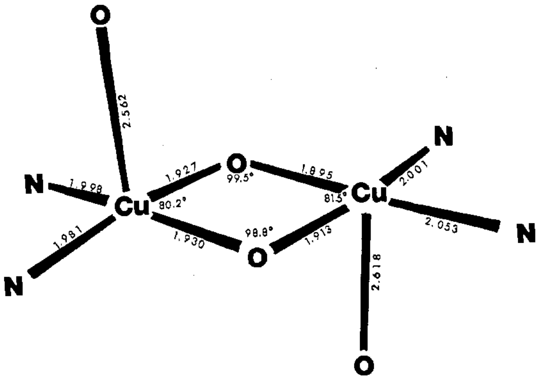

Figure 3.—A view of the coordination around the copper atoms in $[Cu(EAEP)OH]_2(ClO_4)_2$.

$(H_\perp)_1$ is not observed if D is greater than $h\nu$. A graph illustrating the angular dependence of the calculated resonance positions is included in Figure 2. All transitions predicted with the fitted parameters are included.[12] The very broad magnetic field range spanned by this spectrum is characteristic of dimeric copper complexes with large zero-field splittings. These include copper(II) acetate monohydrate,[13,14] copper propionate monohydrate,[15] and several copper benzoates.[16]

Discussion

A complete X-ray structural determination (R factor on $F = 0.042$)[17] has shown that $[Cu(EAEP)OH]_2(ClO_4)_2$ is dimeric consisting of two copper-centered, distorted square pyramids with a shared basal plane edge as represented in Figure 3. The basal plane is made up of two cis hydroxo bridges and the two nitrogen atoms of the EAEP ligand with the fifth coordination site occupied by a perchlorate oxygen at a distance of about 2.6 Å. The angles of the two Cu–O–Cu bridges are approximately 98.8 and 99.5°. The copper and oxygen atoms are approximately coplanar with a Cu–Cu distance of 2.92 Å.

The copper(II) environment found here is similar to those found in di-μ-hydroxo-bis(N,N,N',N'-tetramethylethylenediamine)dicopper(II) bromide (hereafter the ligand is abbreviated as tmen)[18] and di-μ-hydroxo-bis(bipyridyl)dicopper(II) sulfate pentahydrate.[4] The main differences among these complexes are found in the geometric arrangement at the bridging oxygen atoms. In these three complexes, the Cu–O–Cu bridge angles are 97 (bipyridyl), 99 (EAEP), and 104° (tmen). Another structural difference is in the angle between the two basal planes. In both the EAEP and the tmen complexes, the planes are nearly coplanar while in the bipyridyl complex the dihedral angle between the planes is 7.9°. The copper–copper internuclear separations are 2.89 (bipyridyl), 2.92 (EAEP), and 3.00 Å (tmen).

Magnetically, great differences are found among these complexes. An antiferromagnetic interaction giving a singlet–triplet energy separation of 130 cm^{-1} is found in the EAEP complex, whereas the tmen[19] complex has been reported to have $2J = -509$ cm^{-1}. Even more striking is the fact that the data for the bipyridyl complex have been interpreted to indicate a ferromagnetic interaction resulting a triplet ground state with a singlet state about 48 cm^{-1} above it.[5] Since the gross structural features of these three complexes are not radically different, it appears that the magnetic properties may be quite sensitive to minor bridge angle changes. It is postulated that, since the bridge bonding arrangement consists of hybrid oxygen orbitals, the M–O–M angle reflects the amount of s orbital character and that when this contribution is small, the exchange interaction is ferromagnetic. As the amount of s character increases, the interaction ultimately becomes antiferromagnetic. It is further suggested that the magnitude of the interaction, whether ferromagnetic or antiferromagnetic, is a function of the electron density at the bridging oxygen. McWhinnie[20] has shown in his investigation of the alkoxo-bridged complexes of the general formula $[(2\text{-}NH_2py)_2Cu(OR)]_2(NO_3)_2$, where R = H, methyl, or ethyl, that the room-temperature magnetic moments are 1.49, 0.95, and 0.70 BM, respectively. As more electron density is available to the oxygen bridge, the pathway for the antiferromagnetic interaction is enhanced. Similar results obtain in systems in which the hydroxo bridge is hydrogen bonded, thus also altering the oxygen electron density.[21] It seems possible that hydrogen bonding can account, in part, for the difference in magnitude of the interaction between the EAEP and the tmen complexes; it is probable that the hydrogen bonding to a bromide anion found in the tmen complex is stronger than any such bonding to perchlorate which could exist in the EAEP complex.

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Reactions of Carboxamido Complexes with Halogens and Mercuric Chloride

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Transition metal–alkyl bonds may be cleaved by halogens, *e.g.*

$$C_5H_5Fe(CO)_2R + X_2 \longrightarrow C_5H_5Fe(CO)_2X + XR \qquad (1)$$

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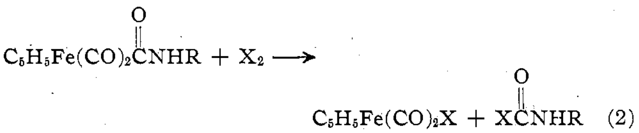
[1] Fellow of the Alfred P. Sloan Foundation, 1970–1972.

to form the corresponding metal halide and alkyl halide.[2] In our studies of carboxamido complexes,[3] it was of interest to determine whether the metal–carbon bond in these derivatives also could be cleaved by halogens. In this reaction, the cleavage may be followed by other reactions due to the reactivity of the initial products



$$C_5H_5Fe(CO)_2\overset{O}{\overset{\|}{C}}NHR + X_2 \longrightarrow C_5H_5Fe(CO)_2X + X\overset{O}{\overset{\|}{C}}NHR \quad (2)$$

$$XC(O)NHR \longrightarrow HX + RNCO \quad (3)$$

$$C_5H_5Fe(CO)_2CONHR + 2HX \longrightarrow [C_5H_5Fe(CO)_3]X + [RNH_3]X \quad (4)$$

Hence the carbamoyl halide formed in eq 2 may decompose[4] to the alkyl isocyanate and hydrogen halide according to eq 3. The hydrogen halide may then react with the starting carboxamido complex according to a known reaction[5] (eq 4) to yield $C_5H_5Fe(CO)_3^+$. Indeed the reaction of $C_5H_5Fe(CO)_2CONHR$ with halogens appears to proceed according to this series of equations. Mercuric chloride reacts in a very similar fashion.

Results and Discussion

Reaction with Halogens.—The carboxamido complex $C_5H_5Fe(CO)_2CONHCH_3$ reacts quantitatively with Br_2 according to the equation

$$3C_5H_5Fe(CO)_2CONHCH_3 + 2Br_2 \longrightarrow 2C_5H_5Fe(CO)_2Br + [C_5H_5Fe(CO)_3]Br + 2CH_3NCO + [CH_3NH_3]Br \quad (5)$$

The products have been isolated and identified. That it is quantitative was established from the reaction of 0.195 mmol of $C_5H_5Fe(CO)_2CONHCH_3$ with 0.140 mmol of Br_2 in CD_3CN solvent in an nmr tube. Spectral data for the reactants and products are given in Table I. The ratio of intensities for $C_5H_5Fe(CO)_2Br$:$[C_5H_5Fe(CO)_3]Br$:CH_3NCO was found to be 10:5.3:5.7. This compares with a calculated ratio (from eq 5) of 10:5:6. No other proton-containing products were observed. The $[CH_3NH_3]Br$ precipitates from solution and is not seen in the nmr spectrum.

TABLE I
^{1}H NMR DATA[a]

Compd	τ	
	C_5H_5	CH_3
$C_5H_5Fe(CO)_2CONHCH_3$[b]	5.13	7.43[c]
$[C_5H_5Fe(CO)_3]PF_6$	4.34	
$C_5H_5Fe(CO)_2Br$	4.97	
$C_5H_5Fe(CO)_2HgCl$	5.02	
CH_3NCO		7.07
$(CH_3NH)_2CO$		7.38[d]

[a] In acetonitrile-d_3 solvent at room temperature, using tetramethylsilane as the internal standard. [b] NH proton at τ 4.2 (broad). [c] Doublet, J_{HCNH} = 5 Hz. [d] NH proton at τ 4.7.

The cyclohexyl analog, $C_5H_5Fe(CO)_2CONHC_6H_{11}$, reacts with I_2 in a similar manner. These reactions presumably follow the mechanism outlined in eq 2–4. It should be emphasized, however, that these results do not rule out a path involving initial formation of an *N*-halocarboxamido group such as occurs in the reaction of organic amides with halogens.[6]

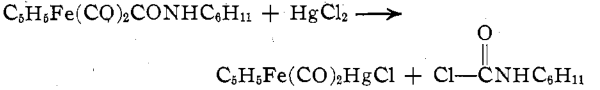
The reaction of $C_5H_5Fe(CO)_2CONHC_6H_{11}$ with Cl_2 appeared to proceed in much the same manner except that much of the carboxamido complex did not react and other unidentified products were also produced.

Although perfluoroalkyl iodides are known[7] to react with low-valent metals in the same way as I_2, there was no perceptible reaction of $C_5H_5Fe(CO)_2CONHC_6H_{11}$ with *n*-heptafluoropropyl iodide at room temperature over a period of 18 hr. Likewise, there was no reaction with methyl iodide under the same conditions. The tertiary carboxamido complex $Hg[CON(C_2H_5)_2]_2$ previously[8] had been reported to yield $BrC(O)N(C_2H_5)_2$ on reaction with bromine.

Reaction with $HgCl_2$.—The reaction of the cyclohexyl carboxamido complex with $HgCl_2$ proceeds according to the equation

$$3C_5H_5Fe(CO)_2CONHC_6H_{11} + 2HgCl_2 \longrightarrow 2C_5H_5Fe(CO)_2HgCl + [C_5H_5Fe(CO)_3]Cl + 2C_6H_{11}NCO + [C_6H_{11}NH_3]Cl \quad (6)$$

The carbonyl-containing products have been isolated and identified. This reaction probably proceeds by a mechanism similar to that suggested for the halogen reactions. In this case the initial step would involve cleavage of the Fe–C bond as in



$$C_5H_5Fe(CO)_2CONHC_6H_{11} + HgCl_2 \longrightarrow C_5H_5Fe(CO)_2HgCl + Cl\text{—}\overset{O}{\overset{\|}{C}}NHC_6H_{11} \quad (7)$$

The resulting carbamoyl chloride would then react as outlined in eq 3 and 4.

Previously Fukuoka, Ryang, and Tsutsumi[9] reported the reaction of $HgCl_2$ with the unstable carboxamido complex $Ni(CO)_3CON(CH_3)_2^-$, generated, *in situ*, by the reaction of $Ni(CO)_4$ and $LiN(CH_3)_2$. The predominant products were $(CH_3)_2N(O)CC(O)N(CH_3)_2$ (*N,N,N′,N′*-tetramethyloxamide), mercury, and LiCl.

Experimental Section

Materials.—The complex $[C_5H_5Fe(CO)_3]PF_6$ was prepared either from $C_5H_5Fe(CO)_2Cl$ and CO with $AlCl_3$[3] or from $C_5H_5Fe(CO)_2^-$ and $ClC(O)OC_2H_5$.[5] The previously described[5] synthesis of $C_5H_5Fe(CO)_2CONHCH_3$ was used to obtain this compound. All reactions were carried out under a nitrogen atmosphere.

$C_5H_5Fe(CO)_2CONHC_6H_{11}$.—A suspension of 6.02 g (17.2 mmol) of $[C_5H_5Fe(CO)_3]PF_6$ in 100 ml of dry diethyl ether was treated with 7.8 g (78.8 mmol) of cyclohexylamine. The colorless solution turned yellow and an orange-yellow oil formed. After removing the solvent under vacuum, the yellow oily residue was washed successively with 80 ml, 40 ml, and finally two 25-ml aliquots of water. The remaining yellow powder was extracted with two 150-ml aliquots of warm ether. On cooling at −20°, 1.75 g (5.8 mmol) of pure yellow crystalline product (mp 116–117°) was obtained. *Anal.* Calcd for $C_5H_5Fe(CO)_2CONHC_6H_{11}$: C, 55.5; H, 5.65; N, 4.62. Found: C, 55.5; H, 6.00; N, 4.61. Its infrared spectrum in heptane solution showed ν(C–O) absorptions at 2032 (s), 1971 (vs), and 1635 (m) cm^{-1}.

Reaction of $C_5H_5Fe(CO)_2CONHCH_3$ with Br_2.—A suspension of 1.40 g (5.97 mmol) of $C_5H_5Fe(CO)_2CONHCH_3$ in 45 ml of

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pentane was treated with 1.12 g (7.0 mmol) of bromine dissolved in pentane. The reaction mixture changed from yellow to orange to red; the infrared spectrum of the red solution showed absorptions for CH_3NCO (2320 (m), 2295 (vs), and 2260 (s) cm^{-1}) and $C_5H_5Fe(CO)_2Br$ (2055 (vs) and 2015 (s) cm^{-1}). The $[C_5H_5Fe(CO)_3]Br$ was insoluble and was, therefore, not seen in the solution spectrum. Under reduced pressure, pentane and CH_3NCO were distilled from the mixture. The presence of the CH_3NCO in the distillate was further confirmed by addition of excess CH_3NH_2 to the solution to yield a white flaky precipitate of $(CH_3NH)_2CO$. This was purified by sublimation under vacuum to give 0.13 g (1.48 mmol) of $(CH_3NH)_2CO$, mp 99–100°. Its proton nmr spectrum in $CDCl_3$ showed a doublet at τ 7.25 (J_{HCNH} = 5 Hz) and a broad N–H absorption at τ 4.45 in a 3:1 intensity ratio.

The residue remaining after the pentane–CH_3NCO distillation was extracted with several aliquots of warm pentane; these were cooled at −20° to give 0.59 g (2.3 mmol) of red crystalline $C_5H_5Fe(CO)_2Br$, identified by its infrared spectrum. The pentane-insoluble residue was treated with excess NH_4PF_6 in 4 ml of water. The solid was filtered off and dried under vacuum. Several washings of the solid with ether removed additional $C_5H_5Fe(CO)_2Br$ (0.47 mmol) which had apparently formed from the reaction of $C_5H_5Fe(CO)_3^+$ with Br^- in water. (In CH_2Cl_2 solvent, we have observed that this reaction does occur.) The remaining yellow powder (0.42 g, 1.20 mmol) was identified as $[C_5H_5Fe(CO)_3]PF_6$ by its infrared spectrum (2120 (s) and 2070 (vs, br) cm^{-1} in KBr).

Reaction of $C_5H_5Fe(CO)_2CONHC_6H_{11}$ with I_2.—This reaction was very similar to that given above and no attempt was made to determine product yields. To a suspension of 0.62 g (2.04 mmol) of $C_5H_5Fe(CO)_2CONHC_6H_{11}$ in 45 ml of hexane was added 0.52 g (2.04 mmol) of I_2. On stirring at room temperature, the solution turned from yellow to black. The infrared spectrum of the solution showed absorptions for $C_6H_{11}NCO$ (2255 cm^{-1}) and $C_5H_5Fe(CO)_2I$ (2040 (s) and 1998 (s) cm^{-1}).

The $C_6H_{11}NCO$ and solvent were distilled off under vacuum. On treatment with CH_3NH_2, the white flaky $C_6H_{11}NHC(O)NHCH_3$ (3330 (s), 2925 (m), 2850 (w), 1620 (vs), and 1580 (s) cm^{-1} in KBr) precipitated.

The black residue from the distillation was extracted with several 60-ml aliquots of warm pentane until the $C_5H_5Fe(CO)_2I$ was completely removed. The orange residue remaining consisted of a mixture of $[C_5H_5Fe(CO)_3]I$ (2115 (s) and 2070 (vs) cm^{-1} in CH_2Cl_2) and $[C_6H_{11}NH_3]I$. The infrared spectrum of $[C_5H_5Fe(CO)_3]I$ in CH_2Cl_2 changed with time to give $C_5H_5Fe(CO)_2I$.

Reaction of $C_5H_5Fe(CO)_2CONHC_6H_{11}$ with $HgCl_2$.—To an ether solution of 0.68 g (2.24 mmol) of $C_5H_5Fe(CO)_2CONHC_6H_{11}$ at −78° was added 0.62 g (2.30 mmol) of $HgCl_2$. The mixture was warmed to near reflux with stirring, during which time a fine white material precipitated. After 1 hr the ether was removed at reduced pressure, leaving a pale yellow solid. The ether distillate contained $C_6H_{11}NCO$, which was identified by treating it with excess CH_3NH_2 to give $C_6H_{11}NHC(O)NHCH_3$; its infrared spectrum in KBr pellet was identical with that reported in the previous section.

Approximately 60 mg of unreacted $C_5H_5Fe(CO)_2CONHC_6H_{11}$ was extracted with hexane from the pale yellow solid. The hexane-insoluble residue in CH_2Cl_2 solution showed terminal C–O absorptions due to only $[C_5H_5Fe(CO)_3]Cl$ and $C_5H_5Fe(CO)_2HgCl$. The latter compound was extracted from the solid with 120 ml of warm ether. On reducing the volume to 60 ml and cooling at −20° overnight, 0.13 g (0.31 mmol) of yellow crystalline $C_5H_5Fe(CO)_2HgCl$ separated from solution; its infrared spectrum in CH_2Cl_2 solution (2020 (s) and 1974 (s) cm^{-1}) was identical with that previously reported for this compound.[10] Additional $C_5H_5Fe(CO)_2HgCl$ was extracted with several 60-ml aliquots of warm ether until the ether was colorless. The residue (0.45 g) showed infrared absorptions (2120 (s) and 2060 (vs) cm^{-1}) characteristic of $[C_5H_5Fe(CO)_3]Cl$; it also contained $[C_6H_{11}NH_3]Cl$.

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Chemical Studies of *closo*-1,5-Dicarbapentaborane(5)

BY ANTON B. BURG* AND THOMAS J. REILLY

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Since the discovery of the carborane 1,5-$C_2B_3H_5$,[1] there has been virtually no further report of its chemical behavior. A generous gift of mixed light carboranes from Drs. R. E. Williams and J. Ditter (Chemical Systems, Inc., Santa Ana, Calif. 92705) has made it possible for us to isolate enough of this carborane for extensive laboratory studies.

The trigonal-bipyramidal structure of $C_2B_3H_5$ is such that the electron pair in the A_1 molecular orbital would be less delocalized, and the E-type orbitals would be constructed of more seriously bent atomic orbitals, than in larger carboranes. Thus only a seriously "strained" and thermodynamically unstable electronic situation seems possible. Indeed, the metastability of liquid $C_2B_3H_5$ is demonstrated by its slow room-temperature conversion to yellow-brown solids—possibly by the catalytic effect of impurities. Also, $C_2B_3H_5$, $C_2B_4H_6$, and $C_2B_5H_7$, passed as vapors at minimal pressure through a 13.56-Mc electrodeless discharge (in a quartz tube) or as solids bombarded by atomic hydrogen, are partially destroyed, forming only nonvolatile products. These range from pure white solids, which are partially soluble in or reactive to acetone or methanol, to brown glassy films inert to strong oxidizers. Thus even $C_2B_4H_6$ or $C_2B_5H_7$ must be regarded as metastable, although more enduring than $C_2B_3H_5$.

The kinetic stability of such carboranes may be ascribed to their cage structures and high electronic symmetry. The present results indicate that the 1,5-$C_2B_3H_5$ skeleton becomes unstable when its electronic symmetry is seriously disturbed.

For example, a solid 1:1 trimethylamine adduct of $C_2B_3H_5$ exists at low temperatures, but when it begins to melt, there is rapid conversion to intractable polymeric material, with no formation of hydrogen or other volatiles. Similar instability appears when halogenation or NO_2 oxidation of $C_2B_3H_5$ is tried.

On the other hand, substitution derivatives lacking polarity seem stable. The suggested 2,3-dimethyl-1,5-dicarbapentaborane (5)[2] would be in this class, and the same argument applies to the methyl derivatives of 1,2-$C_2B_3H_5$.[2,3] The principle is more fully illustrated by our new B–B connected dicarborane $C_4B_6H_8$ and a *B*-1-propenyl derivative made from 1,5-$C_2B_3H_5$ and propyne.

The Trimethylamine Adduct.—An electron-acceptor action (presumably through boron) is indicated by the clean formation of the adduct $C_2B_3H_5 \cdot N(CH_3)_3$ at −78°. In a stopcocked tube on the high-vacuum

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