1130, 1050, 1020, 810 cm^{-1}; mass spectrum m/e (rel intensity) 164 (46, M$^+$), 109 (42), 96 (100), 83 (58), 80 (50), 79 (98), 67 (96), 66 (75), 41 (50).

Anal. Calcd for C$_{11}$H$_{16}$O: C, 80.44; H, 9.83. Found: C, 80.6; H, 9.8.

A mixture of 3.3 g (0.02 mol) of the combined VPC fractions of homoprotoadamantanone obtained above, 93 g (0.165 mol) of potassium hydroxide, 10 mL (0.207 mol) of 100% hydrazine hydrate, and 100 mL of diethylene glycol was heated under gentle reflux (ca. 160 °C) for 3 h. The reaction temperature was elevated gradually to 220 °C while water formed was distilled off, and the mixture was refluxed for an additional 2 h at that temperature. Combined reaction mixture and distillate were diluted with 100 mL of a saturated sodium chloride solution and extracted with three 50-mL portions of n-hexane. Combined hexane extracts were washed with two 50-mL portions of water and dried over anhydrous magnesium sulfate. Evaporation of the solvent and purification of the residue by sublimation under slightly diminished pressure gave 1.3 g (42% yield) of a pure sample of 4-homoprotoadamantane (11): mp 129–130 °C; IR (neat) 2910, 2850, 1460, 1230, 1100, 1020, 920, 800 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.0–2.4 (complex m); ^{13}C NMR (CDCl$_3$) δ_C 21.0 (t), 27.3 (t), 29.3 (d), 32.8 (t), 34.1 (d), 34.7 (t), 35.9 (d), 37.2 (t), 37.5 (t), 37.7 (d), 40.8 (t); mass spectrum m/e (rel intensity) 150 (86, M$^+$), 135 (44), 107 (44), 94 (54), 93 (65), 81 (62), 80 (68), 79 (100), 67 (86), 55 (46), 41 (78).

Anal. Calcd for C$_{11}$H$_{18}$: C, 87.92; H, 12.08. Found: C, 88.1; H, 12.0.

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Selective Formation of Biaryls via Interaction of Polynuclear Arylcopper Compounds with Copper(I) Trifluoromethanesulfonate [Copper(I) Triflate][1]

Gerard van Koten,* Johann T. B. H. Jastrzebski, and Jan G. Noltes

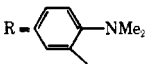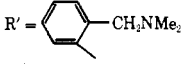*Institute for Organic Chemistry, TNO, Utrecht, The Netherlands*

Selective formation of biaryls is observed upon interacting well-defined arylcopper cluster compounds (2-Me$_2$NCH$_2$C$_6$H$_4$)$_4$Cu$_4$, (4-MeC$_6$H$_4$)$_4$Cu$_4$, (2-Me$_2$NC$_6$H$_4$)$_4$Cu$_6$Br$_2$, and (2-Me$_2$NC$_6$H$_4$)$_4$Cu$_6$OTf$_2$ with equimolar amounts of CuOTf in benzene. It is shown that complex formation of the arylcopper cluster with CuOTf precedes the C–C-coupling process. In some cases these complexes are sufficiently stable to be isolated, e.g., (2-Me$_2$NC$_6$H$_4$)$_4$-Cu$_6$OTf$_2$ (from the 2/1 reaction of 2-Me$_2$NC$_6$H$_4$Cu with CuOTf). Decomposition of the 2-MeC$_6$H$_4$Cu/CuOTf complex with NH$_3$/H$_2$O in the presence of oxygen affords, in addition to toluene and 2,2′-bitolyl, 2-H$_2$NC$_6$H$_4$Me and 2-HOC$_6$H$_4$Me. The formation of the arylcopper–CuOTf complexes and hence biaryl formation can be inhibited by suitable ligands such as PPh$_3$. In the absence of built-in ligands in the arylcopper compound, e.g., (4-MeC$_6$H$_4$)$_4$Cu$_4$, the reaction with CuOTf can be made catalytic in CuOTf. The selective C–C-coupling reaction has been explained in terms of intraaggregate electron-transfer processes occurring in the intermediate arylcopper–copper triflate complexes. A mechanism is proposed based on valence disproportionation inside the copper core induced by charge transfer from the core to the electron-accepting OTf anions.

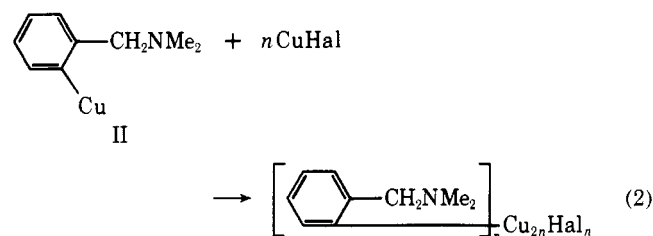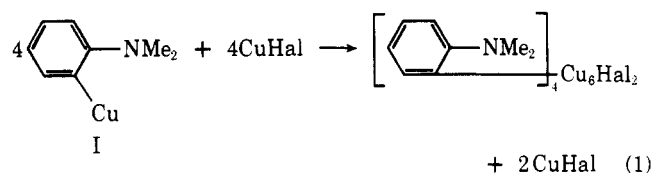The 1/1 reaction of polymeric 2-(dimethylamino)phenylcopper[3] (I) with cuprous halides affords stable hexanuclear copper complexes which have R$_4$Cu$_6$Hal$_2$ stoichiometry.[4] The

interaction of 2-[(dimethylamino)methyl]phenylcopper[5] (II) with cuprous halides gives rise to the formation of polymeric complexes with (R′Cu·CuHal)$_n$ stoichiometry.[6] Both types

Table I. Interaction of 2-Me$_2$NCH$_2$C$_6$H$_4$Cu and 2-Me$_2$NC$_6$H$_4$Cu with (CuO$_3$SCF$_3$)$_2$·C$_6$H$_6$ in Benzene

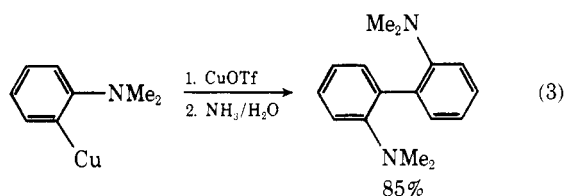| Reagents[a]	Added ligands	Reaction time, h	Products[b]		
			RR	RH	Others
R = [structure]—NMe$_2$					
RCu/CuOTf[c] (2/1)		48	0	0	R$_4$Cu$_6$OTf$_2$ 80
R$_4$Cu$_6$OTf$_2$/CuOTf (1/2)		24	91	9	d
RCu/CuOTf (1/1)		48	85	15	d
RCu/CuOTf (1/0.1)		288	e	e	R$_4$Cu$_6$OTf$_2$/RCu
{ RCu (1/4)	PPh$_3$	24			
{ CuOTf (2)		72	0	0	RCu·3CuOTf·6PPh$_3$[f]
RCu (1/3)	PPh$_3$	48	0	0	No reaction
R$_4$Cu$_6$Br$_2$/CuOTf (1/4)		48	97	Trace	CuBr[d]
R' = [structure]—CH$_2$NMe$_2$			R'R'	R'H	Others
R'Cu/CuOTf (1/1)		48	100	N.D.[g]	
R'Cu/CuOTf (2/1)		3[h]	0	0	i

[a] Molar ratio of the reagents are given in parentheses. [b] Yield (%) calculated on the total amount of R (or R') in the starting organocopper. [c] Pure benzene complex of CuOTf, (CuOTf)$_2$·C$_6$H$_6$, has been used. [d] Quantitative amounts of Cu^0 were formed. After the reaction the total amount of CuOTf was present in the form of a complex with RR and RH. [e] Small amount of RH (< 10%) was present in solution. Heating of the reaction mixture at 80 °C for 12 h afforded 75% R as RH and 25% R as RR (for comparison: the thermal decomposition of pure I in DMF gives 60% R as RH and 40% R as RR[8e]). [f] Composition of the solid isolated (18% yield) from the reaction mixture; see Experimental Section. [g] Not detectable by NMR or by GC/MS. [h] CuOTf was added to II at −20 °C. [i] Yellow solid with 3R'Cu·2CuOTf stoichiometry (elemental analysis; NMR in pyridine confirmed 3/2 molar ratio) was isolated.

$$4\,\overset{\text{[structure]}}{\underset{\text{Cu}}{}}\text{—NMe}_2 + 4\text{CuHal} \longrightarrow \left[\overset{\text{[structure]}}{}\text{—NMe}_2\right]_4 \text{Cu}_6\text{Hal}_2$$

I

$$+\; 2\text{CuHal} \quad (1)$$

$$\overset{\text{[structure]}}{\underset{\text{Cu}}{}}\text{—CH}_2\text{NMe}_2 + n\text{CuHal}$$

II

$$\longrightarrow \left[\overset{\text{[structure]}}{}\text{—CH}_2\text{NMe}_2\right]_n \text{Cu}_{2n}\text{Hal}_n \quad (2)$$

of complexes are stable in the presence of an excess of cuprous halide.

During a study of the interaction of I with copper triflate (CuOTf)[7] we noted that depending on the I/CuOTf molar ratio either stable complexes of the type R$_4$Cu$_6$OTf$_2$ were formed (2/1 molar ratio) or decomposition of the arylcopper with formation of metallic copper occurred (1/1 molar ratio). The results of a study of the 2/1 reaction have been published elsewhere.[2] The high stability of R$_4$Cu$_6$OTf$_2$ has been ascribed to the geometry of the 2-(dimethylamino)phenyl ligands which each are capable of spanning three copper atoms of the octahedral copper core thus stabilizing the R$_4$Cu$_6$$^{2+}$ unit.[2]

A study of the products formed in the 1/1 reaction of 2-Me$_2$NC$_6$H$_4$Cu with CuOTf revealed that a selective coupling of the 2-(dimethylamino)phenyl ligands had taken place. While studies concerning carbon–carbon bond formation via interaction of organocopper intermediates with *divalent* copper salts have recently been reported,[6,8] to our knowledge

$$\overset{\text{[structure]}}{\underset{\text{Cu}}{}}\text{—NMe}_2 \xrightarrow[\text{2. NH}_3/\text{H}_2\text{O}]{\text{1. CuOTf}} \overset{\text{Me}_2\text{N} \;\; [\text{structure}]}{\underset{\text{NMe}_2}{}}\quad (3)$$
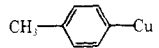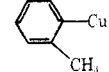
85%

this is the first example of selective coupling of organic groups achieved by interaction of organocopper compounds with a *monovalent* copper salt. In view of the scant knowledge about the relation between reactivity and structure of organocopper intermediates we have studied this reaction in greater detail. Three other, structurally different, arylcopper compounds, 2-Me$_2$NCH$_2$C$_6$H$_4$Cu (II), 4-MeC$_6$H$_4$Cu[9] (III), and 2-Me-C$_6$H$_4$Cu[9] (IV), have been included in this study.

Results

The results of the reaction of 2-Me$_2$NC$_6$H$_4$Cu (I) and 2-Me$_2$NCH$_2$C$_6$H$_4$Cu (II) with CuOTf are presented in Table I. The reaction of I with CuOTf afforded well-defined R$_4$Cu$_6$OTf$_2$ (V)[2] in 80% yield. At I/CuOTf molar ratios between 2/1 and 1/1 metallic copper was formed during the reaction. NMR spectra of a 1/2 reaction mixture of R$_4$Cu$_6$OTf$_2$ with CuOTf in benzene-d_6 revealed that in addition to metallic copper 2,2'-bis(dimethylamino)biphenyl (VI) and N,N-dimethylaniline (VII) had formed. The chemical shift data as well as the broadening of the NMe$_2$ proton resonances of VI and VII indicated that these products were present in solution as their complexes with CuOTf.[10] Decomposition of these complexes by workup procedures involving extraction of the reaction mixture with NH$_3$/H$_2$O solution afforded a mixture of uncomplexed VI and VII. GC/MS analysis revealed that the dimer VI was formed in 91% and the arene VII in 9%

Table II. Interaction of o- and p-Tolylcopper with CuOTf in Benzene

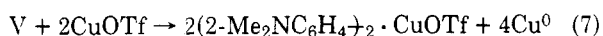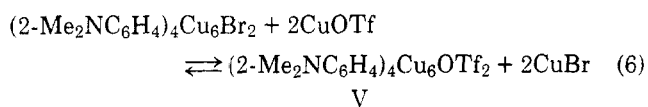| Reagents[a]	Workup conditions	x,x'-Bitolyl	Toluene	Other	
CH_3—⟨⟩—Cu		$x = x' =$ para			
p-TolCu/CuOTf[c] (1/1)		95[d]	0	0	
p-TolCu/CuOTf (1/0.1)		100[d]	0	0	
⟨⟩—Cu with CH₃ ortho		$x = x' =$ ortho		o-H$_2$NTol	o-HOTol
o-TolCu/CuOTf (1/1)	$NH_3/H_2O/O_2$[e]	20	40	10	17[f]
o-TolCu/CuOTf (1/1)	$NH_3/H_2O/N_2$[g]	±20	±80	<1	<1

[a] Molar ratio of the reagents given in parentheses. [b] Yield (%) calculated on the total amount of tolyl in the starting tolylcopper. [c] (CuOTf)$_2$·C$_6$H$_6$ has been used. [d] Quantitative amount of Cu^0 is formed. [e] Reaction time 5 h; workup in the presence of air oxygen. [f] Minor amounts of ditolyl ether (most probably the 2,2' isomer) were detected by GC/MS. [g] NH$_3$/H$_2$O solution added under N$_2$ atmosphere; reaction mixture stirred for 1.5 h before the final workup procedure in air was carried out.
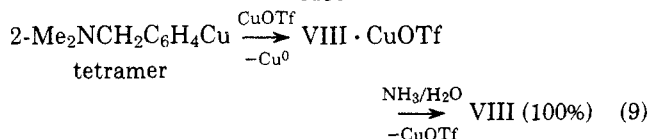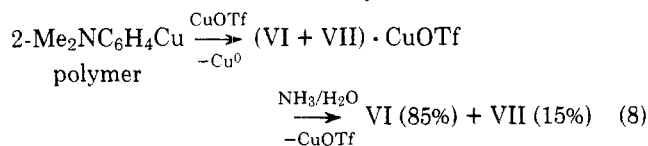
yield (calculated on the amount of R in I).

$$4\ 2\text{-Me}_2\text{NC}_6\text{H}_4\text{Cu} + 2\text{CuOTf} \xrightarrow{\text{C}_6\text{H}_6} (2\text{-Me}_2\text{NC}_6\text{H}_4)_4\text{Cu}_6\text{OTf}_2$$
$$\text{I} \qquad\qquad\qquad\qquad\qquad \text{V}$$
$$(4)$$

$$\text{V} + 2\text{CuOTf} \xrightarrow{\text{C}_6\text{H}_6} 4\text{Cu}^0$$

$$+ 4\text{CuOTf} \cdot [(2\text{-Me}_2\text{NC}_6\text{H}_4)_2 \text{ and } \text{Me}_2\text{NC}_6\text{H}_5] \quad (5)$$

The different reactivity of CuOTf toward arylcopper-copper halide compounds is clearly demonstrated by the formation of the dimer VI in 97% yield in the 1/4 reaction of $(2\text{-Me}_2\text{NC}_6\text{H}_4)_4\text{Cu}_6\text{Br}_2$ with CuOTf in benzene [cf. eq 1, which shows that $(2\text{-Me}_2\text{NC}_6\text{H}_4)_4\text{Cu}_6\text{Br}_2$ is stable toward CuBr[4]]. Most probably this reaction involves ligand displacement with retention of the hexanuclear cluster structure [11] followed by the irreversible interaction of $(2\text{-Me}_2\text{NC}_6\text{H}_4)_4\text{Cu}_6\text{OTf}_2$ with CuOTf.[12]

$$(2\text{-Me}_2\text{NC}_6\text{H}_4)_4\text{Cu}_6\text{Br}_2 + 2\text{CuOTf}$$
$$\rightleftarrows (2\text{-Me}_2\text{NC}_6\text{H}_4)_4\text{Cu}_6\text{OTf}_2 + 2\text{CuBr} \quad (6)$$
$$\text{V}$$

$$\text{V} + 2\text{CuOTf} \rightarrow 2(2\text{-Me}_2\text{NC}_6\text{H}_4)_2 \cdot \text{CuOTf} + 4\text{Cu}^0 \quad (7)$$

The interaction of I with CuOTf in a 1/1 molar ratio afforded the dimer VI in a significantly lower yield (85%) while the arene VII was formed in 15% yield.

$$2\text{-Me}_2\text{NC}_6\text{H}_4\text{Cu} \xrightarrow[-\text{Cu}^0]{\text{CuOTf}} (\text{VI} + \text{VII}) \cdot \text{CuOTf}$$
$$\text{polymer}$$
$$\xrightarrow[-\text{CuOTf}]{\text{NH}_3/\text{H}_2\text{O}} \text{VI (85\%)} + \text{VII (15\%)} \quad (8)$$

$$2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{Cu} \xrightarrow[-\text{Cu}^0]{\text{CuOTf}} \text{VIII} \cdot \text{CuOTf}$$
$$\text{tetramer}$$
$$\xrightarrow[-\text{CuOTf}]{\text{NH}_3/\text{H}_2\text{O}} \text{VIII (100\%)} \quad (9)$$
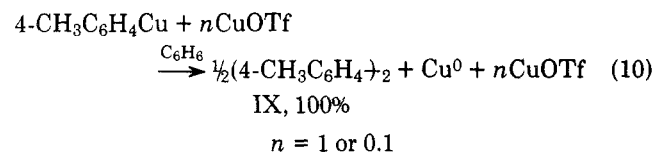
The corresponding 1/1 reaction of tetrameric 2-[(dimethylamino)methyl]phenylcopper (II) with CuOTf resulted in the formation of a 1/2 complex of the dimer with CuOTf. Not a trace of the arene could be detected. Hydrolytic workup of the reaction mixture afforded exclusively the dimer 2,2'-bis-[(dimethylamino)methyl]biphenyl (VIII) (100% yield). Accordingly, reaction sequence 9 provides an excellent synthetic route for the synthesis of pure VIII.[13] It is worthy of note that

complexes with well-defined 2-Me$_2$NCH$_2$C$_6$H$_4$Cu/CuOTf ratios are not formed. Insoluble yellow solids with varying II/CuOTf ratios were obtained starting from reaction mixtures with II/CuOTf molar ratios greater than 1.

As is seen from eq 8 and 9, CuOTf is not consumed in the reaction of the arylcopper compounds. Therefore, in principle reactions of this type might proceed in a catalytic fashion. However, complex formation between CuOTf and the biaryl coupling products VI and VIII (cf. ref 10) may account for the fact that this is not observed. Indeed, the reactions of arylcopper compounds I and II with CuOTf were effectively blocked by the presence of other complexing ligands such as triphenylphosphine (see Table I). In separate experiments it was established that this was not due to the formation of arylcopper triphenylphosphine complexes. Surprisingly, both I and II do not interact with triphenylphosphine.[14] In contrast, CuOTf does form a stable 2/1 complex with triphenylphosphine.[10] It is this complex formation which blocks the interaction of CuOTf with the arylcopper compounds.[15]

These observations strongly suggest that in the absence of external or of built-in ligands (–NMe$_2$ or –CH$_2$NMe$_2$) only catalytic amounts of CuOTf are required to effect the coupling reaction. In order to confirm this hypothesis the interaction of o- and p-tolylcopper with catalytic amounts of CuOTf was studied. The results are compiled in Table II.

The reaction of p-tolylcopper (III) with both stoichiometric and catalytic amounts of CuOTf resulted in the quantitative formation of p,p'-bitolyl (IX).

$$4\text{-CH}_3\text{C}_6\text{H}_4\text{Cu} + n\text{CuOTf}$$
$$\xrightarrow{\text{C}_6\text{H}_6} \tfrac{1}{2}(4\text{-CH}_3\text{C}_6\text{H}_4)_2 + \text{Cu}^0 + n\text{CuOTf} \quad (10)$$
$$\text{IX, 100\%}$$
$$n = 1 \text{ or } 0.1$$

NMR spectroscopy unambiguously showed that this reaction involves the intermediate formation of an insoluble 4-CH$_3$C$_6$H$_4$Cu/CuOTf complex. Addition of CuOTf to a solution of p-tolylcopper in benzene-d_6 causes a complete disappearance of the resonances due to the methyl and the aromatic protons when the CuOTf/III ratio reaches 1/4. NMR spectroscopy further reveals that this insoluble complex decomposes in about 2 h to give p,p'-bitolyl as the only product.

Interestingly, using o- instead of p-tolylcopper different results were obtained. Insoluble purple-colored complexes $(o\text{-CH}_3\text{C}_6\text{H}_4\text{Cu})_x(\text{CuOTf})_4$ were isolated from the reactions of o-tolylcopper (IV) with CuOTf in benzene (see Table II).

Attempts to purify these complexes failed. Essentially, no reaction leading to o,o'-bitolyl (X) or toluene was observed. An NMR spectrum of a 1/1 mixture of o-tolylcopper with CuOTf showed that these complexes are stable at room temperature. After 28 h only minor amounts (<5%) of o,o'-bitolyl were present in solution. It is worthy of note that decomposition of this complex with a NH_3/H_2O solution in the presence of oxygen afforded not only toluene arising from hydrolysis of the organocopper, but also o,o'-bitolyl, 2-aminotoluene (XI), and 2-hydroxytoluene (XII).[16] As shown in Table II the solvolysis products XI and XII are only formed in the presence of oxygen.[17] Addition of NH_3/H_2O to the reaction mixture in a nitrogen atmosphere afforded toluene (80%) and o,o'-bitolyl (20%), but not XI and XII.

$$2\text{-MeC}_6\text{H}_4\text{Cu} + \text{CuOTf} \longrightarrow [\text{complex}] \xrightarrow[\text{O}_2]{\text{NH}_3/\text{H}_2\text{O}} \text{toluene}$$

$$+ \ o,o'\text{-bitolyl} + 2\text{-HOC}_6\text{H}_4\text{Me} + 2\text{-H}_2\text{NC}_6\text{H}_4\text{Me} \quad (11)$$

Discussion

Earlier we had observed that interaction of arylcopper compounds Ar_nCu_n with copper halides CuHal results in the formation of complexes $Ar_nCu_{m+n}Hal_m$ which have equal or higher stability as compared with the parent compound. However, the present study reveals that complex formation of ArCu with copper(I) salts of anions with strong electron acceptor properties gives rise to less stable complexes. This observation establishes for the first time that the nature of the counterion has a great influence on the stability of the arylcopper–copper(I) salt complex. A better understanding of this effect is important in view of the interpretation of reactions involving organocopper compounds as intermediates, e.g., the Ullmann biaryl synthesis.

The elucidation of the mode of interaction of CuOTf with arylcopper compounds[20] requires a discussion of the following factors: (1) the structure of the arylcopper compounds before reaction; (2) the nature of the arylcopper–copper triflate interaction including the nature of the electron-transfer processes resulting in product formation.
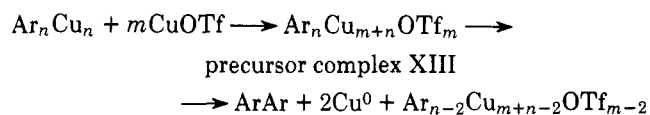
The Structure before Reaction. The structures of (2-$\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_4\text{Cu}_4$[21] as well as of $(2\text{-Me}_2\text{NC}_6\text{H}_4)_4\text{Cu}_6\text{X}_2$, X = halide[4] or triflate,[2] in the solid and in solution are well-documented main structural featurs of these compounds being central tetra- or hexanuclear copper cores to which aryl groups are bound via 2e–3c bonds.

Camus and Marsich[9] have reported that the results of molecular weight determinations of o- and p-tolylcopper were in agreement with low aggregation states (monomers or dimers), but structural details were not given.[22] However, the extreme air sensitivity of o- and p-tolylcopper as well as the fact that $HCCl_3$[24] and CCl_4 had been used as solvents for the osmometric molecular weight determinations led us to redetermine the molecular weight of these compounds. Cryoscopic molecular weight determinations show that p-tolylcopper exists as a tetramer, $(4\text{-MeC}_6\text{H}_4)_4\text{Cu}_4$, in benzene. In contrast, o-tolylcopper exists directly after dissolution in benzene as an apparent hexanuclear species, which equilibrates in about 2 h to a tetranuclear aggregate $(2\text{-MeC}_6\text{H}_4)_4\text{Cu}_4$. Obviously, in solution the $(2\text{-MeC}_6\text{H}_4)_4\text{Cu}_4$ aggregate is thermodynamically the most stable. Other examples of tetranuclear copper cluster species are $(\text{Me}_3\text{SiCH}_2)_4\text{Cu}_4$,[25] $(\text{C}_6\text{F}_5)_4\text{Cu}_4$,[26] and $(2\text{-CF}_3\text{C}_6\text{H}_4)_4\text{Cu}_4$.[26] The copper atoms in these compounds are two-coordinate by participating in two 2e–3c C–Cu interactions, whereas in arylcopper compounds containing built-in ligands, such as $(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_4\text{Cu}_4$ the copper atoms become three-coordinate by an extra Cu–N coordination bond.[21]

$2\text{-Me}_2\text{NC}_6\text{H}_4\text{Cu}$ is the only arylcopper compound used in this study of which the structure is not known with certainty.

The available spectroscopic data[27] strongly support a polymeric structure consisting of 2-(dimethylamino)phenyl groups bridging Cu atoms of one copper chain via 2e–3c Cu–C bonds and coordinating to a copper atom of a second chain via a Cu–N bond.[3]

The C–C Coupling. Interaction of CuOTf with organocopper compounds which have a discrete cluster structure $[(4\text{-MeC}_6\text{H}_4)_4\text{Cu}_4$, $(2\text{-Me}_2\text{NC}_6\text{H}_4)_4\text{Cu}_6\text{Br}_2$, $(2\text{-Me}_2\text{NC}_6\text{H}_4)_4\text{Cu}_6\text{OTf}_2$, and $(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_4\text{Cu}_4]$ results in almost quantitative formation of biaryls. The fact that arenes are formed in less than 9% yield excludes decomposition pathways involving free radicals, but instead points to the occurrence of intramolecular processes leading to pairwise release of aryl groups. It therefore would seem plausible to propose that these processes take place in an arylcopper–copper triflate precursor complex formed by extension of the copper core of the parent organocopper with one or more copper atoms of copper triflate. A representative example of such a complex is $(2\text{-Me}_2\text{NC}_6\text{H}_4)_4\text{Cu}_6\text{OTf}_2$. This complex, which has been isolated and characterized, has a structure consisting of an octahedral copper core to which both aryl groups and anions are bound in a well-defined way.[2]

$$\text{Ar}_n\text{Cu}_n + m\text{CuOTf} \longrightarrow \text{Ar}_n\text{Cu}_{m+n}\text{OTf}_m \longrightarrow$$

$$\text{precursor complex XIII}$$

$$\longrightarrow \text{ArAr} + 2\text{Cu}^0 + \text{Ar}_{n-2}\text{Cu}_{m+n-2}\text{OTf}_{m-2}$$

The driving force in the coupling reaction is charge transfer in the precursor complex XIII from the $\text{Ar}_n\text{Cu}_{m+n}$ skeleton to the strongly electron accepting OTf groups, which reduces the electron density in the Cu_n–C region and thus the kinetic stability of the Cu_n–C bond. The occurrence of Cu_n–C bond weakening as a result of electron transfer can be concluded from the mass spectral fragmentation pattern of $(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_4\text{Cu}_4$. The parent ion $\text{R}_4\text{Cu}_4^{+\cdot}$ undergoes fragmentation to R_3Cu_4^+ (most abundant Cu-containing ion) by cleavage of a Cu_4–C bond indicating that an electron from the bridge-bond MO has been removed rather than from the Cu_4 core.[21] This is also illustrated by the formation of biaryl and aryl halide in the reaction of $(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_4\text{Cu}_4$ with Cu^{II}X_2 which involves inner-sphere-redox reaction in activated complexes of the type $(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_4\text{Cu}_4\cdots\text{X}\cdots\text{Cu}^{II}\text{X}(\text{Cu}^{II}\text{X}_2)_n$.[6]

In the precursor complex XIII aryl groups are at close proximity so that concerted or consecutive Cu–C bond cleavage and C–C bond formation can occur. Three different mechanisms for pairwise release of aryl groups from Cu_n clusters can be envisaged (see Scheme I): (1) two-electron

Scheme I
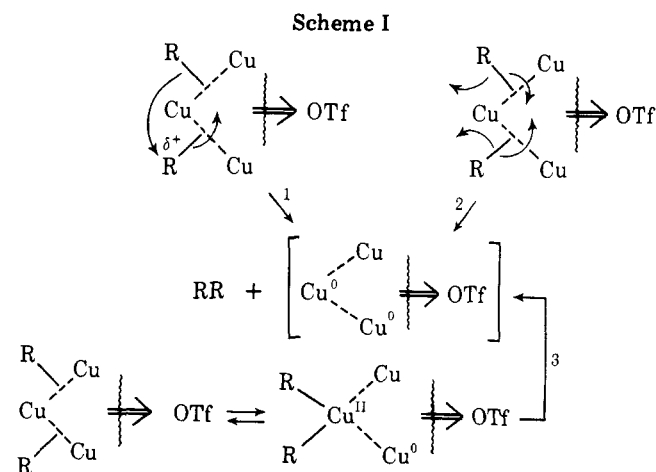
transfer from one Cu–C bond to the Cu_n cluster resulting in reduction of two Cu^I atoms in the metal core and development of a high degree of carbonium ion character at C(bridge) fol-

lowed by intraaggregate nucleophilic attack of a second Cu–C bond; (2) simultaneous one-electron transfer from two Cu–C bonds to the Cu_n cluster and concomitant coupling of the two aryl radicals or one-electron transfer followed by intraaggregate trapping of the aryl radical by a second Cu–C bond; (3) valence disproportionation inside the metal core followed by reductive elimination of R–R.

Process 3 seems to provide a rationale for the large influence of the type of the anion on the occurrence of coupling reactions because the anions attached to the copper core will affect the potentials of the various copper couples.[28,29] The strong electron-accepting properties of the OTf anion favor the Cu^{II} oxidation state, whereas, for example, the electron-donating halide anions favor the Cu^{I} state. As regards the influence of the type of aryl group on the coupling process the kinetic stability of the Cu_n–C bonding will be optimal when the aryl nucleus is oriented about perpendicular to the Cu–Cu axis thus allowing maximum back-bonding to the aryl nucleus.[21] This orientation is favored for steric reasons[30] in the o-methyl substituted aryl derivative whereas in the 2-Me_2N- and 2-Me_2NCH_2-substituted compounds the occurrence of Cu–N coordination further reduces the number of possible rotamers. The lower stability of the precursor complex containing the 2-Me_2NCH_2 grouping as compared with the o-methyl substituted complex can be ascribed to coordination of the hard nitrogen ligand to the copper core which favors valence disproportionation by stabilizing the Cu^{II} oxidation state.

Finally, selective biaryl formation can only be expected for precursor complexes $Ar_nCu_{n+m}OTf_m$ in which n equals 2, 4, 6, etc.[31] In case of polymeric or oligomeric arylcopper compounds chains containing both odd and even numbers of aryl groups will be present. Accordingly, for these compounds the formation of a small amount of arene originating from decomposition of chains with n = 3, 5, 7, etc., must be expected. Indeed, interaction of polymeric 2-$Me_2NC_6H_4Cu$ with CuOTf yields in addition to 85% of the dimer 15% of the arene $Me_2NC_6H_5$.

Experimental Section

General. CuOTf·½C_6H_6 was prepared according to the directions given by Salomon and Kochi.[7] o- and p-tolylcopper and 2-dimethylamino- and 2-dimethylaminomethyl-substituted phenylcopper compounds were prepared by published methods.[3,5,9] The reactions were carried out under dry, oxygen-free nitrogen. Solvents were carefully purified, dried, and distilled before use under nitrogen.

IR spectra were recorded on a Perkin-Elmer 577 grating IR spectrometer. ¹H NMR spectra were recorded on a Varian Associates HA-100 NMR spectrometer. Molecular weight determinations were carried out in benzene using a cryoscopic method. The spectra and the molecular weight data were obtained by Mrs. G. M. Bijlsma-Krüger and Mrs. T. van Montfort-Volp. GC/MS analyses were recorded on a Finnigan 3100D by Mrs. G. G. Versluis-De Haan. Elemental analyses were carried out under the supervision of Mr. W. J. Buis in the Analytical Department of this Institute.

Interaction of 2-(Dimethylamino)phenylcopper with CuOTf. Synthesis of (2-$Me_2NC_6H_4$)₄Cu_6OTf_2 (V). Solid CuOTf·½C_6H_6 (2.45 mmol) was added at room temperature to a well-stirred suspension of 2-(dimethylamino)phenylcopper (I) in benzene (25 mL). The resulting brown-yellow colored reaction mixture was stirred for 48 h. The yellow precipitate was filtered off and extracted twice with benzene (20 mL) and with pentane (2 × 20 mL). The yellow residue (80%) was dried in vacuo. Anal. Calcd for $C_{17}H_{20}Cu_3F_3O_3N_2S$: C, 35.20; H, 3.48; N, 4.83; Cu, 32.86; F, 9.83. Found: C, 34.2; H, 3.5; N, 4.4; Cu, 32.0; F, 9.6. IR (OTf vibrations[2])ν_4, 1315 s, 1298 (sh), 1230 m, 1199 m; ν_1 1010 s; ν_5 632 s; ν_3 521 m. NMR (in toluene-d_8) δ (10 °C) 1.92 and 2.96 (2 s, br, 6 H, NMe_2, coalescence at room temperature to one singlet at 2.50), 6.50 (m, J = 8 Hz, H_3), and 8.84 (m, $J \simeq$ 6 Hz, H_6). Decomposition (under N_2, 5 °C/min) started at 118 °C; explosion occurs at 123 °C.

Reactions of 2-$Me_2NC_6H_4Cu$, (2-$Me_2NC_6H_4$)₄Cu_6OTf_2, and (2-$Me_2NC_6H_4$)₄Cu_6Br_2 with CuOTf. A typical experiment involving the reaction of I with CuOTf in a 1/1 molar ratio is described. The

respective reaction conditions and results of the other reactions are in Table I.

Solid CuOTf·½C_6H_6 (2.36 mmol) was added at room temperature to a suspension of I (2.36 mmol) in benzene (25 mL). This mixture was stirred for 48 h. NMR spectroscopy of the solution showed two broad NMe resonances at δ 2.46 and 2.54 ppm [NMR in benzene-d_6 of (2-$Me_2NC_6H_4$)₂·2CuOTf, NCH_3, 2.52 ppm broad,[10] and of pure VI, NCH_3, δ 2.40 ppm[3]]. A 6 N NH_3/H_2O solution (25 mL) was added to the reaction mixture. The benzene layer was extracted with NH_3/H_2O solution (removal of copper). The benzene layer was extracted with 4 N HCl solution. The acidic water layer was made basic with NaOH solution and extracted with diethyl ether. The ether layer was dried over Na_2SO_4 and concentrated, affording a yellow oil. NMR spectroscopy showed this oil to be a mixture of 2,2'-bis(dimethylamino)-biphenyl (VI) and N,N-dimethylaniline (VII). NMR (C_6D_6) VI, δ 2.40 (12 H, s, NCH_3), 7.52 (m, 2 H, H_3 or H_6), 7.15 (m, 2 H, H_6 or H_3 partly masked by $C_6D_{6-x}H_x$ resonances), and 6.94 (m, 4 H, $H_{4,5}$); VII, 2.50 (3, 6 H, NCH_3). Total recovery of R as VI and VII amounts to 98%, 85% as RR and 15% as RH.

Reaction of 2-(dimethylamino)phenylcopper with Triphenylphosphine. Solid triphenylphosphine (8.17 mmol) was added to a suspension of I (2.72 mmol) in benzene (20 mL). The resulting yellow colored suspension was stirred at room temperature for 48 h. The solid was filtered off and extracted with benzene (2 × 10 mL). NMR and IR spectroscopy revealed that this solid consisted of pure I. The spectra were identical with those of an analytically pure sample of I (see ref 3). I was recovered in 96% yield.

Reaction of I with PPh_3 and CuOTf. A mixture of I (3.3 mmol) and PPh_3 (13.1 mmol) in benzene (25 mL) was stirred at room temperature for 24 h. Subsequently, solid CuOTf·½C_6H_6 (5.68 mmol) was added and the reaction mixture stirred for another 72 h. The yellow precipitate was separated by centrifugation and extracted with benzene (3 × 25 mL). The benzene extract was concentrated, which afforded a yellow solid. Extraction of this solid with pentane (2 × 20 mL) and with ether (3 × 20 mL; removal of PPh_3) afforded an ochre solid which had 2-$Me_2NC_6H_4Cu$·3CuOTf·6PPh_3 stoichiometry (18% yield calculated on the starting amount of I). Decomposition occurred at 140–160 °C. Anal. Calcd for $C_{119}H_{100}NO_9P_6S_3F_9Cu_4$: C, 59.66; H, 4.2; N, 0.58; P, 7.76; F, 7.14; Cu, 10.61. Found: C, 59.2; H, 4.6; N, 0.6; P, 7.5; F, 7.1; Cu, 11.7. NMR (pyridine-d_5) δ 2.90 (br, NCH_3), 7.15–7.60 and 6.4–7.0 (m, br, complexed PPh_3); addition of H_2O afforded VII and PPh_3 in 1/5.7 molar ratio (elemental analysis, 1/6).

Reaction of I with CuO_2CCF_3 in DMF. Solid copper(I) trifluoroacetate[19] (3.6 mmol) was added to a suspension of I (3.6 mmol) in DMF. This mixture was stirred for 96 h. Workup with NH_3 solution (vide supra) afforded a colorless solid which according to NMR spectroscopy was 2,2'-bis(dimethylamino)biphenyl and N,N-dimethylaniline in 9/1 molar ratio. The recovery of R in these products was 70%.

Interaction of 2-[(Dimethylamino)methyl]phenylcopper (II) with CuOTf. Reaction of II with CuOTf. Solid CuOTf·½C_6H_6 (1.62 mmol) was slowly added at room temperature to a solution of II (1.62 mmol) in benzene (20 mL). The color of the solution turned immediately to red upon the addition of the first amount of CuOTf. At 2/1 molar ratios a yellow precipitate was formed which upon continued addition of CuOTf dissolved. Finally, a green solution containing metallic copper was obtained. After 48 h the reaction mixture was worked up following the procedure described above for the I/CuOTf reactions. A yellow oil was isolated which according to NMR spectroscopy consisted of pure 2,2'-bis[(dimethylamino)methyl]biphenyl (VIII). Thus R was quantitatively recovered as the dimer VIII: NMR (C_6H_6) δ 2.01 (s, 2 H, NCH_3), 3.07 (d, 2 H) and 3.28 (d, 2 H, $J_{gem} \simeq$ 13 Hz, NCH_2) (cf. ref 5). N,N-Dimethylbenzylamine was absent.

In a separate experiment the NMR spectrum of the reaction mixture after stirring for 48 h, but before hydrolysis, was recorded: NMR (C_6D_6) δ 2.30 and 2.14 (2 s, br, 12 H, NMe), 3.78 and 2.34 (2 d, br, 4 H, J_{gem} = 12 Hz, NCH_2), identical with the spectrum obtained by mixing VIII and CuOTf in an exact 1/2 molar ratio.

Synthesis of VIII. Crude 2-[(dimethylamino)methyl]phenylcopper (II), isolated by filtration of the reaction mixture of 2-[(dimethylamino)methyl]phenyllithium (59.7 mmol) with an equimolar amount of $CuBr$,[5] was mixed with 120 g of naphthalene and subsequently heated at 165 °C for 6 h. Crude VIII was isolated by an acid/base workup procedure and purified by fractional distillation. The overall yield, calculated on the amount of the aryllithium, was 63%, bp 135–140 °C (0.1 mm), NMR spectrum vide supra.

Attempted Synthesis of II/CuOTf Complexes. A solution of II in toluene (3.29 mmol in 20 mL) was cooled to −20 °C. Under vigorous stirring solid CuOTf (1.65 mmol) was added. The resulting orange-brown suspension was stirred at −45 °C for 1 h and for another 1 h

at room temperature. The orange solution was filtered and concentrated affording a yellow solid. This solid was extracted with pentane (2 × 10 mL) and dried in vacuo. Elemental analysis pointed to the isolation of a complex which had $3(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{Cu})\cdot2\text{CuOTf}$ stoichiometry. Anal. Calcd for $\text{C}_{29}\text{H}_{36}\text{N}_2\text{Cu}_5\text{O}_6\text{S}_2\text{F}_2$: C, 34.19; H, 3.54; Cu, 31.21; N, 4.13; F, 11.20. Found: C, 35.2; H, 3.9; Cu, 28.3; N, 3.7; F, 10.8. This solid decomposed slowly at room temperature.

Interaction of p-Tolylcopper with CuOTf. Pure p-tolylcopper was prepared following the directions of Camus and Marsich.[9] Anal. Calcd for $\text{C}_7\text{H}_7\text{Cu}$: C, 54.36; H, 4.56; Cu, 41.08. Found: C, 52.8; H, 4.6; Cu, 40.8. Mol wt (cryometry in C_6H_6) 604 ($\bar{n}$ = 3.9) concentration independent (calcd for $\text{C}_7\text{H}_7\text{Cu}$, 154.7). NMR ($\text{C}_6\text{D}_5\text{N}$) δ 2.15 (s, 3, CH_3), 7.03 (m, 2, $J_{2,3}$ 7 Hz, H_3) and 8.09 (m, 2, H_2); (in C_6D_6) 1.96 (CH_3), 6.84 (H_3), and 7.98 (H_2).

Reaction of p-Tolylcopper with CuOTf. Solid CuOTf (3.24 mmol) was added to a solution of p-tolylcopper (3.24 mmol) in benzene (40 mL). The color of the solution turned red and a black solid precipitated. A 6 N $\text{NH}_3/\text{H}_2\text{O}$ solution was added. The benzene layer was extracted with $\text{NH}_3/\text{H}_2\text{O}$ solution and with H_2O and dried over MgSO_4. The NMR spectrum indicated that p,p'-bitolyl was formed in 95% yield. NMR (CCl_4) δ 2.32 (3, s, CH_3), 7.08 and 7.34 (2 d, $J = 8$ Hz, $\text{H}_{2,3}$). Concentration of the benzene solution afforded white solid p,p'-bitolyl, mp 115–119 °C (lit.[20] 121 °C).

Interaction of CuOTf with p-Tolylcopper/2-[(Dimethylamino)methyl]phenylcopper Aggregates. p-Tolylcopper (0.8 mmol) and II (2.4 mmol) were dissolved in toluene-d_8 (3 mL). NMR (toluene-d_8) δ (100 °C) H_6 (II), 8.40 (d, br); H_2 (4-TolCu), 7.74 (d); NCH_2 (II), 3.08 (s, br); NMe (II), 1.84 (s, br); CH_3 (4-TolCu), 1.90 (s, br). Solid CuOTf (3.2 mmol) was added to this solution which was then stirred at room temperature for 2 h. $\text{NH}_3/\text{H}_2\text{O}$ solution (10 mL, 6 N) was added. Workup as described above resulted in the isolation of a white solid. NMR spectroscopy indicated that (2-$\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{+}_2$ (VIII) (64 mol %), 2-$\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{CH}_3$-$p$ (15 mol %), p,p'-bitolyl (15 mol %), and N,N-dimethylbenzylamine (6 mol %) were present. NMR (C_6D_6) δ VIII, 2.01 (NCH_3), 3.07 and 3.28 (NCH_2, J_{gem} = 13 Hz); 2-$\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{CH}_3$-$p$, 2.06 ($\text{NCH}_3$), 2.18 ($p$-$\text{CH}_3$), 3.36 ($\text{NCH}_2$); p,p'-bitolyl, 2.18 (CH_3); N,N-dimethylbenzylamine, 2.08 (NCH_3), 3.26 (NCH_2).

The corresponding reaction but now using p-tolylcopper/II/CuOTf in a 1/0.8/2 molar ratio afforded VIII (34 mol %), 2-$\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{CH}_3$-$p$ (16 mol %), and p,p'-bitolyl (51 mol %). GC/MS: VIII, m/e 268; 2-$\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{CH}_3$-$p$, m/e 225; p,p'-bitolyl, m/e 182.

Interaction of o-Tolylcopper with CuOTF. Pure o-tolylcopper was prepared according to ref 9. NMR ($\text{C}_5\text{D}_5\text{N}$) δ 2.39 (s, 3, CH_3), 7.0–7.4 (m, $\text{H}_{3,4,\text{ and }5}$), 8.42 (m, 1, H_6); (in C_6D_6) 2.62 (CH_3), 6.7–7.1 (other H_{arom}), 7.97 (d, br, J = 6 Hz, H_6). Upon heating (75 °C, 1 h) of the benzene-d_6 solution in the NMR tube o,o'-bitolyl was formed exclusively [δ (CH_3) 1.96 ppm]. Mol wt (cryometry in C_6H_6) $\bar{n}_{0h}$ 6.1, $\bar{n}_{3/4h}$ 4.9, $\bar{n}_{2h}$ 4.1; second run $\bar{n}_{1h}$ 4.5, $\bar{n}_{2h}$ 4.0, concentration independent.

Reaction of o-Tolylcopper with CuOTf. Solid CuOTf (1.2 mmol) was added to a solution of o-tolylcopper (1.2 mmol) in benzene (10 mL). A purple colored product precipitated during 5 h of stirring. Workup with $\text{NH}_3/\text{H}_2\text{O}$ solution *in air* afforded a colorless oil which consisted of o,o'-bitolyl, o-hydroxytoluene, and o-aminotoluene. The recovery of tolyl group in these products amounted to 46%. These compounds were identified by NMR and GC/MS techniques. NMR (benzene-d_6) o,o'-bitolyl, δ 1.95 (CH_3); o-aminotoluene, 1.80 (CH_3) and 2.84 (br, NH_2); o-hydroxytoluene, 2.08 (CH_3). Mol % 43/37/21. Their identity was further established by GC/MS analysis. A trace amount of a compound with $\text{C}_{14}\text{H}_{24}\text{O}$ (m/e 198) was identified to be bis(o-methylphenyl) ether (very intensive m/e 107).

Exactly the same result was obtained when after the addition of $\text{NH}_3/\text{H}_2\text{O}$ solution O_2 gas was bubbled through the reaction mixture.

Complex Formation of o-Tolylcopper with CuOTf. An equimolar mixture of CuOTf and o-tolylcopper (CuOTf added to o-tolylcopper) which was dissolved in benzene (50 mL) was stirred for 0.5 h. The purple colored precipitate was filtered off, washed with benzene (3 × 40 mL, removal of uncomplexed CuOTf) and with pentane (2 × 10 mL), and dried in vacuo. Elemental analysis of this solid pointed to the isolation of a CuOTf·1.1 o-tolylcopper complex contaminated with metallic copper. NMR (pyridine-d_5) δ 2.5 (br, NCH_3) and 8.4 (br, H_6).

Registry No.—I, 32691-15-9; II, 38286-29-2; III, 5588-74-9; IV, 20854-03-9; V, 61966-49-2; VI, 20627-78-5; VII, 121-69-7; VIII, 38286-37-2; IX, 613-33-2; X, 605-39-0; XI, 95-53-4; XII, 95-48-7; CuOTf, 42152-44-3; (2-$\text{Me}_2\text{NC}_6\text{H}_4)_4\text{Cu}_6\text{Br}_2$, 58616-70-9; (2-$\text{Me}_2\text{NC}_6\text{H}_4\text{+}_2\cdot2\text{CuOTf}$, 61966-46-9; triphenylphosphine, 603-35-0; 2-$\text{Me}_2\text{NC}_6\text{H}_4\text{Cu}\cdot3\text{CuOTf}\cdot6\text{PPh}_3$, 61966-50-5; CuO_2CCF_3, 25535-55-1; $3(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{Cu})\cdot2\text{CuOTf}$, 61966-48-1; bis($o$-methylphenyl) ether, 4731-34-4; (2-$\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_4\text{Cu}_4$, 37185-48-1; (4-$\text{MeC}_6$-$\text{H}_4)_4\text{Cu}_4$, 61966-47-0; 2-$\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{CH}_3$-$p$, 61846-68-2.

References and Notes

(1) Part 21 in the series Group IB Organometallic Chemistry. For part 20 see G. van Koten, R. W. M. ten Hoedt, and J. G. Noltes, *J. Org. Chem.*, in press.

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(8) (a) A. E. Jukes, *Adv. Organomet. Chem.*, **12**, 215 (1974); (b) M. Tamura and J. K. Kochi, *J. Organomet. Chem.*, **42**, 205 (1972); (c) G. Wittig and G. Klar, *Justus Liebigs Ann. Chem.*, **704**, 91 (1967); (d) T. Kaufmann, M. Schönfelder, and J. Legler, *ibid.*, **731**, 37 (1970); (e) G. van Koten, J. T. B. H. Jastrzebski, and J. G. Noltes, *Tetrahedron Lett.*, 223 (1976).

(9) The synthesis of o- and p-tolylcopper has been described by A. Camus and N. Marsich, *J. Organomet. Chem.*, **14**, 441 (1968). For a redetermination of the aggregation state of these arylcopper compounds in solution, see Discussion and Experimental Section of this paper.

(10) G. van Koten, J. T. B. H. Jastrzebski, and J. G. Noltes, *Inorg. Chim. Acta*, **21**, Lg (1977).

(11) Ligand displacement with retention of the cluster structure has been observed in the 2/1 reaction of LiI with (2-$\text{Me}_2\text{NC}_6\text{H}_4)_4\text{Cu}_6\text{Cl}_2$ in benzene. The iodide cluster 2-$\text{Me}_2\text{NC}_6\text{H}_4\text{Cu}_6\text{I}_2$ and LiCl were isolated quantitatively (cf. ref 4).

(12) The solubility of CuOTf in benzene (cuprous halides are insoluble) favors this equilibrium in spite of the fact that OTf is a weaker bridging ligand than bromide.[2]

(13) Thermal decomposition of 2-$\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{Cu}$ (II) in naphthalene at 165 °C for 6 h, which affords a 9/1 mixture of VIII and the arene (63% overall yield starting from in situ prepared II, see Experimental Section), provides an alternative route to the dimer VIII. Oxidation of II with O_2 gives rise to a mixture of VIII, the arene, and 2-hydroxybenzyldimethylamine [NMR (CCl_4) δ 2.27 (s, 6 H, NCH_3), 3.53 ppm (s, 2 H, NCH_2); in C_6D_6, δ 1.72 (s, 6 H, NCH_3), 3.15 (s, 2 H, NCH_2)].

(14) In general organocopper compounds form complexes with triphenylphosphine [cf. A. Camus and N. Marsich, *J. Organomet. Chem.*, **21**, 249 (1970); A. Miyashita and A. Yamamoto, *ibid.*, **113**, 187 (1976)]. However, the tetranuclear structure of II as well as the polymeric structure of I are not broken down by triphenylphosphine. The fact that in these compounds each copper atom has already trigonal coordination symmetry as a result of intraaggregate N–Cu coordination may account for this observation [cf. G. van Koten and J. G. Noltes, *J. Chem. Soc., Chem. Commun.*, 452 (1972)].

(15) That, however, CuOTf·2PPh_3 is capable of interacting with arylcopper compounds is substantiated by the precipitation of insoluble yellow solids which contain both the arylcopper, CuOTf and PPh_3 (elemental analysis, IR) from homogeneous solutions of I and II and CuOTf·2PPh_3 (see Experimental Section). This is illustrated by the isolation of (2-$\text{Me}_2\text{NC}_6\text{H}_4\text{Cu})\cdot$3CuOTf·6$\text{PPh}_3$.

(16) The 1/1 reaction of 2,6-dimethoxyphenylcopper[3] with CuOTf in benzene affords a stable insoluble complex 2,6-$(\text{MeO})_2\text{C}_6\text{H}_3\text{Cu}\cdot$CuOTf. Decomposition of this complex with $\text{NH}_3/\text{H}_2\text{O}$ in the presence of oxygen affords the arene in 50% yield together with about 12% of 2,6-$(\text{MeO})_2\text{C}_6\text{H}_3\text{NH}_2$ and 37% of [2,6-$\text{MeO})_2\text{C}_6\text{H}_3\text{+}_2$ (calculated on R).

(17) This reaction can be viewed as an electron transfer oxidation of o-tolyl radicals (formed by homolytic cleavage of the Cu–Cu bonds) by the highly electrophilic $\text{Cu}(\text{NH}_3)_x^{2+}$ cation. Oxidative solvolysis[18] of the intermediate [2-$\text{MeC}_6\text{H}_4\text{Cu}(\text{NH}_3)_x^{2+}$] affords XI and XII. Oxidative elimination pathways are not important in view of the constraints of the aromatic nucleus. This route is important in the case of oxidation of alkyl radicals by copper(II) complexes.[18]

(18) C. L. Jenkins and J. K. Kochi, *J. Am. Chem. Soc.*, **94**, 843 (1972).

(19) M. B. Dines, *Inorg. Chem.*, **11**, 2949 (1972).

(20) The use of copper(I) trifluoroacetate instead of copper(I) triflate gives similar results, e.g., the reaction of I with CuO_2CCF_3 in DMF affords the dimer VI in 63% yield and only a minor amount of the arene VII (see Experimental Section).

(21) G. van Koten and J. G. Noltes, *J. Organomet. Chem.*, **84**, 129 (1975).

(22) Camus et al. prefer to describe the bonding in o- and p-tolylcopper in terms of 2e–2c Cu–C bonding. Their NMR spectroscopic data seem to justify this conclusion.[23] However, the symmetry of this bonding does not change on going from 2e–2c to 2e–3c Cu–C interaction. Moreover, the occurrence of rapid interaggregate exchange phenomena can often result in deceptively simple NMR spectra: G. van Koten and J. G. Noltes, to be published.

(23) A. Baici, A. Camus, and G. Pellizer, *J. Organomet. Chem.*, **26**, 431 (1971).

(24) Arylcopper compounds react rapidly with halogen-containing hydrocarbons

|cf. also A. E. Jukes, S. S. Dua, and H. Gilman, *J. Organomet. Chem.* **24**, 791 (1970)]. For example, NMR spectroscopy reveals that a suspension of polymeric 2-Me₂NC₆H₄Cu in CDCl₃ decomposes into CuCl and secondary products, 2-Me₂NC₆H₄D and (2-Me₂NC₆H₄)₂. The formation of CuCl can be deduced from the observation of the resonance pattern of chloroform-soluble (2-Me₂NC₆H₄)₄Cu₆Cl₂. This hexanuclear arylcopper–copper halide is much more stable toward chloroform than the parent organocopper: G. van Koten and J. T. B. H. Jastrzebski, unpublished results.

(25) J. A. Jarvis, B. T. Kilbourn, R. Pearce, and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 475 (1973).

(26) A. Cairncross and W. A. Sheppard, *J. Am. Chem. Soc.*, **93**, 247 (1971).

(27) Nuclear quadrupole resonance spectra of samples of 2-Me₂NC₆H₄Cu polymer show NQR frequencies for both copper isotopes. The observation of two signals at 21.794 (very weak) and 35.892 MHz (medium) (⁶³Cu resonance positions) indicates that the copper atoms occupy chemically inequivalent sites. This conclusion supports the proposed structure (cf.

figure in ref 3) having three-coordinate copper atoms in the polymeric chain whereas the copper atoms at the end of the chains are essentially two-coordinate. H. van Dam and G. van Koten, unpublished results.

(28) H. O. House, *Acc. Chem. Res.*, **9**, 59 (1976).

(29) R. G. Pearson and C. D. Gregory, *J. Am. Chem. Soc.*, **98**, 4098 (1976).

(30) Bulky ortho substituents enlarge the barrier for rotation of a 2e–3c bonded aryl group around the C(bridge)–C(4) axis: G. van Koten and J. G. Noltes, Abstracts, XVIIth Conference on Coordination Chemistry, 1976, p 236.

(31) The formation of asymmetric biaryls in the reaction of CuOTf with premixed benzene solutions of (2-Me₂NCH₂C₆H₄)₄Cu₄ (Ar₄Cu₄) and (4-MeC₆H₄)₄Cu₄ (Ar'₄Cu₄) (see Experimental Section) indicates that (1) interaggregate exchange between these tetranuclear species takes place resulting in the formation of a mixed arylcopper–copper triflate precursor complex ArₓAr'ᵧCuₓ₊ᵧ₊zOTfz, and (2) an even number of aryl groups (x + y) is present in the precursor complex because arenes are formed in very low yields.

A Simple Preparation of Phenols from Diazonium Ions via the Generation and Oxidation of Aryl Radicals by Copper Salts[1a]

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The standard method of preparation of phenols from diazonium salts consists of heating the latter in highly acidic aqueous solution; the high temperature and acidity often cause a variety of unwanted side reactions. We advocate an entirely different procedure which can be performed in a few minutes in neutral solution at room temperature, or below. The method is based on our previous observation that aryl radicals can be oxidized to phenols by cupric ion and it consists of adding cuprous oxide to a dilute solution of the diazonium salt dissolved in a solution containing a large excess of cupric nitrate. In one case the presence of silver(I) appeared to accelerate the radical oxidation. Not only is the redox procedure simpler than the thermal method, but in all cases studied to date, the yields are equivalent or superior to those obtained by the thermal procedure. In four cases in which the latter is unsatisfactory, the redox method is quite successful and it is considered the method of choice for new cases.

As indicated in all textbooks in organic chemistry the standard method for the conversion of an aromatic diazonium ion to a phenol is thermal decomposition of the diazonium ion in a highly acidic aqueous medium. The great deal of controversy concerning the mechanism of this reaction[2] has apparently been resolved recently in favor of a substantially free, singlet, aryl cation intermediate (eq 1).[3]

$$ArN_2^+ \longrightarrow N_2 + Ar^+ \xrightarrow{H_2O} ArO^+H_2 \longrightarrow ArOH + H^+ \quad (1)$$

The high acidity is required in order to suppress the ionization of the product phenol to phenoxide ion which couples readily with unreacted diazonium ion to produce an azo compound.[4,5] In order to obtain high yields of phenol uncontaminated with azo compound, it is frequently necessary to add a solution of the diazonium salt to a boiling sulfuric acid solution,[6] if possible with simultaneous removal of the phenol by steam distillation.[7]

The coupling reaction is only one of a variety of competing reactions which plague the synthesis of phenols by this route. Intramolecular nucleophiles or potential nucleophiles can also attack the diazonium group. For example, an ortho carboxamido group reacts with a diazonium function to yield a benzo-1,2,3-triazene.[8] Similarly, an ortho hydroxyl group leads to the production of a diazoxazole,[9] while an ortho thiol group leads to a benzothiadiazole.[10] Intramolecular diazo coupling with a suitably placed electron-rich ring has also been observed.[11] Nucleophilic attack on the diazonium function by an ortho vinyl group to form an indazole (1) is also common (eq 2).[12]

$$+ \text{ PhCHO} + \text{H}^+ \quad (2)$$
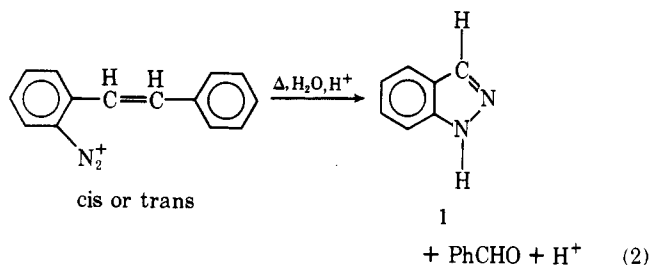
Even a saturated carbon atom in the ortho position to a diazonium function can serve as a nucleophile, presumably after deprotonation.[13-15] For example, the diazonium ion 2
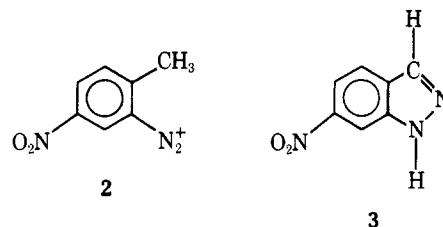
yields 85% of the indazole 3 when heated in acid solution,[13] although the phenol can be produced instead by adding the diazonium solution to a boiling sulfuric acid solution.[14]

Another problem sometimes encountered during thermal decomposition of a diazonium ion is replacement of an ortho or para substituent with a hydroxyl group.[16]

In addition to these competing reactions in which the two nitrogen atoms are retained in the product, several reactions in which nitrogen is lost are known to occur in place of phenol