Trimethylphosphine as a Reactive Solvent: Synthesis and Crystal Structure of $Ta(PMe_3)_3(\eta^2\text{-}CH_2\text{–}PMe_2)(\eta^2\text{-}CH\text{–}PMe_2)$ and Synthesis of Related Molybdenum and Tungsten Compounds

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Reduction of solutions of the metal halides $TaCl_5$, $MoCl_5$, or WCl_6 in pure trimethylphosphine with sodium sand causes smooth stepwise reduction giving $Ta(PMe_3)_3(\eta^2\text{-}CH_2\text{–}PMe_2)(\eta^2\text{-}CH\text{–}PMe_2)$, $Mo(PMe_3)_5H_2$, or $W(PMe_3)_4(\eta^2\text{-}CH_2\text{–}PMe_2)H$ respectively; the *X*-ray crystal structure of the tantalum compound shows the presence of the unique $Ta(\eta^2\text{-}CH\text{–}PMe_2)$ group.

We have been searching for simple high yield routes to high energy compounds such as homoleptic $M(PR_3)_n$ compounds and related derivatives since such compounds are very useful synthetic intermediates. Recently we were able to prepare $Mo(PMe_3)_6$ by co-condensation between molybdenum atoms and trimethylphosphine.[1] However, the analogous reaction with tungsten atoms gave none of the corresponding tungsten analogue.

It has become increasingly clear that low-valent, electron rich transition metal systems can react with carbon–hydrogen bonds *via* oxidative-addition. The classic work of Chatt and Davidson showed that reduction of $Ru(dmpe)_2Cl_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$) with sodium naphthenide gave a ruthenium-naphthyl-hydride derivative.[2]

$$[Ta(PMe_3)_3(\eta^2\text{-}CH_2\text{–}PMe_2)(\eta^2\text{-}CH\text{–}PMe_2)]$$

(1)

$$[W(Me_3P)_4(\eta^2\text{-}CH_2\text{–}PMe_2)H]$$

(2)

We decided to attempt to reduce possible side-reactions and their ensuing complications by carrying out reductions of metal halides in the absence of hydrocarbon solvent and with pure alkali metal as the reductant. Trimethylphosphine is readily available and being highly volatile any excess is readily removed from the reaction mixture. Further, it has only one type of C–H bond and the equilibrium $M(\eta^2\text{-}CH_2\text{–}PMe_2)H \rightleftharpoons M\text{–}PMe_3$ occurs readily.

We have found that reduction of $TaCl_5$ in excess of trimethylphosphine with sodium sand under argon proceeds smoothly giving air-sensitive, bright green crystals of the compound $Ta(PMe_3)_3(\eta^2\text{-}CH_2\text{–}PMe_2)(\eta^2\text{-}CH\text{–}PMe_2)$, **(1)**. In a typical experiment 2 g of $TaCl_5$ in 25 cm^3 of Me_3P were stirred with *ca.* 1 g of sodium sand at room temperature for 2 days giving *ca.* 0.3 g of pure **(1)**.[†] The crystal structure of **(1)** has been determined.

Crystal data: $C_{15}H_{42}P_5Ta$, $M = 558$, monoclinic, space group $P2_1/n$, $a = 10.143(3)$, $b = 18.769(3)$, $c = 13.040(2)$ Å, $\beta = 93.61(2)°$, $U = 2478$ Å^3, $Z = 4$, $D_c = 1.50$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 49.9$ cm^{-1}, data were collected on an Enraf-Nonius CAD4F diffractometer, using monochromated Mo-K_α

[†] N.m.r. data, δ, *J* in Hz, ^1H n.m.r. for **(1)** in C_6D_6: 9.46 {10 lines, dddt, 1H, *J*[P(1)–H] 21.5, *J*[P(5)–H] and *J*[P(2)–H] *ca.* 16.3, *J*[P(3,4)–H] 3.2—3.4, Ta=CH}, 1.65 [d, 9H, *J*(P–H) 6.09, $Me_3P(5)$], 1.49 [dd, 6H, *J*(P–H) 5.55, 1.01, Me_2P], 1.35 [dd, 6H, *J*(P–H) 5.08, 1.03, Me_2P], 1.24 [virtually coupled 'triplet', 18H, $Me_3P(3,4)$], −0.87 [apparent ddt, 2H, *J*(P–H) 13.8, 4.9, 2.3, $TaCH_2$]. Compound **(2)**, ^{31}P n.m.r. in $CD_3C_6D_5$ at −60°C (p.p.m., *J* in Hz): −79.01 [dt, *J*(PMe_2–P*trans*) 10, *J*(PMe_2–P*cis*) 63, *J*(PMe_2–P*cis'*) *ca.* 0, PMe_2], −42.04 [dt, *J*(P*trans*–P*cis*) *ca.* 14, *J*(P*trans*–P*cis'*) *ca.* 11, *J*(^{183}W–P) 730, 2PMe_3(*trans*)], −25.52 [apparent quartet, *J*(PMe_2–P*cis*) *ca.* 0, *J*(P*cis*–P*trans*), and *J*(P*cis*–P*cis'*) *ca.* 11—14, PMe_3(*cis*)], −23.99 [dq, *J*(P*cis'*–PMe_2) 63, *J*(P*cis'*–P*trans*) *ca.* *J*(P*cis'*–P*cis*) *ca.* 11, PMe_3(*cis'*)]. ^1H N.m.r. of **(2)** in $CD_3C_6D_5$ at room temp. (δ, *J* in Hz): −3.75 [br. quintet, 1H, *J*(P–H)average 39, *J*(^{183}W–H) 26, W–H], 0.43 [apparent doublet of sextets, 2H, *J*(P–H) 5.13 and 1.0, W–CH_2], 1.41 [d, *J*(P–H) 7.99, PMe_2], 1.47 (br. s, 4PMe_3); relative intensity of sum of bands at 1.41, 1.47 to bands at 0.43 and −3.75, *ca.* 42:2:1. Partial ^1H n.m.r. spectrum of **(2)** at −60 °C in $CD_3C_6D_5$ (*J* in Hz): δ −3.75 [ddt, *J*(P–H) 78, 54, 9.5, W–H] 0.43 (br. band, CH_2), broad bands centred at 1.69, 1.55, 1.53, 1.46, 1.44, 1.43, 1.41, and 1.21 (14Me).

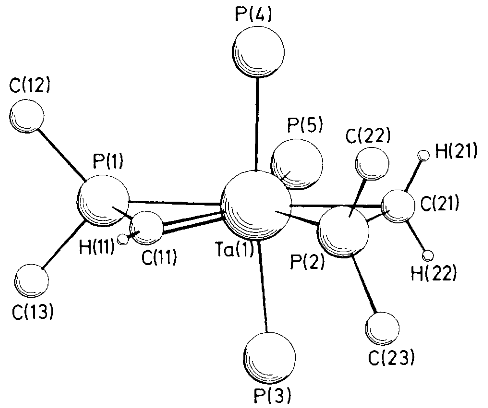

Figure 1. Crystal structure of (**1**). For clarity the carbon atoms bonded to P(3), P(4), and P(5) have been omitted, as have all methyl hydrogen atoms. Selected bond lengths and angles are: Ta–P(1) 2.516(1), Ta–P(2) 2.435(1), Ta–P(3) 2.551(1), Ta–P(4) 2.553(1), Ta–P(5) 2.596(1), Ta–C(11) 2.015(4), Ta–C(21) 2.324(4), P(1)–C(11) 1.716(5), P(1)–C(12) 1.840(6), P(1)–C(13) 1.849(6), P(2)–C(21) 1.776(5), P(2)–C(22) 1.840(5), P(2)–C(23) 1.846(5) Å; Ta–C(11)–P(1) 84.4(2), C(11)–P(1)–Ta 52.9(1), Ta–C(21)–P(2) 71.5(2), C(21)–P(2)–Ta 64.8(1), P(3)–Ta–P(4) 174.3(1), P(1)–Ta–P(5) 91.36(4), P(5)–Ta–C(21) 86.5(1)°.

radiation. After applying an empirical absorption correction, 3132 independent reflections with $I > 3\sigma(I)$ were used in the structure analysis. The structure was solved by Patterson and Fourier methods and has been refined using the large-block approximation. All hydrogen atoms were located and their positions refined subject to 'soft' constraints. The final cycle of refinement of 319 parameters gave an R value of 0.019 (R_w 0.022). The structure is shown in Figure 1 together with selected dimensions.‡

The $M(\eta^2\text{-}CH_2\text{-}PMe_2)$ moiety has been proposed to occur in a number of compounds, *e.g.* $M(PMe_3)_3(\eta^2\text{-}CH_2\text{-}PMe_2)$, M = Fe or Os[3] and has been crystallographically characterised in the compound $Re(\eta^2\text{-}CH_2\text{-}PMe_2)(PMe_3)_4$.[4] The crystal data show that the C(11) is bonded to only one hydrogen atom which is coplanar with the Ta–C–P triangle. The Ta–C(11) bond length is 0.31 Å shorter than the Ta–C(21) bond. Therefore, the Ta–C(11) bond must be described as a tantalum–carbon double bond and the whole group is the first example of a $M(\eta^2\text{-}CH\text{-}PMe_2)$ moiety. The tantalum atom lies 0.02 Å out of the plane formed by the phosphorus atoms P(1), P(2), and P(5), while C(11) and C(21) lie within 0.01 Å of the same plane. A related $W[\eta^2\text{-}C(NEt_2)PMePh]$ grouping has recently been characterised.[5] Complex (**1**) is an example of a seven coordinate, pentagonal bipyramidal, eighteen electron, trivalent tantalum compound. The n.m.r. data for (**1**)† are fully consistent with maintenance of the same structure in solution. In particular, H(11) shows a characteristic low field shift at δ 9.46.

Treatment of tungsten hexachloride in pure Me_3P with sodium sand under dinitrogen at room temperature causes a steady reaction over two days giving air-sensitive, volatile, yellow-brown crystals (in 45% yield). Microanalysis and n.m.r. data† are consistent with the formulation $W(Me_3P)_4(\eta^2\text{-}CH_2\text{-}PMe_2)H$ (**2**) where the H and $CH_2\text{-}PMe_2$ groups adopt a *cis* orientation. The compound (**2**) undergoes complex fluxional rearrangements which may be wholly or partially frozen out at −60 °C. The n.m.r. data do not allow distinction between all possible isomers of (**2**).§

Similarly, reduction of molybdenum pentachloride in excess of pure Me_3P under argon gives the recently described[6] compound $Mo(Me_3P)_5H_2$ in 55% yield [ν(Mo–H) 1960 cm^{-1}; partial ^1H n.m.r. data in C_6D_6: δ −5.23 (sextet, 2H, J 40.41 Hz)].

In conclusion, liquid trimethylphosphine is a very convenient reactive solvent for the synthesis by a one-pot reaction of known and new low-valent trimethylphosphine derivatives of the transition metals.

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ *Added in proof.* The crystal structure of (**2**) has been determined (ref. 7) which supports the proposed formulation. Briefly the P atoms of two PMe_3 and the CH_2-carbon and P atoms of the $\eta^2\text{-}CH_2\text{-}PMe_2$ group lie essentially coplanar whilst the two P atoms of the remaining two PMe_3 groups are collinear with the W atom and normal to this plane.

Compound (**2**) has been previously described as a partially characterised compound formed by reduction of $WCl_4(PMe_3)_3$ in tetrahydrofuran and PMe_3 using sodium amalgam (ref. 8).