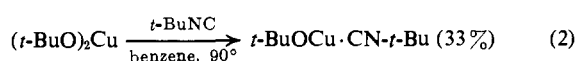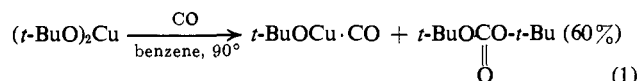upon the nature of metal.[6] The considerable lowering of $\nu(C\equiv N)$ in **2** is significant ($\nu(C\equiv N)$ of free t-BuNC, 2138 cm^{-1}). To our knowledge, this is the first example of a copper–isocyanide complex exhibiting such a remarkable reduction of $\nu(C\equiv N)$. For example, $\nu(C\equiv N)$ of t-BuNC·CuCl and t-BuNC·CuOAc[7] are 2189 and 2169 cm^{-1}, respectively. h^5-C$_5$H$_5$Cu·CN-t-Bu has a value of 2170 cm^{-1}.[8] Thus, t-BuNC ligand in **2** functions as a good π-acceptor for copper by the aid of σ-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.[9] Reduction of (t-BuO)$_2$Cu with carbon monoxide and t-BuNC took place readily, and **1** and **2** were obtained by sublimation (eq 1 and 2).[10]

$$(t\text{-BuO})_2\text{Cu} \xrightarrow[\text{benzene, 90°}]{\text{CO}} t\text{-BuOCu·CO} + t\text{-BuOCO-}t\text{-Bu (60\%)}$$
$$\underset{\text{O}}{\overset{\|}{}} \quad (1)$$

$$(t\text{-BuO})_2\text{Cu} \xrightarrow[\text{benzene, 90°}]{t\text{-BuNC}} t\text{-BuOCu·CN-}t\text{-Bu (33\%)} \quad (2)$$

t-BuOCu·PEt$_3$ complex has been previously shown to induce an instantaneous metalation of cyclopentadiene at $-78°$ producing h^5-C$_5$H$_5$Cu·PEt$_3$.[1,8] Metalation of cyclopentadiene by an equimolar amount of **2** in hexane took place at $-15°$ to give h^5-C$_5$H$_5$Cu·CN-t-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).


$\sim 100\%$
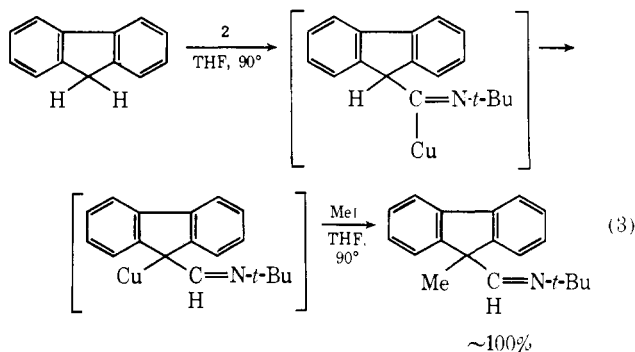
Similarly, in the presence of a tenfold excess of t-BuNC in benzene at 50°, the h^5-C$_5$H$_5$Cu·CN-t-Bu complex gave an organocopper complex, t-BuN=CHC$_5$H$_4$Cu·(CN-t-Bu)$_2$,[11] which produced N-cyclopentylmethyl-$tert$-butylamine (53%) on hydrogenation with Raney nickel. Interestingly, **1** effected 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-C$_5$H$_5$Cu·L complexes (L = PR$_3$, RNC, CO) have been reported: (a) metalation with the Cu$_2$O–L system, *e.g.*, h^5-C$_5$H$_5$Cu·PEt$_3$, G. Wilkinson and T. S. Piper, *J. Inorg. Nucl. Chem.*, **2**, 32 (1956), and h^5-C$_5$H$_5$Cu·CN-t-Bu, T. Saegusa, Y. Ito, and S. Tomita, *J. Amer. Chem. Soc.*, **93**, 5656 (1971); (b) metal exchange reaction, *i.e.*

L·CuX + C$_5$H$_5$Tl $\longrightarrow$ h^5-C$_5$H$_5$Cu·L + TlX
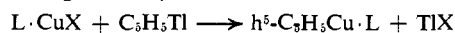
The present method using t-BuOCu·L complexes is characterized by high efficiency and mild reaction conditions.

(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 (σ or π bonding) and the position of t-BuN=CH- group in the cyclopentadiene ring, is currently being studied.

pentadiene to give h^5-C$_5$H$_5$Cu·CO complex which has previously been prepared only with difficulty.[4] The benzene solution resulting from **1** and a slight excess of cyclopentadiene at 20° for 1 hr showed only one ν (C=O) of h^5-C$_5$H$_5$Cu·CO at 2093 cm^{-1} with the formation of t-BuOH (91%).[12]

In the metalation of cyclopentadiene using t-BuOCu·L complexes, variation of their activities with the ligand L (PEt$_3$ > t-BuNC > CO) may reasonably be explained in terms of the σ-donor or π-acceptor strength of the ligand which changes the basic strength of the $tert$-butoxy ligand. This explanation suggests that a "spectrochemical series" for π-bonding ligands[13] 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$_3$P to the reaction mixture released carbon monoxide quantitatively. At 25° for 30 min, the decomposition of h^5-C$_5$H$_5$Cu·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).

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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$_2$GeMn-(CO)$_4$C(O)Me (**1**).[1] 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 ^{1}H nmr spectrum of **1** in CD$_2$Cl$_2$ at ambient temperature exhibited singlets at τ 7.32 and 8.90 in the ratio of 1:2, assigned to C–CH$_3$ and Ge-(CH$_3$)$_2$, respectively. At $-30.5°$ two singlets near τ 7.3 (total intensity 1) and two singlets near τ 8.9 (total intensity 2) were visible. The peaks near τ 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 mol l.$^{-1}$ at $-30.5°$ for the process dimer = 2 monomer.[2] 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$_2$Br$_2$ at conditions (11.4 mg ml^{-1}, 37°) where a negligible amount of the associated form would be present: calcd for monomeric **1**, 313; found, 318.
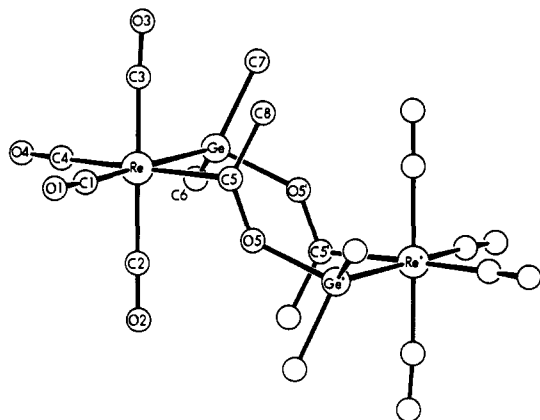
Figure 1. The molecular structure of [Me$_2$GeRe(CO)$_4$C(O)Me]$_2$.[10] Selected bond lengths (Å) are: Re–Ge = 2.591(3); Ge–O5' = 1.96(2); C5–O5 = 1.27(3); Re–C5 = 2.14(3); av Re–C(1-4) = 1.92(3); av C(1-4)–O(1-4) = 1.15 (3). Selected bond angles (deg) are: Re–C5–C8 = 111 (2); Re–C5–O5 = 121 (2); C8–C5–O5 = 128 (2); Ge–O5'–C5' = 139 (2), Ge–Re–C5 = 82.8 (6); Re–Ge–O5' = 107.6 (4).

−25°, thermodynamic parameters for this process were determined to be $\Delta H° = 6.7 \pm 0.3$ kcal and $\Delta S° = 27.9 \pm 1.4$ eu.[3]

The ^{13}C nmr spectrum in CDCl$_3$ at −30° confirmed the presence of two distinct species in solution. Particularly noteworthy were two peaks at −337.72 and −335.20 ppm, relative to TMS, which established that both species contained carbene carbon atoms.[4]

It has not been possible to obtain crystals of 1 suitable for crystallographic study. We therefore prepared the rhenium analog[5] of 1 and have been able to obtain satisfactory crystals of it despite its lesser stability in solution.[6]

The X-ray diffraction study showed that the crystals contained the dimer rather than the monomer.[7] The crystals exhibited twinning and the apparent space group and unit cell were determined to be $I2/m$, $a = 9.639(8)$ Å, $b = 11.504(9)$ Å, $c = 11.140(9)$, Å, and $\beta = 97.22 (1)°$. This cell is a composite of two orientations of a triclinic cell with space group $P\bar{1}$ and approximate dimensions $a \simeq b = 9.05$ Å, $c = 9.63$ Å, $\alpha = 106.9°$, $\beta = 118.0°$, and $\gamma = 101.0°$. The density was measured by flotation as 2.37(2) g cm^{-3} and is in reasonable agreement with the calculated value 2.40 g cm^{-3} (assuming a molecular weight of 887.7 and two molecules in the $I2/m$ cell). Intensity data were collected on an automatic Picker four-circle diffractometer within the angular limits $0 < 2\theta \le 45°, 0 \le \phi < 360°$, $-90° \le \chi \le 90°$ using Mo Kα radiation. The data

were corrected for absorption effects ($\mu = 130$ cm^{-1}) and merged to give 692 significant observations.

The structure was solved and refined by conventional methods and has refined to an R factor of 0.039.[8] The symmetry of the dimer is C_i but the twinning introduces a mirror plane and the composite of the two interpenetrating images (each of occupancy 0.5) has symmetry C_{2h} and is consistent with two molecules in the apparent $I2/m$ cell. The twinning appears to be similar to that described for Co$_4$(CO)$_{12}$.[9] The electron density peaks due to the different half-weight images were well resolved in the important central region and assignment of bonds (i.e., image separation) was straightforward once the dimeric nature of the molecule was recognized.

The molecular structure of [Me$_2$GeRe(CO)$_4$C(O)Me]$_2$ is shown in Figure 1.[10] The molecule contains an unusual eight-membered, heterocyclic ring of rhenium, germanium, oxygen, and carbon atoms. Selected bond lengths and angles are given in the caption to Figure 1. Of particular interest are the planarity of the carbene carbon atoms and the three attached groups and the rather long germanium–oxygen distance, which may result from the strong interaction between the oxygen and carbene carbon.

The structure provides excellent support for the dimer–monomer equilibrium described above, as well as suggesting that the four-membered heterocyclic structure earlier proposed[1] for the monomeric form of 1 is correct.

(3) At the concentration used in the variable temperature study (52.8 mg ml^{-1}), the dimer peak above −25° was of low and not easily measurable intensity and decreased to zero before ambient temperature was reached. This was not a process of peak coalescence. Furthermore, dimer would not be detected at dilutions normally used in infrared spectroscopy.

(4) G. M. Bodner, S. B. Kahl, K. Bork, B. N. Storhoff, J. E. Wuller, and L. J. Todd, *Inorg. Chem.*, 12, 1071 (1973).

(5) This complex has been characterized by analysis and spectroscopy.

(6) Crystals were grown by vigorously bubbling nitrogen through a dichloromethane–n-heptane solution to the point of turbidity, followed by cooling to −15°.

(7) The mass spectrum of this dimeric species shows only peaks due to the monomeric form. On this basis, the mass spectra of 1 and its diphenyl analog,[1] which also show only monomer, would be consistent with a dimeric solid form for these compounds although a monomeric solid cannot be ruled out.

(8) Refinement was carried out in $I2/m$. The space group $P1$ was also used varying the relative weights of the two components but essentially refined to equal weights, which is the $I2/m$ solution.

(9) C. H. Wei, *Inorg. Chem.*, 8, 2384 (1969).

(10) See paragraph at end of paper regarding microfilm material.

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Chirality in Polyisocyanides

Sir:

It has been suggested[1-3] from Stuart models that the backbone of polyisocyanides (1) has the conformation of a tightly coiled helix. In particular this would be

(1) (a) R. J. M. Nolte, R. W. Stephany, and W. Drenth, *Recl. Trav. Chim. Pays-Bas*, 92, 83 (1973); (b) R. J. M. Nolte, Ph.D. Thesis, University of Utrecht, 1973.

(2) F. Millich and R. G. Sinclair, *J. Polym. Sci., Part C*, 22, 33 (1968).

(3) F. Millich and G. K. Baker, *Macromolecules*, 2, 122 (1969).