

Interaction of Hexamethyltungsten(VI) with Trimethylphosphine; X-Ray Crystal Structure of Dimethyltetrakis(trimethylphosphine)tungsten(II)†

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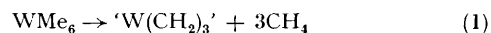
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Summary The synthesis of $\text{WMe}_6 \cdot \text{PMe}_3$, *trans*- $\text{WMe}_2(\text{PMe}_3)_4$, $\text{WH}_2(\text{PMe}_3)_5$, $\text{NbMe}_5(\text{PMe}_3)_2$, and $\text{TaMe}_5(\text{PMe}_3)_2$ is reported; the structure of *trans*- $\text{WMe}_2(\text{PMe}_3)_4$ has been determined by a single crystal X-ray analysis.

THE thermal decomposition of hexamethyltungsten^{1,2} proceeds according to the approximate stoichiometry shown in equation (1), where the nature of the black



† No reprints available.

insoluble material produced is unknown except that it shows C-H stretching frequencies in the i.r. spectrum. It seemed possible that the decomposition of WMe_6 and other permethyls in the presence of co-ordinating ligands might allow compounds with either terminal³ M-CH₂ or bridge⁴ M-CH₂-M groups to be trapped. Recently, mixed alkyl-alkylidene-alkylidene complexes of tungsten have been isolated using PMe_3 and $Me_2PCH_2CH_2PMe_2$.⁵

Interaction of WMe_6 and PMe_3 in light petroleum gives red crystalline $WMe_6 \cdot PMe_3$ which can be handled in air and is stable indefinitely at $-20^\circ C$ under nitrogen or in solution. Other phosphine adducts of WMe_6 have been reported although they are poorly characterised.^{1,2}

¹H and ¹³C n.m.r. spectra show that although $WMe_6 \cdot PMe_3$ is fluxional at room temperature, a more rigid structure such as a capped bipyramid exists at low temperature.

On heating, or better under u.v. irradiation, $WMe_6 \cdot PMe_3$ in PMe_3 gives high yields, not of a methylene complex, but of the unusual tungsten(II) alkyl, *trans*-dimethyltetra-kistrimethylphosphinetungsten(II). The structure (Figure) of this yellow, crystalline diamagnetic compound has been determined by an X-ray crystallographic study.

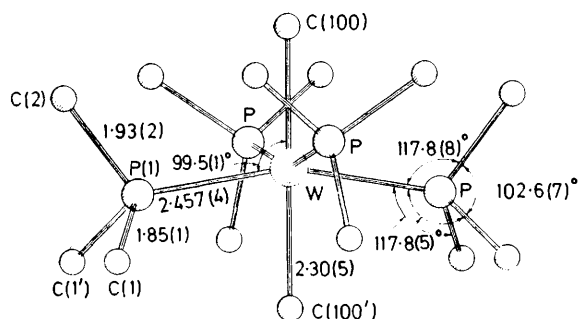


FIGURE. The structure of *trans*- $Me_2W(PMe_3)_4$ showing important bond lengths and angles.

Crystal data: $C_{14}H_{42}P_4W$, M 518.24, tetragonal, $a = 9.699(2)$, $c = 12.593(2)$ Å, $U = 1184.7$ Å³, space group $I\bar{4}2m$, $Z = 2$, $D_c = 1.45$ g cm⁻³, $F(000) = 520$, $\mu(Mo-K\alpha)$

‡ 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.

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$= 54.2$ cm⁻¹. The structure was solved and refined using 787 unique observed [$F_0 > 3\sigma(F_0)$] intensities measured on a Nonius CAD4 diffractometer. The current R value is 0.045. The molecule has $\bar{4}$ symmetry with a distorted octahedral geometry. The Me-W-Me group is linear by symmetry but the WP_4 girdle is considerably puckered due to phosphine-phosphine steric interactions. A similar MP_4 grouping occurs in the $[Rh(PMe_3)_4]^+$ ion.⁶ The W-C bond length is similar to the W-Me bond length found in the W^{VI} compound $W(=CCMe_3)(=CHCMe_3)(CH_2CMe_3)(Me_2PCH_2CH_2PMe_2)$ ⁷ and the W-P bond lengths of 2.457 Å are indicative of $W^{II} \rightarrow P \pi$ -back bonding.‡

The ¹H, ³¹P, and ¹³C n.m.r. spectra are also in accord with the structure, the ¹H and ¹³C {¹H} resonances for the W-CH₃ groups occurring at δ -1.58 [quintet, $^3J(^{31}P-^1H)$ 9.45 Hz] and 18.6 (m), respectively (relative to Me_4Si). The ¹H n.m.r. spectrum suggests that the flattened tetrahedron of P atoms (in the solid state) is rapidly inverting so that each W-CH₃ group couples equally with all four P atoms. The spectrum is unchanged at $-70^\circ C$.

Methane is the only gas formed in the reaction and a small amount of an off-white hydrocarbon-insoluble, pyrophoric powder remains which has not yet been fully characterised.

The interaction of $WMe_6 \cdot PMe_3$ in diethyl ether containing an excess of PMe_3 under hydrogen (3 atm) also leads to a tungsten(II) complex, dihydridopentakistrimethylphosphinetungsten(II). The ¹H and ³¹P n.m.r. spectra of this pale yellow, air sensitive, crystalline compound which is very soluble in light petroleum also show it to be fluxional at room temperature.

We have also isolated $TaMe_5(PMe_3)_2$ and $NbMe_5(PMe_3)_2$ as fawn and yellow, pyrophoric, crystalline materials which, like the $Me_2PCH_2CH_2PMe_2$ adducts are much more thermally stable than the per-methyls.⁸ Although pentamethyltantalum also gives only methane on thermal decomposition,⁸ we have not isolated any identifiable complexes from the products of decomposition of $NbMe_5$ and $TaMe_5$ in PMe_3 .

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