Preliminary communication

AN UNUSUAL DOUBLE C–H ACTIVATION OF COORDINATED TRIMETHYLPHOSPHINE. SYNTHESIS, MOLECULAR STRUCTURE AND REACTIVITY OF $(C_5Me_5)Ta(PMe_3)(H)_2(\eta^2\text{-}CHPMe_2)$ *

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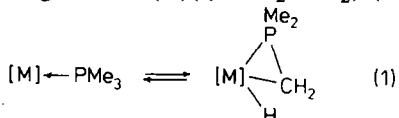
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(Received December 19th, 1986)

Summary

Sodium reduction of $(C_5Me_5)TaCl_4$ in trimethylphosphine solvent results in a double C–H activation to give $(C_5Me_5)Ta(PMe_3)(H)_2(\eta^2\text{-}CHPMe_2)$, whose structure has been determined by X-ray crystallography. Reactions with carbon monoxide and dihydrogen lead to $(C_5Me_5)Ta(PMe_3)_2(CO)_2$ and $(C_5Me_5)Ta(PMe_3)_2H_4$, respectively, whereas treatment with halocarbons gives products in which the $Ta(\eta^2\text{-}CHPMe_2)$ moiety is retained.

A common activation mode of coordinated trimethylphosphine is the oxidative cleavage of a substituent methyl C–H bond to give the 3-membered metallacyclic fragment, $M(H)(\eta^2\text{-}CH_2PMe_2)$ (eq. 1).

$$[M]\leftarrow PMe_3 \rightleftharpoons [M]\overset{\overset{\displaystyle Me_2}{P}}{\underset{H}{\diagdown}}\hspace{-0.3em}CH_2 \qquad (1)$$

Several complexes possessing the cyclometallated PMe_3 moiety have been characterised, either spectroscopically [1–7] or, in one case by X-ray crystallography [8,9]. An important feature of their reactions is the reversibility of the cyclometallation process, allowing the ready generation of a coordinatively unsaturated transition metal fragment, which, most recently has been used to facilitate the activation of aliphatic hydrocarbons under mild conditions [7]. We now report a novel double activation of trimethylphosphine which takes place when $(C_5Me_5)TaCl_4$ is treated with sodium in trimethylphosphine. We envisaged that the sterically demanding

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* Dedicated to Professor G.E. Coates on the occasion of his 70th birthday

C_5Me_5 ligand would disfavour formation of $(C_5Me_5)Ta(PMe_3)_4$ and that a more likely outcome would be intramolecular activation of ligand C–H bonds by the electropositive tantalum centre.

Treatment of $(C_5Me_5)TaCl_4$ with metallic sodium in neat PMe_3 proceeded smoothly during 3 h, to give a good yield of colourless $(C_5Me_5)Ta(PMe_3)(H)_2(\eta^2$-$CHPMe_2)$ (1). X-Ray quality crystals were readily obtained from a concentrated petroleum ether solution by slow cooling to $-50°C$. The molecular structure determination confirmed that two PMe_3 ligand C–H bonds had been oxidatively cleaved and, moreover, that the hydrogens had been abstracted from the same methyl substituent (Fig. 1a).

Crystal data for 1: $C_{16}H_{33}P_2Ta$, $M = 468.33$, orthorhombic, space group $P2_12_12_1$, a 9.131(1), b 13.399(1), c 16.518(2) Å, U 2020.9 Å^3, $Z = 4$, D_c 1.539 g cm^{-1}. Intensities of 3901 reflections were measured on a Siemens AED2 diffractometer using graphite-monochromated Mo-K_α radiation (λ 0.71073 Å). After semi-empirical absorption correction, 3177 independent reflections with $|F| > 4\sigma(F)$ were used in the structure analysis. The structure was solved by Patterson methods and has been refined on F by blocked-cascade least-squares. H atoms were not included. The final R is 0.0331 ($R_w = 0.0382$). The absolute structure was determined by refinement of $\eta = 1.15(3)$ [10]. Selected bond lengths and angles are listed in Fig. 1*.

Analysis of the crystallographic results reveals η^5-coordination of the C_5Me_5 ligand with the ring centroid vector lying approximately coplanar with the Ta, P(1), P(2) and C(23) atoms thus defining a pseudo mirror plane through the molecule (Fig. 1b). The methylidyne hydrogen and the two hydride ligands were not located in the crystal structure determination but infrared (ν(Ta–H) 1635 cm^{-1}) and NMR spectroscopy (vide infra) clearly indicated their presence, and further showed that the hydride hydrogens occupy equivalent solution environments. On the basis of these observations, the established geometry of the other ligands around the metal centre, and consideration of the remaining available space, we favour placement of the two hydride ligands either side of the pseudo mirror plane as represented diagramatically in Scheme 1(a).

The η^2-$CHPMe_2$ moiety is assumed to arise by an unusual double intramolecular C–H activation of a coordinated trimethylphosphine ligand, and such a moiety has been structurally characterised in one other compound [9], although in that case the abstracted hydrogens do not remain bound to the metal centre. The tantalum–carbon bond distance of 2.005(10) Å lies within the range for a tantalum–carbon double bond [11]. However, the P–C bond distance of 1.714(9) Å is considerably shortened from that expected for a P–C single bond (av. P–C bond length excluding P(2)–C(23) is 1.850(16) Å) which suggests a significant contribution from form II (Scheme 1(b)) in which the metallacycle may be formally regarded as a coordinated λ^5-phosphaalkyne ($HC\equiv PMe_2$). III is a delocalised representation of the bonding in the Ta(η^2-$CHPMe_2$) moiety.

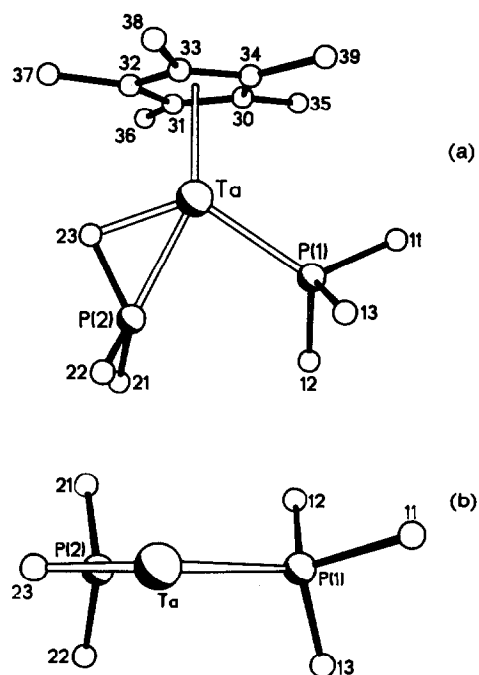High field NMR data are consistent with persistence of the same structure in


Fig. 1. (a) The molecular structure of $(C_5Me_5)Ta(PMe_3)(H)_2(\eta^2\text{-CHPMe}_2)$ (carbon atoms labelled by number only). Selected bond lengths (Å) and angles (degrees): Ta–P(1) 2.590(3), Ta–P(2) 2.480(2), Ta–C(23) 2.005(10), Ta–ring centroid 2.105(8), P(1)–C(11) 1.850(14), P(1)–C(12) 1.860(15), P(1)–C(13) 1.828(16), P(2)–C(23) 1.714(9); P(1)–Ta–P(2) 82.3(1), P(1)–Ta–C(23) 125.6(3), P(2)–Ta–C(23) 43.4(3), P(1)–Ta–ring centroid 124.6(3), P(2)–Ta–ring centroid 153.1(3), C(23)–Ta–ring centroid 109.7(8). (b) View along ring centroid axis (ring omitted) showing approximate co-planarity of Ta, P(1), P(2), and C(23).

solution (at 298 K). In particular, the 250 MHz ^{1}H NMR spectrum (C_6D_6, δ in ppm) revealed a typical low field shift for the methylidyne hydrogen at δ 9.19 ppm and a doublet of doublets resonance at δ 3.87 ppm (^2J(P–H) 54.9, 17.9 Hz) for the equivalent hydride ligands. ^{13}C and ^{31}P NMR spectra (C_7D_8) gave signals con-
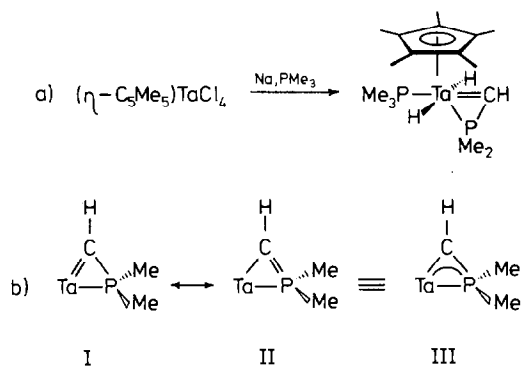
SCHEME 1

sistent with the $Ta(\eta^2\text{-CHPMe}_2)$ metallacycle [12], notably a low field methylidyne carbon resonance at δ 191.2 ppm (J(C–H) 169.8 Hz) and a high field ^{31}P signal at δ −114.3 ppm (J(P–P) 57.2 Hz). The methylidyne C–H coupling constant of 169.8 Hz is larger than that expected for a simple tantalum alkylidene species [13] but is comparable with reported $J(^{13}\text{C}-^1\text{H})$ values for bridging methylidyne ligands [14,15].

In view of the established equilibrium between $M-PMe_3$ and $M(H)(\eta^2\text{-CH}_2PMe_2)$ and its demonstrated utility in synthesis and in the activation of C–H bonds via the generation of a coordinatively unsaturated metal centre, we were interested to see to what extent 1 could be used as a synthon for the 14 electron fragment $[(C_5Me_5)Ta(PMe_3)_2]$.

Preliminary reactivity studies have indicated that reversible hydrogen migrations do indeed occur, to give products bearing two PMe_3 ligands. For example, 1 reacts with carbon monoxide at room temperature to give the previously reported $(C_5Me_5)Ta(PMe_3)_2(CO)_2$ [16], and with dihydrogen at 70°C to afford $(C_5Me_5)Ta(PMe_3)_2H_4$ [16], both of which have been characterised by comparison with data for authentic samples.

In contrast, the metallacycle remains intact when 1 is treated with halocarbon reagents. The reaction with an equimolar amount of CH_3X (X = Br, I) leads to $(C_5Me_5)Ta(PMe_3)(H)(X)(\eta^2\text{-CHPMe}_2)$ (X = Br, 2; X = I, 3) with concomitant formation of CH_4; 2 and 3 are readily identified from the presence of new metal hydride (C_6D_6, δ 5.66, dd, ppm ^2J(P–H) 47.5, 25.0 Hz, 2; δ 4.08, dd ppm, ^2J(P–H) 51.4, 28.0 Hz, 3) and methylidyne hydrogen resonances (δ 9.22 and 9.53 ppm, respectively), in the ^{1}H NMR spectrum. Similarly 1 reacts with chloroform at room temperature to give the chloro derivative $(C_5Me_5)Ta(PMe_3)(H)(Cl)(\eta^2\text{-CHPMe}_2)$ 4 (CDCl$_3$, δ 6.73, dd ppm, ^2J(P–H) 45.8, 27.5 Hz, Ta–H; δ 8.65 ppm, $\eta^2\text{-CHPMe}_2$). On prolonged treatment with CH_3X (X = Br, I) or $CHCl_3$ at room temperature, the second hydride ligand is readily replaced to afford dihalo derivatives in which the metallacyclic fragment again remains unchanged.

In summary, the reduction of $(C_5Me_5)TaCl_4$ in trimethylphosphine solvent provides a convenient route to the unusual cyclometallated complex $(C_5Me_5)Ta(PMe_3)(H)_2(\eta^2\text{-CHPMe}_2)$. Preliminary reactivity studies have indicated that reversible hydrogen migrations occur to generate a bis(trimethylphosphine)metal fragment. The potential application of this system to the activation of simple hydrocarbons is at present under investigation, along with a study of the $Ta(\eta^2\text{-CHPMe}_2)$ metallacycle itself through complexes such as 2–4.

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12 The (η^2-CHPMe$_2$) moiety in Ta(PMe$_3$)$_3$(η^2-CH$_2$PMe$_2$)(η^2-CHPMe$_2$) possesses ^{13}C and ^{31}P NMR resonances at δ 193.5 and -77.5 ppm, respectively. See ref. 9.

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