Synthesis and Characterization of Seven-co-ordinate $TaX(CO)_3(PMe_3)_3$ Complexes (X = Cl, Br, I)

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Treatment of $TaClH_2(PMe_3)_4$ with CO or oxidation of $[Ta(CO)_6]^-$ with $TaCl_5$ in diethyl ether–PMe_3 solutions provides $TaCl(CO)_3(PMe_3)_3$, a capped trigonal prismatic complex whose structure has been determined by *X*-ray diffraction; bromo and iodo analogues have been isolated by oxidation of $[Ta(CO)_6]^-$ with Br_2 or I_2 in diethyl ether–PMe_3 solutions.

Monomeric, non-cyclopentadienyl carbonyl complexes of d^4 niobium(I) and tantalum(I) are very rare and the only well characterized examples are the seven-co-ordinate $MX(CO)_2(R_2PCH_2CH_2PR_2)_2$ (R = alkyl) compounds described by Tebbe,[1] Schrock,[2] Wreford,[3] and Leigh.[4] These adopt capped trigonal prismatic geometries when X, the capping ligand, is a halide, pseudohalide, or alkyl group and capped octahedral geometries when X = H. The synthetic utility of these compounds for further explorations of low-valent group 5 chemistry is necessarily limited by the presence of two, tightly-bound chelating phosphines. Here we describe a number of synthetic strategies for the preparation of mononuclear tantalum(I) carbonyl complexes containing trimethylphosphine and provide structural data on one of these systems.

Diethyl ether solutions of $TaClH_2(PMe_3)_4$[5] react smoothly with CO (40 psi) at 25 °C according to the stoicheiometry of equation (1). Pure $TaCl(CO)_3(PMe_3)_3$, (**1**), is isolated in 90% yield after solvent removal, extraction of solid residue with warm hexane, filtration, and evaporation of the filtrate. Complex (**1**) can also be obtained by treatment of diethyl ether solutions of $Na[Ta(CO)_6]$[6] with solid $TaCl_5$ (1 equiv.) in the presence of excess (8 equiv.) of PMe_3 [equation (2)].

$$\mathrm{TaClH_2(PMe_3)_4 + 3CO \xrightarrow[8\,h,\ 25\ ^{\circ}C]{OEt_2} \underset{(\mathbf{1})}{TaCl(CO)_3(PMe_3)_3} + PMe_3 + H_2} \qquad (1)$$

$$\mathrm{Na[Ta(CO)_6] + TaCl_5 + excess\ of\ PMe_3 \xrightarrow[1\,h,\ -20\ ^{\circ}C]{OEt_2} (\mathbf{1}) + NaCl + CO + [Ta^{III}]} \qquad (2)$$

Tantalum pentachloride functions as a two-electron oxidant and halide source in this reaction and the yield of (**1**), based on $Na[Ta(CO)_6]$, is typically 75%. The insoluble, high-valent, tantalum-containing product of reaction (2) is still uncharacterized. If $TaBr_5$ is substituted for the pentachloride, $TaBr(CO)_3(PMe_3)_3$, (**2**), is obtained in 40% yield.

An obvious and useful alternative to reaction (2) is shown in equation (3). Here bromine or iodine is used to oxidize diethyl ether solutions of $Na[Ta(CO)_6]$ containing excess (8 equiv.) of PMe_3. The yields of (**2**) and $TaI(CO)_3(PMe_3)_3$, (**3**), obtained by this procedure are 50 and 75%, respectively. Because $[Ta(CO)_6]^-$ does not react with PMe_3 at room temperature, phosphine substitution in reactions (2) and (3) must occur *via* $Ta(CO)_6$ or $Ta(CO)_6X$. In view of the mild reaction conditions, substitution *via* the 17-electron radical seems more likely.[7] The potential utility of reaction (3) to prepare a variety of $TaX(CO)_3L_3$ complexes, where L is a two-electron donor, should be noted.

$$\mathrm{Na[Ta(CO)_6] + X_2 + excess\ of\ PMe_3 \xrightarrow[1\,h,\ -20\ ^{\circ}C]{OEt_2} TaX(CO)_3(PMe_3)_3 + NaX + 3CO} \qquad (3)$$

$$\begin{array}{l} (\mathbf{2})\ \mathrm{X = Br} \\ (\mathbf{3})\ \mathrm{X = I} \end{array}$$

Complexes (**1**)—(**3**) are all diamagnetic, moderately air-sensitive red–orange crystalline solids.‡ They are monomeric in benzene and do not exchange with free PMe_3 in C_6D_6 solution on the ^1H n.m.r. time scale at 25 °C. The i.r. spectra (hexane) of (**1**)—(**3**) are nearly superimposable; in each case we observe three sharp C–O stretching modes: 1962, 1862, and 1843 cm^{-1} for (**1**); 1952, 1853, and 1836 cm^{-1} for (**2**); 1957, 1857, and 1836 cm^{-1} for (**3**). All of these seven-co-ordinate complexes are stereochemically nonrigid in solution $\{[^2H_8]$toluene$\}$ at 25 °C, *i.e.*, a single resonance is observed in each $^{31}P\{^1H\}$ n.m.r. spectrum and a single carbonyl resonance is observed in each $^{13}C\{^1H\}$ n.m.r. spectrum. When the samples are cooled to −80 °C, apparent limiting spectra are obtained. Two carbonyl resonances are observed in the respective $^{13}C\{^1H\}$ n.m.r. spectra and AX_2 patterns appear in the $^{31}P\{^1H\}$ n.m.r. spectra. These −80 °C data suggest that the $TaX(CO)_3(PMe_3)_3$ species have C_s or mirror symmetry but do not unambiguously define the stereochemistry about the tantalum(I) centres. In order to establish a structural basis for future work, an *X*-ray study of (**1**) was undertaken.

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‡ Complexes (**1**)—(**3**) gave acceptable C, H, and X microanalyses. Selected n.m.r. data: (**1**) ^{31}P (p.p.m. relative to external 85% H_3PO_4, C_7D_8, 145.8 MHz, $\{^1H\}$, −80 °C): −10.4 [t, 1P, *J*(P-1–P-2) 50.7 Hz] and −24.9 [d, 2P, *J* (P-1–P-2) 50.7 Hz], ^{13}C (C_7D_8, 90.6 MHz, $\{^1H\}$, −80 °C): δ 269.5 (br. s, 1C, CO), 254.8 (br. s, 2C, CO), and 16.4 (m, 9C, PMe_3); (**2**) ^{31}P (p.p.m. C_7D_8, 145.8 MHz, $\{^1H\}$, −80 °C): −14.1 [t, 1P, *J*(P-1–P-2) 46.4 Hz] and −30.0 [d, 1P, *J*(P-1–P-2) 46.4 Hz], ^{13}C (C_7D_8, 90.6 MHz, $\{^1H\}$, −80 °C): δ 265.2 (m, 1C, CO), 254.2 [d, 2C, *J* (C–P) 19.7 Hz, CO], 16.9 [d, 3C, *J*(C–P) 9.0 Hz, PMe_3], and 16.7 [t, 6C, *J*(C–P) 5.4 Hz, PMe_3]; (**3**) ^{31}P (p.p.m., C_7D_8, 145.8 MHz, $\{^1H\}$, −80 °C): −22.6 [t, 1P, *J*(P-1–P-2) 40.3 Hz] and −38.7 [d, 2P, *J*(P-1–P-2) 40.3 Hz], ^{13}C (C_7D_8, 90.6 MHz, $\{^1H\}$, −80 °C): δ 261.7 (m, 1C, CO), 252.1 [d, 2C, *J*(C–P) 18.0 Hz, CO], 17.9 [d, 3C, *J*(C–P) 27.7 Hz, PMe_3], and 17.7 [t, 6C, *J*(C–P) 12.5 Hz, PMe_3].

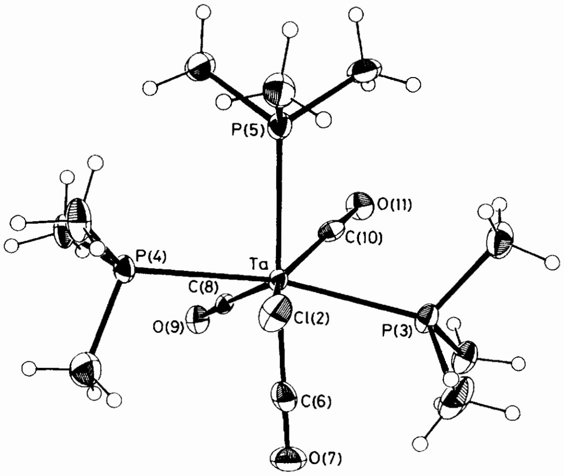

Figure 1. ORTEP drawing of $TaCl(CO)_3(PMe_3)_3$. Selected bond lengths are Ta–Cl(2), 2.545(2) Å; Ta–P(3,4,5), 2.595(3), 2.638(3), and 2.666(3) Å; Ta–C(6,8,10), 2.059(10), 2.021(9), and 2.035(10) Å.

Crystals of (**1**) were grown from concentrated hexane solutions at −40 °C and the structure determined from diffraction data collected at −160 °C.§ There are two crystallographically independent, structurally very similar molecules of (**1**) in the asymmetric unit and one of these is shown in Figure 1. The overall geometry is best described as capped trigonal prismatic with Cl(2) in the capping position, P(3), P(4), P(5), and C(6) in the capped quadrilateral face, and C(8), C(10) on the remaining edge. Note that (**1**) has only C_1 symmetry in the solid state. In order to explain the low temperature n.m.r. data, it seems reasonable to postulate rotation of the edge carbonyl groups about the Ta–Cl(2) axis. This process, an interconversion of capped trigonal prismatic and pentagonal bipyramidal geometries, has a very low activation energy[8] and it averages the environments of the edge carbonyl groups and the *trans* phosphine groups on the quadrilateral face.

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§ *Crystal data:* $C_{12}H_{37}ClO_3P_3Ta$, $M = 528.67$, monoclinic, space group $P2_1/n$, $a = 17.684(3)$, $b = 13.904(5)$, $c = 18.522(5)$ Å, $\beta = 117.60(2)°$, $U = 2018.02$ Å^3, $Z = 8$, $D_c = 1.740$ g cm^{-3}, μ(Mo-K_α) = 57.5 cm^{-1}, λ(Mo-K_α) = 0.71069 Å. 5280 Unique intensity data measured, 4628 observed $[F_0 > 2.33\sigma(F_0)]$, $R_F = 0.039$, $R_w = 0.041$, non-hydrogen atoms anisotropic, hydrogen atoms included as fixed atom contributors in idealized positions. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.