Synthesis and Specific Intramolecular C–C Coupling Reactions of Novel Hexanuclear Copper Cluster Complexes $Ar_4R_2Cu_6$

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Summary The synthesis of novel mixed organocopper cluster complexes, $Ar_4R_2Cu_6$, *via* ligand-substitution of $Ar_4Cu_6X_2$ 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,[1] $(ArCu)_n$ ($Ar = o\text{-}Me_2NC_6H_4$), upon interaction with CuBr forms a hydrocarbon-soluble complex $Ar_4Cu_6Br_2$[1] 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.[2]

The new complexes $Ar_4Cu_6X_2$ ($X = Cl$, decomp. 181—183°; $X = I$, decomp. 195—197°) which were likewise obtained by interaction of $(ArCu)_n$ with CuX have the same octahedral structure (mol. wt., i.r., and ^1H n.m.r. data). The complexes $Ar_4Cu_6X_2$ can undergo halogen exchange with retention of the hexanuclear cluster as illustrated by the quantitative isolation of $Ar_4Cu_6I_2$ from the reaction of $Ar_4Cu_6Cl_2$ with 2 mol of LiI in benzene.

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

$$Ar_4Cu_6Br_2 + 2LiR \rightarrow Ar_4Cu_6R_2 + 2LiBr \qquad (1)$$

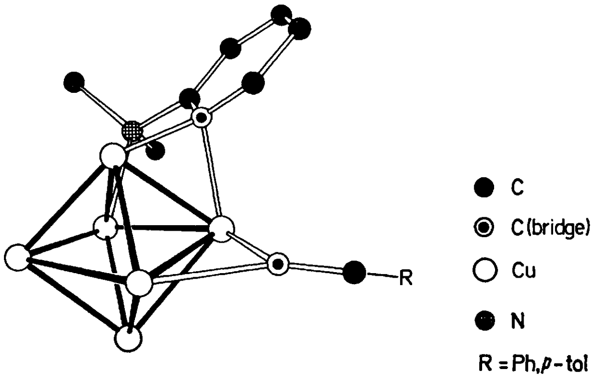
$$\begin{array}{ll} \text{(I)} & R = PhC{\equiv}C \\ \text{(II)} & R = p\text{-}MeC_6H_4C{\equiv}C \\ \text{(III)} & R = 2,4,6\text{-}Me_3C_6H_2C{\equiv}C \end{array}$$

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 $Ar_4R_2Cu_6$ units. The δ-values for the $Me_2NC_6H_4$ protons for $R_4Cu_6Br_2$ and compounds (I)—(III) are nearly identical as would be expected if these compounds had the Ar_4Cu_6 skeleton in common. Comparison of $\nu(C{\equiv}C)$ frequencies for (I)—(III);

[†] In the same way $Ar_4Cu_6(C{\equiv}CSiMe_3)_2$ (decomp. 140°) has been prepared.

[‡] As shown by mass spectrometry tetranuclear copper clusters $R^1{}_4Cu_4$ ($R^1 = 2\text{-}Me_2NCH_2C_6H_4$)[3] and $R^2{}_4Cu_4$ ($R^2 = 5\text{-}Me,2\text{-}Me_2NCH_2\text{-}C_6H_3$)[3,4] undergo ligand exchange in benzene with formation of $R^1{}_3R^2Cu_4$, $R^1{}_2R^2{}_2Cu_4$, and $R^1R^2{}_3Cu_4$ (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 cm^{-1}] with those for various other arylacetylide–copper compounds[5] reveals that each arylacetylide ligand is σ-bonded to two equatorial copper atoms and that π-interactions as occurring in $(PhC{\equiv}CCu)_n$ [$\nu(C{\equiv}C)$ 1933 cm^{-1}][5] are not important. A partial structure is shown in the Figure.



Figure

Thermolysis of $Ar_4R_2Cu_6$ (benzene; 80°) yields ArR without a trace of the biaryl ArAr or the diacetylene RR (Ar = *o*-$Me_2NC_6H_4$; R = $C{\equiv}CC_6H_4Y$). Products ArH or RH resulting from hydrogen abstraction are likewise absent indicating that ArR is formed in an intramolecular reaction which does not proceed *via* free radicals, but involves homolytic Cu–C bond breaking and 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 Ar and one R bridging ligand are present, but Ar_2Cu_3 and R_2Cu_3 faces are absent.

The organocopper species $[Ar_3RCu^I_4Cu^0_2]$ formed upon thermolysis of $Ar_4R_2Cu_6$ is unstable and splits off the benzene-insoluble $(ArCu)_n$. The resulting hydrocarbon-soluble species $[ArRCu^I_2Cu^0_2]$ is under investigation.§

Satisfactory analytical data have been obtained for all compounds described.

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§ Recently an octanuclear Cu^ICu^0 compound $(m\text{-}CF_3C_6H_4)_6Cu^I_6Cu^0_2$ has been isolated by Cairncross and Sheppard.[6]

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