Communications to the Editor

The First Isolable Transition Metal Methylene Complex and Analogs. Characterization, Mode of Decomposition, and Some Simple Reactions

Sir:

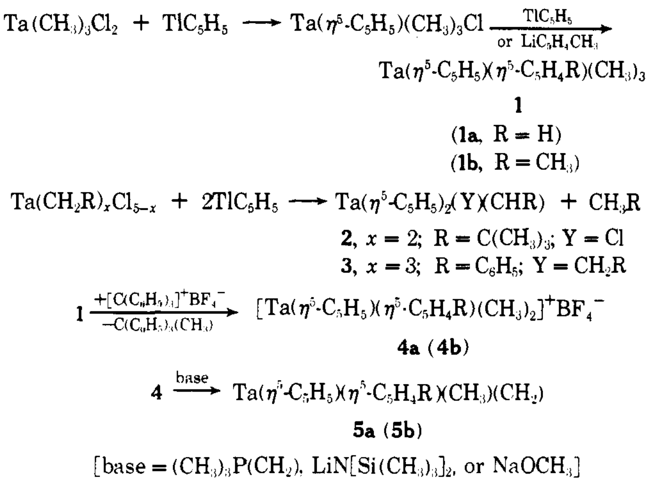
Transition metal methylene[1] complexes have often been postulated as intermediates,[2] yet no example has been characterized. Recent discovery of "unstabilized" carbene complexes,[3] including one in which the carbene ligand has one α-hydrogen,[4] prompted an attempt to isolate a simple methylene complex. The first example, $Ta(\eta^5\text{-}C_5H_5)_2(CH_3)(CH_2)$, is reported here along with some other members of this alkylidene family. Its x-ray structure and the variable temperature NMR spectra of analogous complexes are reported separately.[5]

Intramolecular α-hydrogen abstraction from one alkyl ligand by a second apparently occurs most readily if coordination about the metal is crowded. For example, one can prepare $Ta(CH_3)_5$,[6] but "$Ta[CH_2C(CH_3)_3]_5$" decomposes to neopentane and $Ta[CH_2C(CH_3)_3]_3[CHC(CH_3)_3]$.[4] Steric crowding can also account for the fact that preparation of **1** is straightforward (Scheme I), while similar reactions starting with $Ta[CH_2C(CH_3)_3]_2Cl_3$ and $Ta(CH_2C_6H_5)_3Cl_2$ give **2** and **3**, respectively, the only isolated products.

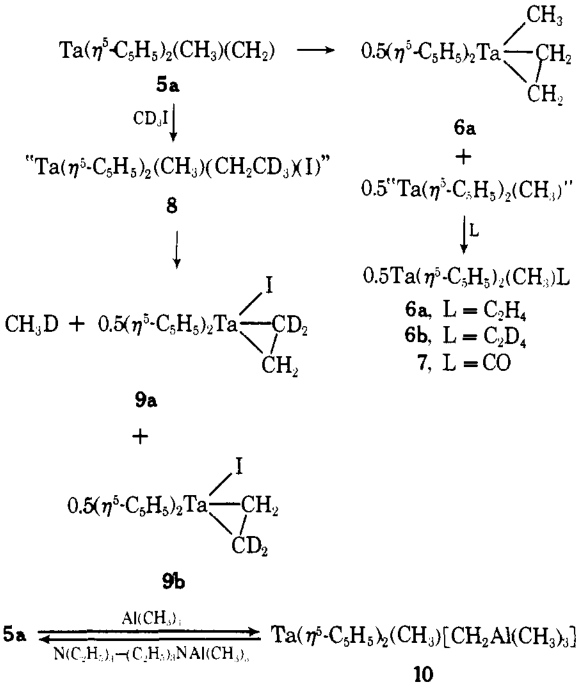
Intermolecular α-hydrogen abstraction can be used to prepare alkylidene complexes in cases where intramolecular abstraction fails or cannot be controlled.[7] Electrophilic attack on **1**[8a] by $C(C_6H_5)_3^+$ gives **4** which can be cleanly deprotonated[8c] to give the methylene complexes, **5**. The cationic route therefore may be not only a potentially valuable but a more general method of preparing Nb and Ta alkylidene complexes.

A typical preparation of **5a** consists of adding 0.95 g of $(CH_3)_3P(CH_2)$ dropwise to a stirred suspension of 4.28 g of **4a** in 25 ml of tetrahydrofuran. After 15 min the solvent was removed in vacuo and the residue extracted with 50 ml of toluene. A quantitative yield of $P(CH_3)_4{}^+BF_4{}^-$ was filtered off and 150 ml of pentane added to the filtrate. After standing at −30° for 1 hr 2.77 g (82%) of pale, buff colored needles was filtered off. (Anal. Calcd for $TaC_{12}H_{15}$: C, 42.38; H, 4.41. Found: C, 42.10; H, 4.44. ^1H NMR (τ, C_6D_6): −0.22 (2, s, CH_2), 4.82 (10, s, $\eta^5\text{-}C_5H_5$), 9.88 (3, s, CH_3). ^{13}C NMR (gated decoupled, ppm downfield from TMS, C_6D_6): 228 (CH_2, t, $^1J_{CH}$ = 132 Hz), 100 ($\eta^5\text{-}C_5H_5$, d, $^1J_{CH}$ = 175 Hz), −4 (CH_3, q, $^1J_{CH}$ = 122). Mol wt (cryoscopic in benzene): calcd, 340; Found, 395). **5a** appears moderately stable to air in the solid state for a short time but is quite sensitive to air and moisture in solution. It decomposes slightly in the solid state in several weeks but can be stored indefinitely under nitrogen at −30°.

Scheme I



Scheme II



Like **5a**, the ^{13}C {^1H} spectrum of **2** and **3** each show a resonance at low-field (273 and 246 ppm downfield from TMS in C_6D_6, respectively). Each is a doublet in the gated decoupled spectrum ($^1J_{CH}$ = 121 and 127 Hz, respectively). The chemical shifts lie within the range characteristic of carbene ligand carbon atoms in other carbene complexes.[9] The structural aspects and ^1H NMR spectra of **2**, **3**, and **5** are more fully discussed in the accompanying communication.[5]

The methylene complex (**5a**) decomposes slowly in C_6D_6 at 25° in 1-2 days to give a ca. 50% yield of $Ta(\eta^5\text{-}C_5H_5)_2(CH_2CH_2)(CH_3)$ (**6a**, by ^1H NMR; Scheme II). Other signals are weak and broad and some solid precipitates in the sample. In the presence of ethylene, no solid precipitates and only **6a** is observed by ^1H NMR. It can be isolated in essentially quantitative yield. In the presence of C_2D_4, decomposition gives a 1:1 mixture of **6a** and $Ta(\eta^5\text{-}C_5H_5)_2(CD_2CD_2)(CH_3)$ (**6b**), and in the presence of CO, a 1:1 mixture of **6a** and **7**. These observations suggest that the primary mode of decomposition of **5a** is intermolecular, most likely the consequence of attack by a fairly nucleophilic[10] methylene ligand (vide infra) on electron-poor Ta. What is possibly preferential cleavage of a doubly methylene-bridged dimer[11] then gives **6a** and "$Ta(\eta^5\text{-}C_5H_5)_2(CH_3)$" which is captured by $C_2H_4(C_2D_4)$ or CO to give **6a** (**6b**) or **7**. The -$C(CH_3)_3$ and -C_6H_5 carbene ligand substituents are large compared to a proton and apparently 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).

(4) R. R. Schrock, *J. Am. Chem. Soc.*, **96**, 6796 (1974).

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

(6) R. R. Schrock and P. Meakin, *J. Am. Chem. Soc.*, **96**, 5288 (1974).

(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. **5a** 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-Ta-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.

(12) H. Schmidbaur and W. Tronich, *Chem. Ber.*, **101**, 595 (1968).

(13) (a) H. Fischer, E. O. Fischer, and C. G. Kreiter, *Chem. Ber.*, **107**, 2459 (1974); (b) F. R. Kreissl and W. Held, *J. Organomet. Chem.*, **86**, C10 (1975).

(14) Address correspondence to the author at the Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

Richard R. Schrock[14]
Contribution No. 2292
Central Research and Development Department
E. I. du Pont de Nemours and Company
Experimental Station
Wilmington, Delaware 19898

Received July 5, 1975

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-Ta-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 $[(CH_3)_3CCH_2]_3Ta{\equiv}CC(CH_3)_3\cdot Li(N,N'\text{-dimethylpiperazine})$[4]). Since the range of known M-C_{carb} bond lengths is so great (ca. 1.95-2.15 Å),[5] it is perhaps not surprising that the Ta-CH_2 length falls within. Yet only M-C_{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.