J.C.S. Снем. Сомм., 1977

Formation of Copper(1) Isocyanate Complexes by the Reaction of Carbon Dioxide and Copper(1) Bis(Trimethylsilyl)amide Complexes

By Tetsuo Tsuda, Hiroshi Washita, and Takeo Saegusa*

(Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan)

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)amide³ 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.

To a stirred toluene (5 ml) solution containing (Me₃Si)₂-NCu (0.44 mmol) and t-butyl isocyanide (1.32 mmol), CO₂ 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, $Cu(NCO)(Bu^{\dagger}NC)_{n}$, which showed i.r. absorptions at 2225, 2175 ($v_{N=C}$, v_{as} NCO), 1350, and 610 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 cm^{-1} (ν_{as} NCO), ca. 1330 cm⁻¹ (v_s NCO), and *ca*. 620 cm⁻¹ (δ, γ NCO).⁴ The copper content determined by iodometry was 20.8%, and the complex evolved CO₂ gas when it was treated with aq. H_2SO_4 ; the ratio of CO₂ gas evolved to Cu content (CO₂:Cu) was 1.09:1. The average co-ordination number of Bu^tNC (n) calculated on the basis of elemental analyses and the copper content by iodometry was ca. 2.5.† An analysis of the Bu^tNC content of the complex by n.m.r. spectroscopy using nitromethane as internal standard showed n = ca. 2.7.

The reaction between CuN(SiMe₃)₂ and CO₂ requires a σ -donating ligand as an essential component. Besides Bu^tNC, PBu₃ⁿ and PEt₃ were also effective. (Me₃Si)₂NCu alone or co-ordinated with P(OMe)₃ could not induce any reaction. The effect of these ligands upon the reaction is similar to that observed in CO₂ insertion into Cu-O⁵ and Cu-C⁶ bonds. The Table summarizes the yields of (Me₃Si)₂O formed under various conditions. The i.r. $(v_{as} \text{ NCO})$

469

absorptions of $Cu(NCO)(PBu_3^n)_n$ and $Cu(NCO)(PEt_3)_n$ were at 2175 and 2160 cm⁻¹, respectively.

TABLE.	Formation	of	(Me ₃ Si) ₂ O from	(Me _s Si) ₂ NCu
Ligand	% Yield		Ligand		% Yield
Bu ^t NC ^a	54		PBu ⁿ , ^b		84
PBu¹₃ª	36		P(OMe)	b	0
P(OMe) ₃ ^a	0		ButNCc	•	60
Bu ^t NC ^b	91		PBu n₃ c		32
Deam tom			h 0 00 1 1	• •	. ,

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

The $Cu(NCO)(Bu^{\dagger}NC)_n$ complex, as prepared above, reacted with a mixture of PrnBr (0.88 mmol) and ethanol (0.88 mmol) in toluene (2.5 ml) at 120 °C to produce PrⁿNHCO₂Et in 69% yield after 5 h. The complex was also prepared from (Me₃Si)₂NCu (0.38 mmol), Bu^tNC (1.14 mmol), and CO₂ (0.38 mmol) in diglyme (2 ml) at ambient temperature and it reacted with BuⁿI (0.76 mmol) in the same solvent at 130 °C to afford Bu nNCO in 58% yield after 2 h. Addition of BuⁿNH₂ to the resulting reaction mixture yielded BunNHCONHBun.

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 CO₂ insertion into the Cu-N bond of the (Me₃Si)₂NCu complex is the first and essential step of the reaction. The reaction of (Me₃Si)₂NNa and CO₂⁷ proceeds via CO₂ insertion into the Na-N bond to produce mainly Me₃SiN=C=NSiMe₃ and NaOCO₂SiMe₃.

(Received, 27th January 1977; Com. 071.)

† Elemental analyses. Calc. for Cu(NCO)(Bu^tNC)_{2.5}: 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 Bu^tNC, the degree of association of the complex was found to be 1·3 bu crucescopy in barrane at a concentration of 1.76 mt $^{\circ}$ by cryoscopy in benzene at a concentration of 1.76 wt %.

¹ H. Felkin and P. J. Knowles, J. Organometallic Chem., 1972, 37, C14; P. Svoboda, T. S. Belopotapova, and J. Hetflejs, J. Organometallic Chem., 1974, 65, C37; R. A. Forder, M. L. H. Green, R. E. Mackenzie, J. S. Poland, and K. Prout, J.C.S. Chem. Comm., 1973, 426; T. Ito and A. Yamamoto, J.C.S. Dalton, 1975, 1398; H. Koinuma, Y. Yoshida, and H. Hirai, Chem. Letters, 1975, 1223.
² T. Tsuda, S. Sanada, and T. Saegusa, J. Organometallic Chem., 1976, 116, C10.
³ H. Bürger and U. Wannagat, Monatsh., 1964, 95, 1099.
⁴ D. Forster and D. M. L. Goodgame, J. Chem. Soc., 1965, 262; A. H. Norbury and A. I. P. Sinha, J. Chem. Soc. (A), 1968, 1598; J. Ellermann and W. Uller, Chem. Ber., 1970, 103, 3932.
⁵ T. Tsuda, S. Sanada, K. Ueda, and T. Saegusa, Inorg. Chem., 1976, 15, 2329.

T. Tsuda, S. Sanada, K. Ueda, and T. Saegusa, Inorg. Chem., 1976, 15, 2329.

⁶ T. Tsuda, Y. Chujo, and T. Saegusa, J.C.Š. Chem. Comm., 1975, 963.

⁷ U. Wannagat, H. Kuckertz, C. Krüger, and J. Pump, Z. anorg. Chem., 1964, 333, 54.