

duced 23% of (2) and, after oxidation, 12% of (4), 13% of (5), and 4% of (6) in addition to 15% of recovered (1).

When a 0.013M-ether solution of (1) alone was irradiated, essentially all the (1) had disappeared (to dimer) after 0.5 h. Therefore, MeLi is an efficient quencher of (1).

Thermal addition of MeLi to (1) in THF-ether proceeded slowly at 50–55°. Reaction of a solution of (1) (0.14M) and MeLi (0.75M) in THF-ether (5:3) for 7 h gave ca. 20% conversion of (1). Analysis of the oxidized product mixture showed the alkylated anthracenes to consist of 92% of (4), ca. 7% of (6), and a trace (ca. 1–2%) of (5). In contrast, photolysis of an identical solution gave 21% of (2), 15% of (4), 21% of (5), and 4% of (6). Therefore, it is clear that (a) MeLi does add to (1) photochemically; (b) MeLi inhibits the photochemical dimerization of (1); and (c) the isomer distribution of methylanthracenes produced photochemically, where a large amount of 2-alkyl product is found, is radically different from that produced thermally and from that reported for other photoalkylations,<sup>1</sup> where exclusive or nearly exclusive 9-alkylation is the case.¶

The e.s.r. spectrum obtained after irradiation of (1) and MeLi in ether was similar to that after irradiation of (1) in

the presence of PhLi.§ The latter reaction has been shown to produce the anthracene radical anion.<sup>1h</sup> Thus an electron transfer-alkyl transfer process is indicated. However, it is also possible that methylation is a separate reaction not proceeding *via* initial complete electron transfer but *via* a direct addition of a methyl carbanion instead. Either process would result in the formation of lithium salts of methylanthracenes. Loss of LiH apparently occurs to some extent (more so with the 1- and 2-methylated intermediates, as expected) to form methylanthracenes during the reaction. We note the analogy between the present reaction and the photoaddition of amines to (1).<sup>2</sup> The reason for the large amount of 2-alkyl product is presently unknown.

MeLi also adds photochemically to naphthalene and phenanthrene.

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¶ These conclusions hold even in the unlikely extreme event that the entire mass deficiency is a result of a photochemical destruction of only 9-alkylated material.

§ A slight difference (line broadening with PhLi) is attributed to a solvent effect; PhLi experiments were in 35% benzene-ether; MeLi in pure ether.

<sup>1</sup> (a) J. A. Dixon and D. H. Fishman, *J. Amer. Chem. Soc.*, 1963, **85**, 1356; (b) J. A. Dixon, D. H. Fishman, and R. S. Dudinyak, *Tetrahedron Letters*, 1964, 613; (c) D. Nicholls and M. Swarc, *J. Amer. Chem. Soc.*, 1966, **88**, 5757; *Proc. Roy. Soc.*, 1967, **A301**, 231; (d) R. G. Harvey and C. C. Davis, *J. Org. Chem.*, 1969, **34**, 3607; (e) R. G. Harvey, L. Nazareno, and H. Cho, *J. Amer. Chem. Soc.*, 1973, **95**, 2376; (f) E. J. Panek, *ibid.*, 1973, **95**, 8460; (g) H. J. S. Winkler, R. Bollinger, and H. Winkler, *J. Org. Chem.*, 1967, **32**, 1700; *Intra-Sci. Chem. Reports*, 1969, **3**, 261; (h) H. J. S. Winkler and H. Winkler, *J. Org. Chem.*, 1967, **32**, 1695.

<sup>2</sup> N. C. Yang and J. Libman, *J. Amer. Chem. Soc.*, 1973, **95**, 5783, and references therein.

## Synthesis and Specific Intramolecular C–C Coupling Reactions of Novel Hexanuclear Copper Cluster Complexes Ar<sub>4</sub>R<sub>2</sub>Cu<sub>6</sub>

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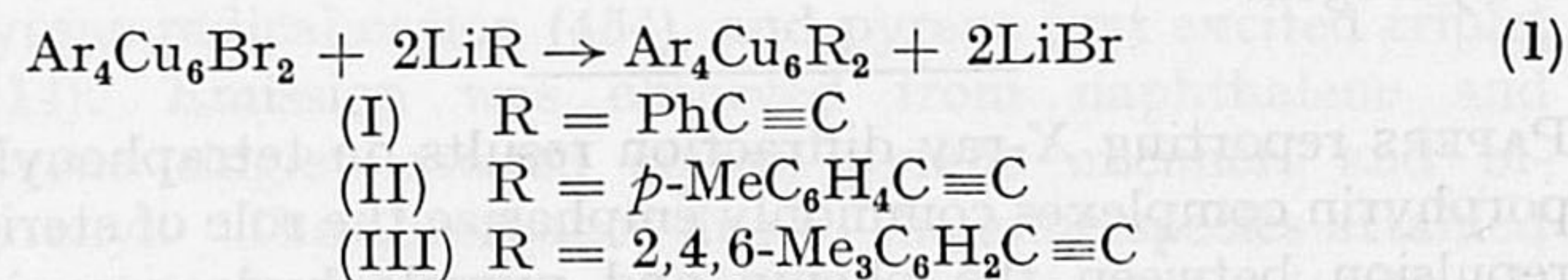
**Summary** The synthesis of novel mixed organocopper cluster complexes, Ar<sub>4</sub>R<sub>2</sub>Cu<sub>6</sub>, *via* ligand-substitution of Ar<sub>4</sub>Cu<sub>6</sub>X<sub>2</sub> with RLi is reported; the exclusive formation of the mixed coupling product ArR upon thermolysis follows from the structure of these complexes.

POLYMERIC 2-(dimethylamino)phenylcopper,<sup>1</sup> (ArCu)<sub>n</sub> (Ar = *o*-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>), upon interaction with CuBr forms a hydrocarbon-soluble complex Ar<sub>4</sub>Cu<sub>6</sub>Br<sub>2</sub><sup>1</sup> which according to an X-ray study possesses an octahedral copper skeleton with the four aryl ligands each bridging one equatorial and one apical Cu atom and the two bromo-ligands each bridging two equatorial Cu atoms.<sup>2</sup>

The new complexes Ar<sub>4</sub>Cu<sub>6</sub>X<sub>2</sub> (X = Cl, decomp. 181–183°; X = I, decomp. 195–197°) which were likewise obtained by interaction of (ArCu)<sub>n</sub> with CuX have the same octahedral structure (mol. wt., i.r., and <sup>1</sup>H n.m.r. data). The complexes Ar<sub>4</sub>Cu<sub>6</sub>X<sub>2</sub> can undergo halogen exchange with retention of the hexanuclear cluster as illustrated by

the quantitative isolation of Ar<sub>4</sub>Cu<sub>6</sub>I<sub>2</sub> from the reaction of Ar<sub>4</sub>Cu<sub>6</sub>Cl<sub>2</sub> with 2 mol of LiI in benzene.

In the presence of lithium arylacetylides (1:2 molar ratio) quantitative ligand-substitution occurs [reaction (1)].†

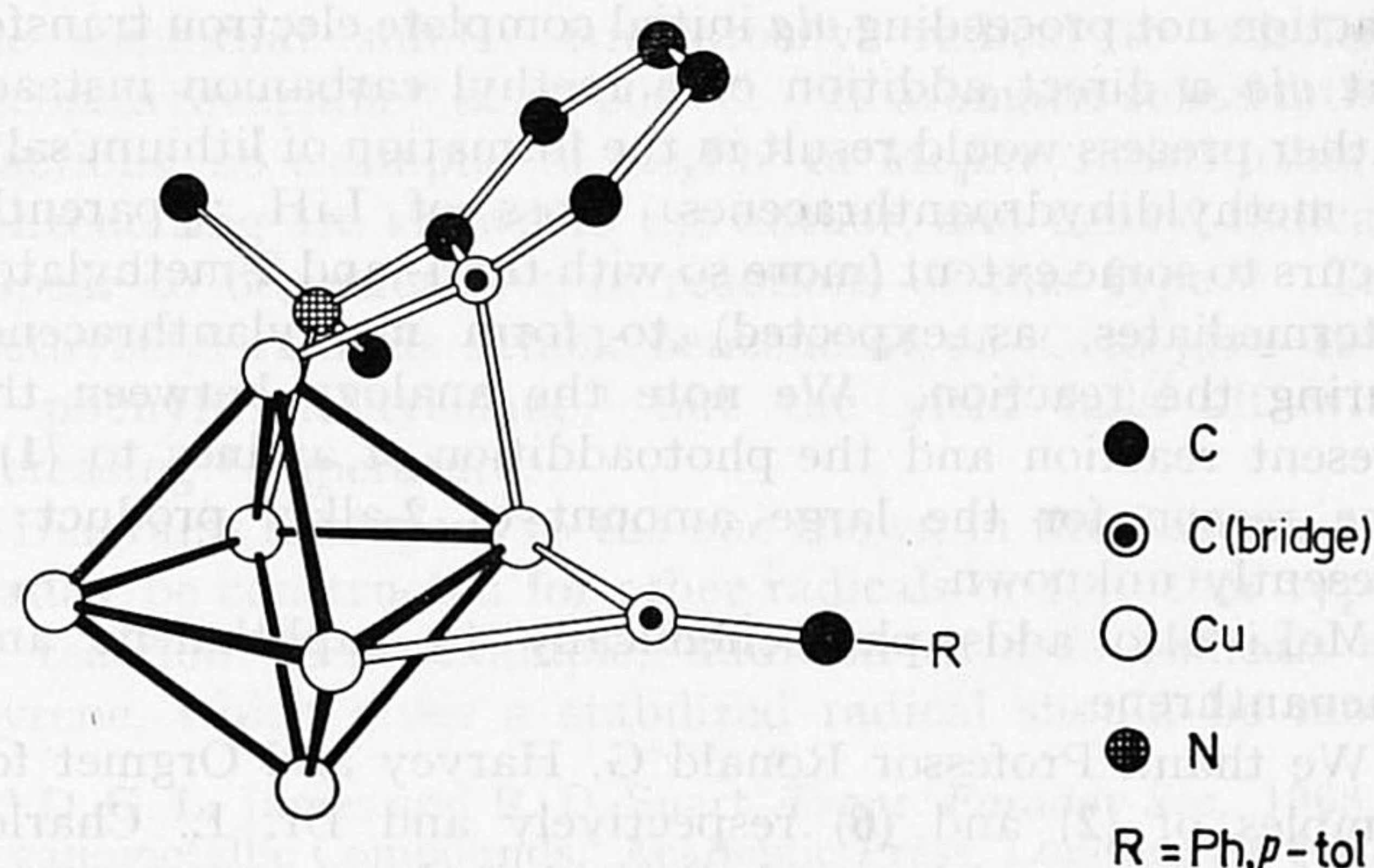


The products (I)–(III), which are the first examples of polynuclear mixed organocopper compounds, have been isolated‡ analytically pure: (I), dark-green, decomp. 127–129°; (II) brown, decomp. 115–120°; (III) bright-yellow, decomp. 186–193°. As shown by cryometry compounds (I)–(III) exist in benzene as discrete Ar<sub>4</sub>R<sub>2</sub>Cu<sub>6</sub> units. The δ-values for the Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub> protons for R<sub>4</sub>Cu<sub>6</sub>Br<sub>2</sub> and compounds (I)–(III) are nearly identical as would be expected if these compounds had the Ar<sub>4</sub>Cu<sub>6</sub> skeleton in common. Comparison of ν(C≡C) frequencies for (I)–(III);

† In the same way Ar<sub>4</sub>Cu<sub>6</sub>(C≡CSiMe<sub>3</sub>)<sub>2</sub> (decomp. 140°) has been prepared.

‡ As shown by mass spectrometry tetranuclear copper clusters R<sub>4</sub>Cu<sub>4</sub> (R<sup>1</sup> = 2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sup>3</sup> and R<sub>2</sub>Cu<sub>4</sub> (R<sup>2</sup> = 5-Me, 2-Me<sub>2</sub>NCH<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sup>3,4</sup> undergo ligand exchange in benzene with formation of R<sub>3</sub>R<sup>2</sup>Cu<sub>4</sub>, R<sub>2</sub>R<sup>2</sup>Cu<sub>4</sub>, and R<sup>1</sup>R<sup>2</sup>Cu<sub>4</sub> (5 parent peaks differing by 14 mass units). However, these polynuclear mixed organocopper compounds cannot be isolated.

[(I) 2051sh, 2041m, and 2037sh; (II) 2046m and 2031sh; (III) 2036m and 2031m  $\text{cm}^{-1}$ ] with those for various other arylacetylide-copper compounds<sup>5</sup> reveals that each



FIGURE

arylacetylide ligand is  $\sigma$ -bonded to two equatorial copper atoms and that  $\pi$ -interactions as occurring in  $(\text{PhC}\equiv\text{CCu})_n$

§ Recently an octanuclear  $\text{Cu}^{\text{I}}\text{Cu}^{\text{0}}$  compound  $(m\text{-CF}_3\text{C}_6\text{H}_4)_6\text{Cu}^{\text{I}}_6\text{Cu}^{\text{0}}_2$  has been isolated by Cairncross and Sheppard.<sup>6</sup>

<sup>1</sup> G. van Koten, A. J. Leusink, and J. G. Noltes, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 227.

<sup>2</sup> J. M. Guss, R. Mason, K. M. Thomas, G. van Koten, and J. G. Noltes, *J. Organometallic Chem.*, 1972, **40**, C79.

<sup>3</sup> G. van Koten, A. J. Leusink, and J. G. Noltes, *Chem. Comm.*, 1970, 1107.

<sup>4</sup> J. M. Guss, R. Mason, I. Sotofte, G. van Koten, and J. G. Noltes, *J.C.S. Chem. Comm.*, 1972, 446.

<sup>5</sup> P. W. R. Corfield and H. M. M. Shearer, cited in G. E. Coates, M. L. H. Green, and K. Wade, eds. 'Organometallic Compounds,' vol. 2, Transition elements, Methuen, London, 1968, pp. 274 and 278; G. E. Coates and C. Parkin, *Adv. Chem. Co-ordination Compounds*, 1961, 173.

<sup>6</sup> A. Cairncross and W. A. Sheppard, *J. Amer. Chem. Soc.*, 1971, **93**, 247.

$[\nu(\text{C}\equiv\text{C}) 1933 \text{ cm}^{-1}]^5$  are not important. A partial structure is shown in the Figure.

Thermolysis of  $\text{Ar}_4\text{R}_2\text{Cu}_6$  (benzene;  $80^\circ$ ) yields  $\text{ArR}$  without a trace of the biaryl  $\text{ArAr}$  or the diacetylene  $\text{RR}$  ( $\text{Ar} = o\text{-Me}_2\text{NC}_6\text{H}_4$ ;  $\text{R} = \text{C}\equiv\text{CC}_6\text{H}_4\text{Y}$ ). Products  $\text{ArH}$  or  $\text{RH}$  resulting from hydrogen abstraction are likewise absent indicating that  $\text{ArR}$  is formed in an intramolecular reaction which does not proceed *via* free radicals, but involves homolytic  $\text{Cu-C}$  bond breaking and  $\text{C-C}$  bond formation in a concerted fashion. The specificity of the thermolysis may be understood in terms of the template effect exerted by the octahedral copper cluster: four triangular faces each containing one  $\text{Ar}$  and one  $\text{R}$  bridging ligand are present, but  $\text{Ar}_2\text{Cu}_3$  and  $\text{R}_2\text{Cu}_3$  faces are absent.

The organocopper species  $[\text{Ar}_3\text{RCu}^{\text{I}}_4\text{Cu}^{\text{0}}_2]$  formed upon thermolysis of  $\text{Ar}_4\text{R}_2\text{Cu}_6$  is unstable and splits off the benzene-insoluble  $(\text{ArCu})_n$ . The resulting hydrocarbon-soluble species  $[\text{ArRCu}^{\text{I}}_2\text{Cu}^{\text{0}}_2]$  is under investigation. §

Satisfactory analytical data have been obtained for all compounds described.

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## Phenyl Ring Rotation in Metal Complexes of Tetraphenylporphyrin Derivatives

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**Summary** Variable-temperature n.m.r. spectra of a series of In, Ru, and Ti complexes of substituted tetraphenylporphyrins show that phenyl ring rotation occurs on the n.m.r. time scale if the phenyl ring *ortho*-substituents are hydrogen.

PAPERS reporting X-ray diffraction results on tetraphenylporphyrin complexes commonly emphasize the role of steric repulsion between the phenyl and pyrrole hydrogens in preventing the phenyl rings from becoming even approximately coplanar with the porphyrin ring.<sup>1</sup> In the tetraphenylporphyrin metal complexes in which the axial sites on the metal are not the same, the *ortho* and *meta* hydrogens on the phenyl rings of the tetraphenylporphyrin are nonequivalent and yield an ABCD pattern in the  $^1\text{H}$  n.m.r. spectrum. In the case of indium tetra-(*p*-tolyl)porphyrin chloride<sup>2</sup> and ruthenium carbonyl tetra-(*p*-isopropylphenyl)porphyrin<sup>3</sup> we have observed that the nonequivalence can be averaged to yield an apparent AB pattern in the temperature range  $30\text{--}120^\circ\text{C}$ . In these reports the averaging of the nonequivalent phenyl proton resonances was attributed to rotation about the porphyrin *meso*-carbon-phenyl-carbon bond, though it was recognized that axial ligand

exchange could result in the same net effect on the n.m.r. spectrum. We now report variable-temperature n.m.r.

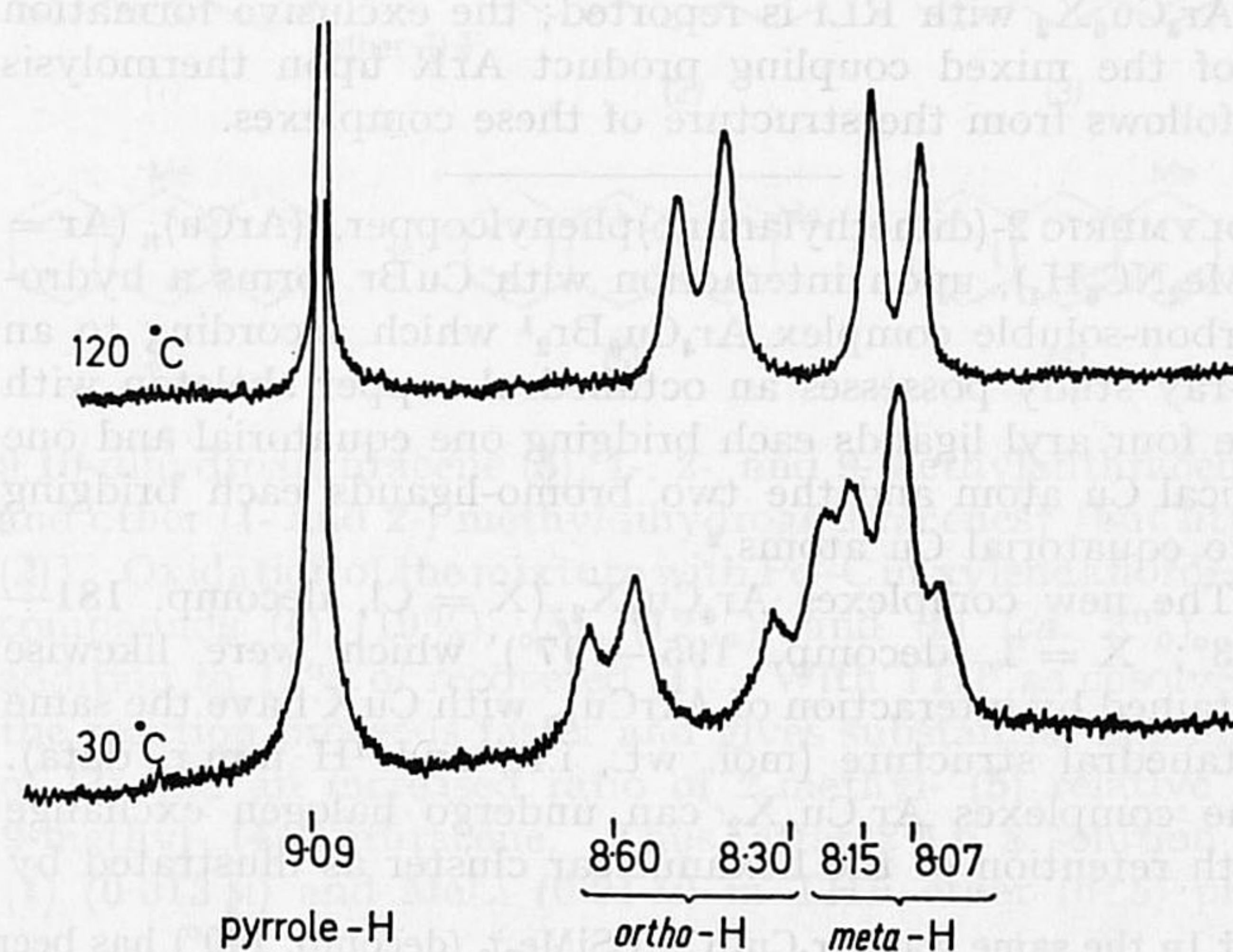


FIGURE.  $^1\text{H}$  N.m.r. spectra (100 MHz) of indium tetra-(*p*-trifluoromethyl)porphyrin chloride in  $\text{Cl}_2\text{HCCHCl}_2$  at  $30$  and  $120^\circ\text{C}$ . Slow exchange chemical shifts are in p.p.m. downfield from  $\text{Me}_4\text{Si}$ .