prevent similar decomposition of **2** and **3** respectively; **2** and **3** can be heated to 100° in toluene-d_8 for 6 hr without change (by ^{1}H NMR).

Some simple reactions of **5a** (Scheme II) confirm that the methylene ligand is nucleophilic. It reacts with CD_3I in benzene or dichloromethane to give pure CH_3D and **9a** (and it isomer, **9b**) probably via intermediate **8**, the exact nature of which is unknown at this time. It forms an adduct with $Al(CH_3)_3$ (**10**; cf. $(CH_3)_3PCH_2Al(CH_3)_3$)[12] which reacts with bases like $N(C_2H_5)_3$ to regenerate **5a.** This moderate, though significant, nucleophilic character of the methylene ligand in **5a** contrasts strongly with the electrophilic character of Fischer-type carbene ligands,[9] or $=C(C_6H_5)_2$ in $(CO)_5W[C(C_6H_5)_2]$,[3a] both of which add tertiary phosphines to form ylide complexes;[13] **5a** does not.

The results presented here (i) suggest that an alkyl ligand's α-hydrogen atoms are, in some instances, quite acidic and can be removed by base leaving a *nucleophilic* carbene ligand; (ii) indicate how some carbene complexes might decompose; and (iii) demonstrate that complexes of the methylene ligand are viable.

References and Notes

(1) "Methylene" terminology is preferred by analogy with phosphorus ylides, e.g., methylenetriphenylphosphorane. "Methylidene" (cf. alkylidene in general) and "carbene" are alternatives. The latter, however, commonly describes substituted carbene ligands in general.[9]

(2) (a) F. D. Mango and I. Dvoretsky, *J. Am. Chem. Soc.*, **88,** 1654 (1966); (b) P. W. Jolly and R. Pettit, *ibid.*, **88,** 5044 (1966); (c) M. L. H. Green, M. Ishaq, and R. N. Whiteley, *J. Chem. Soc. A*, 1508 (1967); (d) M. R. Collier, B. M. Kingston, and M. F. Lappert, *Chem. Commun.*, 1498 (1970); (e) N. J. Cooper and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 761 (1974); (f) W. Kirmse, "Carbene Chemistry", 2nd ed, Academic Press, New York, N.Y., 1971, Chapter 3.

(3) (a) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **95,** 5833 (1973); (b) A. Sanders, L. Cohen, W. P. Giering, D. Kenedy, and C. V. Magatti, *ibid.*, **95,** 5430 (1973).

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(5) L. J. Guggenberger and R. R. Schrock, *J. Am. Chem. Soc.*, following paper in this issue.

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(7) Decomposition of $Ta(\eta^5\text{-}C_5H_5)_2(CD_3)_3$ (in C_6D_6 at 125° for 8 hr) yields 1.4 mol (per Ta) of methane, which is 88% CHD_3 and 12% CD_4, and 0.9 mol of a mixture of 60% H_2, 35% HD, and 5% D_2. Apparently hydrogen atoms are abstracted from $\eta^5\text{-}C_5H_5$ under these conditions. **5**a may form under more carefully controlled conditions but since it is not significantly more stable than **1** (if at all) it would also decompose rapidly.

(8) (a) The structure of **1** is believed one in which all three methyl groups lie in a plane perpendicular to the $C_5H_5\text{–}Ta\text{–}C_5H_5$ plane based on analogy with the structure of $Nb(\eta^5\text{-}C_5H_5)_2(C_2H_4)(C_2H_5)$[8b] and on its ^{1}H NMR spectrum in C_6D_6 (τ 5.23 (10, C_5H_5), 9.69 (6, CH_3), and 9.75 (3, CH_3)). Labeling studies (to be reported separately) showed that $C(C_6H_5)_3^+$ attacks the central methyl group specifically. (b) L. J. Guggenberger, F. N. Tebbe, and P. Meakin, *J. Am. Chem. Sc.* **96,** 5420 (1974). (c) Note even methoxide ion deprotonates **4** which suggests **4** is more acidic than methanol.

(9) (a) F. A. Cotton and C. M. Lukehart, *Prog. Inorg. Chem.*, **16,** 487 (1972); (b) D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, **72,** 545 (1972); (c) D. J. Cardin, B. Cetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, **2,** 99 (1973); (d) E. O. Fischer, *Pure Appl. Chem.*, **30,** 353 (1972).

(10) This terminology is based on the electronic nature of the *coordinated* carbene carbon atom and should not be confused with that (usually opposite) based on the *free* carbene.[9b] The former seems more appropriate since no evidence suggests carbene complexes react via the corresponding free carbenes.[9]

(11) Note that this particular mechanism formally involves intermetallic methylene transfer.

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Structure of Bis(cyclopentadienyl)methylmethylenetantalum and the Estimated Barrier to Rotation about the Tantalum–Methylene Bond

Sir:

The preceding paper[1] describes the characterization of $Ta(\eta^5\text{-}C_5H_5)_2(CH_3)(CH_2)$ (**1**) and some related alkylidene complexes. Since this is the first isolated transition metal methylene complex, we undertook a structural investigation in order to confirm and characterize the Ta-methylene bonding. We report here the crystal structure of **1** and variable temperature ^{1}H NMR behavior of related complexes.

Crystals of **1** are monoclinic (space group $P2_1/c$; a = 6.544 (4), b = 11.685 (2), c = 15.339 (11) Å, and β = 117.13 (5)°) with four molecules per unit cell. We measured one-half the total data sphere to get at least two independent measurements for each reflection, corrected the data for absorption ($\mu(\text{Mo}K\alpha)$ = 110.2 cm^{-1}), and averaged symmetry equivalent reflections. All hydrogen atoms were located and the methyl and methylene hydrogen atoms' positional parameters refined. Final R values[2] for 1279 reflections with $F > \sigma(F)$ are 0.026 for R and 0.032 for R_w.

The molecule (Figure 1) has idealized $C_s(m)$ point symmetry in which $CH_3\text{-}Ta\text{-}CH_2$ (C–Ta–C) is the mirror plane. The two eclipsed cyclopentadienyl rings are 2.10 Å from Ta where their centroids subtend an angle of 135.7 (3)°; the C–Ta–C angle is 95.6 (3)°. Details of the CH_2 ligand and its bonding to Ta are the following. (i) Within experimental error the CH_2 plane is perpendicular to the C–Ta–C plane (88 (3)°) and the methylene carbon atom lies in the Ta–CH_2 plane (0.03 (3) Å out of the plane). (ii) The Ta–C bond distance is 2.026 (10) Å, (iii) The H–C–H angle is 107 (9)°.

The methylene ligand orients perpendicular to the C–Ta–C plane most likely because the p_z orbital on the sp^2-hybridized C_{carb} can thereby overlap well with appropriately hybridized Ta orbitals lying in the C–Ta–C plane. A similar argument involving overlap of ethylene π^* orbitals was put forward to account for ethylene's *in-plane* bonding in $Nb(\eta^5\text{-}C_5H_5)_2(C_2H_5)(C_2H_4)$.[3]

Since C_{carb} in **1** bears no substituents like $-NR_2$, $-OR$, or $-C_6H_5$, it can π-bond only with the metal. The perpendicular orientation and the high barrier to rotation (vide infra) suggest a full double bond between Ta and CH_2. The bond length (2,026 (10) Å) is approximately midway between a single (ca. 2.25 Å, this work and ref 4) and "triple" Ta–carbon bond length (1.76 (2) Å in $[(CH_3)_3CCH_2]_3\text{-}Ta{\equiv}CC(CH_3)_3{\cdot}Li(N,N'\text{-dimethylpiperazine})$[4]). Since the range of known $M\text{–}C_{\text{carb}}$ bond lengths is so great (ca. 1.95–2.15 Å),[5] it is perhaps not surprising that the $Ta\text{–}CH_2$ length falls within. Yet only $M\text{–}C_{\text{carb}}$ bond orders less than two have so far been postulated.[6]

The ^{1}H NMR spectra of $Ta(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH_3)(CH_3)(CH_2)$[1] (**2**), $Ta(\eta^5\text{-}C_5H_5)_2(Cl)[CHC(CH_3)_3]$ (**3**),[1] and $Ta(\eta^5\text{-}C_5H_5)_2(CH_2C_6H_5)(CHC_6H_5)$[1] (**4**) first suggested that the carbene ligand in each did not lie in the C_{carb}–Ta–Z plane (Z = CH_3, Cl, and $CH_2C_6H_5$, respectively); i.e., (i) the $\eta^5\text{-}C_5H_5$ ligands in **3** and **4** are nonequivalent (at 100 MHz); (ii) the benzyl α-protons in **4** are nonequivalent and give an AB quartet (at 100 MHz; τ 7.30 and 8.21, $^2J_{HH'}$ = 10.7 Hz); and (iii) the methylene protons in **2** also give an AB quartet (at 220 MHz; τ 0.02 and 0.10, $^2J_{HH'}$ = 7.7 Hz).

On warming ^{1}H NMR samples of **3** and **4** the characteristic nonequivalencies disappear, e.g., the spectrum of **4** (Figure 2) shows that the nonequivalent $\eta^5\text{-}C_5H_5$ groups and the nonequivalent benzyl α-protons *each* equilibrate.

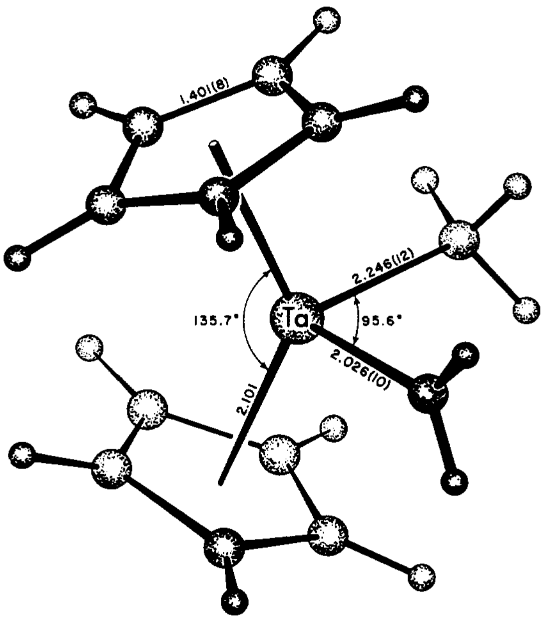

Figure 1. The molecular structure of $Ta(\eta^5\text{-}C_5H_5)_2(CH_3)(CH_2)$.

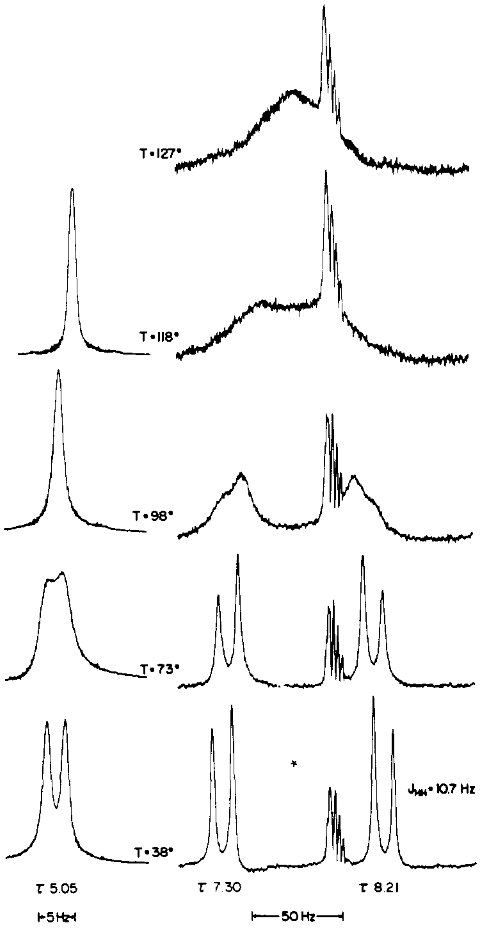

Figure 2. The $\eta^5\text{-}C_5H_5$ (τ 5.05) and benzyl α-proton signals in the 100-MHz ^1H NMR spectrum of $Ta(\eta^5\text{-}C_5H_5)_2(CH_2C_6H_5)(CHC_6H_5)$ in toluene-d_8 (* = toluene-d_7 traces of toluene-d_0).

Rapid hydrogen transfer between $CH_2C_6H_5$ or $\eta^5\text{-}C_5H_5$ and CHC_6H_5 in **4** can be ruled out since the benzylidene proton (at τ −1.03) does not take part in this process. The 220-MHz spectrum of an analog of **3**, $Ta(\eta^5\text{-}C_5H_4CH_3)_2(Cl)[CHC(CH_3)_3]$ (**5**),[7] shows eight nonequivalent cyclopentadienyl proton resonances at 20° (consistent with the molecule's asymmetry) which coalesce[8] to four (two protons each) on warming the sample to 106°. The temperature dependent process therefore creates only *one* symmetry plane.[9] Equilibration of $\eta^5\text{-}C_5H_4CH_3$ groups in **5** and, by analogy, $\eta^5\text{-}C_5H_5$ groups in **3**, via a tetrahedral-planar-tetrahedral conformational change can therefore be ruled out. "Rotation" of -CHR into the C_{carb}-Ta-Z plane (Z = Cl or $CH_2C_6H_5$) in **3**, **4**, and **5**, either to the "inside" or to the "outside", is the only reasonable alternative. The $\Delta G^\ddagger$ values for this process in **3** and **4** are 16.8 ± 0.1 (at 323 K) and 19.3 ± 0.1 kcal/mol (at 393°), respectively.[10]

In contrast, the resonance pattern for the methylene protons in **2**, at 220 MHz (vide infra) and 100 MHz, does not change on heating ^1H NMR samples of **2** to 100° (**2** decomposes rapidly at this temperature). Based on these observations $\Delta G^\ddagger$ for methylene rotation in **2** and, by analogy, in **1**, can be estimated as ≥21.4 kcal/mol.[11] The true value may be significantly larger since $\delta\nu_\infty \simeq {}^2J_{HH'}$ at 100 MHz.[10b] Interestingly, this finding is consistent with the calculated energy difference between a perpendicular and in-plane methylene orientation in hypothetical $[Ti(\eta^5\text{-}C_5H_5)_2(CH_3)(CH_2)]^-$, about 27 kcal/mol.[12]

We believe the ordering of $\Delta G^\ddagger$ (**2** > **4** > **3**) directly reflects the degree to which the -CHR ligand can form a multiple bond by orienting perpendicular to the C_{carb}-Ta-Z plane. A model of **3**, in which the carbene ligand rotates most easily, shows that a strictly perpendicular $CHC(CH_3)_3$ ligand is sterically unfavorable. However, since the CH_2 ligand has minimal steric requirements it can form what must be close to a full double bond to Ta.

References and Notes

(1) R. R. Schrock, *J. Am. Chem. Soc.*, preceding paper in this issue.

(2) $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

(3) L. J. Guggenberger, P. Meakin, and F. N. Tebbe, *J. Am. Chem. Soc.*, **96**, 5420 (1974).

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(5) See ref 9 in ref 1.

(6) (a) Traditionally, M-C_{carb} bond lengths have been compared with M-CO bond lengths in strictly analogous or similar complexes. Though only one, rather difficult structure of a tantalum carbonyl is known,[6b] and the two M-CO bond lengths therefore not representative (1.87 and 2.15 Å; average = 2.01 Å), it is interesting that their average is not much less than the Ta-CH_2 bond length. M-C_{carb} bond lengths are normally significantly longer than M-CO bond lengths.[5] (b) P. Meakin, L. J. Guggenberger, F. N. Tebbe, and J. P. Jesson, *Inorg. Chem.*, **13**, 1025 (1974).

(7) **5** was prepared in a manner analogous to **3** from $Ta[CH_2C(CH_3)_3]_2Cl_3$ and 2 mol of $Tl(C_5H_4CH_3)$ in toluene.

(8) The methyl groups on the cyclopentadienyl rings in **5** concomitantly coalesce to a singlet. The cyclopentadienyl proton signals vary from broad, slightly structured peaks to poor triplets or quartets.

(9) Spectra of other molecules in this general family are consistent with this interpretation. For example, the spectrum of $Ta(\eta^5\text{-}C_5H_4CH_3)_2(CH_3)(CH_2)$ shows four nonequivalent cyclopentadienyl proton resonances while those of $Ta(\eta^5\text{-}C_5H_4CH_3)_2(CH_3)_3$ and $[Ta(\eta^5\text{-}C_5H_4CH_3)_2(CH_3)_2]^+BF_4^-$ show only two.

(10) (a) $\Delta G^\ddagger$ for **3** was calculated by complete line shape analysis courtesy of P. Meakin; Raban's method[10b] ($\delta\nu_\infty$ = 12.96 Hz, T_c = 323 K) gave a value of 16.9 kcal/mol. From the AB quartet in **4** ($\delta\nu_\infty$ = 68 Hz, T_c = 391 K, $^2J_{HH'}$ = 10.5 Hz) $\Delta G_{391}^\ddagger$ equals 19.3 kcal/mol; from the $\eta^5\text{-}C_5H_5$ signals ($\delta\nu_\infty$ = 2.55 Hz, T_c = 349 K) $\Delta G^\ddagger$ equals 19.5 kcal/mol.[10b] (b) D. Kost, E. H. Carlson, and M. Raban, *Chem. Commun.*, 656 (1971).

(11) Assuming $T_c \simeq 413$ K (40° above the highest temperature available), $\delta\nu_\infty$ = 7.7 Hz (at 100 MHz) and $^2J_{HH'}$ = 7.7 Hz, k_c = 45 sec^{-1} and $\Delta G_{413}^\ddagger$ = 21.4 kcal/mol.

(12) J. W. Lauher and R. Hoffmann, private communication.

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Received July 5, 1975