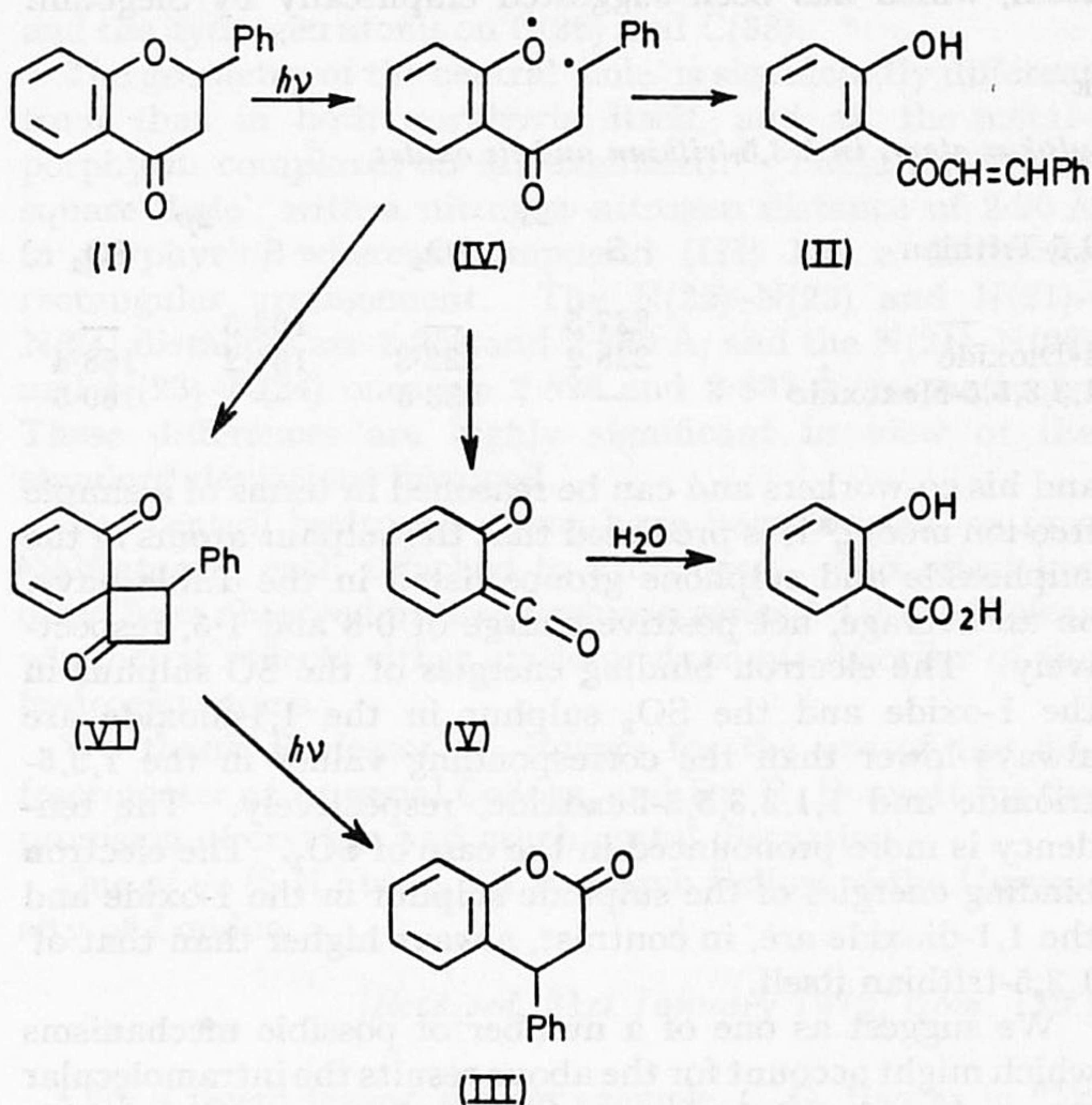


IN a reaction analogous to the photo-Fries rearrangement of aromatic esters,¹ various simple aromatic ethers undergo a



light induced rearrangement to *o*- and *p*-substituted phenols.^{2,3} It was therefore of interest to extend our study²

to cyclic ethers where the potential migrating group is attached to the aromatic ring, and we now report a rearrangement of flavanone (I).

Irradiation (Rayonet reactor fitted with 2537-A source, quartz, 0.7% solution w/v) of (I) in benzene (12 h, 37% reaction) produced 2'-hydroxychalcone (II, 20%), 4-phenyldihydrocoumarin (III, 13%, identical with authentic sample⁴), and salicylic acid (4%). We believe that the initial product of the photolysis is the diradical (IV), in analogy with the behaviour of simple aryl ethers.^{2,3} Intramolecular hydrogen abstraction then leads to 2'-hydroxychalcone (II), while fragmentation gives the keto-keten (V) which reacts with water to yield salicylic acid. It has recently been suggested that the intermediate (V) is produced on photolysis of both 2-phenyl-1,3-benzodioxan-4-one⁵ and 2,3-dihydrobenzofuran-2,3-dione.⁶ We also suggest that the rearrangement of (I) to 4-phenyldihydrocoumarin (III) proceeds through (IV) and the dienone (VI), which yields the product in a further photo-rearrangement. The conversion of (I) into (III) is analogous to the light induced rearrangement of isothiochroman-4-one to thiochroman-3-one, for which an intermediate similar to (VI) has been suggested.⁷

Evidence for the intermediacy of (V) in the formation of salicylic acid was obtained by repeating the photolysis of (I) in benzene containing 5% methanol. Methyl salicylate was produced in 9% yield.

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

By G. VAN KOTEN* and J. G. NOLTES

(Organisch Chemisch Instituut TNO, Utrecht, The Netherlands)

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

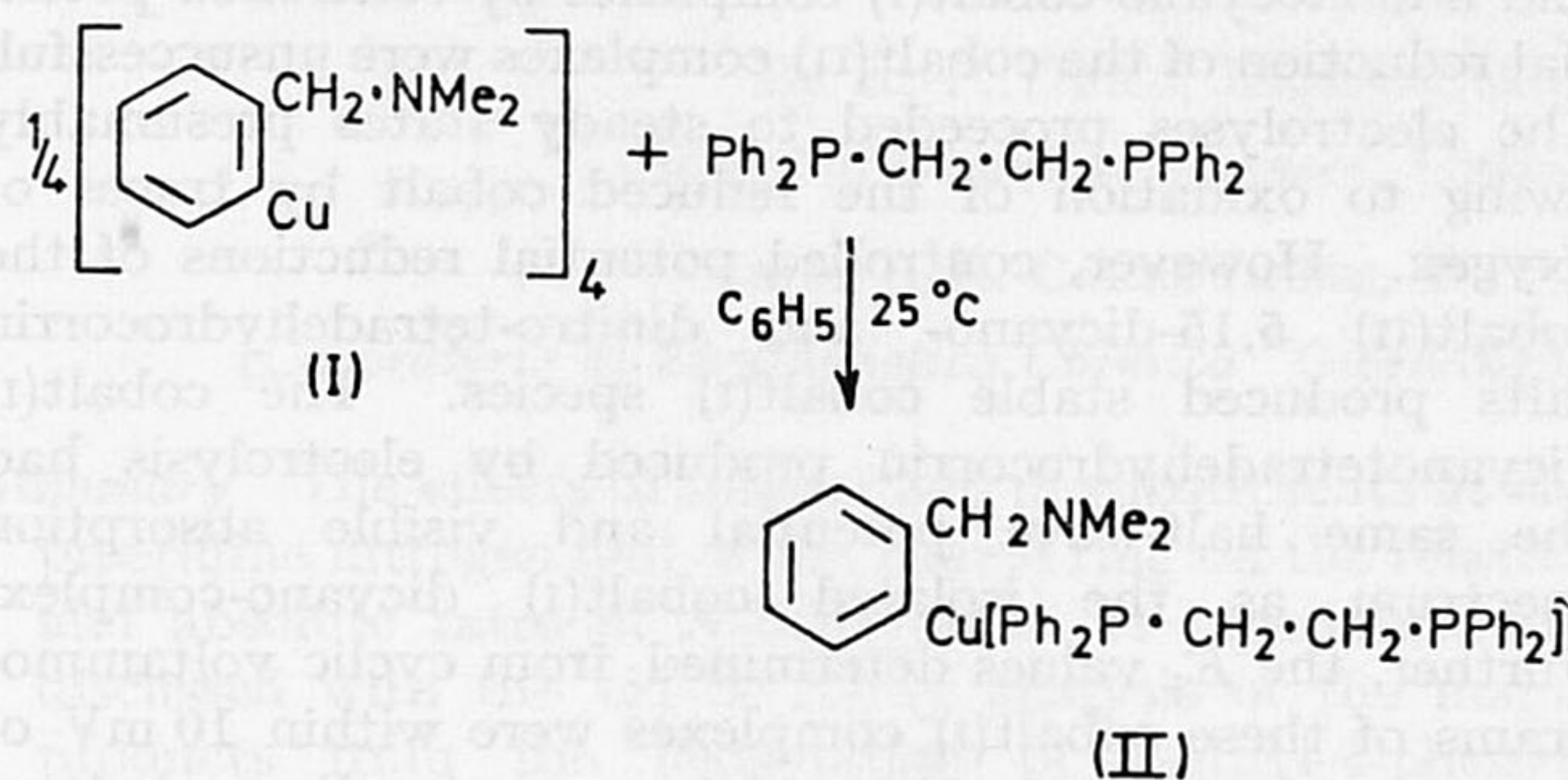
stability of organocopper(I) cluster compounds¹ we have studied the reaction of (2-cupriobenzyl)dimethylamine tetramer† [RCu; (I)] with monodentate and bidentate organophosphorus ligands.‡

Molecular weight determinations and microwave titrations³ 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

† 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. Noltès, *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

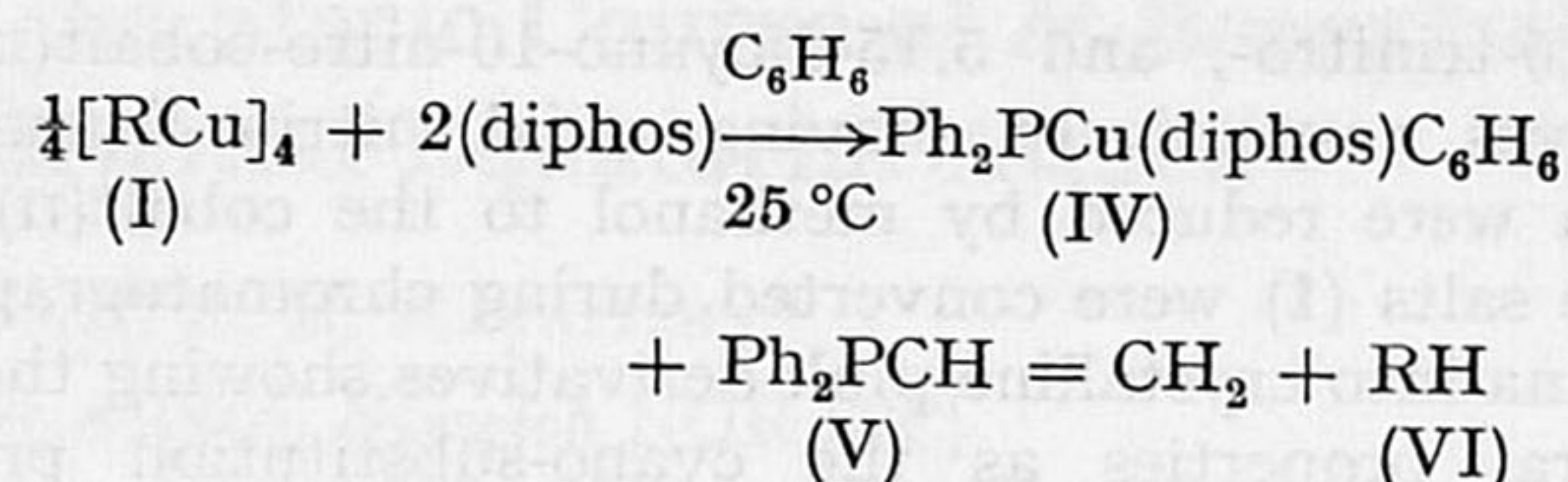
molecular weight determinations suggested that reaction occurred for $\text{RCu}:\text{diphos} < 1$.



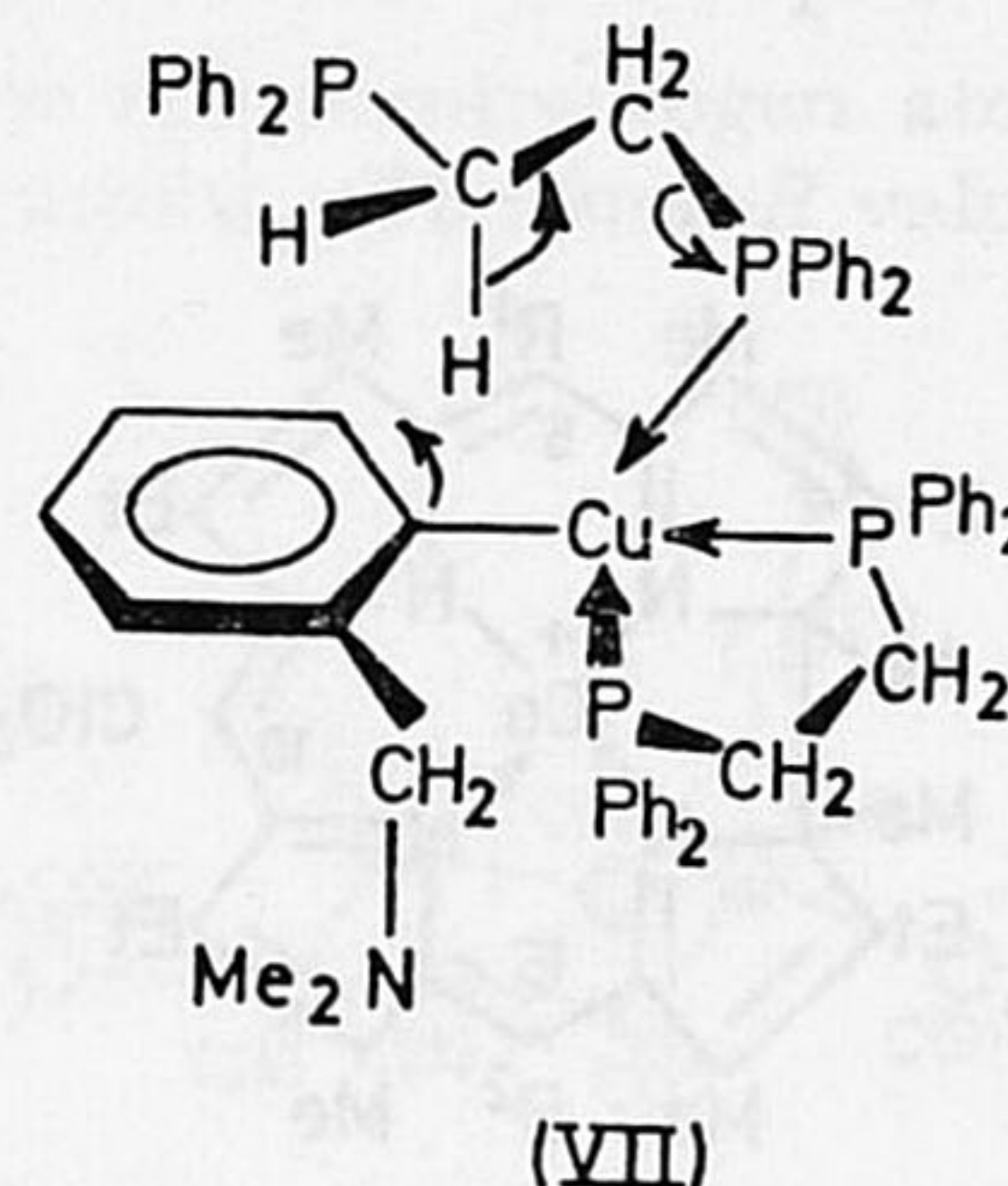
This has been confirmed by a preparative study. From the 1:1 reaction of (I) with diphos white crystalline $\text{RCu}(\text{diphos})_2$ (II) has been isolated.¶ Most probably the copper atom in (II) is tetra-co-ordinate as a result of (diphos) chelation and Cu-N intramolecular co-ordination.

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



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



from the reaction of 1,2-dichloroethane (dce) with $(\text{CuAr})_2(\text{diphos})_3$ complexes² 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 $\text{RCu}(\text{cis-dppe})$ (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.

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³ E. H. Adema and J. Schrama, *Analyt. Chem.*, 1965, 37, 229.

Stable Cobalt(I) Complexes of Tetradehydrocorrins

By C. M. ELSON, A. HAMILTON, A. W. JOHNSON,* and C. STUBBS

(School of Molecular Sciences and A.R.C. Unit of Nitrogen Fixation, University of Sussex, Falmer, Brighton BN1 9QJ)

Summary Cyanation and nitration of cobalt(II) tetradehydrocorrins yield cobalt(III) derivatives which can be converted readily into crystalline neutral cobalt(I) complexes; these substituted cobalt(I) tetradehydrocorrins are reversibly oxidised to stable cobalt(II) complexes at potentials anodic to the oxidation potential of the unsubstituted cobalt(I) complex.

In a study of the substitution reactions of the tetradehydrocorrins (**1**; $\text{R}^1 = \text{R}^2 = \text{H}$)† we have encountered a novel series of pink complexes, prepared as in the following example. Treatment of the purple salt (**1**; $\text{R}^1 = \text{R}^2 = \text{H}$) with cyanide gave, by analogy with earlier work,¹ the neutral dicyanocobalt(III) species (**2**; $\text{R}^1 = \text{R}^2 = \text{H}$), which, when heated in chlorobenzene at 100° under nitrogen, gave a mixture of two crystalline pink, neutral cobalt complexes

which contained respectively one (37%) and two (6%) cyano-*meso*-substituents. The location of these cyano-substituents was established by conversion of the monocyno-derivative with more cyanide into the corresponding dicyanocobalt(III) derivative (**2**; $\text{R}^1 = \text{CN}$, $\text{R}^2 = \text{H}$), which on heating gave the pink dicyano-compound (**3**; $\text{R}^1 = \text{R}^2 = \text{CN}$) and this was shown to contain only one *meso*-hydrogen (n.m.r.). Treatment of the pink complexes with perchloric acid gave the cobalt(II) perchlorates (**1**; $\text{R}^1 = \text{CN}$, $\text{R}^2 = \text{H}$ and $\text{R}^1 = \text{R}^2 = \text{CN}$) respectively.

We have been unable to bring about cyanation at the remaining *meso*-unsubstituted position (C-10) by heating (**2**; $\text{R}^1 = \text{R}^2 = \text{CN}$) obtainable from (**1**; $\text{R}^1 = \text{R}^2 = \text{CN}$) by treatment with excess of cyanide. However, nitration [$\text{Cu}(\text{NO}_3)_2\text{-Ac}_2\text{O}$] of the perchlorates of the cobalt(II) ligands (**1**; $\text{R}^1 = \text{R}^2 = \text{H}$ or CN) gave the 5,15(5,10?)-dinitro-

† Satisfactory analyses and spectra consistent with the assigned structures have been obtained for all new compounds described.