Bis(di-isopropylamino)phosphido and Di-isopropylaminophosphinidene Metal Carbonyl Complexes from Reactions of Manganese and Cobalt Carbonyls with Bis(di-isopropylamino)phosphine: *X*-Ray Crystal Structures of $(Pr^i_2N)_2PMn_2(CO)_8H$ and $Pr^i_2NPCo_3(CO)_9$

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Reactions of $(Pr^i_2N)_2PH$ with $Mn_2(CO)_{10}$ (photochemical in tetrahydrofuran) and $Co_2(CO)_8$ (hexane at ambient temperature) give yellow $(Pr^i_2N)_2PMn_2(CO)_8H$ and green-black $Pr^i_2NPCo_3(CO)_9$, respectively, whose structures have been determined by *X*-ray crystallography; reaction of $(Pr^i_2N)_2PMn_2(CO)_8H$ with HX (X = Cl and Br) results in cleavage of a P–N bond but retention of the Mn–H bond to give $(Pr^i_2NPX)Mn_2(CO)_8H$.

Recently we reported that reactions of the tetrahydrofuran (thf) substituted metal carbonyl complexes (thf)$M(CO)_5$ (M = Cr, Mo, and W), (thf)$Fe(CO)_4$, and (thf)$Mn(CO)_2C_5H_5$ with $(Pr^i_2N)_2PH$ result in simple displacement of the co-ordinated thf to give the corresponding $(Pr^i_2N)_2PH$ complexes.[1] We have now found that reactions of the metal–metal bonded carbonyls $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ with $(Pr^i_2N)_2PH$ are considerably more complicated leading to rupture of the P–H bond in the ligand to give the phosphido complex $(Pr^i_2N)_2PMn_2(CO)_8H$ and the phosphinidene complex $Pr^i_2NPCo_3(CO)_9$, respectively. In view of the unanticipated nature of these reactions, these products have been characterized by single-crystal *X*-ray diffraction. The P–N bonds in these complexes represent possible reactive sites for further reactions leading to transition metal complexes of novel phosphorus ligands as illustrated by our observation of the reaction of $(Pr^i_2N)_2PMn_2(CO)_8H$ with HX (X = Cl and Br) to give $(Pr^i_2NPX)Mn_2(CO)_8H$ containing a novel dialkylaminohalogenophosphido ligand.

For the preparation of $(Pr^i_2N)_2PMn_2(CO)_8H$ a mixture of $(Pr^i_2N)_2PH$[2,3] and $Mn_2(CO)_{10}$ (P/Mn = 1/2) in thf solution was exposed to u.v. irradiation for 1 h. Removal of solvent and unchanged $Mn_2(CO)_{10}$ at 70 °C *in vacuo* (0.001 mmHg) followed by crystallization of the residue from pentane (cooling to −10 °C) gave a 50% yield of yellow $(Pr^i_2N)_2PMn_2(CO)_8H$: decomp. >130 °C; ν(CO) in hexane: 2085w, 2060m, 2000s, 1990s, and 1965s cm^{-1}; ^{31}P n.m.r. (rel. to ext. H_3PO_4): δ 292.7 p.p.m. (br.). The ^1H n.m.r. spectrum ($CDCl_3$) exhibited a broad high-field Mn–H resonance at δ −15.1 in addition to the expected isopropyl resonances.

The complex $(Pr^i_2N)_2PMn_2(CO)_8H$ forms monoclinic crystals from pentane: space group $P2_1/a$; $a = 14.662(4)$, $b = 17.644(10)$, $c = 10.071(4)$ Å, $\beta = 91.27(3)°$, $D_c = 1.444$ g/cm^3, $Z = 4$.† Anisotropic least-squares refinement of all non-hydrogen parameters (Mo-K_α radiation, 1880 observed reflections, $R = 0.057$) indicates the structure depicted in Figure 1. The two $Mn(CO)_4$ groups in this structure are joined by an Mn–Mn bond [2.916(2) Å] which is symmetrically bridged by a bis(di-isopropylamino)phosphido group [Mn–P: 2.334(4) and 2.335(4) Å] and a hydrogen atom, the Mn_2PH group being planar (std. dev. 0.06), similar to the reported[4] structure for $Ph_2PMn_2(CO)_8H$.

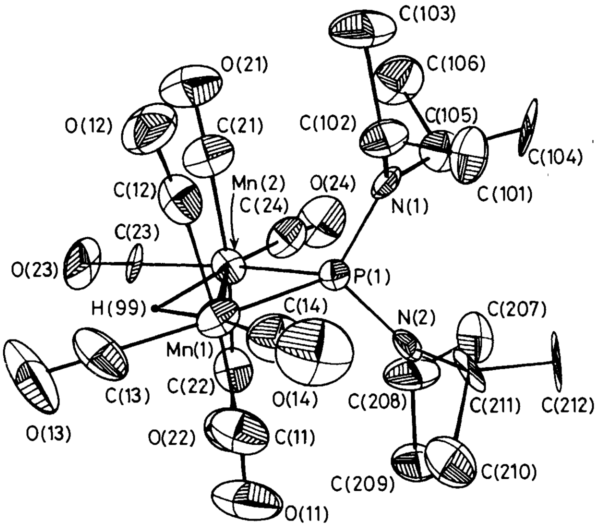

Figure 1. ORTEP diagram of the complex $(Pr^i_2N)_2PMn_2(CO)_8H$.

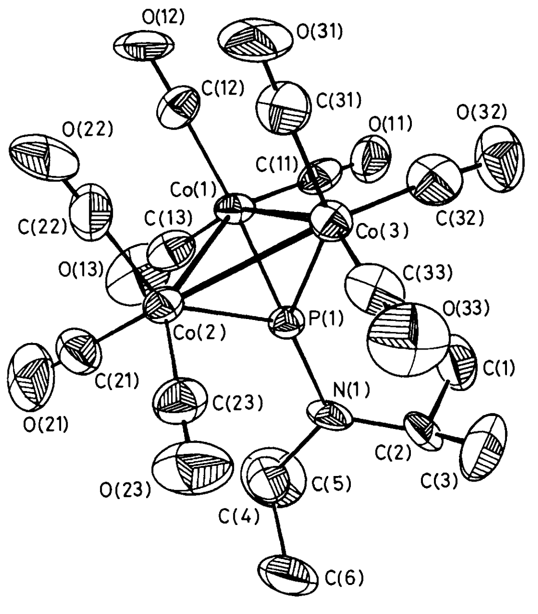

Figure 2. ORTEP diagram of the complex $Pr^i_2NPCo_3(CO)_9$.

The P–N bonds in $(Pr^i_2N)_2PHM(CO)_n$ (n = 5, M = Cr, Mo, and W; n = 4, M = Fe) are readily cleaved selectively to give the corresponding $Pr^i_2NP(H)ClM(CO)_n$ derivatives in good yield with retention of the P–H bond.[1] Similar treatment of a

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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.

hexane solution of $(Pr^i_2N)_2PMn_2(CO)_8H$ with excess of hydrogen chloride at ambient temperature gives a 65% yield of yellow-orange $(Pr^i_2NPCl)Mn_2(CO)_8H$: m.p. >100 °C (decomp.); ν(CO) in hexane: 2096w, 2068m, 2022s, 2010s, and 1975s cm^{-1}; ^{31}P n.m.r.: δ 305.1 p.p.m. (br.); ^1H n.m.r. Mn–H: δ −16.4 (br.). The similarity of the spectroscopic properties of $(Pr^i_2NPCl)Mn_2(CO)_8H$ to those of $(Pr^i_2N)_2PMn_2(CO)_8H$ except for the small changes in i.r. frequencies and n.m.r. chemical shifts indicates analogous structures for both complexes including preservation of the Mn–H–Mn system during the reaction of $(Pr^i_2N)_2PMn_2(CO)_8H$ with HCl. Hydrogen bromide reacts analogously with $(Pr^i_2N)_2PMn_2(CO)_8H$ to give the corresponding orange bromophosphine derivative $(Pr^i_2NPBr)Mn_2(CO)_8H$ with similar spectroscopic properties and hence an analogous structure.

The reaction of $Co_2(CO)_8$ with $(Pr^i_2N)_2PH$ in saturated hydrocarbon solvents at or near room temperature appears to be rather complicated giving a number of dark coloured relatively reactive metal carbonyl derivatives. A limiting product appears to be the μ_3-di-isopropylaminophosphinidene complex $Pr^i_2NPCo_3(CO)_9$, which can be obtained in *ca.* 7% yield by stirring $Co_2(CO)_8$ with $(Pr^i_2N)_2PH$ for 5 days at room temperature in hexane solution using a molar ratio of $Co_2(CO)_8$ to $(Pr^i_2N)_2PH$ of 3:2. The product is isolated as green-black air-sensitive crystals by chromatography on silica gel in pentane solution followed by crystallization from pentane at −10 °C. Related $YPCo_3(CO)_9$ compounds (Y = Et_2N, Ph, and Bu^t) have been obtained by Markó and Markó[5] from reactions of $Co_2(CO)_8$ with $YPCl_2$.

The complex $Pr^i_2NPCo_3(CO)_9$ forms monoclinic crystals from pentane: space group *Cc*; $a = 14.416(7)$, $b = 10.000(5)$, $c = 15.411(6)$ Å, $\beta = 103.84(3)°$, $D_c = 1.684$ g/cm^3, $Z = 4$.† Least-squares refinement (Mo-K_α radiation, 1851 observed reflections, $R = 0.042$) of all non-hydrogen parameters using anisotropic thermal parameters indicates the structure depicted in Figure 2. The three cobalt atoms form an equilateral triangle [average Co–Co 2.712(2) Å] which is face-bridged by a Pr^i_2NP group [Co–P: 2.142(3), 2.131(4), and 2.131(4) Å]. All nine carbonyl groups in $Pr^i_2NPCo_3(CO)_9$ are terminal in accord with the i.r. spectrum (2085w, 2030s, and 2000w cm^{-1}). A related structure has been found[6] for the complex $Bu^tPCo_3(CO)_9$.

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