 1184-58-3; Me₃SiI, 16029-98-4; Me₃SiOSO₂CF₃, 27607-77-8.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (23 pages). Ordering information is given on any current masthead page.

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(19) *R*_F = (Σ||*F*_o| - |*F*_c||/Σ|*F*_o|) × 100 (%); *R*_{wF} = [Σw(|*F*_o| - |*F*_c||)²/Σw|*F*_o|²]^{1/2} × 100 (%); GOF = [Σw(|*F*_o| - |*F*_c||)²(NO - NV)]^{1/2}; NO = number of observations; NV = number of variables.

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