A Complex between Isoprene and Copper(I) Chloride: Synthesis and Structural Characterization

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A polymeric complex $[Cu_2Cl_2(C_5H_8)]$ between isoprene (2-methylbutadiene) and copper(I) chloride has been prepared in ethyl vinyl ketone (1-penten-3-one), utilizing the complex between copper(I) chloride and the solvent as an in situ precursor. The structure of $[Cu_2Cl_2(C_5H_8)]$ has been determined by X-ray diffraction. The compound crystallizes in the monoclinic space group $P2_1/c$ with a = 6.934 (4), b = 16.802 (10), c = 7.198 (4) Å, β = 118.03 (3)° and Z = 4, and the structure was refined to a final R = 0.020 (R_w = 0.029) for 114 parameters and 886 observed reflections. Isoprene exhibits the s-trans conformation and bridges two copper(I) atoms through coordination involving both C=C bonds. These copper(I) atoms are further bridged by chloride, leading to the formation of layers with peripherally bound isoprene ligands. Cu–C distances range from 2.076 (5) to 2.244 (4) Å [$C(CH_3)$]. One copper(I) center exhibits tetrahedral coordination geometry while the other shows a slight trigonal pyramidal distortion. The carbon skeleton of the ligand, including the carbon atom of the methyl group, is approximately planar.

Introduction

In previous studies of π-complexes between α,β-unsaturated carbonyl compounds and copper(I) chloride, we have found evidence for a relationship between the conformation of the ligand and the mode of complexation to copper(I).[1] Most often the ligand assumes the s-trans conformation, despite the preferred conformation of the free molecule, bridging two copper(I) atoms via C=C and the carbonyl oxygen atom.[1] As an extension of this work we are attempting to prepare complexes between conjugated dienes and copper(I). Although the structures of several π-olefinic complexes of copper(I) chloride have been characterized,[2] there appear to be no examples involving conjugated dienes other than the complex with *trans*-1-cyanobutadiene in which the ligand coordinates to copper(I) via nitrogen and the 3,4 C=C bond.[3] For butadiene and its 2-methyl substituted analogue, isoprene, the s-trans conformation is the more stable for the free ligand.[4] On complexation to metal centers, the s-cis conformation and the tetrahapto bonding mode is that, however, most commonly observed for this type of ligand,[5] with exceptions such as $[\{Ni(C_4H_6)(C_{10}H_8N_2)\}_2(C_4H_6)]$,[6] $[\{Mn(C_5H_5)(CO)\}_2(C_4H_6)]$,[7a] $[N(CH_3)_3(C_2H_5)]_2[Pt_2Cl_6(C_4H_6)]$,[7b] $Os_3(CO)_{10}(C_4H_6)$,[7c] and $Cp_2Zr(C_4H_6)$.[7d] In the latter compound the butadiene ligand is, however, coordinated to zirconium in the tetrahapto mode, despite transoid ligand conformation.[7d] We have recently devised a general method for the preparation of crystalline complexes between copper(I) chloride and a variety of conjugated and nonconjugated dienes.[8] The present account of the preparation and structural characterization of a complex between isoprene and copper(I) chloride represents the initial step in this series of investigations.

Experimental Section

General Data. All operations were carried out under nitrogen or argon by using Schlenk techniques. Ethyl vinyl ketone and isoprene were dried with 4 Å molecular sieves, deoxygenated by freeze–pump–thaw cycles and distilled prior to use. Copper(I) chloride was purified according to ref 9. The infrared spectrum of $[Cu_2Cl_2(C_5H_8)]$ (s) was registered on a Mattson Polaris FTIR spectrophotometer, with CaF_2 mull cell windows.

Preparation of $[Cu_2Cl_2(C_5H_8)]$. Approximately 0.2 g of copper(I) chloride was added at ambient temperature to 10 mL of ethyl vinyl ketone; the mixture was stirred to give a clear solution. Isoprene (2.0 mL) was added very slowly to the solution; yellow irregular-shaped plates of $[Cu_2Cl_2(C_5H_8)]$ were deposited overnight. The mother liquor was withdrawn and the compound washed with five 5-mL portions of isoprene at ca. −100 °C.

Once isolated, the compound is extremely unstable at temperatures over ca. −50 °C, crystals decomposing within 10 s on exposure to air at ambient temperature. Preparation of samples for infrared investigation was carried out at −100 °C and spectra were recorded at low temperature.[10] IR: ν(C=C—C=C) 1569, 1520 cm^{-1}. Corresponding frequencies for isoprene: 1640, 1598 cm^{-1}.

X-ray Structure Determination. Crystal Data and Intensity Data Collection. $[Cu_2Cl_2(C_5H_8)]$ crystallizes in the monoclinic space group $P2_1/c$, with a = 6.934 (4), b = 16.802 (10), c = 7.198 (4) Å, β = 118.03 (3)°, V = 740.2 (7) Å^3, Z = 4, D_{calcd} = 2.39 g cm^{-3}, and $F(000)$ = 520. Owing to extremely rapid loss of the isoprene ligand from the compound at ambient temperature vide supra, a crystal with the approximate dimensions 0.20 × 0.20 × 0.10 mm, obtained as described above, was mounted, under argon, at −150 °C in a glass capillary and transferred at the same temperature to a Rigaku AFC6R diffractometer. Diffracted in-

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Table I. Fractional Coordinates and Equivalent Isotropic Thermal Parameters (Å², Non-Hydrogen Atoms) or Isotropic Thermal Parameters (Å², Hydrogen Atoms) in $[Cu_2Cl_2(C_5H_8)]$

atom	x	y	z	B_{eq}[a] or B
Cu(1)	0.771 75 (9)	0.203 90 (3)	0.609.18 (9)	1.21 (2)
Cu(2)	1.247 04 (8)	0.207 15 (3)	1.023 84 (8)	1.06 (2)
Cl(1)	0.949 5 (2)	0.299 24 (6)	0.865 0 (2)	0.91 (4)
Cl(2)	0.459 7 (2)	0.269 40 (7)	0.351 6 (2)	0.88 (4)
C(1)	0.703 9 (8)	0.083 9 (3)	0.620 0 (8)	1.3 (2)
C(2)	0.861 4 (7)	0.103 6 (3)	0.816 3 (7)	0.9 (2)
C(3)	1.096 8 (7)	0.087 9 (3)	0.908 3 (7)	0.8 (2)
C(4)	1.226 3 (8)	0.092 4 (3)	1.119 9 (8)	1.0 (2)
C(5)	1.181 5 (8)	0.048 5 (3)	0.773 8 (8)	1.4 (2)
H(11)	0.748 (7)	0.055 (3)	0.521 (7)	2 (1)
H(12)	0.565 (8)	0.089 (3)	0.589 (7)	1 (1)
H(21)	0.826 (6)	0.121 (2)	0.913 (6)	0 (1)
H(41)	1.381 (7)	0.067 (2)	1.189 (6)	1 (1)
H(42)	1.180 (7)	0.102 (2)	1.205 (7)	0 (1)
H(51)	1.327 (8)	0.048 (3)	0.833 (7)	1 (1)
H(52)	1.135 (7)	0.069 (3)	0.649 (8)	1 (1)
H(53)	1.118 (7)	−0.004 (3)	0.736 (7)	2 (1)

[a] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$.

tensities ($\pm h, k, l$) were measured at -150 ± 1 °C for $3.5 < 2\theta < 55°$, with use of a graphite-monochromated radiation from a RU200 rotating anode source operated at 9 kW (50 kV; 180 mA). The $\omega - 2\theta$ scan mode was employed with a 2θ scan rate of 32° min⁻¹ and an ω scan width of $(1.40 + 0.30 \tan\theta)°$. Weak reflections ($I < 10\sigma(I)$) were rescanned up to three times and counts accumulated to improve counting statistics. Stationary background counts were recorded on each side of the reflection, the ratio of peak counting time vs background counting time being 2:1. Of the 1074 independent reflections measured, excluding those systematically absent, 886 had $I > 3\sigma(I)$ and were regarded as observed. Monitoring three reflections at regular intervals (after every 150 reflections measured) showed no evidence of crystal decay. Intensities were corrected for Lorentz and polarization effects; an empirical correction was made for the effects of absorption (μ = 64.0 cm⁻¹) on the basis of azimuthal scans for several reflections (min/max, transmission factors = 0.69/1.00, respectively). Cell constants were obtained by least-squares refinement by using the setting angles for 20 reflections.

Structure Determination and Refinement. The structure was solved by direct methods (MITHRIL).[11] Full-matrix least-squares refinement of positional and anisotropic thermal parameters for the non-hydrogen atoms and positional and isotropic thermal parameters for the hydrogen atoms, located from a difference map, gave a final R value of 0.020 (R_w = 0.029) for 114 parameters and 886 reflections. Reflections were weighted according to $w = [\sigma^2(F_o)]^{-1}$, the maximum Δ/σ in the final cycle being 0.02 (for H), and the max/min; residual electron density being 0.47 and -0.41 e Å⁻³, respectively. All calculations were performed with use of the TEXSAN[12] software package, and structural illustrations have been drawn with ORTEP.[13] Fractional coordinates and equivalent isotropic/isotropic parameters are listed in Table I.

Results and Discussion

Synthesis. The present complex has been prepared by utilizing the complex between copper(I) chloride and ethyl vinyl ketone,[14] as an in situ precursor. Systematic studies have shown that a solution of copper(I) chloride in ethyl vinyl ketone provides a highly reactive medium which can be used for the preparation of a variety of copper(I) diene complexes,[8,10] and of Cu(CO)Cl.[15] Infrared spectroscopic investigation of solid $[CuCl(C_5H_8O)]$ and of copper(I) chloride dissolved in ethyl vinyl ketone indicates that the species in solution is similar to that in the solid,[10] it being likely that the long Cu–O linkage in the solid[14] is broken in solution, resulting in a dimeric rather than a polymeric species. Since the solid complex between ethyl vinyl ketone and copper(I) chloride, $[CuCl(C_5H_8O)]$,[14] can exist only at temperatures below 0 °C, preparation of $[Cu_2Cl_2(C_5H_8)]$ at ambient temperature eliminates any risk of contamination of the product with $[CuCl(C_5H_8O)]$ (s). Careful control of the concentration of ligand in the reaction solution, by means of slow addition, enables, moreover, the direct formation of crystals suitable for single-crystal X-ray diffraction studies. $[Cu_2Cl_2(C_5H_8)]$ is practically insoluble in isoprene and decomposes with immediate extraction of the isoprene ligand in other solvents,

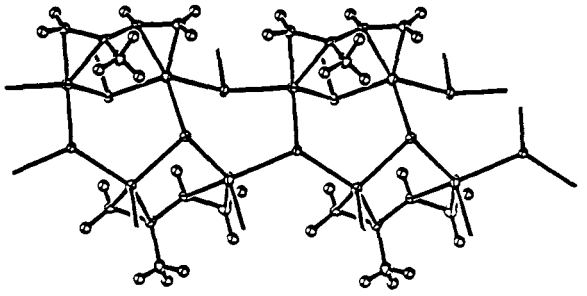

Figure 1. Part of a layer of $[Cu_2Cl_2(C_5H_8)]$.

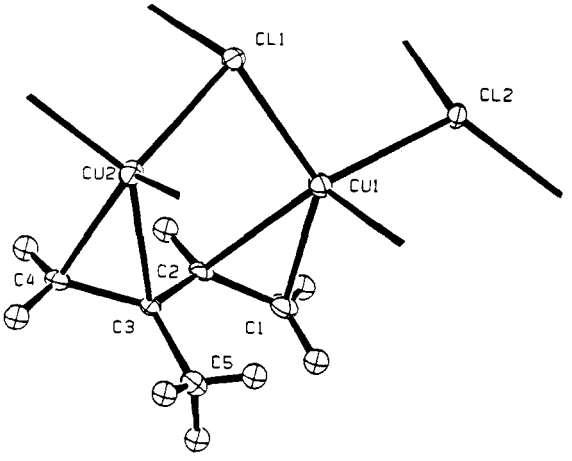

Figure 2. Crystallographic numbering used for the non-hydrogen atoms in $[Cu_2Cl_2(C_5H_8)]$. The thermal ellipsoids enclose 50% probability.

Table II. Interatomic Distances (Å) and Angles (deg) in $[CuCl(C_5H_8)]$[a]

Cu(1)–C(1)	2.080 (5)	Cu(2)–C(3)	2.244 (4)
Cu(1)–C(2)	2.140 (4)	Cu(2)–C(4)	2.076 (5)
Cu(1)–X(1)	1.998	Cu(2)–X(2)	2.052
Cu(1)–Cl(1)	2.311 (2)	Cu(2)–Cl(1)	2.395 (2)
Cu(1)–Cl(1^{i})	2.579 (2)	Cu(2)–Cl(2^{ii})	2.364 (4)
Cu(1)–Cl(2)	2.356 (2)	Cu(2)–Cl(2^{iii})	2.358 (2)
C(1)–C(2)	1.358 (7)	C(3)–C(4)	1.359 (7)
C(2)–C(3)	1.471 (6)	C(3)–C(5)	1.495 (7)
Cl(1)–Cu(1)–X(1)	115.0	Cl(1)–Cu(2)–X(2)	115.8
Cl(1)–Cu(1)–Cl(1^{i})	108.08 (5)	Cl(1)–Cu(2)–Cl(2^{ii})	104.58 (5)
Cl(1)–Cu(1)–Cl(2)	104.54 (6)	Cl(1)–Cu(2)–Cl(2^{iii})	100.58 (6)
Cl(1^{i})–Cu(1)–X(1)	107.9	Cl(2^{ii})–Cu(2)–X(2)	112.6
Cl(1^{i})–Cu(1)–Cl(2)	91.71 (6)	Cl(2^{ii})–Cu(2)–Cl(2^{iii})	101.54 (6)
Cl(2)–Cu(1)–X(1)	126.3	Cl(2^{iii})–Cu(2)–X(2)	119.7
C(1)–C(2)–C(3)	126.9 (4)	C(2)–C(3)–C(5)	118.8 (4)
C(2)–C(3)–C(4)	120.0 (4)	C(4)–C(3)–C(5)	120.1 (4)

[a] X(1) and X(2) are the midpoints of the C(1)–C(2) and C(3)–C(4) bonds, respectively. Symmetry code: (i): $x, 1/2 - y, z - 1/2$; (ii) $1 + x, 1/2 - y, 1/2 + z$; (iii) $1 + x, y, 1 + z$.

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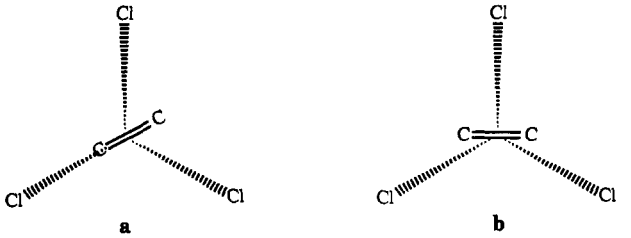

Figure 3. Diagrammatic representation of (*a*) a "quasidodecahedral" and (*b*) a "quasicubical" olefin twist for a tetrahedral $Cu(C{=}C)Cl_3$ fragment.

precluding investigation by e.g. NMR and examination of reactivity in solution.

Molecular Structure of $[Cu_2Cl_2(C_5H_8)]$. In the complex between isoprene and copper(I) chloride, each C=C bond of the ligand coordinates to a copper(I) atom, the latter atoms being further bridged by a chloride ligand. Layer formation, in which the isoprene molecules are peripherally bound on both layer faces, is thus effected via fused six-membered Cu–Cl rings (Figure 1). A smaller part of such a layer, showing the crystallographic numbering, is depicted in Figure 2, and interatomic distances and angle are listed in Table II.

We believe this to be the first example of a structure determination of a complex in which a conjugated diene is bonded to copper(I) through both C=C bonds. As mentioned earlier, in the complex between *trans*-1-cyanobutadiene and copper(I) chloride, the ligand coordinates to copper(I) via nitrogen and the 3,4 C=C bond.[3] As in η^2,η^2-butadienebis[η^2-butadiene-2,2′-(bipyridyl)nickel(0)],[6] the diene ligand in the present complex exhibits the s-trans conformation, bridging two metal centers. In η^2,η^2-butadienebis[η^2-butadiene-2,2′-(bipyridyl)nickel(0)], which is a discrete bimetallic species, there is, however, a further butadiene ligand, also with the s-trans conformation, coordinated terminally to each nickel atom via a single C=C.[6]

Both copper(I) atoms in $[Cu_2Cl_2(C_5H_8)]$ are approximately tetrahedrally coordinated by an olefinic double bond and three chloride ligands. Cu–Cl distances associated with the Cu(1) center are 2.311 (2), 2.356 (2), and 2.579 (2) Å; corresponding distances for Cu(2) are 2.358 (2), 2.364 (2), and 2.395 (2) Å, the former metal center thus exhibiting a coordination geometry slightly distorted toward a trigonal pyramid (Table II). The Cu(1)···Cu(2) distance is 3.242 (2) Å. Copper(I) is asymmetrically coordinated by the olefinic group carrying the methyl group, such that Cu(2)–C(3) is appreciably longer than the remaining three copper(I)–C(olefin) distances. The C=C bonds do not differ from one another, and exhibit a slight, if not significant, lengthening on coordination, together with a concomitant lowering of the infrared frequencies by approximately 75 cm^{-1} (71 and 78 cm^{-1}). The general coordination features are thus similar to those reported previously for π-olefinic complexes of copper(I).[16] In η^2,η^2-butadienebis[η^2-butadiene-2,2′-(bipyridyl)nickel(0)], the C=C bonds coordinated to nickel(0) are 1.401 (3) and 1.415 (3) Å, i.e. appreciably longer than the noncoordinated olefinic bond (1.340 (4) Å).[6]

The dihedral angles between the Cu(2), C(3), and C(4) plane and those through Cu(2), X(2), and Cl(2^{iii}); Cu(2), X(2), and Cl(2^{ii}), and Cu(2), X(2), and Cl(1) are 4, 65, and 55°, respectively, where X(2) is the midpoint of the C(3)–C(4) bond (for symmetry code see Table II), indicating a "quasidodecahedral" olefin twist[17,18] for this tetrahedrally coordinated metal center, cf. Figure 3. The quasidodecahedral structure has been predicted to be the lowest energy alternative for tetrakis(ethylene)nickel(0).[18] Olefin twisting associated with the other copper(I) center can be seen as reflecting the slight trigonal-pyramidal distortion of the coordination geometry for Cu(1), i.e. a twist of the olefin out of the "trigonal plane" through X(1) [the midpoint of the C(1)–C(2) bond], Cl(1) and Cl(2), or, alternatively, as a "quasicubical" twist[17,18] (cf. Figure 3), the dihedral angles between the Cu(1), C(1), and C(2) plane and those through Cu(1), X(1), and Cl(1^{i}); Cu(1), X(1), and Cl(1); and Cu(1), X(1), and Cl(2) being 72, 13, and 34°, respectively.

Table III. Selected Torsion Angles (deg) in $[Cu_2Cl_2(C_5H_8)]$

Cu(1)–C(1)–C(2)–C(3)	−101.0 (4)
Cu(1)–C(1)–C(2)–H(21)	90 (3)
Cu(1)–C(2)–C(1)–H(11)	100 (3)
Cu(1)–C(2)–C(1)–H(12)	−91 (3)
C(1)–C(2)–C(3)–C(4)	−163.9 (5)
Cu(2)–C(4)–C(3)–C(2)	−90.7 (4)
Cu(2)–C(4)–C(3)–C(5)	101.9 (4)
Cu(2)–C(3)–C(4)–H(41)	−106 (3)
Cu(2)–C(3)–C(4)–H(42)	96 (4)
C(1)–C(2)–C(3)–C(5)	3.6 (7)

The ligand skeleton, including the carbon atom of the methyl group, is approximately planar, the mean deviation from the least-squares plane through C(1), C(2), C(3), C(4), and C(5) being 0.07 Å. The C(1)–C(2)–C(3)–C(4) torsion angle is, however, −163.9 (5)°, whereas the C(1)–C(2)–C(3)–C(5) torsion angle is 3.6 (7)° (Table III). In η^2,η^2-butadienebis[η^2-butadiene-2,2′-(bipyridyl)nickel(0)] the bridging butadiene ligand is exactly planar.[6]

Owing to the necessarily low precision associated with the positions of the hydrogen atoms in the present complex, it does not seem meaningful to speculate on the bending back[17] of these substituents on the basis of the torsion angles about the C=C linkages (cf. Table III). On the other hand, C(3) and C(5) are clearly bent back with respect to the C(1)–C(2) and C(3)–C(4) olefinic groups, respectively, whereas C(2) does not appear to be bent back with respect to C(3)–C(4).

Photocatalyzed rearrangements and cycloadditions of polyenes in the presence of copper(I) salts have received considerable attention in recent years.[19] The mechanisms involved are, however, difficult to deduce unambiguously without detailed knowledge of the mode of coordination of the polyene to copper(I). In the present complex, rows of isoprene ligands are positioned by the Cu–Cl framework in such a way that there are several short van der Waals contacts (3.4–3.5 Å) between ligands in adjacent layers, making the compound a possible candidate as a model complex for the study of photochemically induced polymerization.

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Supplementary Material Available: Tables of anisotropic thermal parameters for the non-hydrogen atoms and bond distances involving the hydrogen atoms (2 pages); a listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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