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New Cobalt–Carbonyl–Phosphine Complexes

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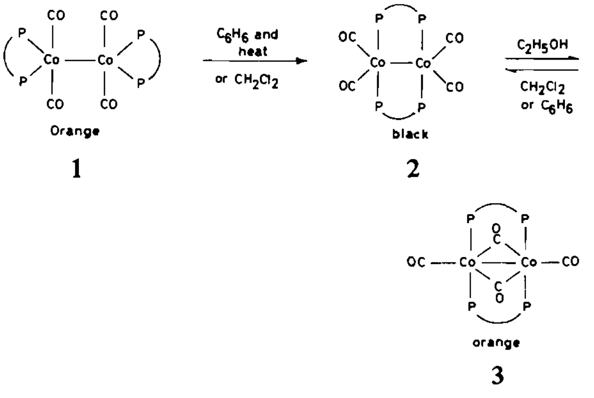
There is extensive literature on reactions between cobalt carbonyls and phosphines [1] and the use of the products of these reactions as catalysts [2, 3]. Interest continues in these systems and, in particular, additional cobalt carbonyl complexes of PPh_3 [3], $Ph_2P(CH_2)_nPPh_2$ ($n = 1$, dppm [4] and $n = 2$, diphos [5]) have been characterized recently. Parallel with our work [6] on reactions between CO-saturated solutions of Ni(II), phosphines and $NaBH_4$, we have carried out similar reactions with Co(II) in the presence of the above phosphines. As with the nickel system, these reactions have produced new complexes, not observed from simple substitution reactions of cobalt carbonyls with the phosphines. The purpose of this communication is to report specifically new interesting dppm complexes.

By suitably adjusting experimental conditions of Co(II), dppm, CO, $NaBH_4$ reactions, at least six products have been obtained. Three of these* appear to be isomers of $[Co(CO)_2(dppm)]_2$ which are interconvertible as shown below:



Thus, 1 shows a singlet at $\delta - 6.1$ in its $^{31}P\{^1H\}$ NMR spectrum consistent with chelating [7] dppm and a complex pattern of (only) terminal CO stretching frequencies in its IR spectrum (2010(vw), 1950(s), 1910(s), 1898(s), 1870(s), 1855(sh) and 1835(w) cm^{-1}). Solutions of 1 slowly turn black as 2 is produced and solutions of 2 show a singlet at δ 36 in $^{31}P\{^1H\}$ NMR spectra, consistent with bridging [7] dppm. The solid state IR spectrum of 2 shows only terminal CO stretching frequencies at 1970(s), 1955(s), 1910(s) and 1878(s) cm^{-1}. Compound 2 is insoluble in ethanol, but suspensions are slowly converted into solid 3 which shows stretching frequencies due to terminal (1968(m), 1950(s), 1945(sh), 1910 and 1905(s, doublet), 1890(m, sh), 1875(m) and 1865(w) cm^{-1}) and bridging (1769(s) and 1745(s) cm^{-1}) CO molecules. Solutions of 3 immediately turn black as 2 is produced, making it impossible to obtain the solution $^{31}P\{^1H\}$ NMR spectrum of 3. We have so far been unable to convert 2 to 1. Structural studies are currently underway on 1, 2 and 3. Compound 2 appears to be analogous to the recently structurally characterized $[Ir(CO)_2\{(CH_3)_2PCH_2P(CH_3)_2\}]_2$ in which the two Ir atoms are in significantly different environments [8].

In addition, solutions of 2 undergo ready oxidative addition with, for example I_2 and HBr. From the former, $[Co_2(CO)_2(\mu\text{-}CO)(\mu\text{-}I)(\mu\text{-}dppm)_2]^+I^-$ has been obtained* in high yield (ν(CO) terminal, 1965(s), 1950(s), 1910(wsh) cm^{-1} and ν(CO) bridging 1825(s) cm^{-1}) and this too, obtained in a quite different way [9], has been recently structurally characterized (with a similar molecular framework to the proposed structure of 3).

Full details of the chemistry and structures of these molecules, together with results from reactions between Co(II), CO, $NaBH_4$ and both PPh_3** and diphos will be published.

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*Satisfactory chemical analyses have been obtained.

**A very recent study on Co(II), PPh_3, CO, $NaBH_4$ reactions reports the formation of Co(I) species [10].

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