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### PHOSPHINENICKEL TRICARBONYL

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Phosphine derivatives often have enough electron-donor bonding power, or P<sub>3d</sub> acceptor strength, or both, to form very stable complexes of transition elements; but phosphine itself has not been much used as a ligand. One reason would be its very poor electrondonor bonding power (correlated with its 93° bond angle, which implies a very large energy-cost for establishment of tetrahedral sp<sup>3</sup> hybridization); <sup>(1)</sup> another would be that the P<sub>3d</sub> orbitals in a metal-PH<sub>3</sub> complex have relatively poor  $\pi$ -acceptor bonding power. Also, in some cases the attempt to use phosphine as a ligand could lead to the formation of unintelligible polymeric metal phosphides or phosphinides. <sup>(2)</sup> However, phosphine can replace carbon monoxide from some metal carbonyls; for example,

 $\pi$ -C<sub>5</sub>H<sub>5</sub>V(CO)<sub>4</sub> + PH<sub>3</sub>  $\rightarrow \pi$ -C<sub>5</sub>H<sub>5</sub>V(CO)<sub>3</sub>PH<sub>3</sub>

meaning that phosphine is far from useless as a ligand for metalcarbonyl analogues. (3)

We now report a simpler example: the displacement of one CO from  $Ni(CO)_4$  by phosphine. This was accomplished by the use of phosphine in excess; and removal of the liberated CO made possible a virtually quantitative process:

Ni(CO)<sub>4</sub> + PH<sub>3</sub> → CO + Ni(CO)<sub>3</sub>PH<sub>3</sub> mmoles: 0.41 0.72 0.38 (remainder)  $-\frac{0.34}{0.38}$ 

For this experiment, the reaction mixture was contained in a sealed NMR tube having a prolongation for opening <u>in vacuo</u> and resealing. A 3-hour exposure to sunlight liberated 70% of the expected CO, which was led through a high-vacuum U-trap at -196°

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for collection and measurement in an automatic Sprengel-pump system.  $^{(4)}$  Then a further 2-hour exposure of the resealed tube to sunlight completed the process. The excess phosphine was distilled off at a low temperature and measured in the high-vacuum system, thereby proving the composition of the remaining liquid. In another such experiment (in sunlight), the use of a five-fold excess of phosphine led to the liberation of 0.9000 per Ni(CO)<sub>4</sub> in one step.

The nuclear magnetic resonance spectra of the liquid product indicated a single substance without observable impurities:

For <sup>1</sup>H,  $\delta = 2.83$  ppm. upfield of Si(CH<sub>3</sub>)<sub>4</sub>; J<sub>HP</sub> = 303 cps. For <sup>31</sup>P,  $\delta = 177$  ppm. upfield of H<sub>3</sub>PO<sub>4</sub>; J<sub>PH</sub> = 302 cps. The phosphorus spectrum showed the expected 1:2:2:1 quartet, with no trace of any other feature such as a triplet which would have indicated a PH<sub>2</sub> unit. Also the proton spectrum showed only the expected simple doublet.

Comparison of these results with free phosphine, for which  $\delta_{\rm H} = 1.1 \ {\rm ppm.} \ {\rm downfield}$  of Si(CH<sub>3</sub>)<sub>4</sub>,  $\delta_{\rm P} = 238 \ {\rm ppm.}$ , and J = 183 cps., <sup>(5)</sup> indicates three effects of metal-PH<sub>3</sub> bonding:  $\delta_{\rm H}$  moves 3.93 ppm. upfield because hydrogen has a better bonding overlap with the tetrahedral P<sub>3SP</sub><sup>3</sup> orbitals; <sup>(6)</sup> J is sharply increased by the larger s character in the P-H bonds; and  $\delta_{\rm P}$  moves downfield because the  $\sigma$ -electron withdrawal is not compensated by the weak Ni<sub>3d</sub>→P<sub>3d</sub> return  $\pi$ -bonding.

Our explanation of the increased J value disagrees with Fischer <u>et al</u>., who suggest that the similar increase of J when phosphine is bonded to vanadium would be ascribed to V $\rightarrow$ P  $\pi$ -dative bonding.<sup>(3)</sup> In our experience with a number of metal-PF<sub>3</sub> complexes, wherein such "return- $\pi$ " bonding would be far more important, Jpp decreases when the complex is formed.

Although accelerated by sunlight, the  $Ni(CO)_4$ -PH<sub>3</sub> reaction can go forward in the dark, approaching equilibrium during a few days in a sealed tube at 38°. Higher temperatures led to an autocatalytic decomposition to form a lustrous black solid. This might be the same as the solid which Grieb and Jones regarded as a

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nickel phosphide; (7) however, in our experiments the absence of hydrogen suggested that it more probably was either nickel with deeply adsorbed phosphine or a H-Ni-PH<sub>2</sub> high-polymeric mixture.

Our volatile product, Ni(CO)<sub>3</sub>PH<sub>3</sub>, proved to be conveniently stable in a sealed tube at 25-35°, possibly because a minute trace of phosphine inhibited decomposition. However, all attempts to distil it under high vacuum led only to rapid and extensive vaporphase decomposition, covering the inner walls of the glass highvacuum system with nonvolatile black solids. For this reason, the usual determinations of physical constants were omitted.

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