

range was 4 kbar. The results, shown in Figure 1, may be summarized by the statement that the activation volume for the concerted shift (I) equals $-30 \pm 5 \text{ cm}^3/\text{mol}$ and that for the stepwise reaction (II) is $+10 \pm 2 \text{ cm}^3/\text{mol}$. These observations clearly confirm that this activation parameter provides a criterion for concertedness in sigmatropic shifts as well as for cycloadditions.

Acknowledgment. The National Science Foundation generously supported this investigation.

References and Notes

- (1) Paper 52 in the Series "Kinetics of Reactions in Solutions under Pressure".
- (2) Summarized in W. J. le Noble, *Prog. Phys. Org. Chem.*, **5**, 207 (1967); T. Asano and W. J. le Noble, *Chem. Rev.*, **78**, 407 (1978).
- (3) C. Walling and J. Peisach, *J. Am. Chem. Soc.*, **80**, 5819 (1958).
- (4) W. J. le Noble and B. A. Ojosi, *J. Am. Chem. Soc.*, **97**, 5939 (1975).
- (5) K. F. Fleischmann and H. Kelm, *Tetrahedron Lett.*, 3773 (1973). W. J. le Noble and R. Mukhtar, *J. Am. Chem. Soc.*, **96**, 6191 (1974); **97**, 5938 (1975).
- (6) K. R. Brower, *J. Am. Chem. Soc.*, **83**, 4370 (1961).
- (7) C. Walling and M. Naiman, *J. Am. Chem. Soc.*, **84**, 2628 (1962).
- (8) The rearrangement of allylic azides is a closely related case: W. J. le Noble, *J. Phys. Chem.*, **67**, 2451 (1963).
- (9) K. R. Brower and T. L. Wu, *J. Am. Chem. Soc.*, **92**, 5303 (1970).
- (10) R. C. Neuman and M. J. Amrich, *J. Am. Chem. Soc.*, **94**, 2730 (1972).
- (11) C. A. Stewart, *J. Am. Chem. Soc.*, **94**, 635 (1972).
- (12) F. J. Dinan and H. Tieckelman, *J. Org. Chem.*, **29**, 1650 (1964). J. E. Lister and H. Tieckelman, *J. Am. Chem. Soc.*, **90**, 4361 (1969). U. Schöllkopf and I. Hoppe, *Tetrahedron Lett.*, 4527 (1970); *Justus Liebigs Ann. Chem.*, **765**, 153 (1971).

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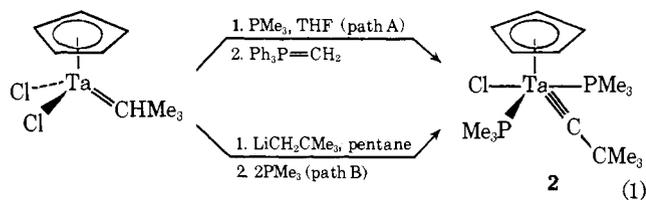
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Multiple Metal-Carbon Bonds. 10.¹ Thermally Stable Tantalum Alkylidyne Complexes and the Crystal Structure of $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\text{CPh})(\text{PMe}_3)_2\text{Cl}$

Sir:

Alkylidene complexes of niobium and tantalum have been prepared by deprotonating (formally² or actually³) the α -carbon atom of an alkyl ligand in a M^{5+} complex. We now can prepare thermally stable Ta neopentylidene^{4,5d} complexes similarly by deprotonating a cationic neopentylidene complex. Both neopentylidene and benzylidene complexes can be prepared more cleanly by accelerating abstraction of the alkylidene α -hydrogen atom by the alkyl ligand in neutral alkyl/alkylidene complexes with trimethylphosphine.

Addition of 1 mol of PMe_3 to red $\text{TaCp}(\text{CHCMe}_3)\text{Cl}_2$ ⁷ in toluene yields the sparingly soluble yellow adduct, $\text{TaCp}(\text{CHCMe}_3)\text{Cl}_2(\text{PMe}_3)$ (**1**).^{8a} In THF in the presence of 3–5 additional mol of PMe_3 , **1** reacts with $\text{Ph}_3\text{P}=\text{CH}_2$ to give $[\text{Ph}_3\text{PCH}_3]^+\text{Cl}^-$ (~90% yield). Removing the THF and extracting the residue with pentane gives moderately soluble, pale yellow, crystalline **2** in 60% crude yield (30% yield of pure, recrystallized **2**; eq 1, path A). Calcd for $\text{TaC}_{16}\text{H}_{32}\text{P}_2\text{Cl}$: C,



38.23; H, 6.41; Cl, 7.05. Found: C, 38.09; H, 6.26; Cl, 6.99. We postulate that $[\text{TaCp}(\text{CHCMe}_3)\text{Cl}(\text{PMe}_3)_2]^+\text{Cl}^-$ is an in-

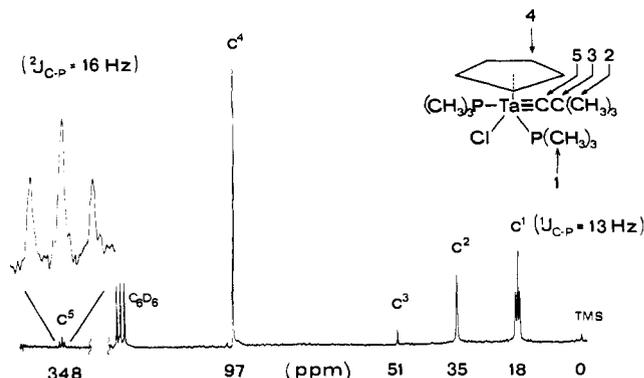


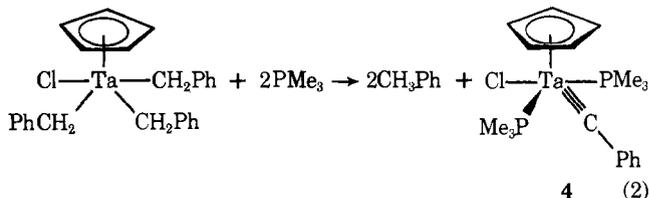
Figure 1. The 22.63-MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)(\text{CCMe}_3)(\text{PM}_3)_2\text{Cl}$ (**2**).

termediate from which a proton is removed by $\text{Ph}_3\text{P}=\text{CH}_2$ to give **2** (cf. the reaction of $\text{TaCp}_2(\text{CHCMe}_3)\text{Cl}$ with PMe_3 to give $[\text{TaCp}_2(\text{CHCMe}_3)(\text{PMe}_3)]^+\text{Cl}^-$ and the deprotonation of $[\text{TaCp}_2\text{Me}_2]^+\text{BF}_4^-$ by $\text{Me}_3\text{P}=\text{CH}_2$ to give $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)^3$). Yellow **2** is indefinitely stable at 25 °C in solution. In the solid state it reacts only slowly with oxygen but is more sensitive to water or other protic solvents. It sublimes with little decomposition at 100 °C and 1 μ and is a monomer in cyclohexane (mol wt, 527 cryoscopically; theory, 503).

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2** is shown in Figure 1. The most important feature is the 1:2:1 triplet at 348 ppm due to the neopentylidene α -carbon atom coupled to two equivalent phosphorus nuclei. Some coupling of the neopentyl methyl carbon atoms (C^2) to phosphorus can also be seen. In the gated decoupled spectrum the resonances for C^5 and C^3 are broad (owing to long-range CH coupling), but every other peak is split into the appropriate multiplet. The neopentylidene C^α resonance is ~100 ppm farther downfield than the neopentylidene C^α resonance in $\text{TaCp}(\text{CHCMe}_3)\text{Cl}_2$ ⁷ and related molecules^{1,2} and is in the same region where the alkylidene α -carbon resonances in group 6 complexes such as $\text{Br}(\text{CO})_4\text{W}=\text{CPh}$ are found.⁵ The ^1H NMR spectrum^{8b} also suggests that the phosphine ligands are equivalent.

The reaction of $\text{LiCH}_2\text{CMe}_3$ with $\text{TaCp}(\text{CHCMe}_3)\text{Cl}_2$ at 25 °C in pentane gives $\text{TaCp}(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)\text{Cl}$ (**3**) in 85–90% isolated yield as a pentane-soluble, thermally stable, sublimable, orange oil.⁹ On adding PMe_3 to a pentane solution of **3** at 25 °C 1 mol of neopentane evolves immediately and **2** forms quantitatively (eq 1, path B); no other products can be seen by ^1H NMR. We believe that PMe_3 coordinates to **3** to give a pseudo-five-coordinate complex in which abstraction of the neopentylidene ligand's α -hydrogen atom by the neopentyl ligand is more favorable than it is in pseudotetrahedral **3**. It is also possible that abstraction of an α -hydrogen atom from the neopentyl by the neopentylidene ligand is similarly "accelerated", but, since this reaction is degenerate, we cannot tell which α -abstraction process is faster.

The reaction of the thermally unstable $\text{TaCp}(\text{CH}_2\text{Ph})_3\text{Cl}$ ¹⁰ in benzene with 2 mol of PMe_3 gives less soluble, red $\text{TaCp}(\text{CH}_2\text{Ph})_3\text{Cl}(\text{PMe}_3)$ (by ^1H NMR) which dissolves completely on heating to 60 °C for 2 h to give an orange solution which contains 2 mol of toluene (by ^1H NMR and GLC) and **4** (eq 2). We do not yet know whether pseudo-six-coordi-



nate $\text{TaCp}(\text{CH}_2\text{Ph})_3\text{Cl}(\text{PMe}_3)$ decomposes more readily than pseudo-five-coordinate $\text{TaCp}(\text{CH}_2\text{Ph})_3\text{Cl}$ or whether $\text{TaCp}(\text{CHPh})(\text{CH}_2\text{Ph})\text{Cl}_x$ ($x = 0$ or 1) is an observable intermediate (cf. $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\text{CHPh})(\text{CH}_2\text{Ph})\text{Cl}$ below). The ^{13}C spectrum of **4** is similar to that of **2**;¹¹ the benzyldiene α -carbon resonance occurs at 334 ppm with $J_{\text{CP}} = 21 \pm 1$ Hz.

Both $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\text{CHCMe}_3)(\text{CH}_2\text{CMe}_3)\text{Cl}^{12a}$ and $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\text{CHPh})(\text{CH}_2\text{Ph})\text{Cl}^{12b}$ react instantly with PMe_3 to give $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\text{CCMe}_3)(\text{PMe}_3)_2\text{Cl}$ (**5a**) and $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\text{CPh})(\text{PMe}_3)_2\text{Cl}$ (**5b**) quantitatively at 25 °C. The ^{13}C NMR spectrum of each is similar to that of the corresponding $\eta^5\text{-C}_5\text{H}_5$ analogue above (for **5a** $\delta_{\text{C}\alpha} 354$ ($J_{\text{CP}} = 19 \pm 1$ Hz); for **5b** $\delta_{\text{C}\alpha} 345$ ($J_{\text{CP}} = 20 \pm 1$ Hz)). **5a** and **5b** are more soluble in pentane, but otherwise their physical properties are very similar to those of **2** and **4**, respectively. They too are monomers (mol wt for **5b**, 576 in cyclohexane (average of 565 and 586); theory, 593).

Bridging alkylidene ligands are found in the complexes,¹³ $[\text{M}(\text{CH}_2\text{SiMe}_3)_2(\text{CSiMe}_3)]_2$ ($\text{M} = \text{Nb}$ or Ta), in which M is in the same formal oxidation state as Ta in **2**, **4**, or **5**, but the valence electron count of hypothetical monomeric $\text{M}(\text{CH}_2\text{SiMe}_3)_2(\text{CSiMe}_3)$ is 10 (and the complex is not crowded) while the valence electron count in **2**, **4**, and **5** is 18 and they are relatively crowded molecules. Since the formal valence electron count about each metal does not change on dimerization through the alkylidene ligand, steric hindrance may be the primary reason why **2**, **4**, and **5** do not dimerize.

We expect the alkylidene α -carbon atom to be nucleophilic since the alkylidene ligand is formed in a manner similar to that of an alkylidene ligand, and alkylidene ligands are nucleophilic in $\text{TaCp}(\text{CHCMe}_3)\text{Cl}_2$ and all other complexes with the metal in that formal oxidation state ($3+$ or $5+$ depending on one's point of view).¹⁻³

The molecular geometry of $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\text{CPh})(\text{PMe}_3)_2\text{Cl}$ (**5b**) has been determined unequivocally by means of a single-crystal X-ray diffraction study. It crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with $a = 10.5129$ (12) Å, $b = 13.8147$ (16) Å, $c = 18.1793$ (21) Å, $\beta = 102.945$ (8)°, $V = 2573.1$ (5) Å³, and $\rho(\text{calcd}) = 1.531$ g cm⁻³ for mol wt 592.90 and $Z = 4$. Intensity data were collected by the θ - 2θ scan technique on a Syntex P2₁ automated four-circle diffractometer and were corrected for absorption via an empirical method based upon a series of ψ scans ($\mu 47.3$ cm⁻¹). The structure was solved via Patterson and difference-Fourier methods; full-matrix least-squares refinement (Ta, Cl, P, and C anisotropic; H isotropic) has led to the final discrepancy indices $R_F = 4.1\%$ and $R_{wF} = 3.5\%$ for those 3140 reflections with $4^\circ < 2\theta < 45^\circ$ (Mo $K\alpha$ radiation) and $|F_o| > \sigma(|F_o|)$. All atoms other than the hydrogen atoms of the $\eta^5\text{-C}_5\text{Me}_5$ ligand were located directly; the molecular geometry is shown in Figure 2.

The central tantalum (5+) atom is surrounded in a "four-legged piano stool" arrangement by the $\eta^5\text{-C}_5\text{Me}_5$ ligand and the four monodentate ligands. The tantalum-benzyldiene linkage ($\text{Ta}-\text{C}^1$) is 1.849 (8) Å in length—i.e., some 0.40 Å shorter than a normal $\text{Ta}-\text{C}(\text{sp}^3)$ single bond and ~ 0.18 Å shorter than the tantalum-neopentylidene linkage of 2.030 (6) Å found in $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)_2(\text{CHCMe}_3)\text{Cl}$.¹⁴ Distortion of the $\text{Ta}-\text{C}^1-\text{C}^2$ angle (171.8 (6)°) from 180° presumably results from repulsive intermolecular interactions. Nevertheless, it seems appropriate to regard the tantalum-benzyldiene linkage as essentially a triple bond. The C^1-C^2 bond length of 1.467 (10) Å is quite in keeping with its being an unperturbed $\text{C}(\text{sp})-\text{C}(\text{sp}^2)$ single bond.

$\text{Ta}-\text{C}(\text{cyclopentadienyl})$ bonding distances are (cyclically) 2.417 (8), 2.460 (8), 2.518 (9), 2.455 (9), and 2.397 (9) Å; the average value is 2.449 Å. The four monodentate ligands define a remarkable regular geometric pattern around the tantalum

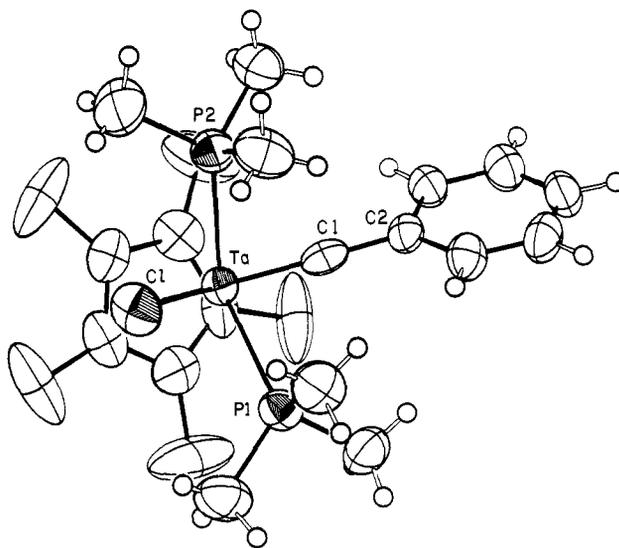


Figure 2. Molecular geometry of the $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\text{CPh})(\text{PMe}_3)_2\text{Cl}$ molecule (ORTEP diagram; 50% probability contours for all atoms except hydrogen atoms).

atom. The two "pseudo-trans" angles, $\text{C}^1-\text{Ta}-\text{Cl}$ and $\text{P}^1-\text{Ta}-\text{P}^2$, are equivalent with values of 125.54 (22) and 125.41 (7)°, respectively. The four cis angles are $\text{C}^1-\text{Ta}-\text{P}^1 = 80.29$ (22), $\text{P}^1-\text{Ta}-\text{Cl} = 76.66$ (7), $\text{Cl}-\text{Ta}-\text{P}^2 = 75.76$ (7), and $\text{P}^2-\text{Ta}-\text{C}^1 = 78.96$ (22)°. The tantalum-phosphorus bond lengths are $\text{Ta}-\text{P}^1 = 2.567$ (2) and $\text{Ta}-\text{P}^2 = 2.565$ (2) Å, while the tantalum-chlorine distance is 2.548 (2) Å. All other distances and angles in the structure are normal.

Acknowledgments. This work was generously supported by the National Science Foundation (Grant NO. CHE76-07410 to R. R. Schrock and CHE77-04981 to M. R. Churchill). We also thank the Francis N. Bitter National Magnet Laboratory for the use of their high field ^1H and ^{13}C NMR facilities.

References and Notes

- (1) Part 9: R. R. Schrock, L. W. Messerle, C. D. Wood, and L. J. Guggenberger, *J. Am. Chem. Soc.*, **100**, 3793 (1978).
- (2) Part 8: R. R. Schrock and J. D. Fellmann, *J. Am. Chem. Soc.*, **100**, 3359 (1978).
- (3) (a) Part 7: R. R. Schrock and P. R. Sharp, *J. Am. Chem. Soc.*, **100**, 2389 (1978); (b) R. R. Schrock, *J. Am. Chem. Soc.*, **97**, 6577 (1975).
- (4) One referee vehemently objected to the use of the alkylidene nomenclature instead of Fischer's⁵ carbyne nomenclature. "Alkylidene" is not only logical (alkyl \rightarrow alkylidene \rightarrow alkylidene) but has been used elsewhere in organic and organometallic chemistry for at least 10 years. (See, for example, alkylidynecobalt nonacarbonyl cluster chemistry.⁶)
- (5) (a) E. O. Fischer and U. Schubert, *J. Organomet. Chem.*, **100**, 59 (1975). (b) E. O. Fischer, *Adv. Organomet. Chem.*, **14**, 1 (1976). (c) E. O. Fischer, T. L. Lindner, and F. R. Kreissl, *J. Organomet. Chem.*, **112**, C27 (1976). (d) The largest class of alkylidene complexes consists of examples of the type $\text{X}(\text{CO})_5\text{M}\equiv\text{CR}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}; \text{M} = \text{Cr}, \text{Mo}, \text{W}; \text{R} = \text{C}_6\text{H}_5, \text{CH}_3$), most of which are barely stable at room temperature.^{5a,b} Other examples, e.g., $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{W}\equiv\text{CR}$,^{5c} are apparently more stable.
- (6) D. Seyferth, *Adv. Organomet. Chem.*, **14**, 97 (1976).
- (7) S. J. McLain, C. D. Wood, and R. R. Schrock, *J. Am. Chem. Soc.*, **99**, 3519 (1977).
- (8) (a) ^1H NMR (τ , CD_2Cl_2): 4.01 (d, 1, $J_{\text{HP}} = 1.6$ Hz, $=\text{CHCMe}_3$), 4.15 (d, 5, $J_{\text{HP}} = 2.9$ Hz, $\eta^5\text{-C}_5\text{H}_5$), 8.40 (d, 9, $J_{\text{HP}} = 8.6$ Hz, PMe_3), 8.87 (s, 9, $=\text{CHCMe}_3$). (b) ^1H NMR (τ , C_6D_6): 4.67 (t, 5, $J_{\text{HP}} \approx 2.5$ Hz, Cp), 8.65 (1:2(br):1, t, 9, $J_{\text{HP}} \approx 3.5$ Hz, PMe_3), 8.76 (s, 9, CMe_3).
- (9) ^1H NMR (τ , C_6D_6): 4.08 (s, 1, $=\text{CHCMe}_3$), 4.27 (s, 5, Cp), 7.90 (d, 1, CH_2CMe_3 , $J = 13$ Hz), 8.90 (s, 9, $=\text{CHCMe}_3$), 8.95 (s, 9, CH_2CMe_3), 9.27 (d, 1, CH_2CMe_3 , $J = 13$ Hz). ^{13}C NMR (gated decoupled, parts per million, C_6D_6): 240 (d, $=\text{CHCMe}_3$, $J_{\text{CH}} = 81$ Hz), 104 (d, Cp, $J_{\text{CH}} = 177$ Hz), 79.1 (dd, CH_2CMe_3 , $J \approx 100, 110$ Hz), 47.3 (s, $=\text{CHCMe}_3$), 34.8 (s, CH_2CMe_3), 34.6 (q, $=\text{CHCMe}_3$, $J_{\text{CH}} = 125$ Hz), 33.4 (q, CH_2CMe_3 , $J_{\text{CH}} = 125$ Hz).
- (10) Brown $\text{TaCp}(\text{CH}_2\text{Ph})_3\text{Cl}$ can be prepared from $\text{Ta}(\text{CH}_2\text{Ph})_3\text{Cl}_2$ (R. R. Schrock, *J. Organomet. Chem.*, **122**, 209 (1976)) and NaCp in THF at -78°C , followed by warming to room temperature, removal of solvent, and recrystallization from benzene-pentane. ^1H NMR (τ , C_6D_6): 4.65 (s, 5, Cp), 7.13 (s, 6, CH_2); phenyl region is complex (relative area 15).
- (11) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4** (parts per million from Me_4Si in C_6D_6): 334 (t, C^α , $J_{\text{CP}} = 21 \pm 1$ Hz), 153.2 (C_{ipso}), 128.5 and 127.6 (C_o and C_m), 122.7 (C_p), 98.7 (s, C_p), 16.9 (t, PMe_3 , $J_{\text{CP}} = 13 \pm 1$ Hz).
- (12) (a) $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\text{CH}_2\text{CMe}_3)(\text{CHCMe}_3)\text{Cl}$ is formed when $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)$ -

(CH₂CMe₃)Cl₃ is treated with 2 mol of LiCH₂CMe₃ in pentane at -78 °C: δ (CHCMe₃) 232 ($J_{\text{CH}} = 76 \pm 2$ Hz), τ (CHCMe₃) 6.25, τ (CH_AH_BCMe₃) 9.08, τ (CH_AH_BCMe₃) 9.25 ($J_{\text{H}_A\text{H}_B} = 14$ Hz). (b) Ta(η^5 -C₅Me₅)(CHPh)(CH₂Ph)Cl is formed when Ta(CH₂Ph)₃Cl₂ is treated with LiC₅Me₅ in THF for 1 day: δ (CHPh) 222 ($J_{\text{CH}} = 85 \pm 2$ Hz), τ (CHPh) 6.71, τ (CH_AH_BPh) 7.66, τ (CH_AH_BPh) 7.82 ($J_{\text{H}_A\text{H}_B} = 11$ Hz). Ta(η^5 -C₅Me₄Et)(CHPh)(CH₂Ph)Cl forms similarly and has been analyzed. Calcd for TaC₂₅H₃₀Cl: C, 54.91; H, 5.52; Cl, 6.48. Found: C, 54.30; H, 5.40; Cl, 6.37.

- (13) (a) W. Mowat and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1120 (1973); (b) F. Huq, W. Mowat, A. C. Skapski, and G. Wilkinson, *Chem. Commun.*, 1477 (1971).
 (14) (a) M. R. Churchill, F. J. Hollander, and R. R. Schrock, *J. Am. Chem. Soc.*, **100**, 647 (1978); (b) M. R. Churchill and F. J. Hollander, *Inorg. Chem.*, **17**, 1957 (1978).
 (15) (a) National Science Foundation Predoctoral Fellow, 1975–1978; (b) Dow Chemical Central Research Fellow, 1976–1977; (c) Alfred P. Sloan Fellow, 1976–1978.

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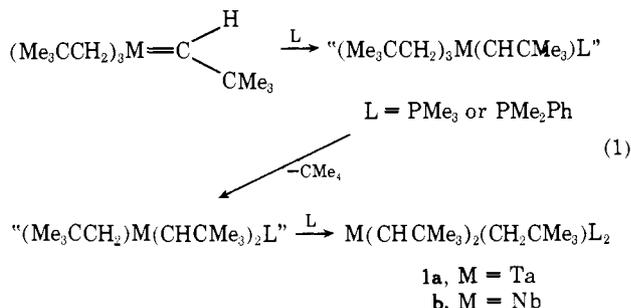
Received January 20, 1978

Multiple Metal–Carbon Bonds. 11.¹ Bisneopentylidene Complexes of Niobium and Tantalum

Sir:

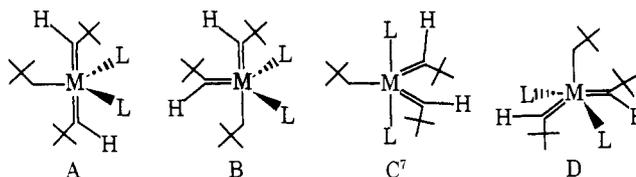
In a recent communication¹ we showed that alkylidyne complexes can be prepared from alkyl/alkylidene complexes by "accelerating" (with PMe₃) the nondegenerate α -hydrogen atom transfer from the alkylidene α -carbon atom to the alkyl α -carbon atom. An interesting question is what happens if α -hydrogen abstraction occurs in a di- or trialkyl-alkylidene complex? Either an alkyl/alkylidyne or a bisalkylidene complex in principle could be formed. Dimeric alkyl-"alkylidyne" complexes are known.^{1,2} We now want to show that bisneopentylidene complexes (of Nb and Ta) can also be the ultimate products of accelerated α -hydrogen abstraction reactions in di- or trineopentyl-neopentylidene complexes. They can also be prepared from alkylidyne-chloride complexes by substituting the chloride with the alkyl.^{3a}

Ta(CH₂CMe₃)₃(CHCMe₃)^{3b,c} is relatively stable thermally as a solid or in pentane or benzene (for weeks at 25 °C) probably because (i) intermolecular decomposition pathways are slow and (ii) the first observed change is a degenerate intramolecular scrambling of α -hydrogen atoms ($\Delta G^\ddagger \approx 28$ kcal mol⁻¹; no neopentane evolves during the scrambling process^{3b}). In the presence of at least 2 mol of L (L = PMe₃ or PMe₂Ph), however, neopentane (1 mol) does evolve, comparatively rapidly when L = PMe₃ (2 h at 25 °C) but more slowly (2 weeks at 25 °C) when L = PMe₂Ph. We therefore propose that a five-coordinate intermediate is formed (eq 1) in which α -



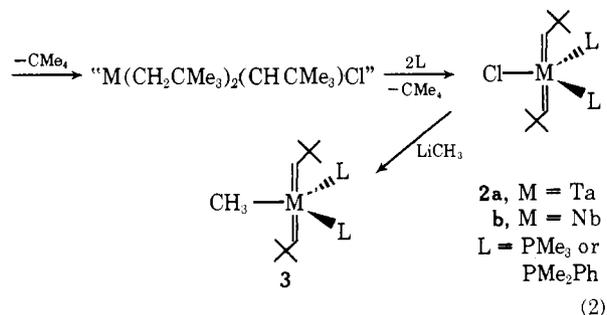
hydrogen atom abstraction^{3b} and that the final product (in essentially quantitative yield) is a bisneopentylidene complex, **1a**. It is not necessarily true that the immediate precursor is also a bisneopentylidene complex (see later), although this is what we have assumed for the present. The evolution of neopentane from Nb(CH₂CMe₃)₃(CHCMe₃)^{3b} is also accelerated dramatically on adding L and the analogous products, **1b**, can be isolated in ~75% yield. All complexes are orange to red, crystalline, sensitive to air and moisture, and moderately soluble in pentane. A molecular weight determination for Ta(CHCMe₃)₂(CH₂CMe₃)(PMe₃)₂ in cyclohexane (cryoscopically) showed it to be a monomer (mol wt found, 540 \pm 40; two runs at 0.006 and 0.011 M). The presence of two neopentylidene ligands is suggested by the instantaneous reaction of **1** with acetone to give 2 mol of disobutylene.⁴

The ¹H and ¹³C NMR spectra of **1** show that (i) it has a plane of symmetry and (ii) the neopentylidene ligands are nonequivalent on the NMR time scales (60–270 MHz) at 30 °C. For example, the ¹H NMR spectrum of Ta(CHCMe₃)₂(CH₂CMe₃)(PMe₃)₂ at 270 MHz shows three CMe₃ singlets, a PMe₃ triplet ($J_{\text{HP}} = 2.4$ Hz), a neopentyl H $_{\alpha}$ triplet at τ 9.39 ($J_{\text{HP}} = 19$ Hz), and two neopentylidene H $_{\alpha}$ resonances at τ 7.92 and 3.07 ($J_{\text{HP}} \leq 2$). On broad-band-decoupling ³¹P the neopentyl H $_{\alpha}$ triplet resonance becomes a singlet and the broadened neopentylidene H $_{\alpha}$ resonances sharpen. In the gated decoupled ¹³C spectrum we find two neopentylidene C $_{\alpha}$ doublet resonances at τ 274 and 246 with low CH coupling constants ($J_{\text{CH}} = 95$ and 85 Hz, respectively, $J_{\text{CP}} \leq 5$ Hz) characteristic of neopentylidene ligands in crowded environments.⁵ When L = PMe₂Ph (and M = Ta) the gated decoupled ¹³C NMR spectrum establishes that the phosphine's methyl groups are diastereotopic; two *P*-Me quartets are found (at δ 22.5 and 19.2; $J_{\text{CH}} = 128$ Hz) but only one type of phenyl ring. In the four most likely structures



(A–D) the neopentylidene ligands *must not freely rotate about the M=C axis*.⁶ We favor A, based only on the relatively large -CH₂-phosphorus coupling constant (19 Hz) vs. the relatively small =CH-phosphorus coupling constant (≤ 5 Hz).

Thermally unstable Ta(CH₂CMe₃)₄Cl can be prepared by adding HCl to Ta(CH₂CMe₃)₃(CHCMe₃) at -78 °C in pentane.^{3b} We added PMe₃ in an attempt to trap the proposed decomposition product, M(CH₂CMe₃)₂(CHCMe₃)Cl,⁸ the high yield product is, instead, Ta(CHCMe₃)₂(Cl)(PMe₃)₂ (**2a**, eq 2). Analogous procedures give thermally stable products



where L = PMe₂Ph or M = Nb. Apparently even the larger, less basic PMe₂Ph can coordinate to incipient M(CH₂CMe₃)₂(CHCMe₃)Cl to give (most likely) thermally