

Phosphenitrosylcobalt Dicarbonyl

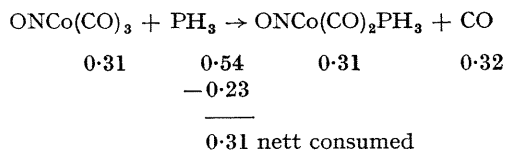
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Summary The replacement of CO by PH_3 , as in the formation of the new compound $\text{ONCo}(\text{CO})_2\text{PH}_3$, demonstrates that differences in strength between donor-acceptor ligands vary with the bonding competition among such ligands.

PHOSPHINE is normally regarded as a weak ligand for any kind of complex bonding to transition elements, but there is current interest in its limited replacement of strong π -acceptor ligands such as CO or PF_3 . This "strong" behaviour of a reputedly weak ligand seems to be correlated with the presence of more than enough π -acceptor ligands for effective employment of all available metal d_π electrons, so that little π -bonding energy is lost by replacing one strong π -acceptor ligand even by such a weak σ -donor (and even weaker π -acceptor) as phosphine. The simplest examples are the conversion of the $\text{M}(\text{CO})_6$ type into $(\text{CO})_4\text{M}(\text{PH}_3)_2$,¹ the formation of $\text{HCo}(\text{PF}_3)_3\text{PH}_3$ from $\text{HCo}(\text{PF}_3)_4$,² and the action of PH_3 upon $\text{Ni}(\text{CO})_4$ to make the very unstable $(\text{CO})_3\text{NiPH}_3$.³

A further example is the new volatile compound $\text{ONCo}(\text{CO})_2\text{PH}_3$, which is decidedly more stable than the analogous $(\text{CO})_3\text{NiPH}_3$. It was made by the action of PH_3 upon $\text{ONCo}(\text{CO})_3$ in a sealed Pyrex tube, in sunlight or at 60° in the dark. By frequent removal of the displaced CO, the following quantitative stoichiometry was achieved.



The orange-red liquid product is indefinitely stable in a sealed tube at 25° , but decomposes slightly during high-vacuum distillation.

Like other phosphine complexes, $\text{ONCo}(\text{CO})_2\text{PH}_3$ has a

far higher P-H coupling constant (^1H n.m.r. spectrum: J 326 c./sec., at 4.62 p.p.m. downfield from Me_4Si) than that of free phosphine (183 c./sec), because the P-H bond gains P_{3s} character when the P \rightarrow metal dative bond demands more P_{3p} character than the lone-pair electrons would have. Correlated with this effect is stronger P-H bonding, as shown by an increase in the i.r. frequency assigned to P-H stretching (here 2334 cm^{-1} for the vapour phase, as against 2312 cm^{-1} for phosphine vapour). The effect seems very similar to what was observed for $\text{Me}_2\text{PH}\cdot\text{BH}_3$, in which the P-H stretching frequency is nearly 5% higher than in free Me_2PH , against the expectation of a lower frequency for a quaternary P-H bond.⁴ Accordingly, it should be understood that an important part of the overall gain of bond energy due to PH_3 complex formation is in the increased strength of the three P-H bonds.

Also significant is the following comparison of i.r. frequencies (cm^{-1}) for C-O and N-O stretching, recorded for the vapour phase with the same instrument.

Understanding that these modes increase frequency when the bound CO or NO meets stronger competition for the metal $3d_\pi$ electrons, we infer that CO may be a slightly stronger π -acceptor than PF_3 , and that PH_3 runs a poor third in this comparison. Accordingly, we cannot agree that the replacement of CO by PH_3 , or the loss of CO before PH_3 in mass spectrometry, would indicate any strong π -acceptor action by phosphine.¹

The comparison of bonding action by PF_3 and CO is further aided by the failure of two experiments directed toward the synthesis of $\text{ONCoCOPF}_3\text{PH}_3$. In the first, an equimolar mixture of PF_3 and $\text{ONCo}(\text{CO})_2\text{PH}_3$ was exposed to sunlight through Pyrex, but the sole result was the replacement of PH_3 by PF_3 . In the second, $\text{ONCo}(\text{CO})_2\text{PF}_3$ was similarly exposed to PH_3 for long periods of time, with no detectable reaction. Such results suggest that PF_3 is a stronger σ -donor than CO, and probably a weaker π -acceptor.

TABLE

Assignment		ONCo(CO) ₃ ⁵	ONCo(CO) ₂ PF ₃	ONCo(CO) ₂ PH ₃
C-O stretching	2108	2087	2057
		2047	2044	2006
N-O stretching	1822	1825	1796

In sum, then, there can be no dependable order of overall bonding strength for donor-acceptor ligands, even when all are compared by attachment to the same metal, for their donor and acceptor bonding must vary with the competition; and it is well understood that donor and acceptor action by the same ligand are mutually supportive. For

the latter reason, even separate order-lists of donor and acceptor strengths, such as might be developed by means of the i.r. criterion,⁶ along with extensive displacement experiments, may not be quite realistic.

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⁵ Strictly agreeing with R. S. McDowell, W. D. Horrocks, jun., and J. T. Yates, *J. Chem. Phys.*, 1961, **34**, 530.

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