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# ARE ARYLCOPPER COMPOUNDS INTERMEDIATES IN THE EXCHANGE REACTION BETWEEN ARYL HALIDES AND COPPER(I) SALTS?

Gerard van Koten*, Johann T. B. H. Jastrzebski and Jan G. Noltes
Institute for Organic Chemistry TNO, Utrecht, The Netherlands

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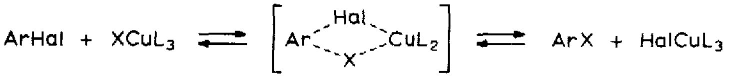
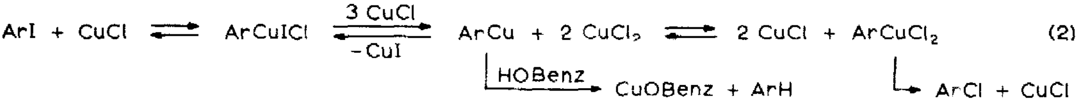
Halogen-anion exchange between aryl halides and anions of copper salts has generally been rationalized in terms of a copper-assisted nucleophilic displacement reaction involving a four-center transition state or intermediate[1,2], eq. 1.



$$\mathrm{ArHal} + \mathrm{XCuL_3} \rightleftharpoons \left[\mathrm{Ar}\overset{\mathrm{Hal}}{\underset{\mathrm{X}}{\diamond}}\mathrm{CuL_2}\right] \rightleftharpoons \mathrm{ArX} + \mathrm{HalCuL_3} \qquad (1)$$

Recently, Cohen et al.[3] proposed an alternative mechanism, which involves an organocopper compound, $ArCu^{I}$, as an intermediate[4], eq. 2. Cohen et al. propose that the observed reaction products ArCl and ArH are formed by reaction of ArCu with $CuCl_2$ and by protonation of ArCu, respectively.



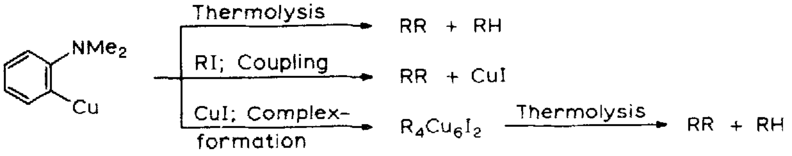
$$\mathrm{ArI} + \mathrm{CuCl} \rightleftharpoons \mathrm{ArCuICl} \xrightleftharpoons[\mathrm{-CuI}]{\mathrm{3\,CuCl}} \mathrm{ArCu} + 2\,\mathrm{CuCl_2} \rightleftharpoons 2\,\mathrm{CuCl} + \mathrm{ArCuCl_2} \qquad (2)$$
$$\mathrm{ArCu} \xrightarrow{\mathrm{HOBenz}} \mathrm{CuOBenz} + \mathrm{ArH} \qquad \mathrm{ArCuCl_2} \rightarrow \mathrm{ArCl} + \mathrm{CuCl}$$

However, in our view this proposal does not take into account the known chemistry of arylcopper compounds[5]. (i). It must be expected that, if ArCu is an intermediate, in addition to protonation also coupling with ArI to give ArAr will take place[5,6]. (ii). Reactions between ArCu and $CuCl_2$ give other products (ArH and ArAr) in addition to ArCl[7]. (iii). Arylcopper compounds are not stable under the conditions applied for these reactions and more importantly, thermolysis of ArCu generally gives rise to the formation of both ArH and ArAr[7,8].

We report here some results for the halogen-halogen exchange reaction of CuCl with $2\text{-}Me_2NC_6H_4I$ (RI). This system had been selected for study because the possible arylcopper intermediate (cf. eq. 2) in this reaction, RCu ($R = 2\text{-}Me_2NC_6H_4\text{-}$) had been the subject of earlier synthetic and structural studies[9]. Relevant experimental data have been compiled in the Table.

The RI/CuCl-exchange reaction (DMF; 130° C; $N_2$-atmosphere) results in the formation of RCl in >90 % yield. Addition of proton donors ($H_2O$ or HOBenz) has no effect on the amount or type of products formed. Furthermore, the reaction of RI with CuOBenz[12] gives the ester ROBenz[13] as well as RR. Both products are absent in RI/CuCl/HOBenz reaction mixtures indicating that CuOBenz (cf. eq. 2) is not formed. Finally, in the RI/CuCl/Allyl bromide reaction mixture R-All[10], which is readily formed by coupling of RCu with AllBr, could not be detected. Instead, competitive I/Cl, I/Br and Br/Cl exchange occurred. These results show that the arylcopper, RCu, is not an intermediate in the RI/CuCl reaction. This conclusion is further supported by the results of separate experiments carried out with the pure arylcopper compound RCu.

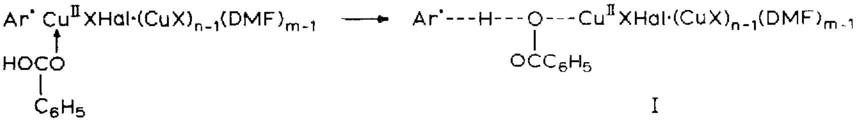
Thermolysis (DMF; 130°C; $N_2$-atmosphere) of RCu affords RH and RR in a 3/1 molar ratio, whereas the thermal decomposition of $R_4Cu_6Cl_2$ and $R_4Cu_6I_2$ gives RR as the major product. This difference in thermolysis behaviour will be connected with the different structures of RCu (polymeric[9]) and $R_4Cu_6X_2$ (discrete hexanuclear cluster[11]; intraaggregate coupling of two R groups can occur[8]). Oxidation (DMF, 25°C, $N_2$) of RCu and $R_4Cu_6I_2$ with $CuCl_2$ affords not only RCl but also RR. In analogy with the explanation given for the oxidation of tetranuclear $(2\text{-}Me_2NCH_2C_6H_4)_4Cu_4$[9] with $CuCl_2$[7] we postulate that in these reactions an innersphere-activated complex of the type $R_4I_2Cu_5Cu\cdots X\cdots Cu^{II}X(CuX_2)_n$ is formed as an intermediate. Intramolecular electron-transfer from the $Cu_6$-cluster to the $Cu^{II}X_2$-polymer then leads to coupling of the bridging groups within the activated complex. C—C coupling with formation of RR (DMF; 130°C; $N_2$) takes place upon heating a mixture of RI and RCu. Coupling is accompanied by competitive thermolysis of RCu and of the intermediately formed $R_4Cu_6I_2$[15], see eq. 3.



(3)

Our experiments with pure RCu show that the formation of RR must be expected if RCu is an intermediate in the RI/CuCl exchange reaction.

ArH, detected among the reaction products[3], need not be formed by protolysis of an organocopper intermediate. A possible route for the exchange reaction involves the interaction of ArHal with $(CuX)_n(DMF)_m$-oligomeric species[16]. Single electron-transfer leads via a transient species of the type $Ar^{\cdot}Cu^{II}XHal\cdot(CuX)_{n-1}(DMF)_m$ to the exchanged product ArX and $CuHal\cdot(CuX)_{n-1}(DMF)_m$. In the presence of proton-active compounds, e.g. BenzOH, competitive proton transfer from coordinated BenzOH to Ar$^{\cdot}$ in the bridged intermediate I



$$Ar^{\cdot}\,\underset{\underset{\underset{C_6H_5}{|}}{HOCO}}{\overset{}{\underset{\uparrow}{Cu^{II}}}}XHal\cdot(CuX)_{n-1}(DMF)_{m-1} \longrightarrow Ar^{\cdot}{-}{-}{-}H{-}{-}{-}\underset{\underset{OCC_6H_5}{|}}{O}{-}{-}{-}Cu^{II}XHal\cdot(CuX)_{n-1}(DMF)_{m-1}$$

I

(cf. ref. 17) then results in the formation of ArH and $Cu^{II}XHal\cdot Cu^{II}XOBenz\cdot(CuX)_{n-2}(DMF)_m$.

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Table. Experimental data[13] concerning the exchange reaction of RI ($R = 2\text{-}Me_2NC_6H_4$) with CuCl and the reactivity of the possible organocopper intermediate

| Reactants | Reaction time (h) | Products[a] | | | | |
|---|---|---|---|---|---|---|
| | | RH | RCl | RR[b] | RX[b] | |
| Exchange reaction (DMF; 130° C) | | | | | | |
| RI/2 CuCl | | ≤0.05[c] | 0.93 | — | — | |
| RI/1.6 CuCl/1 $H_2O$ | | ≤0.05 | 0.94 | — | — | |
| RI/2 CuCl/½ HOBenz[d] | 3 | ≤0.02 | 0.90 | — | X = OBenz<br>— | |
| RI/2 CuCl/½ AllBr[e] | 4 | ≤0.02 | 0.71 | — | X = Br<br>0.10 | X = All<br>— |
| RI/CuOBenz[f,g] | | 0.16 | — | 0.20 | X = OBenz<br>0.10 | |
| Thermal decomposition of RCu (DMF; 130° C) | | | | | | |
| RCu | [h] | 0.6 | — | 0.4 | | |
| $R_4Cu_6Cl_2$ | <2 | 0.4 | — | 3.6 | | |
| $R_4Cu_6I_2$[i] | | 0.2 | — | 3.8 | | |
| Oxidation of RCu with $Cu^{II}X_2$ (DMF; 25° C) | | | | | | |
| RCu to 4 $CuCl_2$[j] | | 0.03 | 0.22 | 0.42 | | |
| $R_4Cu_6I_2$ to 4 $CuCl_2$[j] | | <0.01 | 0.04 | 0.58 | X = I<br>0.05 | |
| RI to $CuCl_2$[k] | | — | — | — | X = I<br>0.93 | |
| $CuCl_2$ to RCu[l] | | 0.13 | 0.10 | 0.74 | | |
| Coupling of RCu with RI (DMF; 130° C) | | | | | | |
| RCu/1.25 RI[m] | 3/4 | 0.08 | — | 1.30 | X = I<br>0.83 | |
| RCu/1.3 RI | 4 | 0.24[n,o] | — | 1.88 | X = I<br>0.40 | |

[a] Mol. R-. [b] Not detected unless indicated otherwise. [c] Directly present after mixing of the reagents (from NMR experiment in DMF-$d_7$). [d] Amount of benzoic acid, BenzOH, remained unchanged. [e] After 3 h; 0.28 RBr, 0.54 RCl, 0.07 RI. [f] Pure CuOBenz. [g] 0.47 RI recovered. [h] After 4 h. After ½ h 72 % of the total amount of RH was detected. [i] Clean decomposition. [j] Reversed addition gave the same results. [k] At 130° no RI could be recovered. [l] A yellow precipitate was isolated which analysed for 2.3 CuCl•DMF. [m] NMR experiment using DMF-$d_7$. [n] Partly due to hydrolysis of RCu. [o] See ref. 15.

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4. This scheme suggests that $ArCu^{I}$ is rather stable, whereas $ArCu^{III}Cl_2$ and $ArCu^{III}ClI$ are transient intermediates.

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10. $2\text{-}Me_2NC_6H_4CH_2CH{=}CH_2$; b.p. 60-61°C/5 mm; NMR ($CCl_4$, $\delta$ ppm), 2.60 ($NMe_2$, 6 H, s), 3.41 ($PhCH_2$-, 2 H, m), 5.02 ($=CH_2$, 2 H, m), 5.7-6.1 (-CH=, 1 H, m), 6.8-7.2 (PhH, 4 H, m).

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13. The reactions were carried out in an $N_2$-atmosphere. Reaction products were identified by comparison with pure samples using NMR, IR and GS-MS techniques.

14. RI has been detected in the reaction mixture which indicates that also intraaggregate trapping of $R^{\bullet}$ by a $Cu_n$–I bond takes place[7,8].

15. In refluxing benzene $R_4Cu_6I_2$ and RR are formed. Both RCu and $R_4Cu_6I_2$ are stable at 80°C

$$6\,RCu + 6\,RI \xrightarrow[C_6H_6]{80^{\circ}C} R_4Cu_6I_2 + 2\,RR + 4\,RI$$

16. $Cu^{I}$ halide complexes have often polynuclear structures in which the halide anion bridges two (e.g. $L_2CuX_2CuL$) or three Cu atoms (e.g. complexes with "step" or "cubane" $Cu_4X_4$ skeletons); cf., M. R. Churchill and K. L. Kalra, Inorg. Chem., 13 (1974) 1899.

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