Complex-forming Reactions of an Arylcopper(I) Cluster Compound with Organophosphines. An Unexpected C(alkyl)–P Bond Cleavage in 1,2-Bis(diphenylphosphino)ethane

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Summary Whereas the 1:1 reaction of (2-cupriobenzyl)-dimethylamine (RCu) with 1,2-bis(diphenylphosphino)-ethane (diphos) affords the 1:1 complex RCu(diphos), 1:2 reaction results in cleavage of the C(alkyl)–P bond with formation of $Ph_2PCu(diphos)(solv)$, RH, and $Ph_2PCH = CH_2$.

IN the course of our investigation of the structure and stability of organocopper(I) cluster compounds[1] we have studied the reaction of (2-cupriobenzyl)dimethylamine tetramer† [RCu; (I)] with monodentate and bidentate organophosphorus ligands.‡

Molecular weight determinations and microwave titrations[3] failed to reveal any appreciable breakdown of tetrameric (I) by PPh_3. Microwave titrations showed the formation of a 1:1 complex with bidentate diphos, and

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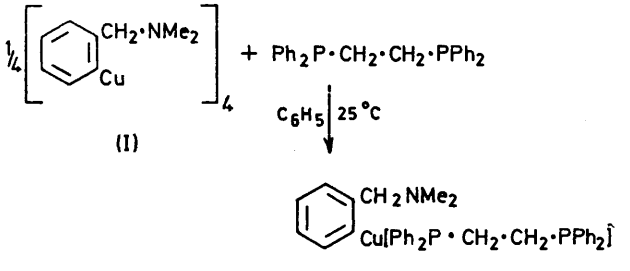
† The solid state structure of (4-methyl-2-cupriobenzyl)dimethylamine tetramer has been established by *X*-ray diffraction (J. M. Guss, R. Mason, I. Sotofte, G. van Koten, and J. G. Noltes, *J.C.S. Chem. Comm.*, in the press).

‡ Costa and Camus have shown that the polymeric structures of phenyl-, tolyl-, and anisyl-copper(I) are broken down to lower arylcopper aggregates upon complexation with phosphorus- and nitrogen-containing ligands.[2]

molecular weight determinations suggested that reaction occurred for RCu:diphos < 1.



(II)

This has been confirmed by a preparative study. From the 1:1 reaction of (I) with diphos white crystalline RCu(diphos)§ (II) has been isolated.¶ Most probably the copper atom in (II) is tetraco-ordinate as a result of (diphos) chelation and Cu–N intramolecular co-ordination.

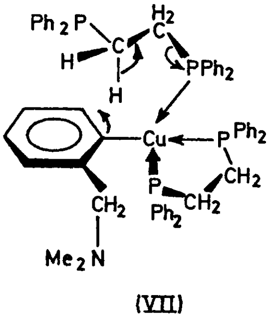
Product analysis [n.m.r. and i.r. spectroscopy, elemental analysis, and degradation of (IV) with DCl and HCl] showed that the 1:2 reaction involved a novel C(alkyl)–P bond cleavage in (diphos). The products (IV)—(VI) were isolated in 70—99% yield.

This C(alkyl)–P bond cleavage can be explained by a concerted mechanism which takes place in complex (VII·(This is supported by the fact that the reaction of (II) with

$$\underset{\text{(I)}}{\tfrac{1}{4}[\mathrm{RCu}]_4} + 2(\mathrm{diphos}) \xrightarrow[25\,°\mathrm{C}]{\mathrm{C_6H_6}} \underset{\text{(IV)}}{\mathrm{Ph_2PCu(diphos)C_6H_6}}$$

$$+ \underset{\text{(V)}}{\mathrm{Ph_2PCH = CH_2}} + \underset{\text{(VI)}}{\mathrm{RH}}$$

an equimolar amount of diphos likewise produces (IV). The formation of $(CuCl)_2(diphos)_3(dce)_2$, ArH, and vinyl chloride



(VII)

from the reaction of 1,2-dichloroethane (dce) with $(CuAr)_2$-$(diphos)_3$ complexes[2] can be explained on the same basis.

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§ The 1:1 reaction of (I) with *cis*-1,2-bis(diphenylphosphino)ethylene (*cis*-dppe) afforded yellow crystalline RCu(*cis*-dppe) (III). Both (II) and (III) (*ca.* 80%), are monomeric in benzene (by ebullioscopy). Both compounds melt at about 160—165 °C (decomp. 170 °C) and are very stable in air.

¶ All compounds gave satisfactory analyses. Complete spectroscopic and degradative details will be given later.

[1] G. van Koten, A. J. Leusink, and J. G. Noltes, *Chem. Comm.*, 1970, 1107; *Inorg. Nuclear Chem. Letters*, 1971, **7**, 227.
[2] G. Costa, A. Camus, N. Marsich, and L. Gatti, *J. Organometallic Chem.*, 1967, **8**, 339; A. Camus and N. Marsich, *ibid.*, 1970, **21**, 249
[3] E. H. Adema and J. Schrama, *Analyt. Chem.*, 1965, **37**, 229.