The Reaction of Coarse-grain Metal Powders with Phosphoranes: a Facile Activation of Metallic Reagents and a Novel Route to Metal–Phosphine Complexes. The X-Ray Crystal Structures of $MnI_2(PPhMe_2)$ and $FeBr_3(PPhMe_2)_2$

Stephen M. Godfrey, David G. Kelly, Anthony G. Mackie,* Philomena P. Mac Rory, Charles A. McAuliffe,* Robin G. Pritchard and (the late) Susan M. Watson

Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD, UK

A route to new and existing transition metal phosphine complexes is provided by the reaction of coarse-grain metal powders and phosphoranes in diethyl ether, as exemplified here by $NiI_3(PMe_3)_2$, $FeBr_3(PPhMe_2)_2$ and $MnI_2(PPhMe_2)$.

Several groups have successfully employed transition metals rather than their salts for the synthesis of complexes. For instance, Timms[1] and Green[2] and their co-workers have used metal vapours as an alternative route to conventionally synthesised complexes and also to produce novel complexes. Finely dispersed metals have been used by Rieke,[3] whilst the electrolytic reaction of cathodic metals has been used to produce Schiff's base and other complexes.[4]

However, each of these techniques contains experimental difficulties or limitations. Vapour-phase reactions require high temperatures in order to volatalise the reactants and very low temperatures to co-condense the vapours. In contrast, involatile ligands can be reacted with dispersed metals in solution; but the formation of these solutions can be laborious. Finally, whilst electrolytic syntheses are straightforward, the range of applicable ligands is limited.

We here report a series of an entirely new type of reaction between metals and phosphoranes, which employ reagent grade metal powders (15–50 μ) without purification or activation, to produce metal phosphine complexes.

The reactions of tertiary phosphines, arsines and stibines with dihalogens to produce compounds of formula R_3EX_2 (R = alkyl, aryl; E = P, As, Sb; X = F, Cl, Br, I) have been extensively examined.[5–10] Whilst single crystal X-ray studies clearly show that the antimony compounds are five-coordinate, the situation for the phosphorus- and arsenic-containing compounds is less clear. Both five-coordinate and ionic formulations have been proposed,[7–10] but our recent studies show that Ph_3PI_2[11] and Ph_3AsI_2[12] are, in fact, four-coordinate $R_3E{-}I{-}I$ species. Irrespective of their precise formulation, the apparent coordinatively saturated nature of the compounds has militated against their use in the synthesis of transition metal complexes.

We have reacted phosphoranes with the first row transition elements chromium to zinc and some second and third row elements, to yield, for example complexes of stoichiometry $MoI_4(PPh_3)_2$ and $HgBr_2(PPh_3)$; in each case standard reagent grade metal powders have been used, and reactions have been conducted under strictly anhydrous conditions in diethyl ether at ambient temperature or in sealed tubes at 60 °C. Of these we now report some examples which illustrate the utility and variety of the reactions.

(*i*) $NiI_3(PMe_3)_2$: Reagent grade nickel powder reacts with two equivalents of Me_3PI_2 to yield $NiI_3(PMe_3)_2$. Eqn. (1) is balanced by the quantitative spectrophotometric detection of diiodine. Recrystallisation of the red powder from diethyl

$$Ni + 2Me_3PI_2 \rightarrow NiI_3(PMe_3)_2 + \tfrac{1}{2}I_2 \qquad (1)$$

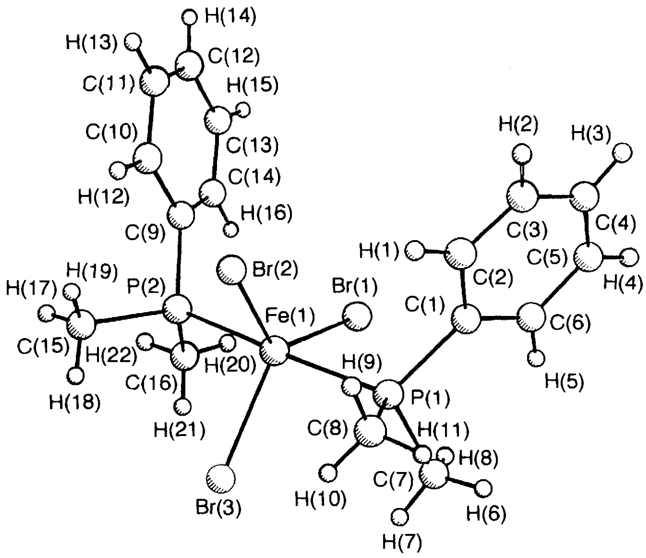

Fig. 1 Structure of $FeBr_3(PPhMe_2)_2$: selected bond lengths (Å) and angles (°): Fe(1)–Br(1) 2.350(6), Fe(1)–Br(2) 2.394(5), Fe(1)–Br(3) 2.414(6), Fe(1)–P(1) 2.345(9), Fe(1)–P(2) 2.343(9), Br(1)–Fe(1)–Br(2) 127.5(2), Br(1)–Fe(1)–Br(3) 120.8(2), Br(2)–Fe(1)–Br(3) 111.7(2), Br(1)–Fe(1)–P(1) 87.2(3), Br(1)–Fe(1)–P(2) 88.2(3)

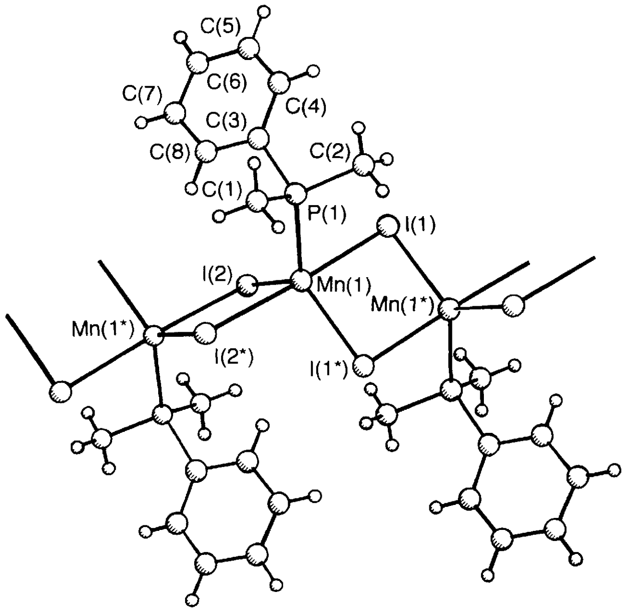

Fig. 2 Section of $[MnI_2(PPhMe_2)]_n$ polymer: selected bond lengths (Å) and angles (°): Mn(1)–I(1) 2.777(6), Mn(1)–I(1)′ 2.569(5), Mn(1)–I(2) 2.669(5), Mn(1)–I(2)″ 2.902(5), Mn(1)–P(1) 2.573(9), I(1)–Mn(1)–I(1)′ 89.9(1), I(1)–Mn(1)–I(2) 92.5(2), I(1)–Mn(1)–P(1) 86.4(2), I(1)–Mn(1)–I(2) 113.8(2), I(1)–Mn(1)–P(1) 123.6(3), I(2)–Mn(1)–P(1) 122.6(3), where (′) denotes $1 - x, -y, 2 - Z$ and (″) $2 - x, -y, 2 - z$

ether produced needles, the X-ray crystal structure of which shows them to be isostructural with the recently reported trigonal bipyramidal $NiI_3(PMe_3)_2$.[13] Whilst such nickel(III) complexes are not unknown,[14–16] they are rare and are formed from the use of an oxidising agent on a Ni^{II} species. The Ni^{III} complex described here is formed directly from the reaction of metal and phosphorane without the use of any subsequent oxidising agent.

(*ii*) $FeBr_3(PPhMe_2)_2$: In contrast to the well-established coordination chemistry of nickel salts with tertiary phosphines, reports of such iron complexes are relatively rare. No iron(II) complex has been crystallographically characterised and only $FeCl_3(PMe_3)_2$ and $FeCl_3(PPh_3)_2$ represent the (+3) oxidation state.[17]

We find that iron powder reacts rapidly, *ca.* 12 h, to consume two equivalents of $PhMe_2PBr_2$ to form a white solid which is partially soluble in diethyl ether and is acutely sensitive to dioxygen. Prolonged exposure to dioxygen results in the formation of an orange complex which exhibits a strong (PO) band in the infrared spectrum; however, at low O_2 partial pressures (<100 ppm) we are able to isolate an intensely purple trigonal bipyramidal $FeBr_3(PPhMe_2)_2$ complex, the X-ray crystal structure† of which is shown in Fig. 1. It might have been expected that the reaction of the white intermediate with O_2 would have yielded a μ-oxo complex.

(*iii*) $MnI_2(PPhMe_2)$: The X-ray crystal structure of $MnI_2(PPhMe_2)$ made by direct reaction of MnI_2 with $PPhMe_2$ in diethyl ether has been reported by King and co-workers.[18] It consists of an infinite chain of $[MnI_2]$ units with two $PPhMe_2$ ligands additionally coordinated to alternate manganese atoms, producing a 4,6,4,6 structure.

In an attempt to produce a mixed halogen complex we have reacted manganese metal with one equivalent of $PhMe_2PBrI$ (made from $PhMe_2P$ and IBr and shown by ^{31}P to be an authentic mixed-halogen phosphorane). Although we have been unable to separate completely the two products formed, eqn. (2), by fractional crystallisation we were able to isolate samples of $MnBr_2(PPhMe_2)$ and $MnI_2(PPhMe_2)$ with only trace contamination of one with the other, and eventually obtained crystals of the latter from dry diethyl ether. To our surprise an X-ray crystal structure shows this to be a pentacoordinated polymer, Fig. 2, a 5,5,5,5 structure,† contrasting with the 4,6,4,6 isomer obtained by the conventional synthesis.[18] We have re-examined the conventional synthesis and confirmed by X-ray powder diffraction that the 4,6,4,6 isomer is invariably formed. Like the 4,6,4,6 isomer the 5,5,5,5 isomer reacts rapidly and reversibly with dioxygen, a toluene solution of the complex turning deep green on exposure to dioxygen; a quantitative 1:1 uptake to form $MnI_2(PPhMe_2)(O_2)$ was measured using a gas burette and the solution displays an electronic spectral band at 620 nm as seen earlier.[19]

$$PhMe_2PIBr + Mn \rightarrow MnBr_2(PPhMe_2) + MnI_2(PPhMe_2) \quad (2)$$

In conclusion, these results suggest that a route to novel metal phosphine complexes is available by simple reaction of metal powders with phosphoranes. Such unusual complexes as

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† *Crystal data for*: $C_{16}H_{22}P_2FeBr_3$. M = 811.57, monoclinic, $P2_1/n$, Z = 4, a = 11.760(5), b = 12.745(7), c = 14.819(7) Å, β = 107.72(4)°, V = 2116(2) Å³, D_c = 2.548 Mg m⁻³, μ(Mo-Kα) = 12.09 mm⁻¹, Rigaku AFC6S diffractometer, graphite monochromated Mo-Kα radiations (λ = 0.71069 Å), ω–2θ scan mode, 4051 reflections recorded (0 < θ < 25°), Lorentz, polarization, decomposition and absorption corrections applied. The structure was solved by direct methods and refined by full-matrix least-squares analysis to final residuals R = 0.067 and R_w = 0.073 for 946 observed reflections with $F > 5\sigma(F)$ and reflection : parameters ratio 7.95. Heavier atoms were refined anisotropically, carbon isotropically and hydrogen atoms constrained to chemically reasonable positions.

For $C_8H_{11}PMnI_2$, M = 446.90, monoclinic, $P2_1/n$, Z = 4, a = 7.251(6), b = 12.984(8), c = 13.220(8) Å, β = 91.79(6)°, V = 1244(2) Å³ D_c = 2.386 Mg m⁻³, μ(Mo-Kα) = 6.017 mm⁻¹, Rigaku AFC6S diffractometer, graphite monochromated Mo-Kα radiation (λ = 0.71069 Å), ω–2θ scan mode, 2503 reflections recorded (0 < θ < 25°) Lorentz, polarization, absorption and decomposition corrections applied. The structure was solved by Patterson methods and refined by full-matrix least-squares analysis to find residuals R = 0.064, R_W = 0.077 for 814 reflections with $F > 5\sigma(F)$ and reflection : parameters ratio 11.80. Heavier atoms were refined anisotropically, carbon isotropically and hydrogen atoms constrained to chemically reasonable positions. Atomic coordinates, bond lengths and bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

the nickel(III) $NiI_3(PMe_3)_2$ and the self-assembled pentacoordinate polymeric $MnI_2(PPhMe_2)$ species suggest that this new synthetic method can yield rare and unconventional products.

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