

nism, and against the operation of competing SN1 and SN2 processes of the classic Ingold types.<sup>3</sup> We do not deny the possibility that the Snee mechanism may operate in certain special cases. The results,<sup>21</sup> however, seem to us to be capable of an alternate explanation. The calculations of Sims and coworkers<sup>15</sup> indicate that "the chlorine isotope effect... increases continuously as ones goes from a reactant-like to a product-like transition state..." in classical SN2 processes. This is just the situation expected for the SN2 component of borderline solvolyses with increasing concentrations of sodium azide.

**Acknowledgment.** One of us (C. J. C.) wishes to thank Professor V. J. Shiner for helpful comments.

(22) Participant in the Great Lakes Colleges Association Fall Semester Program 1972.

Vernon F. Raaen, Timothy Juhlke<sup>22</sup>  
Frederick J. Brown,<sup>22</sup> Clair J. Collins\*

Chemistry Division, Oak Ridge National Laboratory  
Oak Ridge, Tennessee 37830

Received June 10, 1974

### *t*-BuOCu·CO and *t*-BuOCu·CN-*t*-Bu. New and Sublimable Copper-Carbonyl and -Isocyanide Complexes

Sir:

We wish to report the preparations, characterizations, and reactions of new and sublimable copper-carbonyl and -isocyanide complexes, *t*-BuOCu·CO (**1**) and *t*-BuOCu·CN-*t*-Bu (**2**). These complexes demonstrate an interesting property of *t*-BuOCu,<sup>1</sup> *i.e.*, a strong affinity toward a  $\pi$ -accepting ligand which has not been observed in common cuprous salts. This feature of *t*-BuOCu may be ascribed to the high  $\sigma$ -donating character of the *tert*-butoxy ligand which enhances the back-donation from the copper to the  $\pi$ -accepting ligand. **1** and **2** offer a convenient method of preparing  $h^5$ -cyclopentadienyl-copper complexes *via* metalation of cyclopentadiene.

The following operations were carried out under nitrogen. On passing a stream of carbon monoxide through a suspension of *t*-BuOCu<sup>1</sup> in benzene at room temperature, *t*-BuOCu was dissolved to produce a yellow-brown solution. After filtration of a small amount of precipitate, evaporation of benzene *in vacuo* from the filtrate gave a pale yellow solid which was identified as **1** by the following analyses: Cu content by iodometry 37.9% (calcd for **1**, 38.6%); ir (Nujol) 2062  $\text{cm}^{-1}$  ( $\nu(\text{C}\equiv\text{O})$ ). When an excess of phenylacetylene was added to **1**, stoichiometric amounts of cuprous phenylacetylidyde (97%), *t*-BuOH (98%), and carbon monoxide (97%) were generated.

When **1** was once isolated, it became insoluble in common organic solvents. However, the Cu/*t*-BuO/CO ratio did not change during the evaporation of benzene. Addition of phenylacetylene to the benzene solution of **1** prepared by the above-mentioned procedure produced cuprous phenylacetylidyde, *t*-BuOH, and carbon monoxide in a ratio of 1:0.97:0.92. Insolubilization of **1** may probably be due to the association of **1** by the removal of solvated benzene. The nmr spectrum of

(1) T. Tsuda, T. Hashimoto, and T. Saegusa, *J. Amer. Chem. Soc.*, **94**, 658 (1972).

benzene solution of **1** showed one sharp singlet at  $\tau$  8.59. **1** is sensitive to oxygen and moisture, but it is stable to heat. On heating to 150° under nitrogen, a partial decarbonylation of **1** took place with a simultaneous formation of *t*-BuOCu. At 60° (1 mm), **1** was isolated by sublimation. **1** is the first example of sublimable copper carbonyl complex. The isolation of **1** by sublimation is especially noteworthy, because most of the carbonyl complexes of copper salts have been known to be unstable. For example,  $\text{Cu}\cdot\text{CO}^2$  can exist only under carbon monoxide atmosphere.  $\text{CF}_3\text{COOCu}\cdot\text{CO}^3$  loses carbon monoxide at room temperature *in vacuo*.  $h^5\text{-C}_5\text{H}_5\text{Cu}\cdot\text{CO}^4$  decomposes rapidly at room temperature. Recently, an air- and heat-stable copper carbonyl complex of  $[\text{HB}(\text{pz})_3]\text{Cu}\cdot\text{CO}^5$  (pz = pyrazolyl) has been prepared using a tridentate ligand of hydrotris(1-pyrazolyl)borate having a strong  $\sigma$ -donor character.

The thermal stability of **1** is due to strengthening of the copper-carbonyl bond. Compared with  $\nu(\text{C}\equiv\text{O})$  of free carbon monoxide (2143  $\text{cm}^{-1}$ ), the remarkable reduction of  $\nu(\text{C}\equiv\text{O})$  of **1** (2062  $\text{cm}^{-1}$ ) suggests that the increased back-donation of copper 3d electrons to  $\text{CO}\pi^*$  orbital is responsible for the strengthening of copper-carbonyl bond. This increased back-donating ability of the copper atom probably results from the strong  $\sigma$ -donor character of the *tert*-butoxy ligand. On the basis of  $\nu(\text{C}\equiv\text{O})$  of copper carbonyl complex, the  $\sigma$ -donating ability of the *tert*-butoxy ligand may be higher than that of the hydrotris(1-pyrazolyl)borate ligand ( $\nu(\text{C}\equiv\text{O})$  2083  $\text{cm}^{-1}$ ) and may be comparable to that of hydrotris(3,5-dimethylpyrazolyl)borate ligand ( $\nu(\text{C}\equiv\text{O})$  2066  $\text{cm}^{-1}$ ).<sup>5</sup> These findings indicate the peculiarity of *tert*-butoxy ligand in copper-complex chemistry.

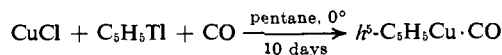
The addition of an equimolar amount of *n*-Bu<sub>3</sub>P, (MeO)<sub>3</sub>P, or *t*-BuNC to a suspension of **1** in benzene resulted in an immediate and quantitative liberation of carbon monoxide with a formation of the corresponding phosphine or isocyanide complex of *t*-BuOCu. However, no decarbonylation was observed by the additions of nitrogen-containing ligands (pyridine,  $\alpha,\alpha'$ -bipyridyl, and tetramethylethylenediamine) and unsaturated hydrocarbons (1,5-cyclooctadiene, styrene, and 3-hexyne).

**2** was isolated as a yellow crystalline solid by sublimation at 90° (1 mm) from an equimolar mixture of *t*-BuOCu and *t*-BuNC in benzene: Cu content by iodometry 28.7% (calcd for **2** 29.0%); *tert*-butoxy group content by benzyl alcoholysis 98%; ir (Nujol) 2102  $\text{cm}^{-1}$  ( $\nu(\text{C}\equiv\text{N})$ ); nmr (C<sub>6</sub>D<sub>6</sub>)  $\tau$  8.10 (S, *t*-BuO) and 9.01 (S, *t*-BuNC). An isocyanide ligand is known to behave as either  $\sigma$ -donor or  $\pi$ -acceptor depending

(2) "Gmelins Handbuch der Anorganischen Chemie," Verlag Chemie GmbH, Weinheim/Bergstr., Kupfer, Teil B, Lieferung 1, 1958, p. 240.

(3) A. F. Scott, L. L. Wilkening, and B. Rubin, *Inorg. Chem.*, **8**, 2533 (1969).

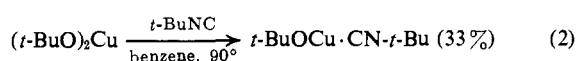
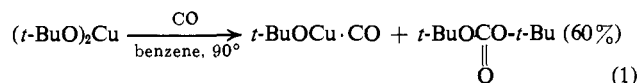
(4) F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, **92**, 5114 (1970); the  $h^5\text{-C}_5\text{H}_5\text{Cu}\cdot\text{CO}$  was prepared as an unstable compound according to the following reaction catalyzed by *n*-Bu<sub>3</sub>P



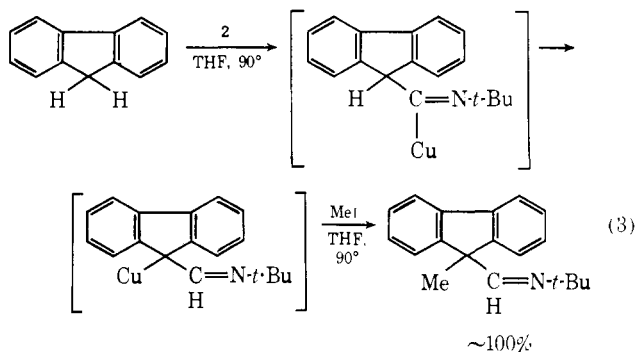
(5) M. I. Bruce and A. P. P. Ostazewski, *J. Chem. Soc., Chem. Commun.*, 1124 (1972). For the polypyrazolylborate ligand, see S. Trofimenko, *Accounts Chem. Res.*, **4**, 17 (1971); *Chem. Rev.*, **72**, 497 (1972).

upon the nature of metal.<sup>6</sup> The considerable lowering of  $\nu(\text{C}\equiv\text{N})$  in **2** is significant ( $\nu(\text{C}\equiv\text{N})$  of free *t*-BuNC, 2138  $\text{cm}^{-1}$ ). To our knowledge, this is the first example of a copper–isocyanide complex exhibiting such a remarkable reduction of  $\nu(\text{C}\equiv\text{N})$ . For example,  $\nu(\text{C}\equiv\text{N})$  of *t*-BuNC·CuCl and *t*-BuNC·CuOAc<sup>7</sup> are 2189 and 2169  $\text{cm}^{-1}$ , respectively.  $h^5\text{-C}_5\text{H}_5\text{Cu}\cdot\text{CN-}t\text{-Bu}$  has a value of 2170  $\text{cm}^{-1}$ .<sup>8</sup> Thus, *t*-BuNC ligand in **2** functions as a good  $\pi$ -acceptor for copper by the aid of  $\sigma$ -donation from *tert*-butoxy ligand.

The inertness of the univalent copper–alkoxy bond toward insertions of carbon monoxide and isocyanide sharply contrasts with a high reactivity of the divalent copper–alkoxy bond.<sup>9</sup> Reduction of (*t*-BuO)<sub>2</sub>Cu with carbon monoxide and *t*-BuNC took place readily, and **1** and **2** were obtained by sublimation (eq 1 and 2).<sup>10</sup>



*t*-BuOCu·PEt<sub>3</sub> complex has been previously shown to induce an instantaneous metalation of cyclopentadiene at  $-78^\circ$  producing  $h^5\text{-C}_5\text{H}_5\text{Cu}\cdot\text{PEt}_3$ .<sup>1,8</sup> Metalation of cyclopentadiene by an equimolar amount of **2** in hexane took place at  $-15^\circ$  to give  $h^5\text{-C}_5\text{H}_5\text{Cu}\cdot\text{CN-}t\text{-Bu}$  which was isolated by sublimation in a good yield. In the case of fluorene, **2** acted as a metalation agent with concomitant insertion of isocyanide (eq 3).

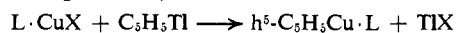


Similarly, in the presence of a tenfold excess of *t*-BuNC in benzene at  $50^\circ$ , the  $h^5\text{-C}_5\text{H}_5\text{Cu}\cdot\text{CN-}t\text{-Bu}$  complex gave an organocopper complex, *t*-BuN=CHC<sub>5</sub>H<sub>5</sub>Cu·(CN-*t*-Bu)<sub>2</sub>,<sup>11</sup> which produced *N*-cyclopentylmethyl-*tert*-butylamine (53%) on hydrogenation with Raney nickel. Interestingly, **1** effected the metalation of cyclo-

(6) F. A. Cotton and F. Zingales, *J. Amer. Chem. Soc.*, **83**, 351 (1961).

(7) T. Saegusa, I. Murase, and Y. Ito, *J. Org. Chem.*, **38**, 1753 (1973).

(8) Two general methods of preparing  $h^5\text{-C}_5\text{H}_5\text{Cu}\cdot\text{L}$  complexes (L = PR<sub>3</sub>, RNC, CO) have been reported: (a) metalation with the Cu<sub>2</sub>O–L system, e.g.,  $h^5\text{-C}_5\text{H}_5\text{Cu}\cdot\text{PEt}_3$ , G. Wilkinson and T. S. Piper, *J. Inorg. Nucl. Chem.*, **2**, 32 (1956), and  $h^5\text{-C}_5\text{H}_5\text{Cu}\cdot\text{CN-}t\text{-Bu}$ , T. Saegusa, Y. Ito, and S. Tomita, *J. Amer. Chem. Soc.*, **93**, 5656 (1971); (b) metal exchange reaction, i.e.



The present method using *t*-BuOCu·L complexes is characterized by high efficiency and mild reaction conditions.

(9) T. Saegusa, T. Tsuda, and K. Isayama, *J. Org. Chem.*, **35**, 2976 (1970).

(10) In eq 1, **1** was isolated from the reaction mixture by sublimation in a separate experiment. In eq 2, an unidentified organic product having the *t*-BuNC component was obtained.

(11) The exact structure of this complex, i.e., the nature of the copper–carbon bond ( $\sigma$  or  $\pi$  bonding) and the position of *t*-BuN=CH– group in the cyclopentadiene ring, is currently being studied.

pentadiene to give  $h^5\text{-C}_5\text{H}_5\text{Cu}\cdot\text{CO}$  complex which has previously been prepared only with difficulty.<sup>4</sup> The benzene solution resulting from **1** and a slight excess of cyclopentadiene at  $20^\circ$  for 1 hr showed only one  $\nu(\text{C}\equiv\text{O})$  of  $h^5\text{-C}_5\text{H}_5\text{Cu}\cdot\text{CO}$  at 2093  $\text{cm}^{-1}$  with the formation of *t*-BuOH (91%).<sup>12</sup>

In the metalation of cyclopentadiene using *t*-BuOCu·L complexes, variation of their activities with the ligand L (PEt<sub>3</sub> > *t*-BuNC > CO) may reasonably be explained in terms of the  $\sigma$ -donor or  $\pi$ -acceptor strength of the ligand which changes the basic strength of the *tert*-butoxy ligand. This explanation suggests that a “spectrochemical series” for  $\pi$ -bonding ligands<sup>13</sup> may be useful for the elucidation of the ligand effect in the reactions of copper complexes.

(12) Although a small amount of carbon monoxide was evolved (14%), the deposit of metallic copper was not observed. Addition of *n*-Bu<sub>3</sub>P to the reaction mixture released carbon monoxide quantitatively. At  $25^\circ$  for 30 min, the decomposition of  $h^5\text{-C}_5\text{H}_5\text{Cu}\cdot\text{CO}$  was appreciable and carbon monoxide was evolved in 25% yield.

(13) W. D. Horrocks, Jr., and R. C. Taylor, *Inorg. Chem.*, **2**, 723 (1963).

Tetsuo Tsuda, Haruo Habu  
Sadashige Horiguchi, Takeo Saegusa\*

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

Received April 27, 1974

### Heterocyclic Carbene Complexes from Trimethylgermylpentacarbonylmanganese and -rhenium. Dimer–Monomer Equilibrium and X-Ray Structure

Sir:

We recently described the conversion of trimethylgermylpentacarbonylmanganese to a carbene complex formulated on spectroscopic evidence as Me<sub>3</sub>GeMn(CO)<sub>4</sub>C(O)Me (**1**).<sup>1</sup> More detailed nmr studies of **1** have now shown that it is in equilibrium with its dimer. We present here a preliminary account of this unusual equilibrium, together with the X-ray structure of the rhenium analog of the dimer.

The 100-MHz <sup>1</sup>H nmr spectrum of **1** in CD<sub>2</sub>Cl<sub>2</sub> at ambient temperature exhibited singlets at  $\tau$  7.32 and 8.90 in the ratio of 1:2, assigned to C–CH<sub>3</sub> and Ge(CH<sub>3</sub>)<sub>2</sub>, respectively. At  $-30.5^\circ$  two singlets near  $\tau$  7.3 (total intensity 1) and two singlets near  $\tau$  8.9 (total intensity 2) were visible. The peaks near  $\tau$  7.3 were well separated (17.5 Hz) and their intensity relative to one another served as the basis for subsequent study. At this temperature, the relative intensity was strongly concentration dependent and could be quantitatively treated in terms of a dimer–monomer equilibrium, leading to the equilibrium constant  $0.92 \pm 0.10 \text{ mol l}^{-1}$  at  $-30.5^\circ$  for the process dimer = 2 monomer.<sup>2</sup> From the variation of the equilibrium constant with temperature over the range  $-70$  to

(1) M. J. Webb, R. P. Stewart, Jr., and W. A. G. Graham, *J. Organometal. Chem.*, **59**, C21 (1973).

(2) The peak at lower field increased in relative intensity as concentration increased and was accordingly assigned to the dimer. That the equilibrium involves dimer and monomer rather than tetramer and dimer (or higher species) was shown by the osmometric molecular weight of **1** in CH<sub>2</sub>Br<sub>2</sub> at conditions (11.4 mg ml<sup>-1</sup>,  $37^\circ$ ) where a negligible amount of the associated form would be present: calcd for monomeric **1**, 313; found, 318.