Formation of an η²-Formaldehyde Compound from Methanol and its Hydrogenation Giving Methanol

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Addition of methanol to $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ gives the η²-formaldehyde derivative $W(PMe_3)_4(\eta^2\text{-}CH_2O)H_2$ which reacts sequentially with dihydrogen forming initially the methoxyhydrido compound $W(PMe_3)_4(OMe)H_3$ and then $W(PMe_3)_4H_4$ accompanied by the production of MeOH.

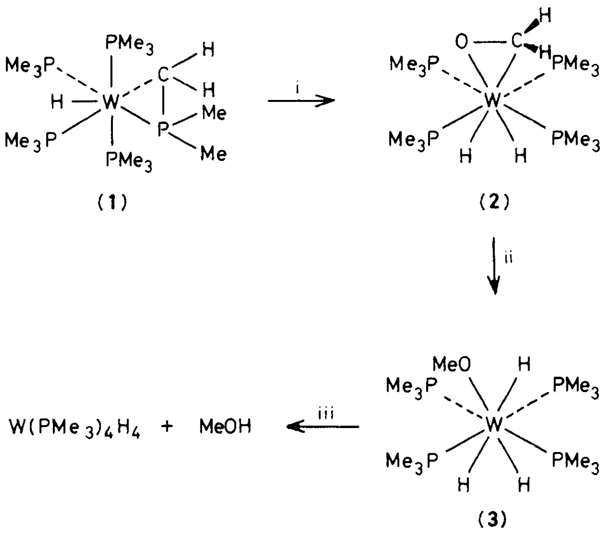
The compound $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$, (**1**), reacts readily with H_2, SiH_4, and HF giving the compounds $W(PMe_3)_4H_2X_2$, X = H, SiH_3, and F respectively.[1] These reactions show that the tungsten centre of (**1**) is very readily oxidised. Treatment of (**1**) with methanol (Scheme 1) gives yellow crystals of $W(PMe_3)_4(\eta^2\text{-}CH_2O)H_2$, (**2**), which has been characterised by microanalysis, and n.m.r. spectroscopy.† A partial crystal structure determination supports the proposed structure: the *X*-ray radiation caused sample decomposition.

η²-Formaldehyde compounds have recently been prepared by reactions with CH_2O, *e.g.* $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$[2] and $V(\eta\text{-}C_5H_5)_2(\eta^2\text{-}CH_2O)$[3] and also by oxidation of a $Re{=}CH_2$ system with PhIO giving the cation $[Re(\eta\text{-}C_5H_5)(NO)(PPh_3)(\eta^2\text{-}CH_2O)]^+$.[4] The bridging μ-formaldehyde complexes $[Zr(\eta\text{-}C_5H_5)_2Cl]_2(\mu\text{-}CH_2O)$[5] and $[Zr(\eta\text{-}C_5H_5)_2(\mu\text{-}CH_2O)]_3$[6] have also been described.

The synthesis of compound (**2**) is the first example of the formation of an η²-formaldehyde ligand by dehydrogenation of methanol. We assume that the reaction proceeds *via* initial oxidative addition of MeOH to (**1**) giving the intermediate $W(PMe_3)_5(MeO)H$ or $W(PMe_3)_5(CH_2OH)H$, followed by loss of PMe_3 and intramolecular oxidative addition of the C–H bond of the methoxy group, or O–H bond of the hydroxymethyl group. We note that the catalytic dehydrogenation of methanol, using cyclohexanone as the hydrogen acceptor, giving methyl formate has been recently demonstrated by Maitlis.[7]

The detailed mechanism of the hydrogenation of CO to methanol under Fischer–Tropsch conditions is not certain. However, ligands such as formyl, formaldehyde, and hydridomethoxy have been postulated, *inter alia,* as intermediates.[8] The overall reaction forming (**2**) may be viewed as the reverse of the final sequence of CO hydrogenation.

We have also observed, for the first time, the hydrogenation of an η²-formaldehyde ligand to give methanol. Thus, treatment of (**2**) with H_2 (2 atm., 60 °C) gives initially the previously described trihydridomethoxy compound $W(PMe_3)_4H_3(OMe)$,[9] (**3**), as pale brown crystals. Compound (**3**) reacts further with H_2 (15 atm., 65 °C) to produce $W(PMe_3)_4H_4$ and methanol (g.l.c.). The reaction of (**2**), with H_2 forming (**3**), may therefore proceed *via* reductive-elimination of the $\eta^2\text{-}CH_2O$ and H ligands giving a methoxy hydride which is followed by oxidative addition of H_2. A second reductive elimination from (**3**) produces MeOH and $W(PMe_3)_4H_4$ by reaction of the intermediate with H_2.



Scheme 1. i, Methanol at room temp. for 2 h, >80%; ii, dihydrogen at 2 atm., 60 °C, 12 h, >80%; iii, dihydrogen at 15 atm., 65 °C, 3 days, *ca.* 20%.

The stoicheiometric conversion of CO to a methoxy hydride $Zr(\eta\text{-}C_5Me_5)_2(H)(OMe)$ has been observed previously, but no intermediates have been isolated; the product may be induced to eliminate MeOH but this requires the addition of a mineral acid.[10]

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† N.m.r. data (C_6D_6, *J* in Hz). ¹H: 3.05 (2H, 5 lines, CH_2O), 1.45 [18H, d, *J*(P–H) 2.8, $2PMe_3$], 1.21 (18H, s, $2PMe_3$), −1.17 [2H, quintet, *J*(P–H) 34.2, 2W-H]. $^{13}C\{^1H\}$: 56.14 (5 lines, CH_2O), 28.70 [d, *J*(P–C) 19.5, PMe_3], 24.43 [d, *J*(P–C) 4.7, PMe_3], 20.12 (s, $2PMe_3$). $^{13}C\{^1H$ off-resonance decoupled$\}$ (only extra couplings given): 56.14 (t, CH_2O), 28.70 (quartet, PMe_3), 24.43 (quartet, PMe_3), 20.12 (quartet, $2PMe_3$). $^{31}P\{^1H\}$: −30.75 [s, *J*(P–W) 209]. $^{31}P\{^1H\text{-}Me\}$ −30.75 [t, *J*(P–H) shows reduced coupling constant owing to off-resonance decoupling].

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