Zerovalent Metal Phosphite Chemistry: Photochemistry of $W[P(OMe)_3]_6$

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Summary The new zerovalent metal phosphite complex, $W[P(OMe)_3]_6$, has been synthesized and shown to be photochemically very reactive as illustrated in the synthesis of a series of new seven- and eight-co-ordinate tungsten hydrides.

In the course of our development[1–4] of low-valent metal phosphine and phosphite chemistry, we have prepared the new complex, $W[P(OMe)_3]_6$, a colourless compound which has extraordinary photochemical reactivity. The complex in solution turns purple on brief exposure to ordinary light to yield free trimethyl phosphite. This photoreactivity has been utilized in the synthesis of new polyhydrides of tungsten and we have established that this photochemical activation can be extended to other zerovalent metal phosphite compounds, *e.g.*, $Mo[P(OMe)_3]_6$ [4] and $Fe[P(OMe)_3]_5$ [1] for the synthesis of metal hydrides. There appears to be a very extensive synthetic photochemistry for zerovalent complexes of the type $M[P(OR)_3]_x$.

The new tungsten complex was prepared by agitating a mixture of a benzene solution of $WCl_4(NC_5H_5)_2{\cdot}2NC_5H_5$ with potassium and potassium iodide at 80 °C for 2 h. Solvent was removed *in vacuo* and an excess of trimethyl phosphite was added. The resultant heterogeneous mixture was heated to 112 °C for 2 h and then held at 70 °C for 20 h. Hexane recrystallization yielded colourless crystals (20%)† [m.p. 153 °C with decomp., electronic spectrum: 228 nm (m) ϵ *ca.* $1{\cdot}5 \times 10^4$; ^1H n.m.r. spectrum (C_6D_6); δ, 3·64 (m);‡ $^{31}P\{^1H\}$ n.m.r. spectrum (C_6D_6) δ, $-3{\cdot}9$, ref. $P(OMe)_3$ (s, J_{WP} 449 Hz)].

In protonation, $W[P(OMe)_3]_6$ showed behaviour analogous to that of the molybdenum analogue in that $W[P(OMe)_3]_5[P(OMe)_2]^+$ and $HW[P(OMe)_3]_6^+$ were formed; however, the susceptibility to phosphite dissociation in $W[P(OMe)_3]_6$ was substantially higher than for the close analogue, $Mo[P(OMe)_3]_6$.[4] Solutions of the tungsten complex in hexane quickly became discoloured at 20 °C on exposure to laboratory light, and on exposure to Pyrex-filtered light from a mercury lamp, the solution turned a deep brown and displayed an n.m.r. spectrum that clearly showed the presence of substantial quantities of free trimethyl phosphite which on longer exposure was transformed to dimethyl methylphosphonate. In the dark, solutions of $W[P(OMe)_3]_6$ did not become discoloured and did not react with hydrogen.

Photolysis of hexane solutions of $W[P(OMe)_3]_6$ in a hydrogen atmosphere rapidly yielded a mixture of three new higher-co-ordinate tungsten hydrides, $H_2W[P(OMe)_3]_5$, $H_4W[P(OMe)_3]_4$, and a very small amount of a third hydride tentatively characterized as $H_2W[P(OMe)_3]_3[PMe(OMe)_2]_2$.§ All these hydrides are stereochemically non-rigid on the n.m.r. time scale to *ca.* -100 °C: $H_2W[P(OMe)_3]_5$ has a ^1H hydride sextet and a $^{31}P\{^1H\}_{CH}$ triplet (av. J_{PH} 36 Hz) that only slightly broaden (viscosity effects) at *ca.* -85 °C; and $H_4W[P(OMe)_3]_4$ has a ^1H hydride quintet and a $^{31}P\{^1H\}_{CH}$ quintet (av. J_{PH} 33 Hz) that at *ca.* -10 °C began to transform to the respective parts of the limiting $AA'A''A'''XX'X''X'''$ spectrum (the satellites due to ^{183}W–H spin–spin coupling were readily resolved and were 18·6 and 29·9 Hz, respectively, for the seven- and eight-co-ordinate hydrides). The barrier to intramolecular rearrangement in the seven-co-ordinate hydride $H_2W[P(OMe)_3]_5$ is expectedly low,[5] $<$ *ca.* 8 kcal/mol, and the barrier for the eight-co-ordinate hydride $H_4W[P(OMe)_3]_4$ is comparable to that for $H_4W[PPh(OEt)_2]_4$.[6]

The general efficacy of photochemical activation in the $M[P(OMe)_3]_x$ class of complexes is neatly illustrated by results for $Mo[P(OMe)_3]_6$ and $Fe[P(OMe)_3]_5$. Our previous attempts[4] to prepare $H_2Mo[P(OMe)_3]_5$ by thermal activation of $Mo[P(OMe)_3]_6$ failed but photochemical activation gave a high-yield mixture of $H_2Mo[P(OMe)_3]_5$ and $H_4Mo[P(OMe)_3]_4$ (the n.m.r. and dynamic n.m.r. features of these two new complexes were very similar to those of the tungsten analogues). Similarly, the thermal reaction of $Fe[P(OMe)_3]_5$ and hydrogen is exceedingly slow[1] but with photochemical activation $H_2Fe[P(OMe)_3]_4$ was formed within *ca.* 30 min.

The hydrogen addition reaction serves to illustrate the utility of photochemical activation in zerovalent or low-valent metal phosphite chemistry, a photochemical chemistry that appears to be very broad in extent with respect to inorganic reactants and organic reactants such as acetylenes. We are attempting to assess spectroscopically the significance of $W[P(OMe)_3]_5$ and $W[P(OMe)_3]_4$ in the photochemical reactions of the tungsten complex.

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† Satisfactory analyses were obtained for C, H, P, and W.

‡ An intermediate degree of P–P coupling is present in this complex as in the analogue $Mo[P(OMe)_3]_6$.[4]

§ The hydride region of the ^1H n.m.r. spectrum consists of triplet of quartets at 25 to -80 °C.

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