Interaction of Arylmetal Compounds of Group 1B with Copper(I) and Silver(I) Trifluoromethanesulphonate; a Novel Biaryl Synthesis and a Route to Hexanuclear Aryl–CuAg, –AgAu, and –CuAu Clusters

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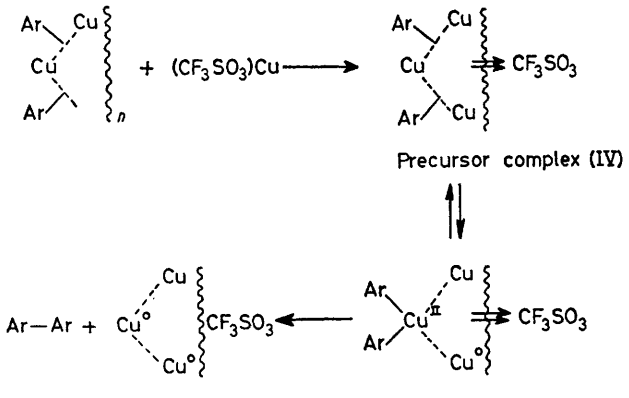
Summary Whereas selective biaryl formation is observed when arylcopper compounds 4-MeC_6H_4Cu, 2-$Me_2NC_6H_4Cu$, and 2-$Me_2NCH_2C_6H_4Cu$ are treated in exact 1 : 1 molar ratio with $(CF_3SO_3)Cu$, reactions of 2-$Me_2NC_6H_4M$ (M = Cu or Au) with $(CF_3SO_3)Cu$ (2 : 1) and of $Ar_4Au_2Li_2$ with $(CF_3SO_3)Cu$ or $(CF_3SO_3)Ag$ (1 : 2) afford novel hexanuclear cluster compounds of the type $Ar_4M_4M'_2(CF_3SO_3)_2$.

Known procedures for coupling of aryl groups in arylcopper compounds involve either interaction with O_2,[1] $Cu^{II}X_2$,[1,2] and RNO_2[1] or thermal decomposition.[1,3] These reactions often proceed with little selectivity. We now report a novel route for selective formation of biaryls from arylcopper compounds which emerged from our study concerning the influence of the nature of the counter-ion X on the stability of copper cluster compounds of the type $Ar_nCu_{n+m}X_m$ (Ar = aryl).

Reaction of copper(I) halides, CuX, with tetrameric $(2\text{-}Me_2NCH_2C_6H_4)_4Cu_4$ (I)[4] and polymeric $(2\text{-}Me_2NC_6H_4)_nCu_n$ (II)[4] gives stable, well defined complexes of the types $(ArCu{\cdot}CuX)_n$ and $Ar_4Cu_6X_2$, respectively.[2,5] In contrast, reactions of $(CF_3SO_3)Cu$ with (I) and $(4\text{-}MeC_6H_4)_4Cu_4$ (III)† (1 : 1) afford, in addition to Cu^0, corresponding biaryls (Ar–Ar) in 100% yield; the reaction of (II) with $(CF_3SO_3)Cu$ (1 : 1), on the other hand, gives both Ar–Ar (85%) and ArH (15%).

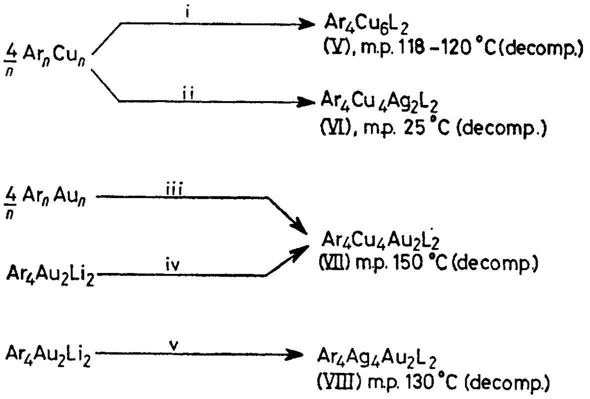


(Ar = Aryl)

Scheme 1

The presence of stoicheiometric amounts of N- or P-containing ligands, such as PPh_3, in the reaction of (I) with $(CF_3SO_3)Cu$ (1 : 4) inhibits the formation of Ar–Ar as a result of complex formation with $(CF_3SO_3)Cu$ [*e.g.*, $(Ph_3P)_2Cu(CF_3SO_3)$; m.p. 178—179 °C; *M* (C_6H_6, cryom.) 744 (737)]. In contrast to (III), (I) and (II) do not react with PPh_3.[6] Because of complex formation with the Me_2NCH_2- and Me_2N-substituents in the biaryls formed, the coupling reactions of (I) and (II) require stoicheiometric amounts of $(CF_3SO_3)Cu$. In the absence of built-in ligands in the aryl nucleus, the arylcopper–$(CF_3SO_3)Cu$ interaction is catalytic; *e.g.*, interaction of (III) with 10 mole % of $(CF_3SO_3)Cu$ affords 4,4′-bitolyl quantitatively.

The quantitative formation of biaryls in the reactions of $(CF_3SO_3)Cu$ with the discrete cluster species (I) and (III) excludes decomposition involving free radicals, but instead points to the occurrence of intramolecular processes leading to pairwise release of aryl groups. The presence of oligomers with odd numbers of aryl groups in polymeric Ar_nCu_n accounts for the formation of ArH in the $Ar_nCu_n(CF_3SO_3)Cu$ reaction. The formation of a precursor complex (IV) is proposed (Scheme 1) as the first step in biaryl formation. A representative example of such a complex is $Ar_4Cu_6(CF_3SO_3)_2$ (V) (Scheme 2) (*vide infra*).‡



($Ar = 2\text{-}Me_2NC_6H_4$, $L = CF_3SO_3$)

Scheme 2. i, $2(CF_3SO_3)Cu$, C_6H_6, 80%; ii, $2(CF_3SO_3)Ag$, C_6H_6; iii, $4(CF_3SO_3)Cu$, C_6H_6, 95%, $-2(CF_3SO_3)Au$; iv, $4(CF_3SO_3)Cu$, Et_2O, 91%, $-2(CF_3SO_3)Li$; v, $4(CF_3SO_3)Ag$, Et_2O, 91%, $-2(CF_3SO_3)Li$.

One of the possible mechanisms for the formation of (V) is a process involving valence disproportionation inside the Cu_n core followed by reductive elimination of biaryl which would also explain the large influence of the counter-ion on the coupling reactions. The anions attached to the Cu_n core would affect the potentials of the various Cu couples;[7] the strongly electron-accepting[8] CF_3SO_3 anion would favour the Cu^{II} oxidation state whereas electron-donating[8] halide anions, for example, would favour the Cu^I state. The recent[9] proposal that organocopper(III) compounds are intermediates in the Ullman type coupling of 2-$XC_6H_4NO_2$ with $(CF_3SO_3)Cu$ must be considered less likely in view of these results.

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† Contrary to an earlier report (A. Camus and N. Marsich, *J. Organometallic Chem.*, 1968, **14**, 441) *o*- and *p*-tolylcopper are tetrameric in freezing benzene.

‡ All compounds gave satisfactory analyses. Complete spectroscopic and degradation data will be published later.

I.r. and n.m.r. spectroscopic data reveal that the structure of (V, Ar = 2-$Me_2NC_6H_4$) is analogous to that of $Ar_4Cu_6Br_2$[5,10] with Ar groups spanning triangular faces of an octahedral Cu_6 core by 2*e*–3*c* C–Cu and 2*e*–2*c* N–Cu bonds and the anions (Br or CF_3SO_3)§ bridging equatorial Cu atoms. Stable hexanuclear complexes $Ar_4M_4M'_2(CF_3SO_3)_2$ (VI—VIII) have been prepared using either Ar_nCu_n or Ar_nAu_n¶ and $Ar_4Au_2Li_2$¶ as starting compounds (Scheme 2).

N.m.r. spectroscopy shows that the Au atoms in $Ar_4M_4Au_2X_2$ occupy apical positions which is in line with the strong preference of Au^I for a digonal co-ordination geometry.[11] Only one resonance pattern for the Ar protons is observed which confirms a symmetric $Ar_4M_4Au_2$ skeleton while in X only one *J*(H-6–^{107,109}Ag) of 6 Hz (C_6D_6, doublet at 8·06 p.p.m. upon irradiation at δH-5) is observed. The bridging carbon atom C-1 in (V), (VII), and (VIII) is a centre of chirality [Ar group bridges metal atoms which have different co-ordination geometries, *e.g.* (V), (VII) and (VIII) and/or are unlike, *e.g.* (VII) and (VIII)]. The NMe resonances [δ (C_6D_6), (V), 1·92–2·96 (2 × s); (VII), 1·84—2·88 (2 × s); and (VIII), 1·90—2·79 (2 × s)] are anisochronous as a result of rate-determining metal–NMe_2 co-ordination (stable prochiral NMe_2 assembly). The NMe resonances in (VII) and (VIII) remain anisochronous up to 90 °C whereas those in (V) coalesce at 40 °C.** This is explained in terms of increased N–M_{eq} bond strength in the AuM (M = Cu or Ag) clusters resulting from a contribution to the bonding of canonical structures such as $[Ar_2Au]_2^{2-}[M_4X_2]_2^{+}$ in which 2*e*–3*c* ArAuM bonding has been replaced by 2*e*–2*c* ArAu interactions. Corresponding high values for isomer shift (3·88 mm s^{-1}) and quadrupole splitting (9·14 mm s^{-1}) in the ^{197}Au Mössbauer spectrum[12] of $Ar_4Au_2Cu_4(CF_3SO_3)_2$ (VII) support this idea.

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§ I.r. spectroscopy reveals a symmetry below C_{v3} [ν_4(*E*) 1218s and 1296s cm^{-1}; ν_5(*E*) 633m cm^{-1}] for the (CF_3SO_3) anion in (V). Accordingly, (V) is, like $Ar_4Cu_6Br_2$ (ref. 5) and $H_6Cu_6(PPh_3)_6$ (M. R. Churchill, J. A. Bezman, J. A. Osborn, and J. Wormald, *Inorg. Chem.*, 1972, **11**, 1818), an 84-electron cluster compound (CF_3SO_3 and Ar groups each contribute 3 electrons to 66 electrons of Cu_6).

¶ $Ar_4Au_2Li_2$ [according to mol. wt. data in boiling C_6H_6, m.p. 155—160 °C (decomp.)] has been prepared from the reaction of ArLi with Ph_3PAuBr (2 : 1). Reaction of Ar_4 Au_2Li_2 with Me_3SnBr (1 : 1) affords polymeric Ar_nAu_n [δ C_6D_5N, 3·10 (NMe), 7·95 (H-6), m.p. 50—55 °C (decomp.)].

** The NMe protons become isochronous by a process involving Cu–N bond dissociation and inversion at N with concomitant rotation around the C–N bond. A process involving Cu–N bond dissociation followed by rapid rotation of the phenyl nucleus around the axis through C(1)–C(4) which inverts the configuration of C(1) represents a higher energy path (G. van Koten and J. G. Noltes, unpublished results).

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[12] M. P. A. Viegers and G. van Koten, unpublished results.