Formation of Copper(I) Isocyanate Complexes by the Reaction of Carbon Dioxide and Copper(I) Bis(Trimethylsilyl)amide Complexes

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Summary Copper(I) bis(trimethylsilyl)amide deoxygenates carbon dioxide in the presence of an added ligand to produce hexamethyldisiloxane and a copper(I) isocyanate complex which is converted into an alkyl isocyanate by treatment with an alkyl iodide.

Recently there has been considerable interest in the organic reactions of carbon dioxide with transition metal complexes. In order to extend the scope of these reactions, apart from carboxylation, the possibility of deoxygenation of CO_2 was investigated. Preparations of transition metal carbonyl complexes using CO_2 have been reported,[1] and recently we have found that the copper-promoted deoxygenation of CO_2 by alkyl isocyanide gave CO and alkyl isocyanate.[2] We now report the deoxygenation of carbon dioxide by copper(I) bis(trimethylsilyl)amide[3] in the presence of a suitable ligand which produces a copper(I) isocyanate complex and hexamethyldisiloxane (Scheme). The copper(I) isocyanate complex thus formed would yield an alkyl isocyanate on reaction with an alkyl iodide, and the present reaction provides a new route to copper(I) isocyanate complexes,[4] in which CO_2 is converted into isocyanate, urea, or urethane.

$$\begin{tikzcd}
 & \mathrm{CuN(SiMe_3)_2 + CO_2} \arrow[d, "\mathrm{L}"', "-\,(\mathrm{Me_3Si})_2\mathrm{O}"] & \\
\mathrm{R^1NHCONHR^2} & \mathrm{Cu(NCO)L}_n \arrow[l, "\mathrm{i,\ R^1I}"', "\mathrm{ii,\ R^2NH_2}"] \arrow[r, "\mathrm{R^1I}"] \arrow[d, "\mathrm{R^1Br + R^2OH}"] & \mathrm{R^1NCO} \\
 & \mathrm{R^1NHCO_2R^2} &
\end{tikzcd}$$

To a stirred toluene (5 ml) solution containing $(\mathrm{Me_3Si})_2\mathrm{NCu}$ (0·44 mmol) and t-butyl isocyanide (1·32 mmol), $\mathrm{CO_2}$ gas (0·44 mmol) was introduced at 0 °C under nitrogen, and the homogeneous reaction mixture was stirred for 3 h. Hexamethyldisiloxane was produced in 91% yield. The precipitate was filtered off and the toluene solution was evaporated *in vacuo* at ambient temperature to give a white copper(I) isocyanate complex, $\mathrm{Cu(NCO)(Bu^tNC)}_n$, which showed i.r. absorptions at 2225, 2175 ($\nu_{\mathrm{N\equiv C}}$, ν_{as} NCO), 1350, and 610 $\mathrm{cm^{-1}}$. These i.r. absorptions suggest that the (NCO) group may be co-ordinated to copper through nitrogen, since transition metal isocyanate complexes, including those of copper, having the nitrogen end of the (NCO) group bonded to the metal atom absorb in three principal regions namely *ca.* 2200 $\mathrm{cm^{-1}}$ (ν_{as} NCO), *ca.* 1330 $\mathrm{cm^{-1}}$ (ν_s NCO), and *ca.* 620 $\mathrm{cm^{-1}}$ (δ, γNCO).[4] The copper content determined by iodometry was 20·8%, and the complex evolved $\mathrm{CO_2}$ gas when it was treated with aq. $\mathrm{H_2SO_4}$; the ratio of $\mathrm{CO_2}$ gas evolved to Cu content ($\mathrm{CO_2}$: Cu) was 1·09 : 1. The average co-ordination number of $\mathrm{Bu^tNC}$ (n) calculated on the basis of elemental analyses and the copper content by iodometry was *ca.* 2·5.† An analysis of the $\mathrm{Bu^tNC}$ content of the complex by n.m.r. spectroscopy using nitromethane as internal standard showed $n = ca.\ 2{\cdot}7$.

The reaction between $\mathrm{CuN(SiMe_3)_2}$ and $\mathrm{CO_2}$ requires a σ-donating ligand as an essential component. Besides $\mathrm{Bu^tNC}$, $\mathrm{PBu_3{}^n}$ and $\mathrm{PEt_3}$ were also effective. $(\mathrm{Me_3Si})_2\mathrm{NCu}$ alone or co-ordinated with $\mathrm{P(OMe)_3}$ could not induce any reaction. The effect of these ligands upon the reaction is similar to that observed in $\mathrm{CO_2}$ insertion into Cu–O[5] and Cu–C[6] bonds. The Table summarizes the yields of $(\mathrm{Me_3Si})_2\mathrm{O}$ formed under various conditions. The i.r. (ν_{as} NCO) absorptions of $\mathrm{Cu(NCO)(PBu_3{}^n)}_n$ and $\mathrm{Cu(NCO)(PEt_3)}_n$ were at 2175 and 2160 $\mathrm{cm^{-1}}$, respectively.

TABLE. Formation of $(\mathrm{Me_3Si})_2\mathrm{O}$ from $(\mathrm{Me_3Si})_2\mathrm{NCu}$

Ligand	% Yield	Ligand	% Yield
$\mathrm{Bu^tNC}$[a]	54	$\mathrm{PBu^n_3}$[b]	84
$\mathrm{PBu^n_3}$[a]	36	$\mathrm{P(OMe)_3}$[b]	0
$\mathrm{P(OMe)_3}$[a]	0	$\mathrm{Bu^tNC}$[c]	60
$\mathrm{Bu^tNC}$[b]	91	$\mathrm{PBu^n_3}$[c]	32

[a] Room temp. in toluene. [b] 0 °C in toluene. [c] Room temp. in tetrahydrofuran.

The $\mathrm{Cu(NCO)(Bu^tNC)}_n$ complex, as prepared above, reacted with a mixture of $\mathrm{Pr^nBr}$ (0·88 mmol) and ethanol (0·88 mmol) in toluene (2·5 ml) at 120 °C to produce $\mathrm{Pr^nNHCO_2Et}$ in 69% yield after 5 h. The complex was also prepared from $(\mathrm{Me_3Si})_2\mathrm{NCu}$ (0·38 mmol), $\mathrm{Bu^tNC}$ (1·14 mmol), and $\mathrm{CO_2}$ (0·38 mmol) in diglyme (2 ml) at ambient temperature and it reacted with $\mathrm{Bu^nI}$ (0·76 mmol) in the same solvent at 130 °C to afford $\mathrm{Bu^nNCO}$ in 58% yield after 2 h. Addition of $\mathrm{Bu^nNH_2}$ to the resulting reaction mixture yielded $\mathrm{Bu^nNHCONHBu^n}$.

The mechanism for the formation of the copper(I) isocyanate complex has not been examined. However, promotion of the reaction by σ-donating ligands may be taken to suggest that $\mathrm{CO_2}$ insertion into the Cu–N bond of the $(\mathrm{Me_3Si})_2\mathrm{NCu}$ complex is the first and essential step of the reaction. The reaction of $(\mathrm{Me_3Si})_2\mathrm{NNa}$ and $\mathrm{CO_2}$[7] proceeds *via* $\mathrm{CO_2}$ insertion into the Na–N bond to produce mainly $\mathrm{Me_3SiN{=}C{=}NSiMe_3}$ and $\mathrm{NaOCO_2SiMe_3}$.

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† Elemental analyses. Calc. for $\mathrm{Cu(NCO)(Bu^tNC)_{2\cdot5}}$: C, 51·73; H, 7·23; N. 15·64; Cu, 20·27. Found: C, 50·88; H, 7·24; N, 14·60; Cu 20·61. In connection with the average co-ordination number of $\mathrm{Bu^tNC}$, the degree of association of the complex was found to be 1·3 by cryoscopy in benzene at a concentration of 1·76 wt%.

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