Tris[methylaminobis(difluorophosphine)]metal(0) Derivatives of Chromium, Molybdenum, and Tungsten: New Volatile Carbonyl-free Zerovalent Metal Derivatives of High Thermal and Oxidative Stabilities

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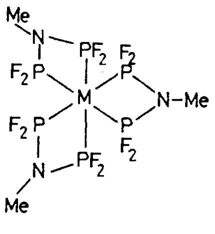
Summary U.v. irradiation of $[M(CO)_6]$ (M = Cr, Mo, and W) with excess of $MeN(PF_2)_2$ in Et_2O solution results in complete substitution of all six carbonyl groups to give colourless volatile compounds $[M\{(PF_2)_2NMe\}_3]$ (M = Cr, Mo, and W) which exhibit high thermal and oxidative stabilities.

THE photochemical substitution of carbonyl groups in $[M(CO)_6]$ (M = Cr, Mo, and W) by trivalent phosphorus ligands to give $[ML_n(CO)_{6-n}]$ derivatives has been known for more than a decade and there are now numerous examples of this type of reaction.[1] However, reported examples of complete substitution of all six carbonyl groups in $[M(CO)_6]$ by reaction with a trivalent phosphorus ligand are very rare, being restricted to PF_3 (M = Mo),[2] Pr^nOPF_2 (M = Cr, Mo, and W),[3] $(MeO)_2PF$ (M = Cr, Mo, and W),[3] and $(MeO)_3P$ (M = Mo).[3] This communication describes the ready photochemical substitution of all six carbonyl groups in the metal hexacarbonyls $[M(CO)_6]$ (M = Cr, Mo, and W) with the readily accessible[4] bidentate chelating strong π-acceptor $MeN(PF_2)_2$. The resulting new zerovalent metal complexes $[M\{(PF_2)_2NMe\}_3]$, which contain carbon-free chelate rings, are the first known carbonyl-free chelate $[ML_6]$ derivatives that are volatile and stable to air oxidation except under extreme conditions.



(I)

Mixtures of the metal hexacarbonyl (5—10 mmol), excess of $MeN(PF_2)_2$ {5—6 mmol per mmol of $[M(CO)_6]$}, and *ca.* 250 ml of diethyl ether were exposed under nitrogen at atmospheric pressure in an open system to u.v. irradiation from a 450 W Hanovia medium pressure quartz mercury vapour lamp in a water-cooled Pyrex immersion well. Irradiation was discontinued when an i.r. spectrum of the reaction solution showed an absence of ν(CO) frequencies (*ca*. 22, *ca*. 16, and *ca*. 56 h for M = Cr, Mo, and W, respectively). Evaporation of solvent from the filtered reaction mixture followed by addition of pentane and cooling gave 45—50% isolated yields of the corresponding $[M\{(PF_2)_2NMe\}_3]$ derivatives. White solids, m.p. 182—183 (M = Cr), 216—218 (M = Mo), and 221—223 °C (M = W) were obtained by vacuum sublimation at 90 °C and 0·1 mmHg.†

The $[M\{(PF_2)_2NMe\}_3]$ derivatives (M = Cr, Mo, and W) are stable towards air-oxidation in the solid state. Solutions of the chromium derivative begin to decompose in air over a period of a week whereas solutions of the molybdenum and tungsten derivatives decompose in air somewhat more rapidly. The $[M\{(PF_2)_2NMe\}_3]$ derivatives (M = Cr, Mo, and W) also exhibit high thermal stabilities. They melt to clear liquids and begin to sublime unchanged at atmospheric pressure above their m.p. The chromium derivative $[Cr\{(PF_2)_2NMe\}]_3$ distils unchanged at *ca*. 256 °C and 1 atm.

The i.r. spectra (KBr pellets) of the $[M\{(PF_2)_2NMe\}_3]$ derivatives (M = Cr, Mo, and W) show the expected strong ν(P–F) band at 835—840 cm^{-1}. Their ^1H n.m.r. spectra each exhibit a broad methyl resonance at τ 7·35. The proton-decoupled ^{31}P n.m.r. spectra of the $[M\{(PF_2)_2NMe\}_3]$ complexes (M = Cr, Mo, and W) exhibit broad triplets at −180·3, −157·6, and −125·2 p.p.m. relative to 85% H_3PO_4, respectively, with $|^1J(P-F)|$ coupling constants of *ca*. 1250, 1220, and 1230 Hz, respectively. The width of these ^{31}P resonances (width at half-height 100—200 Hz) can arise from longer-range $^3J(P-F)$ couplings.[5]

These data on the $[M\{(PF_2)_2NMe\}_3]$ complexes are consistent with their formulation as the zerovalent tris(bidentate) chelates (I) (M = Cr, Mo, and W) containing three four-membered carbon-free chelate rings. The volatility, relatively high oxidative and thermal stability, and ease of formation of these complexes undoubtedly arise from the unique combination of low molecular weight, bidentate chelating ability with a small 'bite,' and strong π-acceptor characteristics of the $MeN(PF_2)_2$ ligand. Reactions of this unusual ligand with other metal carbonyls, such as those of iron and cobalt, give a complex variety of products, some with novel formulae and structures, which are still under investigation.

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† Satisfactory analyses were obtained for C, H, N, P and F; mol. wts. in C_6H_6 agreed with the proposed formulations.

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