

Tertiary Phosphine and Arsine Complexes of Copper(II)

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Summary Copper(II) bishexafluoroacetylacetonate forms green, stable 1:1 adducts with tertiary phosphines.

ALTHOUGH tertiary phosphine complexes of copper(I) are well known, reports of analogous complexes of copper(II) have never been substantiated. The reaction of a tertiary phosphine with a copper(II) salt in a polar solvent has invariably led to a redox reaction and the formation of a copper(I)-phosphine complex.^{1,2} We report that the powerful Lewis acid $\text{Cu}^{\text{II}}(\text{hfac})_2$ [hfac = hexafluoroacetylacetonate] reacts readily with an equimolar amount of triphenylphosphine in non-polar organic solvents to form the dark green, crystalline (m.p. 65–66.5°) complex $\text{Cu}(\text{hfac})_2 \cdot \text{PPh}_3$. The complex is monomeric in chloroform solution, in which it has a magnetic moment at 25 °C of 1.65 B.M. The e.s.r. spectrum in chloroform solution at 25 °C consists of six lines centred at g 2.13 (see Table) and can be interpreted in terms of two overlapping quartets. Although the lower-field lines are broadened because the tumbling rate does not average out the anisotropies, the ratios of the line intensities are, as expected, (*ca.* 1:1:2:2:1:1). The copper hyperfine splitting decreases from *ca.* 71 G in $\text{Cu}(\text{hfac})_2$ to *ca.* 59 G in the phosphine adduct. The phosphorus superhyperfine splitting in the latter is *ca.* 132 G.

Similar adducts have been formed with PET_3 , PBu_2 , PMe_2Ph , PMePh_2 , and AsPh_3 . These compounds give satisfactory analyses, although the arsine derivative dissociates in chloroform solution, and all are to a certain extent unstable since Cu^{II} is readily reduced. The magnetic moments fall in the range 1.65–1.76 B.M., possibly suggesting slight reduction. Reaction of two mol of triphenylphosphine with one mol of $\text{Cu}(\text{hfac})_2$, either in methanol at room temperature or in the melt *in vacuo* yields yellow crystals of $\text{Cu}(\text{hfac})_2 \cdot 2\text{PPh}_3$, m.p. 153–154°. The oxidized product is a mixture containing hexafluoroacetylacetone and other fluorocarbons with a very irritating odour.

E.s.r. data for phosphine complexes in chloroform solution

Complex	g	A_{Cu} (G)	A_{P} (G)
$\text{Cu}(\text{hfac})_2 \cdot \text{PPh}_3$	2.13	59	132
$\text{Cu}(\text{hfac})_2 \cdot \text{PPh}_2\text{Me}$	2.13	62	140
$\text{Cu}(\text{hfac})_2 \cdot \text{PPhMe}_2$	2.14	60	146
$\text{Cu}(\text{hfac})_2 \cdot \text{PET}_3$	2.13	58	139
$\text{Cu}(\text{hfac})_2 \cdot \text{PBu}_3$	2.13	59	137

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