Reversible Binding of Carbon Monoxide by the (Dimethylmethyleneammonium)copper(I) Chloride Cation

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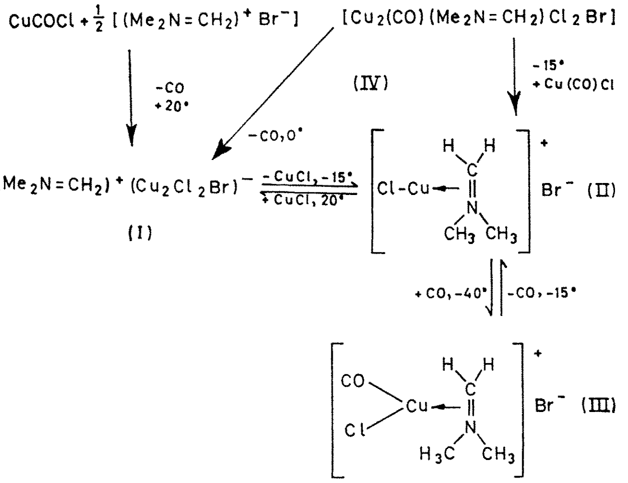
Summary Reactions of the dimethylmethyleneammonium cation with CuCl and Cu(CO)Cl are described; the carbon monoxide ligand in $[Cu(CO)Cl(Me_2N{=}CH_2)]^+$ is reversibly co-ordinated over the temperature range −40° to −15°.

THE dimethylmethyleneammonium cation, the synthesis of which has been described by Eschenmoser,[1] is potentially a useful ligand for the stabilisation of low-valent metal complexes. We report that complexes of this ligand with Cu^I, having stabilities comparable with related complexes,[2] have been characterised and are summarised in the Scheme.



SCHEME

Carbon monoxide is liberated when Cu(CO)Cl and $(Me_2NCH)_2{}^+Br^-$ react in anhydrous tetrahydrofuran (THF), the resulting solid being $(Cu_2Cl_2Br)^-(Me_2N{=}CH_2)^+$ (I) [analysis and *X*-ray molecular weight]. This formulation was also suggested by the i.r. spectrum which shows $\nu(C{=}N)$ as 1690 cm^{-1} in (I) compared with a value of 1680 cm^{-1} in $(Me_2N{=}CH_2)^+Br^-$.

Compound (I) suspended in THF at −40°, absorbs carbon monoxide quantitatively (1Cu : 1CO) and a pale yellow solid, sparingly soluble in THF, is obtained which is stable up to −15° only. The i.r. spectrum (−60°, THF mull) has $\nu(C{=}O)$ 2080 cm^{-1} and two intense $\nu(C{=}N)$ bands centred at 1640 and 1610 cm^{-1}, consistent with the formulation (III) if $\nu(C{=}N)$ is 'split' by solid state effects. A suspension of (III) in THF releases CO quantitatively with pseudo-first-order kinetic dependence at −15°, (II) being formed, which at room temperatures reverts to (I).

In the presence of Cu(CO)Cl, (II) evolves an equimolar amount of CO at temperatures above −15° and it seems that a polynuclear complex (IV) is formed between (II) and Cu(CO)Cl. This complex dissociates quantitatively at 0° to give (I). By contrast, Cu(CO)Cl is stable in THF at room temperature.

We have discovered reactions of (I) with nitric oxide which appear to parallel those described here; further work is in progress.

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[1] A. Eschenmoser, Symposium on Stereochemistry, Sheffield, 1970.

[2] F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, 1970, **92**, 5114; G. Rucci, C. Zanzottera, M. P. Lachi, and M. Camia, *Chem. Comm.*, 1971, 652 and refs. therein.