as metal–enzyme systems and catalysts, if the intensity is compared with those measured on appropriate reference compounds by using the same monochromator.

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Characterization of Matrix-Isolated Cu(CO)Cl. IR Spectroscopic Investigation and ab Initio Calculation

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Cocondensation of CuCl and CO in an argon matrix leads to new IR absorptions near 2157 and 362 cm^{-1}, which are assigned to a linear molecule Cl–Cu–CO. By means of large-scale ab initio calculations (CPF, MP2) the CuC distance is predicted to be 181 pm (CPF) and the reaction energy of CuCl + CO → ClCu–CO is reported to be 155 kJ mol^{-1} exothermic (CPF). Bonding in this complex is discussed. The CuC bond is found to be formed by predominant σ-bonding from carbon to copper while $d\pi^*$-back-donation from Cu to C plays a minor role.

Solutions of copper(I) chloride in hydrochloric acid are known to absorb CO.[1] Until recently, all attempts failed to isolate a well-defined solid containing CuCl and CO from these solutions or from similarly treated solutions of CuCl in organic solvents, e.g. THF or methanol.[2] In 1990, a simple preparation and structural characterization of solid Cu(CO)Cl was reported.[3] In this solid, copper was found to be tetrahedrally coordinated by three chlorine atoms and the CO ligand. This type of bonding differs from that of gold in Au(CO)Cl, a molecule that has been shown to be linear in the solid state.[4]

The purpose of this paper is to describe our investigations on the products of the reaction of monomeric copper(I) chloride with CO in solid argon by means of IR spectroscopy and ab initio calculations. It is shown that experimental findings are in good agreement with data expected for a linear molecule Cu(CO)Cl.

Experimental Results

After cocondensation of monomeric CuCl[5] and CO in an argon matrix,[6] three additional absorptions at 2156.5, 361.6, and 356.1 cm^{-1} arise. They cannot be observed in experiments performed with one of the reactants only. Using isotopically substituted CO, $^{13}C^{16}O$ and/or $^{12}C^{18}O$, shifts in frequencies for these three bands have been detected as documented in Table I and Figure 1.

The absorptions in the CO region of the IR spectra only show isotopic shifts for ^{13}C- and ^{18}O-substitution; no chlorine or copper splitting can be observed. For this reason, the band at 2156.5 cm^{-1} is assigned to a fairly uncoupled CO vibration (ν_{CO}) of the species under investigation. The absorptions at 361.6 and 356.1 cm^{-1} exhibit an intensity pattern expected for a $^{35}Cl/^{37}Cl$ splitting.[7] As these bands are also shifted by ^{13}C- and ^{18}O-substitution, they must be assigned to a highly coupled mode in the observed molecule, called $\nu_{ClCu/CuCO}$ in the following text.[8] Even at very low concentrations of CuCl or CO in the matrix, the bands just described are detected. Thus, it is plausible to assign the observed absorptions to a species Cu(CO)Cl formed by reaction of monomeric CuCl with one molecule of CO.

Normal-Coordinate Analysis

In order to interpret the observed IR absorptions in terms of bond strengths, we performed a normal-coordinate analysis on the molecule Cu(CO)Cl with $C_{\infty v}$ symmetry. As all detectable frequencies belong to the irreducible representation Σ^+, vibrations of this symmetry type have been considered only. We assume that there is no change in the CuCl bond during complexation; therefore, the force constant of uncoordinated monomeric CuCl[9] has been inserted for f_{CuCl} in Cu(CO)Cl. The observed isotopic shifts have been corrected with respect to anharmonicity.[10] Together with the calculated shifts, these values are collected in Table II, exhibiting good agreement with each other.

Table I. IR Absorptions Assigned to Cu(CO)Cl (cm^{-1})

	ν_{CO}	$\nu_{^{35}Cl-Cu-CO}$	$\nu_{^{37}Cl-Cu-CO}$
Cu($^{12}C^{16}O$)Cl	2156.5	361.6	356.1
Cu($^{13}C^{16}O$)Cl	2107.4	358.7	353.9
Cu($^{12}C^{18}O$)Cl	2107.8	355.8	350.0

Table II. Results of the Normal-Coordinate Analysis for Cu(CO)Cl[a]

	$\Delta\nu_{CO}$	$\Delta\nu_{ClCu/CuCO}$	$\Delta\nu_{^{35}Cl/^{37}Cl}$
Cu($^{12}C^{16}O$)Cl			5.53 (5.50)
Cu($^{13}C^{16}O$)Cl	49.98 (49.78)	2.66 (2.91)	5.42 (4.86)
Cu($^{12}C^{18}O$)Cl	49.18 (49.30)	5.79 (5.82)	5.26 (5.83)

[a] Force constants: f_{CuCl} = 2.34 mdyn/Å; f_{CuC} = 2.35 mdyn/Å; f_{CO} = 18.59 mdyn/Å; $f_{CuCl/CuC}$ = 0.1 mdyn/Å; $f_{CuC/CO}$ = 0.5 mdyn/Å; $f_{CuCl/CO}$ = 0.0 mdyn/Å.

The force constant for the CuC bond (f_{CuC} = 2.35 mdyn/Å) is found to be of the magnitude of that for the CuCl bond (f_{CuCl} = 2.34 mdyn/Å) in monomeric CuCl. This value of f_{CuC} is low

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(7) According to the simple model of two vibrating masses, the absorption of a copper–chlorine vibration ($\nu \approx$ 360 cm^{-1}) should exhibit a $^{35/37}Cl$ splitting of about 6.3 cm^{-1}.

(8) According to normal-coordinate analysis and ab initio calculations, the vibration $\nu_{ClCu/CuCO}$ corresponds to an in-phase motion of chlorine versus copper on one hand and of the CO group versus copper on the other hand.

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Table III. Results of the ab Initio Calculations for CO and CuCl Compared to the Experimental Values

	d, pm				ω_0, cm^{-1}			
	CPF	MP2	MOD[a]	exp	CPF	MP2	MOD[a]	exp
CuCl	207.8	205.8	207.4	205.1	412.5	420.3	397.7	415.3
CO	112.8	113.4		112.8	2207.9	2133.1		2169.8

[a] Calculations on MP2 level with reduced basis set on copper.[16]

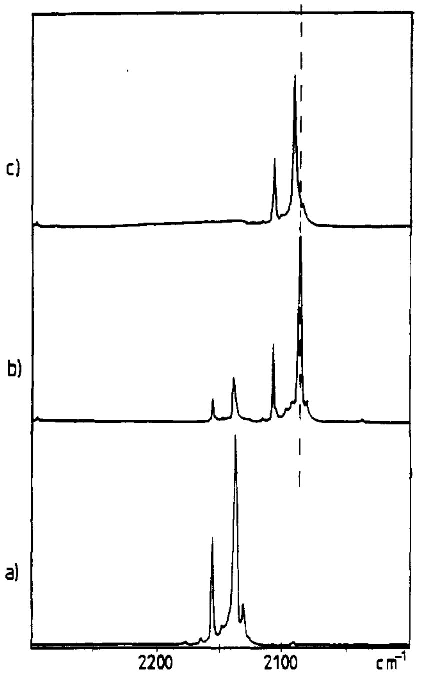

Figure 1. IR spectra after cocondensation of CO and CuCl in an argon matrix: (a) $^{12}C^{16}O$; (b) $^{12}C^{18}O$ (with impurities of $^{12}C^{16}O$); (c) $^{13}C^{16}O$.

compared to that of other metal–carbon force constants calculated for metal ion–CO complexes ([Au(CO)Cl], 2.55 mdyn/Å; [$PtCl_2(CO)_2$], 3.06 mdyn/Å; [$PtBr_2(CO)_2$], 2.93 mdyn/Å).[11] The weak CuC bond may be described as a consequence of predominant charge transfer from the HOMO of isolated CO to the copper center and only poor back-donation of charge density from the d^{10} copper(I) into π^*-type orbitals at CO (v.i.). As the HOMO at CO is known to be of antibonding character,[12] it is not surprising to find a higher value for f_{CO} in Cu(CO)Cl than in uncoordinated CO itself (f_{CO} in CO 18.47 mdyn/Å).

In this model of bonding, the ligand CO in Cu(CO)Cl tends to become CO^+ when coordinated to CuCl. As the ionization of CO is reported to raise the frequency (ω_0) of the CO vibration from 2169 to 2214 cm^{-1},[13] the observed blue-shift for ν_{CO} in matrix-isolated Cu(CO)Cl compared to that of matrix-isolated CO (CO, ν_{CO} = 2138 cm^{-1}; Cu(CO)Cl, ν_{CO} = 2157 cm^{-1}) is plausible.

This view of bonding in Cu(CO)Cl is supported by the high value for the interaction force constant $f_{CuC/CO}$. It is as high as in $Cu(N_2)Cl$[14] and indicates the close correlation between the bond strengths of the CuC and CO bonds. Shortening the CuC bond during vibration will cause an extended overlap between π-type d orbitals at the copper center with antibonding π^* orbitals at the ligand, which will tend to weaken the CO bond.

Table IV. Results of the ab Initio Calculations for Cu(CO)Cl and Cu(OC)Cl

	Cu(CO)Cl			Cu(OC)Cl		
	CPF	MP2	MOD[a]	CPF	MP2	MOD[a]
d(CuCl), pm	207.0	204.7	205.3	207.0	204.1	205.7
d(CuC), pm	180.7	175.0	169.9			
d(CuO), pm				194.4	191.0	187.5
d(CO), pm	112.8	113.7	113.5	113.6	113.9	113.7

[a] Calculations on MP2 level with reduced basis set on copper.[16]

Table V. Calculated Harmonic Frequencies and IR Intensities (MOD[a]) of Cu(CO)Cl and Cu(OC)Cl

	Cu(CO)Cl		Cu(OC)Cl	
irrep	ν, cm^{-1}	I_{rel}	ν, cm^{-1}	I_{rel}
Π	103	2	93	18
Σ^+	389	12	288	12
Π	442	<1	233	1
Σ^+	580	3	467	29
Σ^+	2144	100	2118	100

[a] Calculations on MP2 level with reduced basis set on copper.[16]

Quantum-Chemical Calculations

For the sake of better insight into the bonding properties, energetics of the complexation reactions, and geometry, ab initio calculations for CuCl, CO, and their reaction products have been carried out using the CPF and MP2 methods.[15,16]

To judge the reliability of the methods and basis sets used, the data calculated for the isolated species CuCl and CO are presented in Table III. These results indicate a somewhat fortuitous error cancellation of the MP2-level calculations in which relativistic effects are neglected.[17] The MP2 results obtained with the smaller basis set (denoted as MOD) still provide reasonable accuracy.

According to the results of the calculations with a reduced basis set at the copper atom,[18] the two most stable isomers have been investigated using extended basis sets: a molecule Cu(CO)Cl with CO coordinated to copper via the C atom ($C_{\infty v}$ symmetry) and Cu(OC)Cl with the ligand oxygen-coordinated to the copper atom ($C_{\infty v}$ symmetry).

For both isomers investigated, geometrical data are collected in Table IV. Since there are pronounced effects of electron correlation,[17] we have not documented SCF results, which differ markedly from those of CPF and MP2. With regard to the results of the calculations using a reduced basis set at the copper atom

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(16) CPF calculations have been carried out with the following basis sets: relativistic pseudopotentials at the copper atom[17] (Ne core) (8s7p6d2f)/[6,5,3,2]; at chlorine (12s2p2d1f)/[7,5,2,1]; and at carbon and oxygene (10s6p2d1f)/[6,4,2,1]. The s,p sets were contractions of Huzinaga's primitive sets;[23] the exponents of the polarization functions were as follows: Cu 4.962, 1.221; Cl 1.0, 0.32, 0.78; C 1.5822, 0.4371, 0.9642; O 2.4722, 0.6829, 1.5066. Basis sets for calculations on the MP2 level of theory: copper (14s11p6d3f)/[8,6,4,2]; chlorine (12s9p2d)/[7,5,2]; carbon (9s5p2d)/[5,3,2]; oxygen (9s5p2d)/[5,3,2]. In order to reduce computation time and file space needed to obtain harmonic frequencies, additional computations using a smaller basis set at the copper atom have been performed: model potential at copper (Ne core + 3s) (6s4p5d3f)/[2,2,2,2] referred to as MOD in all tables. Sakai, Y.; Miyoshi, E.; Klobukowski, M.; Huzinaga, S. *J. Comput. Chem.* **1987**, *8*, 226, 256.

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(18) Using the MOD basis set at the copper atom, it was possible to perform energy optimizations for a CO side-on bonded to CuCl (C_s symmetry) as well as for Cu(CO)Cl and Cu(OC)Cl. These calculations show Cu(CO)Cl to be approximately 150 kJ mol^{-1} more stable than the other isomers. The difference in energy between the remaining molecules is about 10 kJ mol^{-1}, preferring Cu(OC)Cl.

(MOD),[16] it is not surprising to find d_{CuC} and d_{CuO} much shorter than those obtained by the other calculations. This is due to the enlarged basis set extention error (BSSE),[19] which tends to shorten the bonds formed during complexation.

The results of MP2 and CPF calculations are in good agreement. Coordination of one CO ligand to the copper atom of CuCl changes neither the length of the CO bond nor that of the CuCl bond very much. On the other hand, there is a pronounced difference in the copper–ligand distance between the two complexes; coordination via the C atom brings the ligand CO more than 10 pm closer to the central atom.

The calculated distances in Cu(CO)Cl are close to the equivalent values in copper(I) carbonyl complexes obtained with X-ray methods. To give an example, for the recently characterized solid Cu(CO)Cl,[3] the CO and CuC distances are 111.2 and 185.6 pm, respectively. Because of the polymeric character of this compound, the CuCl bond is longer (d_{CuCl} = 237.0 pm) than in the monomeric species.

From the differences in total energy between isolated CuCl and CO on one side and Cu(CO)Cl and Cu(OC)Cl, respectively, on the other side, the energies for the reactions of complexation have been determined by the CPF method (values obtained by MP2 calculations are given in parentheses):

$$\mathrm{CuCl + CO \rightarrow Cu(CO)Cl + 155.2\ kJ\ mol^{-1}\ (195.6\ kJ\ mol^{-1})}$$

$$\mathrm{CuCl + CO \rightarrow Cu(OC)Cl + 49.3\ kJ\ mol^{-1}\ (53.3\ kJ\ mol^{-1})}$$

As expected, coordination of CO with the C atom is the favored process. The energy for this reaction is of the magnitude of the energy for the first coordination of a CO molecule to a nickel atom, which is found to be approximately 140 kJ mol^{-1}.[20]

Frequencies and intensities within the harmonic approximation could only be computed on the MOD level. The results are presented in Table V. Obviously, the best agreement between experiment and calculation is obtained for Cu(CO)Cl. In accordance with the experimental IR spectra, the most intense band is calculated for the CO absorption. It is shifted to higher wavenumbers compared to that of the isolated molecule CO (observed shift +19 cm^{-1}; calculated shift +11 cm^{-1}). The only other absorption ($\nu_{\mathrm{ClCu/CuCO}}$) that is predicted to be observable for Cu(CO)Cl is about 10 times weaker in intensity than the corresponding CO band. Compared to the frequency of isolated CuCl, $\nu_{\mathrm{ClCu/CuCO}}$ is calculated to be shifted to lower wavenumbers.

According to our calculations for the molecule Cu(OC)Cl, one would have expected a red-shifted CO absorption compared to that of isolated CO. A second band expected for this molecule is calculated to be 3 times weaker in intensity than the first one, which is blue-shifted with respect to that of isolated CuCl. Both predictions are in contrast to the experimental observations. Therefore, only the calculated spectra of Cu(CO)Cl provide an accurate fit with the experimental findings for both intensities and frequencies.

An analysis of the CPF wave function shows that bonding between copper and carbon in Cu(CO)Cl mainly is of the σ type. A smaller amount of π-back-bonding from d orbitals located at Cu into the π^* LUMO of CO is detectable, however. In terms of a Roby–Davidson population analysis,[21] the σ shared electron number (σ-SEN) for the CuC bond is 1.4 whereas the π-SEN is 0.1 only. This point of view of CO as a σ-donor and a weak π-acceptor is further supported by the results of a Mulliken population analysis,[22] which shows a transfer of electrons from CO to Cu in the σ-space of about 0.4 e; π-back-bonding amounts to about 0.2 e.

Conclusion

Experimental as well as theoretical results confirm the assignments to a linear molecule Cu(CO)Cl formed under cryogenic matrix isolation conditions. The CuC bond is mainly formed by electron transfer out of the σ HOMO of the ligand into d_σ orbitals of the copper atom; there is evidence for some π-back-bonding from Cu to C, which plays a minor role.

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Boron in New Environments. Structure and Reaction Properties of Discrete, Mixed-Metal, Hexanuclear Borides

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The preparation and characterization of two discrete, mixed-metal, hexanuclear transition-metal borides, *trans*-$[\mathrm{Fe_4Rh_2(CO)_{16}B}]^-$ and *mer*-$\mathrm{H_2Fe_3Rh_3(CO)_{15}B}$, are described. The former is prepared from the boride precursor, $[\mathrm{HFe_4(CO)_{12}BH}]^-$, by a cluster expansion reaction with $[\mathrm{Rh(CO)_2Cl}]_2$, while the latter forms spontaneously on protonation of *trans*-$[\mathrm{Fe_4Rh_2(CO)_{16}B}]^-$. Both have been characterized spectroscopically and crystallographically. However, *mer*-$\mathrm{H_2Fe_3Rh_3(CO)_{15}B}$ is severely disordered in the solid state, prohibiting definition of the interatomic distances of this species. Both compounds exhibit an octahedral metal framework with a centered, six-coordinate boron atom. The IR absorptions associated with the interstitial boron atom have been identified in both. The formation of *trans*-$[\mathrm{Fe_4Rh_2(CO)_{16}B}]^-$ is preceded by the formation of *cis*-$[\mathrm{Fe_4Rh_2(CO)_{16}B}]^-$, and the mechanism of the isomerization process has been investigated. Evidence is presented for a Lewis base promoted process in which rapid, reversible base coordination precedes isomerization as well as ligand substitution. The isomerization process is more rapid than ligand substitution for $\mathrm{PMe_2Ph}$ as the entering ligand.

The boron atom in mononuclear compounds is usually found with three or four nearest neighbors. This is consistent with the atomic structure of boron, the concept of a two-center–two-electron bond, and Lewis acid–base chemistry.[1] However, the fact that

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