A Convenient Route to a Ni(0) A-frame Carbonyl Complex and Related Compounds

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The recent review [1] on the coordination chemistry of bis(diphenylphosphino)methane, Ph_2PCH_2-PPh_2 (dppm), clearly illustrates the ability of this ligand to act in a chelating, a monodentate, or a bridging fashion towards metal ions. Part of our interest in this, and related phosphines, has been in their ability to stabilize low oxidation state products in reactions between metal ions and either $NaBH_4$ [2] or $NaBH_3CN$ [3]. We have now extended these reactions to include CO as both an additional reducing agent and stabilizing ligand [4]. For example, reactions between Ni(II), dppm and $NaBH_3CN$ lead to Ni(I)–cyanide–dppm complexes [3], but in the presence of CO a variety of Ni(0)–CO–dppm complexes are formed. Thus, yellow–orange crystals* of $Ni_2(CO)_3(dppm)_2$ (**1**) have been obtained in high yield, the empirical formula suggesting an A-frame structure with a Ni–Ni bond to achieve an 18 electron count on each Ni atom.

It is clear from the IR spectrum that **1** contains both terminal (ν(CO) at 2000(w), 1972(s), 1955(s), 1940(s) cm^{-1}) and bridging (ν(CO) at 1790(s) cm^{-1}) carbonyl groups. The ^{31}P NMR spectrum of the complex shows, at room temperature, a singlet at δ 22.7 which is consistent [5] with dppm bridging two metal centers. The ^1H spectrum of **1** shows two methylene proton signals centered on δ 2.58 and 3.40 respectively with J(H–H) = 12.5 Hz. The signal at δ 2.58 appears as two well-defined overlapping quintets with a line separation (the apparent J(P–H), the average of ^2J(P–H) and ^4J(P–H) of 4.32 Hz. In the signal at δ 3.40, the two overlapping quintets are less well defined and the line separation is *ca.* 5 Hz. This ^1H NMR spectrum, which is typical of A-frame compounds [6], is due to the non-equivalent methylene protons of the coordinated dppm virtually coupled with the four magnetically equivalent P atoms in **1** to give a doublet of quintets in an ABXX′-X″X‴ system. This, therefore, confirms the A-frame nature of **1** and rules out an alternative non-A-frame structure as in, for example, $Rh_2(CO)_3(dppm)_2$ [7] which has IR and ^{31}P spectra remarkably similar to those of **1** but a quite different ^1H spectrum in which the two methylene protons are equivalent.

The above reaction is, then, a particularly convenient route to the A-frame compound and avoids the use of $Ni(CO)_4$ as in the syntheses of the related A-frames $Ni_2(CO)_3[Y_2PXPY_2]_2$, Y = CF_3, X = NH [8] or NCH_3 [8] or S [9] and Y = F, X = NCH_3 [10]. Interestingly, reactions of $Ni(CO)_4$ with $(CH_3)_2PCH_2P(CH_3)_2$ do not lead to the analogue of **1**, but produce (ligand)$Ni(CO)_2$ [11].

There are several aspects of this project which are under very active investigation.

Firstly, A-frame compounds are typically reactive species, and **1** is no exception. For example, it reacts instantly with dry HCl in several stages, and there is rapid evolution of CO when it reacts with I_2. Secondly, **1** is only one of several products formed in these reactions. Of particular interest is a compound, **2**, which, from ^{31}P NMR studies, appears to contain three monodentate dppm ligands, one of which is in a different environment from the other two. The IR spectrum of **2** shows two ν(CO) absorptions at 1992 and 1930 cm^{-1} and chemical analyses, which, while not totally reproducible, suggest the formulation $Ni_2(CO)_3(dppm)_3$ which would be consistent with the ^{31}P spectrum. In solution, **2** rapidly decomposes at room temperature to produce **1**, free dppm and a new symmetrically bridged dppm species with a sharp singlet at δ 17 in the ^{31}P NMR spectrum. We are currently attempting to grow single crystals of **2** for X-ray studies. Another interesting feature of **2** is that it is very reactive towards trace amounts of O_2, to form the monoxide of dppm. Thirdly, we have extended these reactions to phosphines of the type $Ph_2P(CH_2)_nPPh_2$ (n = 2–6). For example, one of the many additional products we have obtained, with n = 3, dppp, is $Ni_2(CO)_2(dppp)_3$ (**3**)** which, from spectral data, clearly contains two tetrahedral Ni(0) centers each with a chelating dppp ligand and a terminal CO (ν(CO) 1912, 1930(vs) doublet) bridged by the third dppp ligand. (^{31}P NMR doublet at δ 13.1 and triplet at δ 26.1 (J(P–P) = 17.7 Hz).)

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