Copper(I) Ethylenediamine Carbonyl Complexes: 'Models' for Carbon Monoxide Activation. *X*-Ray Structure of the Ion-pair Carbonylethylenediaminetetraphenylboratocopper

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Summary Copper (I) iodide absorbs carbon monoxide in methanol in the presence of ethylenediamine (en), giving solutions from which $[Cu_2(en)_3(CO)_2]I_2$, $[Cu_2)en)_3(CO)_2](BPh_4)_2$, and $[Cu(en)_2CO]I$ have been obtained as thermally stable compounds; the reaction of CuCOCl with en allowed the isolation of $[Cu(en)(CO)PhBPh_3]$, an *X*-ray structure determination of which shows the presence of a three-co-ordinate copper(I) interacting with the BPh_4^- anion.

Despite their interesting properties,[1,2] copper carbonyls have hitherto hardly been investigated. Their extreme lability and ready disproportionation have frustrated attempts to explore reactions of copper(I) with carbon monoxide in the presence of suitable nitrogen ligands.[1,2] Ethylenediamine (en), while it seems to stabilize Cu–CO bonds,[3] provides a potentially unsaturated copper(I) atom able to co-ordinate two additional molecules. This system could be an interesting model for copper(I)-promoted transfer of carbon monoxide to organic substrates.[4] A preliminary study on the reaction of CuCOCl with ethylenediamine[3] failed to establish the various species which could be generated by the copper(I)–en–carbon monoxide system and to isolate thermally stable carbonyl complexes.

Herein we report the synthesis of the following thermally stable copper(I) carbonyls: $[Cu_2(en)_3(CO)_2]I_2$ (I), $[Cu_2(en)_3(CO)_2](BPh_4)_2$ (II), $[Cu(en)_2(CO)]I$ (III), and $[Cu(en)CO(BPh_4)]$ (IV), along with results of an *X*-ray analysis of complex (IV).†

CuI suspended in methanolic solutions of en (en : Cu molar ratio 4 : 1) reversibly absorbs carbon monoxide (1 mol of CO per Cu) at room temperature and atmospheric pressure, giving a solution from which either $[Cu_2(en)_3(CO)_2]I_2$ (I) [ν_{CO}(Nujol) 2062 cm^{-1}] or, by addition of $NaBPh_4$, $[Cu_2(en)_3(CO)_2](BPh_4)_2$ (II)‡ [ν_{CO}(Nujol) 2078 cm^{-1}] can be obtained as white crystalline solids. A much larger excess of en over CuI allows the isolation of $[Cu(en)_2CO]I$ (III) [ν_{CO}(Nujol) 2060 cm^{-1}].

As previously described, CuCOCl (1 mol) reacts in methanol at −30 °C with en (1 mol) producing a solution from which the rather unstable [Cu(en)COCl] was recovered.[3] The addition of $NaBPh_4$ to the same solution allowed the isolation of the thermally stable $[Cu(en)CO(BPh_4)]$ (IV) [ν_{CO}(Nujol) 2117 cm^{-1}]. On reaction with en, (IV) gives

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† Satisfactory elemental analytical data were obtained for all the compounds reported.

‡ The molecular complexity of (II) is deduced from on *X*-ray analysis which is in progress.

(II). Thus the reaction occurring between copper(I) and en in the presence of carbon monoxide is a stepwise process, which can be summarized by reaction (1).

$$2\,\mathrm{Cu}^+ + 2\,\mathrm{CO} + 2\,\mathrm{en} \rightarrow 2[\mathrm{Cu(en)CO}]^+ \xrightarrow{\mathrm{en}} [\mathrm{Cu_2(en)_3(CO)_2}]^{2+} \xrightarrow{\mathrm{en}} 2[\mathrm{Cu(en)_2CO}]^+ \qquad (1)$$

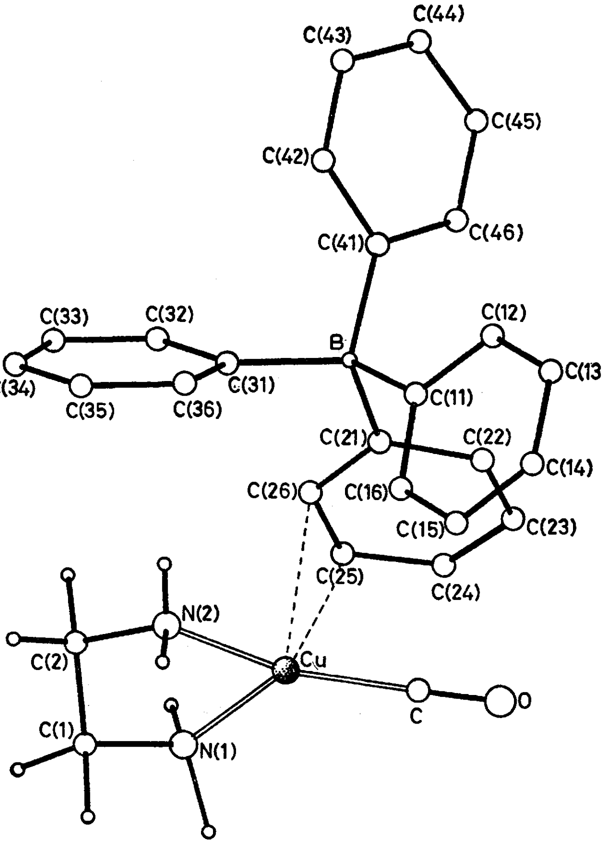

FIGURE. Molecular structure of $[\mathrm{Cu(en)COPhBPh)_3}]$ (IV). Bond distances (in Å): Cu–N(1), 2·038(4); Cu–N(2), 2·043(4); Cu–C, 1·806(6); Cu–C(25), 2·919(5); Cu–C(26), 2·706(4); Cu–A, 2·725(5); C–O, 1·110(7); bond angles (°): N(1)–Cu–N(2), 87·2(2); N(1)–Cu–C, 132·9(2); N(2)–Cu–C, 133·7(2); A–Cu–N(1), 95·0(2); A–Cu–N(2), 108·7(2); A–Cu–C, 92·0(2); Cu–C–O, 178·3(5). A = midpoint of C(25)–C(26).

All the cationic species have been isolated as tetraphenylborate or iodide derivatives, which can be stored in the solid state at room temperature under an N_2 atmosphere for a long time. The carbon monoxide can be displaced in every case by a molecule of $\mathrm{P(OEt)_3}$. The ν_{CO} stretching frequency (2060—2117 cm^{-1}) is sensitive to the number of the basic donor atoms complexing the metal.[2] An *X*-ray structure determination of (IV) was undertaken in order to establish the co-ordination geometry of copper(I) in a potential model complex for carbon monoxide activation.

Crystal data: $\mathrm{C_{27}H_{28}BCuN_2O}$, $M = 470{\cdot}9$, monoclinic, $a = 10{\cdot}301(1)$, $b = 12{\cdot}234(1)$, $c = 18{\cdot}390(2)$ Å, $\beta = 91{\cdot}11(1)^\circ$, $U = 2317{\cdot}1$ Å^3; $Z = 4$, $D_c = 1{\cdot}350\ \mathrm{g\,cm^{-3}}$, space group $P2_1/c$. Intensity data ($6 < 2\theta < 140^\circ$) were recorded on a Siemens AED computer-controlled diffractometer, with Ni-filtered Cu-K_α radiation. 4396 independent reflections were collected, 3150 of which [$I > 2\sigma(I)$] were used in the analysis. The structure was solved by the heavy-atom method and refined by full-matrix least-squares techniques[5] with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were located from a difference Fourier map and refined isotropically. The final R index is 4·9%.§

The crystals are built up of discrete ion-pair units $\mathrm{Cu(en)COPhBPh_3}$. The Figure shows a view of the complex with the more relevant bond distances and angles. N(1), N(2), and C are arranged in a nearly trigonal planar geometry around the metal. A rather long but significant interaction with two carbon atoms of one of the phenyl rings of the $\mathrm{BPh_4}^-$ completes the pseudo-trigonal pyramidal co-ordination around copper(I). The aromatic ring distances have normal values. The Cu–C [1·806(6) Å] and C–O [1·110(7) Å] bond distances are the longest and the shortest, respectively, of the few examples known.[6] The copper atom is displaced by 0·26 Å from the plane defined by N(1), N(2), and C toward the C(25)–C(26) bond. The long Cu–phenyl distances indicate only weak binding of the aromatic unit.[7] This is an ideal situation for the ready replacement of aromatic molecules by other unsaturated groups including carbon monoxide acceptor molecules. Coupling reactions promoted by copper(I), in which the $\mathrm{Cu^I}$ atom acts as a template, have been extensively employed,[4,8] and (IV) might be considered a structural model for this kind of reaction.

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§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 IEW. Any request should be accompanied by full literature citation for this communication.

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