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Preliminary communication

A mild, phosphine-assisted synthesis of (η-C_5Me_5)Ta(CO)$_4$. Isolation and crystal structure of intermediate (η-C_5Me_5)$TaCl_2(CO)_2(PMe_3)$

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Abstract

Mild, reductive carbonylation of (C_5Me_5)$TaCl_4$ in the presence of trimethylphosphine gives (C_5Me_5)Ta(CO)$_4$ in 47% yield. The intermediate (C_5Me_5)$TaCl_2$-$(CO)_2(PMe_3)$ has been isolated from the reaction of (C_5Me_5)$TaCl_2(PMe_3)_2$ with carbon monoxide and its crystal structure determined (space group $P2_12_12_1$).

Half-sandwich carbonyl complexes of the general type Cp′M(CO)$_4$ (Cp′ = C_5H_5, C_5Me_5; M = V, Nb, Ta) are potentially valuable precursors of low oxidation state half-sandwich complexes of these elements [1], and have found use as reagents in organic synthesis [2]. However, forcing conditions are generally necessary for their preparation, typically involving CO pressures of ca. 330 bar and temperatures above 100 °C [3]. During our studies on the reductive activation of tantalum in $Cp^\star TaCl_4$ ($Cp^\star$ = C_5Me_5) [4], we have found that ligated trimethylphosphine facilitates the preparation of $Cp^\star$Ta(CO)$_4$ under mild conditions and in reasonable yield. Here, we report its synthesis in a direct "one-pot" reaction and by a stepwise procedure.

Treatment of $Cp^\star TaCl_4$ with one equivalent of magnesium in THF in the presence of an excess of PMe_3 (typically 3 equiv.) affords the red, petroleum ether soluble d^2 complex $Cp^\star TaCl_2(PMe_3)_2$ (**1**) in ca. 70% yield.

$$Cp^\star TaCl_4 \xrightarrow[PMe_3]{Mg,\ THF} \underset{(\mathbf{1})}{Cp^\star TaCl_2(PMe_3)_2} \qquad (1)$$

Compound **1** is paramagnetic, exhibiting broadened ($\Delta\frac{1}{2}$ = 60 Hz), contact-shifted ^{1}H NMR resonances at δ 91.45 and 20.56 ppm (0.037 *M* solution in benzene-d_6) attributable to the methyl hydrogens of the ring and the phosphine ligands, respectively. No signals are observed in the $^{31}P\{^1H\}$ NMR spectrum at ambient temperature. Similar solution behaviour has been observed for the d^2 vanadium analgoue, $CpVCl_2(PMe_3)_2$ [5].

When a toluene solution of **1** is treated with carbon monoxide (1 atm) the solution rapidly turns purple, and crystalline $Cp^{\star}TaCl_2(CO)_2(PMe_3)$ 2 can be isolated in 90% yield (eq. 2). **2** has been characterised by elemental analysis, IR and NMR spectroscopies, and a single crystal X-ray structure determination.

$$\mathrm{Cp^{\star}TaCl_2(PMe_3)_2} \xrightarrow[\text{toluene}]{\text{CO (1 atm)}} \underset{(\mathbf{2})}{\mathrm{Cp^{\star}TaCl_2(CO)_2(PMe_3)}} + \mathrm{PMe_3} \tag{2}$$

The molecular structure is shown in Fig. 1, and important bond distances and angles are included in the figure caption *. If the C_5Me_5 ligand is assumed to occupy a single coordination site, the molecule may be described as a distorted octahedron with the ring and phosphine ligands lying mutually *trans*. The chloro and carbonyl ligands also adopt a mutually *trans* orientation, resulting in a *cis*-dichloro/*cis*-dicarbonyl arrangement. An interesting feature of the molecular structure is an apparent ring-slip distortion of the C_5Me_5 ligand, with the tantalum atom displaced towards ring carbons C(6) and C(7). Consequently, the Ta–C(6) and Ta–C(7) distances at 2.386(6) and 2.373(6) Å, respectively, are significantly shorter than the other Ta–ring–carbon distances (av. 2.446(6) Å). The ring-slippage also results in an elongated C(6)–C(7) bond (1.475(9) Å) and a shortened C(8)–C(9) distance (1.379(9) Å) compared with the mean inter-ring carbon distances found in other half-sandwich tantalum compounds (typically ca. 1.42 Å [6]). Similar distortions have been noted for half-sandwich oxo-rhenium systems [7], and correlated with the strong *trans* influence of the oxo ligand. Whilst similar effects may be present in **2** owing to the *trans* PMe_3 ligand other factors such as inter-ligand and crystal packing forces may be significant. A more detailed discussion of this feature will be presented in a future report.

The reduction of **2** by sodium amalgam ($2\frac{1}{2}$ equiv.) in THF under ca. 1.5 atmospheres of CO resulted in a dark orange solution from which $Cp^{\star}Ta(CO)_4$ (**3**) was obtained in ca. 65% yield (characterised by elemental analysis, IR, ^{1}H-NMR and mass spectrometries) (eq. 3). The remaining supernatant solution was found to contain an additional product, which is formulated as $Cp^{\star}Ta(CO)_3(PMe_3)$ (**4**) on the basis of its ^{1}H NMR spectrum. In particular, a singlet resonance is observed at δ 1.85 ppm for the ring methyls and a doublet resonance at δ 1.03 ppm, J(PH) 8.1 Hz is indicative of a single metal bound PMe_3 ligand. Complexes **3** and **4** are readily separated by fractional crystallisation. It is likely that the two compounds are formed by competing pathways since **4** does not react with CO to produce **3** under the conditions employed.

$$\underset{(\mathbf{2})}{\mathrm{Cp^{\star}TaCl_2(CO)_2(PMe_3)}} \xrightarrow[\text{CO}]{\text{Na/Hg}} \underset{(\mathbf{3},\ 65\%)}{\mathrm{Cp^{\star}Ta(CO)_4}} + \underset{(\mathbf{4})}{\mathrm{Cp^{\star}Ta(CO)_3(PMe_3)}} \tag{3}$$

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* The atomic coordinates 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.

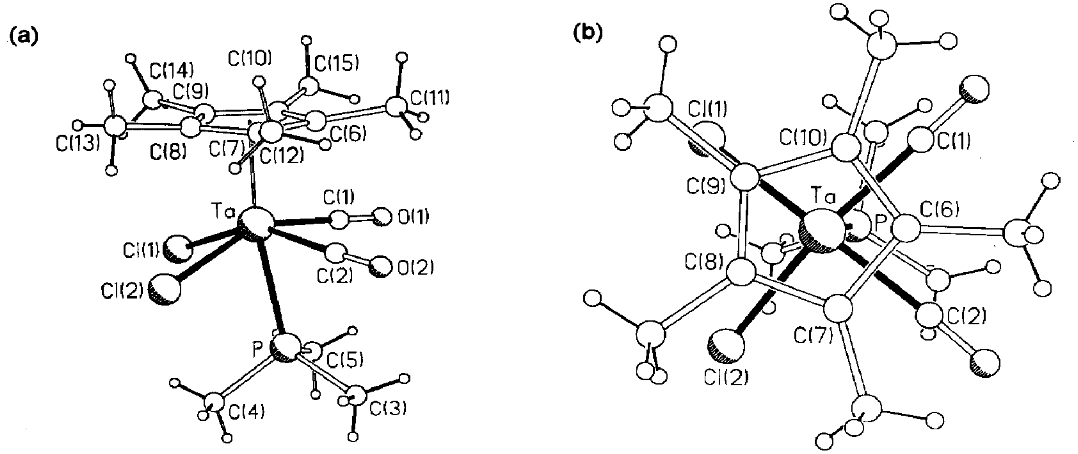

Fig. 1. (a) The molecular structure of $(C_5Me_5)TaCl_2(CO)_2(PMe_3)$ showing the atom labelling. Selected bond lengths (Å) and angles (degrees): Ta–C(1) 2.070(6), Ta–C(2) 2.079(7), Ta–P 2.707(2), Ta–Cl(1) 2.504(2), Ta–Cl(2) 2.512(2), Ta–C(6) 2.386(6), Ta–C(7) 2.373(6), Ta–C(8) 2.438(6), Ta–C(9) 2.474(6), Ta–C(10) 2.426(6), C(6)–C(7) 1.475(9), C(6)–C(10) 1.420(9), C(7)–C(8) 1.417(9), C(8)–C(9) 1.379(9), C(9)–C(10) 1.438(9), C(1)–O(1) 1.136(7), C(2)–O(2) 1.117(8), Ta–rc (ring centroid) 2.094(6); C(1)–Ta–C(2) 83.9(3), C(1)–Ta–P 74.0(2), C(2)–Ta–P 76.9(2), C(1)–Ta–Cl(1) 92.2(2), C(2)–Ta–Cl(1) 151.8(2), P–Ta–Cl(1) 75.2(1), C(1)–Ta–Cl(2) 152.4(2), C(2)–Ta–Cl(2) 86.5(3), P–Ta–Cl(2) 78.7(1), Cl(1)–Ta–Cl(2) 84.2(1), C(1)–Ta–rc 97.7(3), C(2)–Ta–rc 98.9(3), P–Ta–rc 170.9(3), Cl(1)–Ta–rc 109.3(3), Cl(2)–Ta–rc 109.4(3). (b) View a long the tantalum-ring centroid vector, showing the displacement of the PMe_3 ligand.

The formation of $Cp^{\star}Ta(CO)_4$ in a stepwise reduction of $Cp^{\star}TaCl_4$ prompted us to attempt a direct 'one-pot' synthesis of 3. Thus $Cp^{\star}TaCl_4$ was treated with 4 equiv. of sodium amalgam in THF under ca. 1.5 atmospheres CO and in the presence of one equivalent of PMe_3. Extraction of the dried residue with toluene followed by concentration and cooling to −50 °C afforded 3 cleanly in 47% yield. Thus, the method described here has made $Cp^{\star}Ta(CO)_4$ accessible by a mild 'one-pot' synthetic procedure and in reasonable overall yield.

Since $Cp^{\star}Ta(CO)_4$ cannot be obtained by direct reduction of $Cp^{\star}TaCl_4$ under mild conditions, the presence of ligated PMe_3 is clearly crucial to the success of this reaction, and its assistance in the preparation of otherwise inaccessible species has been noted previously [8]. While the precise role of coordinated PMe_3 remains obscure, an important influence is likely to be the coordinative and redox stabilisation of otherwise short-lived chloro-tantalum intermediates.

X-ray data collection, solution and refinement

Crystal data for 2. $C_{15}H_{24}Cl_2O_2PTa$, $M_r = 519.18$, orthorhombic, a 9.876(1), b 12.122(1), c 15.567(1) Å, V 1863.6 Å^3 (from 2θ values of 32 reflections in the range 20–25°, Mo-$K\alpha$ radiation, λ 0.71073 Å, Siemens AED2 diffractometer at room temperature), $Z = 4$, $D_c = 1.850$ g cm^{-3}, $F(000) = 1008$, μ 6.21 mm^{-1}, space group $P2_12_12_1$. Of 15106 reflections with $2\theta < 50°$, corrected for absorption, 3295 were unique, and 3164 with $F > 4\sigma(F)$ were used for structure determination by heavy atom methods ($R_{int} = 0.033$, σ_c based on counting statistics only). Least-squares refinement [9] on F, with anisotropic thermal parameters and constrained H atoms, and with weighting $w^{-1} = \sigma_c^2(F) + 15 - 214G + 346G^2 + 25S - 29S^2 + 73GS$ ($G =$

F_0/F_{max}, $S = \sin\theta/\sin\theta_{max}$) [10] gave $R = 0.033$, $wR = 0.024$, goodness of fit 1.09. The refined value of the anomalous dispersion parameter $\eta = 0.45(5)$ indicates possible partial twinning [11].

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