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Production of Co(III) Complexes from Reactions of Co(II) with $NaBH_4$ or $NaBH_3CN$ in the Presence of Bis(diphenylphosphino)methane

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It has been established [1] that reactions between Co(II) and $NaBH_4$ in the presence of $Ph_2P(CH_2)_n$-PPh_2 (n = 2–6) lead *only* to reduced Co species. Similar reactions with dppm (n = 1), however, proceed differently and lead, not only to Co(I) but also, unexpectedly, to Co(III) species. While the formation of Co(III) by oxidative addition of H_2 [2a] or HX [2b] to monomeric Co(I)–monodentate phosphine complexes and of HX to monomeric Co(I)–bidentate phosphine complexes [3] has been observed previously, the situation with dppm is more complex. This communication therefore focuses on the fundamental difference between monodentate phosphines and the bidentate phosphines with n = 2–6 on the one hand, and dppm on the other hand, namely the tendency of dppm to bridge two metal centers [4].

Thus, the first (air sensitive, paramagnetic) product which has been isolated from $CoCl_2$/dppm/$NaBH_4$ reactions has the empirical formula $CoCl_{1.5}$(dppm)·S (**1**)*. The structure of **1** is currently under investigation, but the important point here is that this type of binuclear Co(I)–Co(II) mixed oxidation state product appears to be unique to reactions involving dppm. We believe that **1** contains bridging dppm ligands and that analogous compounds have not been observed for phosphines with n = 2–6 because they show greatly reduced bridging tendencies. If this is so, then the formation of products from the further reaction of **1** (in a solution which contains BH_4^- and H_2) can be rationalized in terms of the oxidative addition of H_2 to the Co(I) and Co(II) centers of **1** to produce Co(II) and Co(III) species respectively. This process should continue, along with the reduction of the Co(II) so formed by BH_4^-, until the solution eventually contains only Co(III) and Co(I). This is supported by the fact that the two major products which have been isolated in the later stages of the reaction are the Co(III) species $CoHCl_2(dppm)_2 \cdot 2C_2H_5OH$ (**2**)** and the highly crystalline Co(I) complex $CoCl(dppm)_3 \cdot S$ (**3**)** (S = benzene or toluene). Compound **2** is probably an ionic 6-coordinated species since it reacts smoothly with $NaBPh_4$ to produce $[CoHCl(dppm)_2]BPh_4$ (**4**)**.

That **2** is a mono- instead of a di- or tri-hydrido species is further support for its formation by the addition of H_2 to two Co centres rather than to a mononuclear species. The absence of Co(III) complexes as products from similar reactions with other phosphines (n = 2–6) therefore emphasizes the fundamentally different behaviour of dppm through the formation of compounds of type **1**.

Reactions between Co(II) and $NaBH_3CN$ in the presence of bidentate phosphines with n = 1–4 behave in a similar way in that Co(III) is apparently produced *only* from the dppm reactions. From these, crystals of $[CoH(BH_3CN)(dppm)_2](ClO_4)$ (**5**)**, analogous to **2**, have been obtained as one of the major products. An intermediate analogous to **1** has not yet been isolated although transient precursors of **5** are observable. Again, it is difficult to see how any kind of oxidative addition to a mononuclear Co(I) species could give rise to such a product under these conditions, and be unique to dppm.

The solid state and solution spectra of the three Co(III) hydrides, **2**, **4** and **5**, are remarkably similar to those of arsine–Co(III)–hydrido species [5] of the type $[CoH(As)_4X]^+$, and show only a single peak in the 22000–25000 cm^{-1} region ($\epsilon_{max} \sim 1000$). Other spectroscopic data (ν_{Co-H} at ~ 2000 cm^{-1}, quintet in the ^1H NMR spectrum at $\delta \sim -18$ with J_{P-H} ~ 50 Hz, singlet in the ^{31}P NMR spectrum at $\delta \sim 0$ for all three species) are all consistent with the hydride being *trans* to either Cl^- or BH_3CN^- and the presence of chelating dppm ligands is clear from the ^{31}P shifts [6].

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*S = dimethylformamide, introduced during recrystallization. After one recrystallization, 0.5S, and after two recrystallizations, 1.25S were retained in the crystals. These formulations are based on excellent and reproducible elemental analyses for Co, Cl, P, C, H and N.

Excellent chemical analyses have been obtained. ^1H NMR integration shows a dppm: C_2H_5OH ratio of 1:1 in **2.

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