

Complexes of Cyclotetraphosphines with Copper(I) Halides

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FOWLES and JENKINS have recently reported¹ the composition $M(\text{CO})_4(\text{PhP})_4$. Data indicated that preparation of some monomeric products of the the $(\text{PhP})_4$ ring compound had two points of

¹ G. W. A. Fowles, and D. K. Jenkins, *Chem. Comm.*, 1965, 61.

attachment to the metal. Other workers² have reported substituted carbonyl species involving a single point of attachment of $(\text{PhP})_4$ to the metal. We have been interested in complexes of Group V element ring compounds with metal salts, and are therefore prompted to report the preparation of some species having the compositions $(\text{RP})_4\text{CuX}$ and $(\text{RP})_4\text{CuX}_2$. In our studies with alkyl- $(\text{RP})_4$ derivatives, nonoxidizing and very mild heat conditions were employed during preparation of the complexes.

The colourless $(n\text{-C}_8\text{H}_{17}\text{P})_4$ and $(i\text{-C}_4\text{H}_9\text{P})_4$ ligands yielded yellow solid complexes, whereas $(\text{cyclo-C}_6\text{H}_{11}\text{P})_4$ gave colourless solids. All 1:1 (ligand : CuX) complexes have melting points in the range 220—350°. A gradual increase in temperature of the 1:1 complex during an hour produced an oil and solid which persisted until decomposition occurred in the same temperature range as the 1:2 species. The 1:1 product is very soluble in benzene, carbon tetrachloride, and several other nonpolar solvents, but the 1:2 entity is virtually insoluble. Conductance studies have not been made yet, but the extensive solubility of the 1:1 species in nonpolar solvents indicates non-ionic character. Although both complex types are relatively stable in air, the 1:2 species appear to be the more stable.

The 1:1 complexes were prepared easily either by using a carbon tetrachloride solution of ligand to extract the copper(I) halide from aqueous halide media containing ascorbic acid as reducing agent or by direct reaction of anhydrous copper(I) halide

with $(\text{RP})_4$ in the presence of a small amount of nonpolar solvent such as carbon tetrachloride. Distribution ratios in extraction procedures were as high as 2000:1 in some cases. All procedures were conducted under nitrogen (including solvent removal); the temperature during all operations was in the range 25—50°. The 1:2 complexes were obtained by direct reaction of ligand with anhydrous copper(I) halide as above, or in one case by shaking the ligand in carbon tetrachloride with aqueous media containing copper(I) halide. No 1:4 species could be prepared by the latter method. These preparatory techniques are similar to known methods for complexes like $\text{R}_3\text{P}_2\text{CuX}$.

Normal-range infrared spectra of $(n\text{-C}_4\text{H}_9\text{P})_4$ and $(n\text{-C}_4\text{H}_9)_3\text{P}$ are very similar, but $(n\text{-C}_4\text{H}_9\text{P})_4$ exhibits characteristic absorption bands³ in the ultraviolet range 280—300 $\text{m}\mu$, while R_3P type compounds do not. Ultraviolet spectra of the 1:1 and 1:2 complexes, taken in chloroform solution, have shoulder-plateaux in the same wavelength range as for the ligands. However, the shoulder-plateaux of the complexes are not as outstanding as those of the ligands, and the complexes have a much greater absorptivity [per mole of $(\text{RP})_4$] than the ligands. In benzene, $(i\text{-C}_4\text{H}_9\text{P})_4\cdot\text{CuCl}$ exhibited a molecular weight corresponding to a dimer. The 1:1 complexes may be halogen-bridged dimers involving two points of attachment of a puckered^{3,4} $(\text{RP})_4$ ring to the metal, while the 1:2 species are perhaps an interesting type of coordination block polymer.

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² H. G. Ang, T. S. Shannon, and B. O. West, *Chem. Comm.*, 1965, 10.

³ Wm. A. Henderson, Jr., M. Epstein, and F. S. Seichter, *J. Amer. Chem. Soc.*, 1963, **85**, 2462.

⁴ G. J. Palenik, and J. Donahue, *Acta Cryst.*, 1962, **15**, 564.