(22) S. Jeannin, Y. Jeannin, and G. Lavigne, *Transition Met. Chem.*, **1**, 192 (1976).

(23) H. Alper and A. S. K. Chan, *Inorg. Chem.*, **13**, 225 (1974).

(24) J. P. Chesick and J. Donohue, *Acta Crystallogr., Sect. B*, **27**, 1441 (1971).

(25) S. Jeannin, Y. Jeannin, and G. Lavigne, *Transition Met. Chem.*, **1**, 195 (1976).

(26) L. P. Battaglia, A. B. Corradi, M. Nardelli, and M. E. V. Tani, *J. Chem. Soc., Dalton Trans.*, 143 (1976).

(27) M. R. Caira and L. R. Nassimbein, *J. Chem. Soc., Dalton Trans.*, 4 (1976).

(28) J. S. Thompson, T. J. Marks, and J. A. Ibers, *Proc. Natl. Acad. Sci. U.S.A.*, **74**, 3114 (1977).

(29) T. Ottersen, L. G. Warner, and K. Seff, *Inorg. Chem.*, **13**, 1904 (1974).

(30) M. M. Madooka, L. G. Warner, and K. Seff, *J. Am. Chem. Soc.*, **98**, 7569 (1976), and references therein.

(31) H. W. Chen, J. P. Fackler Jr., D. P. Schussler, and L. D. Thompson, *J. Am. Chem. Soc.*, **100**, 2370 (1978).

(32) G. R. Brubaker, J. N. Brown, M. K. Yoo, R. A. Kinsey, T. M. Kutchan, and E. A. Mottel, *Inorg. Chem.*, **18**, 299 (1979).

(33) J. A. Pappas, *J. Am. Chem. Soc.*, **101**, 561 (1979).

(34) R. Havlin and G. R. Knox, *J. Organomet. Chem.*, **4**, 247 (1965).

(35) Shaw, German Offen 2 709 989; German Offen 2 709 990.

(36) C. C. Ashworth, N. A. Bailey, M. Johnson, J. A. McCleverty, N. Morrison, and B. Tabbiner, *J. Chem. Soc., Chem. Commun.*, 743 (1976).

Contribution from the Istituto di Chimica Generale, Università di Pisa, 56100 Pisa, Italy,
and the Istituto di Strutturistica Chimica, Università di Parma, 43100 Parma, Italy

Synthetic and Structural Studies on Monomeric Olefin and Isocyanide Complexes of Copper(I): (Diethylenetriamine)(1-hexene)copper(I) Tetraphenylborate and (*N*,*N*,*N*′,*N*′-Tetramethylethylenediamine)bis(cyclohexyl isocyanide)copper(I) Tetraphenylborate

MARCO PASQUALI, CARLO FLORIANI,* A. GAETANI-MANFREDOTTI, and A. CHIESI-VILLA

Received February 27, 1979

The reaction of a suspension of CuI in methanol containing diethylenetriamine (dien) with 1-hexene gives the olefin complex $[Cu(dien)(1\text{-}hexene)]^+$, which was isolated as a tetraphenylborate derivative. In the complex cation, dien is coordinated through the three nitrogen atoms to the metal, while the C=C bond of the 1-hexene molecule completes the pseudotetrahedral coordination around copper(I). The reaction of a suspension of CuI in methanol containing ethylenediamine (en) or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmen) with carbon monoxide followed by the addition of CNC_6H_{11} produces $[Cu(en)(CNC_6H_{11})_2]^+$ [ν_{CN} (Nujol) 2143 and 2177 cm^{-1}] or $[Cu(tmen)(CNC_6H_{11})_2]^+$ [ν_{CN} (Nujol) 2160 and 2180 cm^{-1}], respectively. The tetrahedral structure of the cationic complex in which copper(I) coordinates a chelating tmen and two C-bonded isocyano groups, was confirmed by an X-ray analysis. Both the Cu–C–N and C–N–R moieties are practically linear with Cu–C and C–N bond lengths of 1.899 (8) and 1.895 (7) Å and C–N bond lengths of 1.15 (1) and 1.13 (1) Å. Crystallographic details for $[Cu(dien)(C_6H_{12})](BPh_4)$: space group $P2_1/c$ (monoclinic), $a = 15.835$ (2) Å, $b = 20.346$ (3) Å, $c = 20.219$ (3) Å, $\beta = 96.21$ (2)°, $Z = 8$. The final *R* factor was 11.5% for 4297 observed reflections. Crystallographic details for $[Cu(tmen)(CNC_6H_{11})_2](BPh_4)$: space group $P2_1/n$ (monoclinic), $a = 15.626$ (2) Å, $b = 14.753$ (3) Å, $c = 18.024$ (4) Å, $\beta = 97.47$ (2)°, $Z = 4$. The final *R* factor was 6.9% for 3860 observed reflections.

Introduction

Few copper(I) complexes have been used as "model compounds" in homogeneous catalysis because monomeric copper(I) compounds tend not to complex with molecules which could be activated. Copper(I) coordination and organometallic chemistry is dominated by the formation of stable cluster compounds[1,2] or by the disproportionation of copper(I) to copper(II) and copper metal.[1] As a part of our continuing investigation into the synthesis and the chemical and structural properties of copper(I) complexes,[3-6] we report here the synthesis and the structure of $[Cu(dien)(C_6H_{12})](BPh_4)$ (dien = diethylenetriamine, C_6H_{12} = 1-hexene) and $[Cu(tmen)(CNC_6H_{11})_2](BPh_4)$ (tmen = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine). Both kinds of complexes could be considered as structural models for electrophilic metal-promoted activation of olefins and isocyanides toward nucleophilic reagents.[7] Moreover, much attention was devoted to the catalytic activity of copper(I)–isocyanide systems, which have been found to promote several versatile organic reactions, such as dimerizations and cycloadditions. In all of these reactions, an organocopper(I)–isocyanide complex is assumed as an active intermediate.[7,8] In spite of a rather rich copper(I)–isocyanide chemistry,[7-10] the polymeric $[CuI{\cdot}CNCH_3]_n$ complex is the only copper(I)–isocyanide compound so far structurally studied.[11]

Experimental Section

Syntheses were carried out under an atmosphere of purified nitrogen. Methanol, ethylenediamine, and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine were dried and distilled before use, and cyclohexyl isocyanide was distilled before use. Infrared spectra were recorded with a Perkin-Elmer 282 spectrophotometer. Considerable difficulty was encountered in obtaining satisfactory elemental analyses, especially for carbon.

Preparation of $[Cu(en)(CNC_6H_{11})_2](BPh_4)$. CuI (1.5 g, 7.88 mmol) is suspended in methanol (50 mL) containing ethylenediamine (4 mL, 60 mmol). The blue color disappears when the suspension is reacted with carbon monoxide, producing a nearly colorless solution. Some undissolved CuI is eventually filtered out. On addition of $C_6H_{11}NC$ (2.2 mL, 21.9 mmol), the solution loses carbon monoxide. The further addition of $NaBPh_4$ (2.8 g, 8.19 mmol) dissolved in methanol (10 mL) produces a white crystalline solid (2.7 g, 51.8%) sensitive to oxygen and moisture. Anal. Calcd for $[Cu(en)(CNC_6H_{11})_2](BPh_4)$, $C_{40}H_{50}N_4BCu$: C, 72.69; H, 7.57; N, 8.48. Found: C, 71.62; H, 7.70; N, 8.51. The IR spectrum (Nujol) displays two strong bands at 2143 (vs) and 2177 (ms) cm^{-1}.

Synthesis of $[Cu(tmen)(CNC_6H_{11})_2](BPh_4)$. CuI (1.0 g, 5.25 mmol) is suspended in CH_3OH (50 mL) containing *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, tmen (2.5 g, 21.5 mmol). Upon exposure

---

* To whom correspondence should be addressed at the Università di Pisa.

0020-1669/79/1318-3535$01.00/0

Table I. Summary of Crystal Data and Intensity Collection

	[Cu(tmen)-($CNC_6H_{11})_2$](BPh$_4$)	[Cu(dien)-(C_6H_{12})](BPh$_4$)
formula	$C_{44}H_{58}BCuN_4$	$C_{34}H_{45}BCuN_3$
a, Å	15.626 (2)	15.835 (2)
b, Å	14.753 (3)	20.346 (3)
c, Å	18.024 (4)	20.219 (3)
β, deg	97.47 (2)	96.21 (2)
Z	4	8
M_r	717.3	570.1
ρ(calcd), g/cm^3	1.157	1.169
space group	$P2_1/n$	$P2_1/c$
radiation	Cu K*α*	Cu K*α*
μ, cm^{-1}	9.59	10.7
scan type	*θ*–2*θ*	*θ*–2*θ*
scan range	±0.5° from peak center	±0.5° from peak center
scan speed	2.5–10°/min	2.5–10°/min
bgd	stationary crystal at ±0.5°	stationary crystal at ±0.5°
2*θ* limits, deg	6–140	6–120
criterion for obsn	$I > 2\sigma(I)$	$I > 2\sigma(I)$
unique obsd data	3860	4297
unique total data	7798	9618
crystal dimens, mm	0.14 × 0.37 × 0.43	0.19 × 0.35 × 0.84

to carbon monoxide, CuI goes into solution. A small amount of a white solid precipitates. The addition of $C_6H_{11}NC$ (2.0 g, 1.83 mmol) causes dissolution of the solid along with the evolution of carbon monoxide. When NaBPh$_4$ (2.0 g, 5.85 mmol) is added, an oil is formed. Further addition of CH_3OH (10 mL) gives a microcrystalline solid (2.0 g, 53.2%). The crystal used in the structure analysis was slowly precipitated from the mother liquor. Both solids have the same IR spectrum[ν_{CN} (Nujol) 2160 (vs), 2180 (ms)]. Anal. Calcd for [Cu(tmen)($CNC_6H_{11})_2$](BPh$_4$), $C_{44}H_{58}N_4BCu$: C, 73.71; H, 8.10; N, 7.82. Found: C, 73.03; H, 8.09; N, 7.67.

Synthesis of [Cu(dien)(C_6H_{12})](BPh$_4$). CuI (1.6 g, 8.30 mmol) is suspended in a methanolic (50 mL) solution of diethylenetriamine, dien (2 mL, 18.5 mmol). On addition of 1-hexene (2 mL, 15.99 mmol), CuI dissolves giving a slight blue solution. After 20 min, a small amount of a blue crystalline solid precipitates, which is filtered out. The addition of NaBPh$_4$ (2.5 g, 7.31 mmol) to the resulting solution gives a white microcrystalline solid (2.5 g, 56% yield). Anal. Calcd for [Cu(dien)(C_6H_{12})](BPh$_4$), $C_{34}H_{45}N_3BCu$: C, 71.66; H, 7.90; N, 7.38. Found: C, 70.95; H, 7.72; N, 7.87. The solid is very sensitive to air. It reacts with carbon monoxide, giving [Cu(dien)-CO](BPh$_4$).[3]

X-ray Data Collection. The crystal of [Cu(tmen)($CNC_6H_{11})_2$]-(BPh$_4$) chosen for data collection was wedged into a thin-walled glass capillary. Preliminary X-ray diffraction measurements (rotation and Weissenberg photographs) indicated monoclinic symmetry with systematic absences consistent with the space group $P2_1/n$. Crystal data and details of data collection are presented in Table I. Cell parameters were refined from a least-squares fit of the setting angles of 40 reflections ($\theta > 30°$).

A prismatic crystal of [Cu(dien)(C_6H_{12})](BPh$_4$), mounted inside a capillary under a nitrogen atmosphere, was used for the X-ray study. Weissenberg photographs revealed lattice symmetry $2/m$ and systematic absences $h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$), defining uniquely the monoclinic space group $P2_1/c$. Preliminary cell dimensions, determined from Weissenberg photographs, were subsequently adjusted by a least-squares procedure applied to the setting angles of 42 reflections ($\theta > 40°$). A summary of the crystal data and intensity collection is reported in Table I.

Data for the two compounds were collected following essentially the same procedure. Intensities were measued by a Siemens AED computer-controlled diffractometer using Ni-filtered Cu Kα radiation (λ 1.541 78 Å). The intensity of a standard reflection was measured every 20 reflections for both compounds as a check on crystal or instrument stability. No significant or systematic change in the measured intensities was observed during data collection. For intensity and background the "five-point technique"[12] was used. The data were reduced in the conventional manner with corrections for Lorentz and polarization factors. The effects for absorption were judged to be minimal and were not compensated for (μr = ca. 0.1 for both crystals examined).

Solution and Refinement of the Structures. Both structures were solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares techniques.[13] Scattering factors of neutral atoms were taken from standard sources.[14] The effects of anomalous dispersion were included in all structure factor calculations.

[Cu(tmen)($CNC_6H_{11})_2$](BPh$_4$). The position of the copper atom was determined from a Patterson map. Successive Fourier calculations, based upon the phases generated from the coordinates of the copper, revealed the location of all the nonhydrogen atoms, excepting those of the cyclohexyl group [C(8) through C(13)]. Two cycles of isotropic full-matrix refinement (the phenyl rings of the BPh$_4^-$ anion were considered as rigid groups) led to $R = 21.7\%$. A three-dimensional difference Fourier map computed at this stage revealed in the region of the missing cyclohexyl group the presence of nine peaks, six of which had an electron density of nearly half the others. The lighter peaks were interpreted by treating three carbon atoms [C(10), C(11), C(12)] of the cyclohexyl group as statistically distributed over two positions with site occupation factors of 0.5. Subsequent complete isotropic refinement of the structure improved *R* to 14.1%. All nonhydrogen atoms, excepting those affected by disorder, were assigned in the next cycles of anisotropic thermal parameter refinement. A difference electron density map calculated at $R = 8.3\%$ revealed most of the hydrogen atom positions; enough methyl group hydrogen atoms were located to calculate the positions of those unobserved. The missing hydrogen atoms, excluding those of the disordered cyclohexyl group, were introduced in calculated positions. All the hydrogen atoms were subjected to one cycle of isotropic refinement and then kept fixed. After two further "blocked" (two blocks) least-squares cycles, the structure converged at 6.9% for 3860 independent observed data. The final difference Fourier map showed no peaks above the general background.

The function minimized in the refinement was $\sum w|\Delta F|^2$ with unit weights. Three reflections, probably affected by counting errors, were rejected. No evidence for secondary extinction was found. The final positional and thermal parameters are listed in Tables II and III. A listing of structure factor amplitudes is available.[15]

[Cu(dien)(C_6H_{12})](BPh$_4$). The coordinates of the two copper atoms were deduced from the Patterson synthesis. A Fourier map, phased on the contributions of the heavy atoms, revealed all nonhydrogen atoms excluding the hexene molecule around Cu(2). Two cycles of full-matrix least-squares refinement of the scale factor and the positional and anisotropic thermal parameters (the phenyl rings in BPh$_4^-$ anions were considered as rigid groups during the entire refinement[13]) yielded $R = 19.3\%$. A ΔF synthesis calculated at this stage showed a set of diffuse peaks in the neighborhood of Cu(2), indicating disorder in the hexene molecule. Attempts to deal with this in terms of partial occupancy were successful only for C(20), all the other peaks not being consistent with the geometries of two "partial" hexene molecules. Disorder was resolved by considering the set of peaks having the most reliable distribution and refining them isotropically. The anisotropic refinement of these atoms was not satisfactory due to their extremely large thermal parameters.

Full-matrix least-squares refinement of positional, anisotropic (Cu, dien, hexene), and isotropic (hexene, BPh$_4^-$ anions) thermal parameters for all atoms converged to $R = 11.8\%$. Most of the hydrogen atoms of the BPh$_4^-$ groups were revealed from a ΔF map. They were introduced as fixed-atom contributions with free isotropic temperature factors and with idealized parameters (recalculated every few refinement cycles) constrained to fixed values. The final *R* was 11.5%. Because of severe disorder associated with the cations (as indicated by the large thermal parameters), a better fit could not be achieved. The function minimized was $\sum w|\Delta F|^2$ with unit weights. There were no peaks of height greater than 0.7 e/Å^3 on the final electron density difference map. One reflection (011) affected by counting errors was rejected.

Final positional and thermal parameters are included in Tables V and VI. A listing of observed and calculated structure factors is available.[15]

Results and Discussion

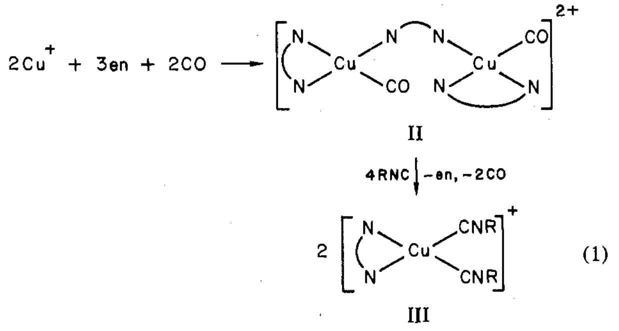
It was recently reported that a methanolic suspension of CuI absorbs, in the presence of ethylenediamine (en), carbon monoxide, producing a solution from which stable copper(I) carbonyls can be isolated: [Cu(en)$_2$CO]I (I) and [Cu$_2$-(en)$_3$(CO)$_2$]X$_2$ (II) [X = I$^-$, BPh$_4^-$].[5,6]

Table II. Final Atomic Fractional Coordinates ($\times 10^4$) for $[Cu(tmen)(CNC_6H_{11})_2](BPh_4)$[a]

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
Cu	1645 (1)	2371 (1)	196 (1)	C(54)	548 (5)	−335 (4)	3311 (4)
N(1)	2752 (3)	3100 (4)	−95 (3)	C(55)	123 (4)	1 (5)	3868 (4)
N(2)	2574 (4)	1623 (5)	938 (3)	C(56)	370 (4)	827 (4)	4211 (3)
N(3)	743 (4)	3592 (4)	1217 (4)	H(1)	4013 (47)	2957 (47)	360 (37)
N(4)	1100 (3)	969 (4)	−990 (4)	H(2)	3564 (45)	1974 (49)	−23 (40)
C(1)	3494 (4)	2599 (7)	268 (5)	H(3)	3248 (46)	2648 (51)	1381 (41)
C(2)	3345 (5)	2156 (8)	950 (6)	H(4)	3840 (46)	1688 (46)	1143 (38)
C(3)	2771 (5)	3110 (7)	−916 (5)	H(5)	2124 (45)	3477 (49)	−1199 (39)
C(4)	2761 (5)	4045 (6)	167 (5)	H(6)	2677 (46)	2501 (52)	−1161 (41)
C(5)	2675 (7)	688 (7)	720 (6)	H(7)	3307 (46)	3518 (48)	−1067 (39)
C(6)	2336 (7)	1563 (8)	1691 (5)	H(8)	2812 (46)	4064 (50)	727 (42)
C(7)	1047 (4)	3132 (5)	805 (5)	H(9)	2113 (46)	4441 (48)	−167 (39)
C(8)	354 (5)	4178 (7)	1748 (6)	H(10)	3298 (46)	4435 (48)	22 (38)
C(9)	−569 (5)	4370 (7)	1324 (7)	H(11)	2830 (47)	690 (52)	136 (42)
C(10)	−489 (13)	5119 (12)	775 (10)	H(12)	2085 (46)	324 (51)	655 (43)
C(10*)	−940 (12)	5197 (14)	1567 (11)	H(13)	3166 (45)	412 (49)	1122 (39)
C(11)	−5 (15)	5882 (16)	1107 (13)	H(14)	2238 (48)	2164 (51)	1861 (41)
C(11*)	−418 (12)	6063 (13)	1580 (11)	H(15)	2863 (44)	1223 (48)	2103 (41)
C(12)	936 (12)	5583 (12)	1308 (9)	H(16)	1734 (47)	1130 (53)	1710 (43)
C(12*)	560 (12)	5922 (14)	1946 (11)	H(151)	598 (42)	406 (44)	−1977 (38)
C(13)	959 (7)	4941 (8)	1954 (7)	H(161)	2208 (44)	334 (48)	−1789 (38)
C(14)	1248 (4)	1538 (5)	−573 (4)	H(162)	2228 (43)	−319 (47)	−1018 (39)
C(15)	992 (4)	182 (5)	−1489 (4)	H(171)	2364 (44)	−1100 (47)	−2219 (36)
C(16)	1870 (5)	−158 (6)	−1618 (5)	H(172)	1330 (43)	−719 (47)	−2731 (40)
C(17)	1758 (7)	−959 (9)	−2135 (6)	H(181)	1263 (39)	−2178 (49)	−2125 (36)
C(18)	1313 (11)	−1690 (8)	−1788 (7)	H(182)	1659 (42)	−1791 (46)	−1320 (40)
C(19)	441 (8)	−1379 (7)	−1648 (7)	H(191)	−18 (46)	−1203 (49)	−2217 (41)
C(20)	498 (6)	−539 (6)	−1131 (5)	H(192)	213 (43)	−173 (50)	−1411 (37)
B	1285 (4)	2328 (5)	4397 (3)	H(201)	927 (44)	−666 (48)	−584 (40)
C(21)	2202 (3)	2717 (4)	4149 (3)	H(202)	−50 (45)	−233 (46)	−1073 (37)
C(22)	2218 (4)	3073 (5)	3438 (4)	H(22)	1679 (38)	3108 (41)	2989 (34)
C(23)	2982 (5)	3371 (5)	3182 (5)	H(23)	2858 (36)	3594 (42)	2590 (36)
C(24)	3740 (5)	3322 (6)	3629 (5)	H(24)	4331 (39)	3585 (41)	3417 (33)
C(25)	3765 (4)	3000 (6)	4328 (5)	H(25)	4393 (40)	2827 (41)	4778 (34)
C(26)	2989 (4)	2687 (5)	4586 (4)	H(26)	3161 (37)	2251 (43)	4979 (35)
C(31)	541 (4)	3077 (4)	4100 (3)	H(32)	1172 (39)	4120 (41)	4681 (34)
C(32)	637 (4)	3986 (5)	4307 (4)	H(33)	216 (37)	5301 (43)	4227 (33)
C(33)	27 (5)	4646 (5)	4079 (4)	H(34)	−1194 (38)	4903 (42)	3378 (33)
C(34)	−701 (5)	4445 (5)	3613 (4)	H(35)	−1315 (39)	3352 (41)	3002 (34)
C(35)	−824 (4)	3566 (6)	3376 (4)	H(36)	−349 (38)	2323 (45)	3430 (34)
C(36)	−200 (4)	2910 (4)	3613 (3)	H(42)	2159 (38)	1038 (42)	5372 (33)
C(41)	1356 (3)	2189 (4)	5308 (3)	H(43)	2310 (38)	869 (43)	6624 (33)
C(42)	1859 (4)	1504 (4)	5663 (4)	H(44)	1674 (36)	1737 (41)	7570 (34)
C(43)	1955 (4)	1386 (5)	6442 (4)	H(45)	691 (38)	3128 (43)	6805 (33)
C(44)	1539 (5)	1947 (6)	6896 (4)	H(46)	562 (38)	3264 (43)	5570 (33)
C(45)	1025 (5)	2589 (6)	6561 (4)	H(52)	1961 (38)	1282 (42)	3274 (33)
C(46)	928 (4)	2737 (4)	5786 (3)	H(53)	1637 (39)	−6 (42)	2807 (33)
C(51)	1052 (3)	1351 (4)	4007 (3)	H(54)	348 (37)	−926 (43)	3028 (33)
C(52)	1474 (4)	973 (4)	3443 (3)	H(55)	−350 (39)	−267 (41)	4106 (33)
C(53)	1226 (5)	153 (5)	3100 (4)	H(56)	63 (38)	1117 (42)	4609 (33)

[a] Standard deviations in this table and following tables are given in parentheses.

A carbonylated solution, from which the isolation of II was achieved, readily reacts with cyclohexyl isocyanide ($C_6H_{11}NC$), losing carbon monoxide. Upon addition of $NaBPh_4$, $[Cu(en)(CNC_6H_{11})_2](BPh_4)$ (III) crystallizes out. The two probable steps in the synthesis of III are given in eq 1. The reaction of $C_6H_{11}NC$ on the preformed carbonyl species, rather than the direct synthesis, allows one both to carry out the reaction on soluble copper(I) species and to produce a mixed-ligand complex. Since in all carbonyl complexes of this class copper(I) achieves tetracoordination,[5,6] the reaction of $C_6H_{11}NC$ can be depicted as the displacement of CO and en or solvent molecules by the incoming isocyanide ligand. A displacement of en by $C_6H_{11}NC$ is expected on the basis of the significant σ-basic properties of cyclohexyl isocyanide.



II

III

(1)

N⌒N = en
R = C_6H_{11}

The same reaction (1), when carried out in the presence of *N,N,N′,N′*-tetramethylethylenediamine (tmen), produces the analogous complex $[Cu(tmen)(CNC_6H_{11})_2](BPh_4)$ (IV).

The IR spectra of III and IV show two sharp and strong bands [for III, ν_{CN} (Nujol) 2143 (vs) and 2177 (ms) cm^{-1} and for IV, ν_{CN} (Nujol) 2160 (vs) and 2180 (ms) cm^{-1}], suggesting a pseudotetrahedral arrangement of the four donor atoms: two nitrogens from en or tmen, and two carbons from isocyanides. This was further confirmed by an X-ray analysis carried out on $[Cu(tmen)(CNC_6H_{11})_2](BPh_4)$ (IV). The presence around the metal of basic σ donor ligands (en or tmen) enhances the

Table III. Thermal Parameters (×10^4) for $[Cu(tmen)(CNC_6H_{11})_2](BPh_4)$[a]

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu	584 (5)	808 (6)	922 (7)	−132 (6)	111 (4)	39 (5)
N(1)	591 (31)	916 (42)	866 (40)	73 (34)	93 (28)	15 (30)
N(2)	788 (39)	1089 (52)	758 (41)	73 (36)	118 (31)	158 (36)
N(3)	847 (43)	948 (50)	1450 (61)	−90 (45)	422 (41)	64 (37)
N(4)	708 (36)	850 (43)	1014 (49)	−143 (38)	8 (33)	−28 (32)
C(1)	567 (40)	1569 (80)	1243 (66)	363 (64)	89 (41)	65 (50)
C(2)	610 (46)	2278 (119)	1662 (93)	819 (87)	−90 (52)	68 (61)
C(3)	1077 (61)	1655 (88)	996 (64)	239 (61)	356 (50)	114 (59)
C(4)	956 (57)	938 (61)	1524 (77)	−24 (56)	82 (53)	−233 (48)
C(5)	1820 (99)	1156 (80)	1740 (99)	48 (74)	−446 (78)	574 (73)
C(6)	1859 (103)	2344 (126)	898 (69)	432 (76)	265 (67)	666 (92)
C(7)	718 (45)	828 (53)	1331 (68)	−66 (50)	365 (45)	−9 (40)
C(8)	873 (58)	1357 (81)	1765 (90)	−668 (71)	317 (58)	238 (58)
C(9)	682 (52)	1617 (92)	2187 (115)	−730 (86)	298 (63)	198 (56)
C(13)	1107 (81)	1863 (124)	2985 (178)	−1421 (130)	87 (96)	159 (83)
C(14)	627 (40)	1018 (59)	947 (57)	−225 (48)	−59 (37)	000 (41)
C(15)	792 (45)	783 (51)	921 (53)	−94 (43)	−62 (39)	−19 (39)
C(16)	921 (58)	1285 (75)	1377 (78)	−306 (64)	225 (53)	45 (53)
C(17)	1684 (101)	1540 (105)	1455 (96)	−375 (87)	139 (76)	632 (88)
C(18)	2710 (168)	990 (85)	1407 (99)	−399 (70)	−648 (104)	643 (99)
C(19)	1956 (117)	902 (75)	1921 (116)	−286 (75)	173 (95)	−534 (75)
C(20)	1246 (71)	983 (65)	1590 (86)	−78 (62)	448 (63)	−182 (56)
B	531 (33)	562 (40)	586 (39)	−71 (35)	84 (28)	−46 (32)
C(21)	608 (33)	598 (37)	671 (38)	−127 (33)	161 (29)	−67 (30)
C(22)	782 (44)	872 (49)	916 (51)	157 (41)	286 (38)	−62 (38)
C(23)	1071 (59)	911 (57)	1167 (63)	158 (48)	479 (52)	−187 (48)
C(24)	971 (58)	1144 (67)	1239 (70)	−207 (56)	456 (54)	−425 (51)
C(25)	658 (40)	1618 (79)	1168 (67)	−371 (61)	204 (43)	−312 (45)
C(26)	753 (42)	1158 (60)	860 (49)	−71 (45)	174 (36)	−182 (43)
C(31)	616 (36)	607 (39)	574 (36)	−18 (31)	177 (29)	−19 (30)
C(32)	825 (46)	719 (48)	834 (49)	−29 (39)	132 (38)	13 (38)
C(33)	1128 (60)	679 (48)	1017 (58)	10 (42)	425 (48)	163 (45)
C(34)	785 (47)	904 (57)	988 (57)	180 (46)	277 (42)	214 (43)
C(35)	681 (42)	1020 (59)	888 (51)	184 (47)	82 (36)	93 (42)
C(36)	680 (38)	726 (46)	717 (42)	30 (35)	116 (32)	33 (34)
C(41)	527 (30)	627 (39)	616 (35)	−46 (31)	99 (27)	−122 (28)
C(42)	716 (40)	749 (45)	699 (44)	20 (37)	52 (33)	−38 (36)
C(43)	833 (47)	865 (53)	903 (56)	142 (45)	−89 (41)	−148 (41)
C(44)	972 (54)	1099 (61)	644 (46)	26 (46)	53 (40)	−270 (48)
C(45)	976 (52)	1182 (64)	705 (48)	−123 (49)	226 (39)	−84 (50)
C(46)	754 (39)	815 (46)	680 (40)	−16 (37)	160 (32)	−7 (35)
C(51)	526 (30)	564 (36)	554 (35)	12 (29)	86 (26)	−1 (27)
C(52)	743 (39)	637 (42)	729 (42)	21 (35)	223 (33)	−14 (33)
C(53)	1049 (54)	742 (50)	786 (48)	−135 (40)	217 (41)	65 (42)
C(54)	1017 (51)	640 (45)	739 (46)	−35 (37)	−134 (40)	−52 (40)
C(55)	692 (41)	743 (48)	903 (51)	87 (41)	1 (37)	−182 (35)
C(56)	637 (36)	688 (43)	699 (42)	−20 (35)	146 (31)	−70 (33)

atom	U_{iso}, Å^2	atom	U_{iso}, Å^2	atom	U_{iso}, Å^2
C(10)	1303 (68)	H(13)	1278 (217)	H(25)	1574 (188)
C(10*)	1342 (66)	H(14)	1116 (247)	H(26)	771 (193)
C(11)	1561 (75)	H(15)	1296 (219)	H(32)	728 (190)
C(11*)	1220 (60)	H(16)	2028 (258)	H(33)	1154 (188)
C(12)	1116 (57)	H(151)	1143 (214)	H(34)	1173 (187)
C(12*)	1331 (64)	H(161)	1183 (220)	H(35)	834 (188)
H(1)	1127 (218)	H(162)	1159 (222)	H(36)	620 (189)
H(2)	1471 (239)	H(171)	1346 (207)	H(42)	747 (187)
H(3)	2329 (254)	H(172)	1473 (217)	H(43)	1295 (189)
H(4)	1337 (212)	H(181)	1202 (199)	H(44)	1104 (187)
H(5)	1588 (221)	H(182)	1116 (206)	H(45)	963 (189)
H(6)	1463 (245)	H(191)	1627 (239)	H(46)	757 (190)
H(7)	1342 (220)	H(192)	1417 (207)	H(52)	1133 (188)
H(8)	1196 (252)	H(201)	1326 (234)	H(53)	972 (191)
H(9)	1408 (225)	H(202)	1246 (215)	H(54)	1176 (187)
H(10)	1294 (216)	H(22)	1053 (187)	H(55)	923 (189)
H(11)	1795 (253)	H(23)	1372 (189)	H(56)	683 (191)
H(12)	1577 (255)	H(24)	1483 (187)		

[a] The anisotropic thermal factors are defined as $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$.

back-bonding by the metal, so that the CN stretching frequencies fall in a rather low range.[7-10] This gives rise to a rather low electrophilic activation of the coordinated isocyano groups, which are unreactive toward the methanol used as the reaction solvent.[7,8]

In this context, it should be remembered that such mixed-ligand complexes have been postulated as intermediates in the copper-catalyzed reactions of isocyanides with nucleophiles.[8,10] While copper(I)–carbonyl chemistry is a rather recent area,[3,5,6,16-18] at least in terms of isolated and fully characterized complexes, many copper(I)–isocyanide complexes have so far been reported, with a general formula $(RNC)_nCuX$ (X =

Table IV. Bond Distances (Å) and Angles (deg) in the Cation $[Cu(tmen)(CNC_6H_{11})_2]^+$

Cu-N(1)	2.159 (6)	Cu-C(7)	1.899 (8)
Cu-N(2)	2.147 (7)	Cu-C(14)	1.895 (7)
N(1)-Cu-N(2)	84.8 (2)	N(2)-Cu-C(7)	106.7 (3)
N(1)-Cu-C(7)	108.4 (3)	N(2)-Cu-C(14)	104.6 (3)
N(1)-Cu-C(14)	110.0 (3)	C(7)-Cu-C(14)	131.9 (3)
N(1)-C(1)	1.46 (1)	N(1)-C(4)	1.47 (1)
N(2)-C(2)	1.44 (1)	N(2)-C(5)	1.45 (1)
C(1)-C(2)	1.44 (1)	N(2)-C(6)	1.46 (1)
N(1)-C(3)	1.48 (1)		
Cu-N(1)-C(1)	104.7 (5)	Cu-N(1)-C(3)	111.5 (4)
Cu-N(2)-C(2)	103.0 (5)	Cu-N(1)-C(4)	111.6 (4)
N(1)-C(1)-C(2)	114.0 (6)	Cu-N(2)-C(5)	114.2 (5)
N(2)-C(2)-C(1)	117.7 (8)	Cu-N(2)-C(6)	112.2 (5)
C(1)-N(1)-C(3)	109.6 (6)	C(2)-N(2)-C(6)	109.6 (7)
C(1)-N(1)-C(4)	111.3 (6)	C(3)-N(1)-C(4)	108.1 (6)
C(2)-N(2)-C(5)	113.9 (8)	C(5)-N(2)-C(6)	104.2 (8)
C(7)-N(3)	1.15 (1)	C(9)-C(10)	1.50 (2)
N(3)-C(8)	1.48 (1)	C(10)-C(11)	1.44 (3)
C(8)-C(9)	1.57 (1)	C(11)-C(12)	1.53 (3)
C(8)-C(13)	1.49 (1)	C(12)-C(13)	1.50 (2)
Cu-C(7)-N(3)	174.4 (7)	C(8)-C(9)-C(10)	107.7 (10)
C(7)-N(3)-C(8)	179.7 (8)	C(9)-C(10)-C(11)	112.7 (16)
N(3)-C(8)-C(9)	102.7 (8)	C(10)-C(11)-C(12)	108.0 (18)
N(3)-C(8)-C(13)	107.7 (7)	C(11)-C(12)-C(13)	106.9 (15)
C(9)-C(8)-C(13)	120.0 (9)	C(12)-C(13)-C(8)	109.5 (11)
C(9)-C(10*)	1.44 (2)	C(11*)-C(12*)	1.60 (3)
C(10*)-C(11*)	1.51 (3)	C(12*)-C(13*)	1.58 (2)
C(8)-C(9)-C(10*)	112.7 (11)	C(11*)-C(12*)-C(13)	118.7 (14)
C(9)-C(10*)-C(11*)	118.9 (16)	C(12*)-C(13)-C(8)	117.1 (11)
C(10*)-C(11*)-C(12*)	112.3 (15)		
C(14)-N(4)	1.13 (1)	C(16)-C(17)	1.50 (2)
N(4)-C(15)	1.46 (1)	C(17)-C(18)	1.47 (2)
C(15)-C(16)	1.51 (1)	C(18)-C(19)	1.49 (2)
C(15)-C(20)	1.51 (1)	C(19)-C(20)	1.55 (1)
Cu-C(14)-N(4)	170.7 (6)	C(15)-C(16)-C(17)	108.8 (7)
C(14)-N(4)-C(15)	173.8 (7)	C(16)-C(17)-C(18)	109.7 (9)
N(4)-C(15)-C(16)	108.9 (6)	C(17)-C(18)-C(19)	109.9 (10)
N(4)-C(15)-C(20)	108.7 (6)	C(18)-C(19)-C(20)	111.5 (10)
C(16)-C(15)-C(20)	111.0 (7)	C(19)-C(20)-C(15)	107.5 (8)

halogen,[11,19-21] CN^-,[19] ClO_4^-,[22] C_2Ph,[19] C_5H_5,[8,23] *tert*-butoxy,[24] acetylacetonate[25]). The number of isocyanides present in these complexes depends on the nature of X, and it can vary from 1 to 4,[10] while in carbonyl chemistry, copper(I) binds only one carbon monoxide. In contrast to this wide range of known isocyanide–copper(I) complexes, there is only one structural determination, carried out several years ago[11] on the polymeric complex $[CuI{\cdot}CNCH_3]_n$.

Description of the Structure of $[Cu(tmen)(CNC_6H_{11})_2](BPh_4)$. The crystals contain discrete $[Cu(tmen)(CNC_6H_{11})_2]^+$ cations and BPh_4^- anions. A view of the coordination environment of the copper atom is given in Figure 1. The pseudotetrahedral geometry is provided by tmen and two C-bonded cyclohexyl isocyanides. The degree of deviation from tetrahedral geometry is mainly indicated by the following angles: N(1)–Cu–N(2) = 84.8 (2)°, C(7)–Cu–C(14) = 131.9 (3)°. The two coordination planes N(1),Cu,N(2) and C(7),Cu,C(14) are mutually orthogonal, the dihedral angle being 91.4°. The Cu–C–N and C–N–C moieties are nearly linear (Table IV), with a Cu–C bond distance which compares well with that expected for a Cu–C(sp) bond[26] and a C–N bond distance for the isocyanide moiety which falls in the range of a triple bond[27,28] [Cu–C(7) = 1.899 (8), Cu–C(14) = 1.895 (7), C(7)–N(3) = 1.15 (1), C(14)–N(4) = 1.13 (1) Å]. These values can be compared with those found in polymeric $[CuI{\cdot}CNCH_3]_n$,[11] which is the only Cu(I)–CNR compound so far structurally studied. The complex is in fact formed by the coordination polyhedra $[CuI_4]$ and $[CuI_2(CNCH_3)_2]$ sharing iodide ligands, and the coordination geometry for the second moiety compares very well with that found in IV. The rather approximate Cu–C and N–C bond distances are 1.81 and 1.24 Å, respectively. Both bond distances and angles within the tmen[29] and cyclohexyl isocyanide[27] ligands fall in the usual range.

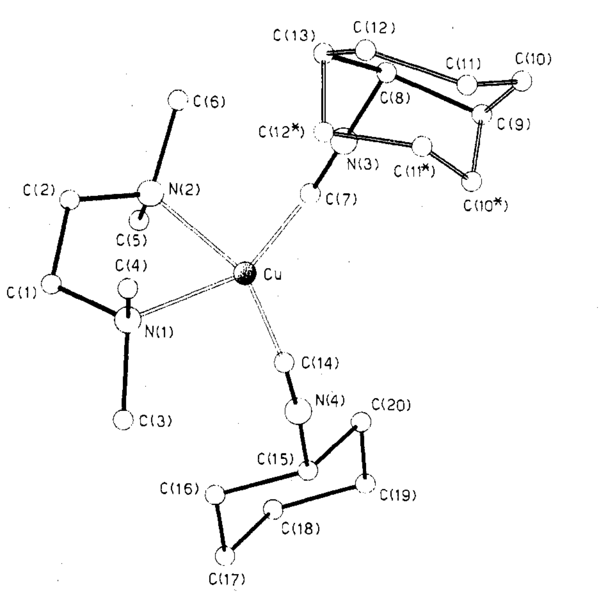


Figure 1. Perspective view of the cation $[Cu(tmen)(CNC_6H_{11})_2]^+$.

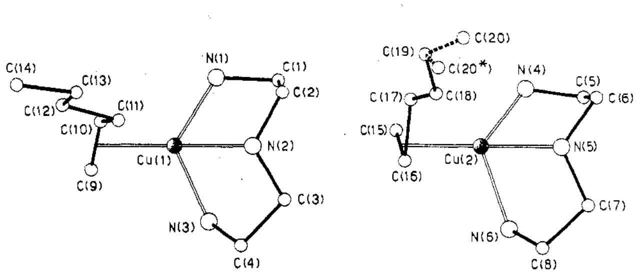


Figure 2. Molecular structure of the two crystallographically independent cations $[Cu(dien)(C_6H_{12})]^+$.

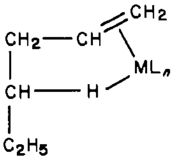
The conformation of the five-membered ring is practically gauche, with C(1) and C(2) lying at 0.21 and −0.31 Å, respectively, from the coordination plane. The dihedral angle between the planes N(1),C(1),C(2) and N(2),C(1),C(2) is 48.6°. The cyclohexyl ring [C(15) through C(20)] is in the equatorial chair form. No flattening or disorder was found for this ring although all the carbon atoms show relatively high thermal parameters. The two cyclohexyl groups, originating from the statistical distribution of the C(8) to C(13) ring, exhibit rather distorted chair conformations and differ in their orientation with respect to the N(3)–C(8) bond direction, which is nearly axial for the C(8) to C(13) ring and intermediate between axial and equatorial for the C(8), C(9), C(10*), C(11*), C(12*), and C(13) ring.

1-Hexene Complexation by Copper(I). Our recent results have shown that diethylenetriamine, when coordinated to copper(I), provides a useful 16-electron "model" compound, $[Cu(dien)]^+$, capable of adding π-acid ligands.[3,4] In $[Cu(dien)(norbornene)]^+$ we found, however, that the interaction of the olefin occurs both through the C=C and an aliphatic C–H bond.[4] This complex provides a structural model for one of the proposed metal-promoted C–H bond activations.[30,31] In order to establish, in other cases, the nature of the olefin–

Table V. Final Atomic Coordinates ($\times 10^4$) for $[(Cu(dien)(C_6H_{12})](BPh_4)$

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
Cu(1)	−398 (1)	2291 (1)	4037 (1)	C(66)	11109 (6)	3433 (5)	1981 (5)
Cu(2)	5706 (2)	4060 (1)	2341 (1)	C(71)	10435 (5)	4501 (4)	3136 (4)
N(1)	619 (8)	2743 (7)	3614 (7)	C(72)	9712 (5)	4524 (4)	3473 (4)
N(2)	573 (1)	2189 (7)	4932 (6)	C(73)	9788 (5)	4466 (4)	4164 (4)
N(3)	−249 (7)	1273 (6)	3972 (6)	C(74)	10587 (5)	4385 (4)	4518 (4)
N(4)	4594 (9)	3717 (8)	2740 (7)	C(75)	11310 (5)	4361 (4)	4182 (4)
N(5)	5001 (11)	4996 (7)	2217 (7)	C(76)	11234 (5)	4419 (4)	3490 (4)
N(6)	5414 (8)	4005 (7)	1284 (5)	C(81)	11139 (6)	4977 (5)	2037 (4)
C(1)	1433 (11)	2550 (9)	4020 (11)	C(82)	11482 (6)	5503 (5)	2420 (4)
C(2)	1299 (13)	2606 (10)	4747 (12)	C(83)	12086 (6)	5910 (5)	2176 (4)
C(3)	775 (13)	1462 (9)	4972 (9)	C(84)	12348 (5)	5791 (5)	1550 (4)
C(4)	−26 (12)	1062 (8)	4681 (9)	C(85)	12006 (6)	5265 (5)	1168 (4)
C(5)	3958 (13)	4175 (13)	2514 (10)	C(86)	11401 (6)	4858 (5)	1411 (4)
C(6)	4230 (14)	4896 (13)	2615 (9)	C(91)	9479 (6)	4950 (4)	1995 (4)
C(7)	4755 (13)	5069 (9)	1468 (9)	C(92)	9236 (6)	5516 (4)	2315 (4)
C(8)	5380 (11)	4714 (9)	1089 (8)	C(93)	8541 (6)	5882 (4)	2038 (4)
C(9)	−1719 (11)	2391 (11)	4014 (13)	C(94)	8089 (6)	5682 (4)	1442 (4)
C(10)	−1389 (11)	2948 (11)	4225 (11)	C(95)	8333 (6)	5117 (4)	1121 (4)
C(11)	−1268 (13)	3097 (11)	4982 (8)	C(96)	9028 (6)	4751 (4)	1398 (4)
C(12)	−2028 (11)	3546 (11)	5088 (9)	H(22)	3425	3016	4355
C(13)	−1901 (12)	3825 (9)	5800 (9)	H(23)	3178	4212	4227
C(14)	−2756 (11)	4208 (9)	5905 (9)	H(24)	4399	4978	4294
C(15)	6800 (16)	3653 (13)	2768 (12)	H(25)	5866	4547	4489
C(16)	7039 (12)	4113 (10)	2485 (9)	H(26)	6113	3351	4618
C(17)	6971 (14)	4388 (12)	3214 (11)	H(32)	6227	2217	3693
C(18)	6987 (16)	5063 (14)	3327 (13)	H(33)	6125	2002	2482
C(19)	7388 (22)	5536 (19)	3913 (17)	H(34)	4733	1737	1861
C(20)	7628 (28)	6170 (22)	3847 (21)	H(35)	3444	1687	2451
C(20*)	7102 (27)	6116 (22)	3847 (21)	H(36)	3546	1902	3661
B(1)	4933 (10)	2294 (8)	4545 (7)	H(42)	5762	2874	5704
B(2)	10359 (10)	4542 (8)	2310 (7)	H(43)	7061	2534	6413
C(21)	4785 (5)	3107 (5)	4495 (4)	H(44)	7869	1558	6109
C(22)	3958 (5)	3350 (5)	4385 (4)	H(45)	7378	922	5097
C(23)	3818 (5)	4024 (5)	4312 (4)	H(46)	6079	1262	4387
C(24)	4506 (5)	4456 (5)	4350 (4)	H(52)	4167	1037	4400
C(25)	5334 (5)	4213 (5)	4460 (4)	H(53)	3192	476	5093
C(26)	5473 (5)	3539 (5)	4532 (4)	H(54)	2665	1060	6041
C(31)	4893 (5)	2073 (5)	3754 (5)	H(55)	3114	2206	6295
C(32)	5620 (5)	2101 (5)	3422 (5)	H(56)	4089	2768	5602
C(33)	5562 (5)	1980 (5)	2740 (5)	H(62)	9009	3634	2126
C(34)	4778 (5)	1831 (5)	2389 (5)	H(63)	9012	2443	1876
C(35)	4051 (5)	1803 (5)	2722 (5)	H(64)	10356	1885	1693
C(36)	4109 (5)	1924 (5)	3404 (5)	H(65)	11697	2518	1760
C(41)	5838 (6)	2090 (4)	5001 (4)	H(66)	11694	3709	2010
C(42)	6115 (6)	2448 (4)	5572 (4)	H(72)	9093	4587	3198
C(43)	6847 (6)	2256 (4)	5971 (4)	H(73)	9228	4484	4425
C(44)	7302 (6)	1706 (4)	5800 (4)	H(74)	10646	4340	5054
C(45)	7025 (6)	1348 (4)	5229 (4)	H(75)	11929	4299	4456
C(46)	6293 (6)	1540 (4)	4829 (4)	H(76)	11794	4401	3229
C(51)	4190 (6)	1938 (4)	4957 (4)	H(82)	11279	5595	2904
C(52)	3937 (6)	1292 (4)	4813 (4)	H(83)	12352	6317	2472
C(53)	3387 (6)	976 (4)	5204 (4)	H(84)	12816	6106	1361
C(54)	3091 (6)	1305 (4)	5739 (4)	H(85)	12208	5173	683
C(55)	3344 (6)	1951 (4)	5882 (4)	H(86)	11136	4451	1115
C(56)	3893 (6)	2268 (4)	5491 (4)	H(92)	9585	5671	2777
C(61)	10351 (6)	3747 (5)	2084 (5)	H(93)	8352	6320	2286
C(62)	9595 (6)	3390 (5)	2046 (5)	H(94)	7551	5966	1227
C(63)	9597 (6)	2719 (5)	1905 (5)	H(95)	7983	4962	659
C(64)	10354 (6)	2405 (5)	1802 (5)	H(96)	9216	4313	1150
C(65)	11110 (6)	2761 (5)	1840 (5)				

Cu(dien) interaction, we investigated by an X-ray analysis $[Cu(dien)(C_6H_{12})](BPh_4)$, which potentially would allow a "chelating interaction" of the olefin ligand



This bonding mode of an olefin was invoked in some Pt or Pd complexes to account for a metal-promoted C–H bond activation.[31] A general procedure was used in which CuI was reacted in CH_3OH in the presence of dien to coordinate various olefins[4] (eq 2). Compound V was isolated as a crystalline

$$CuI + dien + C_6H_{12} \xrightarrow[-NaI]{+NaBPh_4} \underset{V}{[Cu(dien)(C_6H_{12})](BPh_4)} \qquad (2)$$

white solid when $NaBPh_4$ was added to the colorless solution. No spectroscopic determination could give insight to the structure of V, except for X-ray analysis and, far better, neutron diffraction studies.[30]

Description of the Structure of $[Cu(dien)(C_6H_{12})](BPh_4)$. The crystals are built up by two crystallographically independent cations, $[Cu(dien)(C_6H_{12})]^+$, and BPh_4^- anions, which

Table VI. Thermal Parameters (×10^4) for [Cu(dien)(C$_6$H$_{12}$)](BPh$_4$)[a]

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu(1)	817 (16)	730 (15)	715 (14)	2 (13)	−81 (12)	28 (14)
Cu(2)	888 (18)	820 (16)	766 (15)	15 (14)	−160 (13)	75 (15)
N(1)	812 (96)	904 (97)	1051 (105)	97 (86)	34 (79)	−328 (82)
N(2)	1400 (130)	861 (106)	769 (95)	−123 (83)	−474 (89)	225 (103)
N(3)	636 (89)	704 (83)	876 (94)	−22 (75)	57 (71)	−103 (71)
N(4)	762 (103)	1248 (126)	941 (104)	67 (94)	316 (83)	21 (96)
N(5)	1515 (148)	825 (104)	842 (104)	−127 (84)	−269 (103)	464 (102)
N(6)	997 (106)	829 (97)	521 (72)	3 (70)	89 (68)	59 (84)
C(1)	741 (138)	1079 (143)	1175 (164)	69 (27)	−332 (123)	−2 (109)
C(2)	984 (162)	837 (143)	1704 (217)	72 (146)	−834 (153)	−170 (126)
C(3)	1630 (191)	712 (124)	970 (135)	294 (106)	−403 (128)	144 (130)
C(4)	1214 (161)	775 (128)	962 (139)	166 (111)	201 (122)	−105 (118)
C(5)	947 (160)	1438 (199)	1070 (156)	168 (150)	−130 (119)	310 (158)
C(6)	1078 (170)	1719 (229)	872 (135)	58 (149)	321 (124)	674 (170)
C(7)	1542 (187)	901 (135)	737 (123)	174 (104)	−79 (121)	333 (132)
C(8)	1011 (140)	900 (135)	727 (116)	59 (104)	69 (100)	−36 (116)
C(9)	286 (116)	1086 (248)	2237 (248)	−248 (186)	−26 (127)	194 (117)
C(10)	170 (125)	1618 (289)	3695 (435)	110 (297)	108 (173)	178 (148)
C(11)	988 (171)	1549 (180)	612 (108)	−238 (117)	44 (107)	121 (142)
C(12)	750 (131)	1565 (191)	973 (146)	−86 (138)	90 (107)	267 (133)
C(13)	1196 (147)	865 (131)	982 (136)	−252 (106)	−14 (108)	30 (115)
C(14)	672 (130)	1174 (149)	1287 (161)	−287 (125)	−40 (111)	260 (116)

atom	U_{iso}, Å^2	atom	U_{iso}, Å^2	atom	U_{iso}, Å^2	atom	U_{iso}, Å^2
C(15)	1921 (93)	C(45)	950 (57)	C(85)	966 (55)	H(53)	1061 (311)
C(16)	1120 (60)	C(46)	756 (45)	C(86)	822 (47)	H(54)	1294 (314)
C(17)	2231 (78)	C(51)	541 (37)	C(91)	565 (37)	H(55)	1002 (311)
C(18)	1516 (93)	C(52)	739 (44)	C(92)	654 (40)	H(56)	649 (309)
C(19)	2165 (135)	C(53)	924 (52)	C(93)	861 (47)	H(62)	483 (317)
C(20)	1142 (139)	C(54)	838 (49)	C(94)	870 (51)	H(63)	1233 (316)
C(20*)	1047 (129)	C(55)	862 (52)	C(95)	871 (49)	H(64)	1434 (313)
B(1)	527 (41)	C(56)	714 (42)	C(96)	761 (46)	H(65)	1443 (316)
B(2)	550 (42)	C(61)	662 (43)	H(22)	995 (313)	H(66)	798 (317)
C(21)	615 (39)	C(62)	824 (50)	H(23)	1767 (320)	H(72)	1059 (314)
C(22)	726 (44)	C(63)	1028 (58)	H(24)	1073 (312)	H(73)	1143 (315)
C(23)	946 (51)	C(64)	1136 (62)	H(25)	1211 (313)	H(74)	1050 (316)
C(24)	947 (55)	C(65)	1075 (58)	H(26)	1051 (318)	H(75)	1263 (319)
C(25)	771 (45)	C(66)	803 (48)	H(32)	979 (312)	H(76)	698 (316)
C(26)	659 (40)	C(71)	577 (37)	H(33)	1028 (315)	H(82)	1095 (316)
C(31)	647 (41)	C(72)	666 (40)	H(34)	1810 (315)	H(83)	1005 (315)
C(32)	788 (47)	C(73)	802 (47)	H(35)	1716 (314)	H(84)	1520 (317)
C(33)	1092 (62)	C(74)	775 (46)	H(36)	677 (314)	H(85)	1439 (314)
C(34)	1219 (68)	C(75)	749 (44)	H(42)	923 (313)	H(86)	999 (315)
C(35)	1121 (62)	C(76)	662 (41)	H(43)	1037 (316)	H(92)	995 (319)
C(36)	869 (50)	C(81)	601 (39)	H(44)	1792 (314)	H(93)	1024 (317)
C(41)	529 (35)	C(82)	716 (43)	H(45)	1367 (311)	H(94)	1785 (310)
C(42)	660 (41)	C(83)	993 (56)	H(46)	1125 (317)	H(95)	1608 (316)
C(43)	928 (53)	C(84)	948 (55)	H(52)	675 (315)	H(96)	1061 (318)
C(44)	937 (52)						

[a] The anisotropic thermal factors are defined as $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$.

are separated by usual van der Waals distances. Figure 2 shows a perspective view of the two independent cations, with the atomic numbering scheme. While the high degree of disorder present in the cation containing Cu(2) prevents any significant discussion of its crystallographic parameters, the cation nevertheless displays an overall geometry which is very similar to that found for the cation containing Cu(1). Therefore, from now on, the discussion will be restricted to the cation containing Cu(1).

The dien acts as tridentate ligand, while the C═C of the hexene molecule completes the pseudotetrahedral coordination geometry around copper. No additional metal–H–C interaction can be inferred in this case from the X-ray analysis.[4] The deviation from tetrahedral geometry is mainly given by the L–Cu–L (L = donor atoms) angles, which range from 83.2 (7) to 127.4 (9)° (Table VII). While Cu(1) deviates only 0.26 Å from the plane through N(1), N(3), and A [A is the midpoint of the C═C bonded unit], larger deviations occur from the planes defined by the other faces of the coordination polyhedron, which could be alternatively described as a trigonal pyramid with N(2) occupying the apex. The trend in Cu–N bond distances strongly resembles that found in [Cu(dien)CO]$^+$[3] and [Cu(dien)(norbornene)]$^+$,[4] with the central nitrogen atom, N(2), bonding copper at a significantly longer distance [Cu(1)–N(2) = 2.25 (1) Å] than the terminal nitrogens (Table VII). The Cu–A distance, where A is the midpoint of the olefinic C(9)–C(10) double bond, is 2.01 (2) Å vs. the 2.08 Å distance found for the same interaction in [Cu(dien)(norbornene)]$^+$.[4] Bond distances and angles within the dien ligand compare very well with those found in [Cu(dien)CO]$^+$[3] and [Cu(dien)(norbornene)]$^+$.[4] The ethylene units display the gauche conformation, with C(1) and C(2) displaced by 0.45 and −0.26 Å, respectively, from the Cu(1),N(1),N(2) plane and with C(3) and C(4) displaced by 0.01 and −0.73 Å, respectively, from Cu(1),N(2),N(3) plane. Bond distances and angles of the hexene molecule are in good agreement with the reported values for analogous systems. The C═C bond length is only slightly affected upon the coordination to copper(I), the C(9)–C(10) distance being 1.30 (3) Å.

In both complexes the structural data relating to the BPh$_4^-$ anions show the usual features (Table SI). No significant short

Table VII. Important Bond Distances (Å) and Angles (deg) in the $[Cu(dien)(C_6H_{12})]^+$ Cations

Coordination Sphere			
Cu(1)-N(1)	2.11 (1)	Cu(1)-C(9)	2.10 (2)
Cu(1)-N(2)	2.25 (1)	Cu(1)-C(10)	2.13 (2)
Cu(1)-N(3)	2.09 (1)	Cu(1)-A[a]	2.01 (2)
N(1)-Cu(1)-N(2)	83.2 (7)	N(2)-Cu(1)-C(9)	128.2 (9)
N(1)-Cu(1)-N(3)	108.0 (7)	N(2)-Cu(1)-C(10)	111.5 (8)
N(1)-Cu(1)-C(9)	138.6 (9)	N(2)-Cu(1)-A	121.1 (9)
N(1)-Cu(1)-C(10)	114.1 (8)	N(3)-Cu(1)-C(9)	102.4 (8)
N(1)-Cu(1)-A	127.4 (9)	N(3)-Cu(1)-C(10)	136.4 (8)
N(2)-Cu(1)-N(3)	83.5 (6)	N(3)-Cu(1)-A	119.7 (9)
		C(9)-Cu(1)-C(10)	35.9 (9)
Cu(2)-N(4)	2.13 (2)	Cu(2)-C(15)	2.03 (2)
Cu(2)-N(5)	2.21 (2)	Cu(2)-C(16)	2.10 (2)
Cu(2)-N(6)	2.14 (1)	Cu(2)-B[b]	1.98 (2)
N(4)-Cu(2)-N(5)	84.1 (8)	N(5)-Cu(2)-C(15)	143.0 (11)
N(4)-Cu(2)-N(6)	105.2 (8)	N(5)-Cu(2)-C(16)	117.3 (9)
N(4)-Cu(2)-C(15)	114.1 (10)	N(5)-Cu(2)-B	130.8 (11)
N(4)-Cu(2)-C(16)	145.3 (10)	N(6)-Cu(2)-C(15)	119.1 (10)
N(4)-Cu(2)-B	130.1 (11)	N(6)-Cu(2)-C(16)	104.3 (9)
N(5)-Cu(2)-N(6)	83.1 (7)	N(6)-Cu(2)-B	112.4 (10)
		C(15)-Cu(2)-C(16)	33.2 (10)
Dien Ligand			
N(1)-C(1)	1.50 (2)	N(3)-C(4)	1.50 (2)
N(2)-C(2)	1.51 (3)	C(1)-C(2)	1.51 (3)
N(2)-C(3)	1.51 (2)	C(3)-C(4)	1.57 (3)
Cu(1)-N(1)-C(1)	108 (1)	N(1)-C(1)-C(2)	108 (2)
Cu(1)-N(2)-C(2)	103 (1)	N(2)-C(2)-C(1)	113 (2)
Cu(1)-N(2)-C(3)	105 (1)	N(2)-C(3)-C(4)	109 (2)
Cu(1)-N(3)-C(4)	104 (1)	N(3)-C(4)-C(3)	108 (2)
		C(2)-N(2)-C(3)	114 (2)
N(4)-C(5)	1.41 (3)	N(6)-C(8)	1.49 (2)
N(5)-C(6)	1.55 (3)	C(5)-C(6)	1.54 (4)
N(5)-C(7)	1.53 (2)	C(7)-C(8)	1.50 (3)
Cu(2)-N(4)-C(5)	105 (1)	N(4)-C(5)-C(6)	114 (2)
Cu(2)-N(5)-C(6)	104 (1)	N(5)-C(6)-C(5)	106 (2)
Cu(2)-N(5)-C(7)	106 (1)	N(5)-C(7)-C(8)	110 (1)
Cu(2)-N(6)-C(8)	102 (1)	N(6)-C(8)-C(7)	110 (2)
		C(6)-N(5)-C(7)	113 (2)
Hexene Ligand			
C(9)-C(10)	1.30 (3)	C(12)-C(13)	1.54 (3)
C(10)-C(11)	1.55 (3)	C(13)-C(14)	1.60 (2)
C(11)-C(12)	1.54 (3)		
Cu(1)-C(9)-C(10)	73 (1)	C(10)-C(11)-C(12)	104 (2)
Cu(1)-C(10)-C(9)	71 (1)	C(11)-C(12)-C(13)	109 (2)
Cu(1)-C(10)-C(11)	107 (1)	C(12)-C(13)-C(14)	106 (2)
C(9)-C(10)-C(11)	120 (2)		
C(15)-C(16)	1.18 (3)	C(18)-C(19)	1.60 (4)
C(16)-C(17)	1.59 (3)	C(19)-C(20)	1.36 (6)
C(17)-C(18)	1.39 (4)	C(19)-C(20*)	1.32 (6)
Cu(2)-C(15)-C(16)	77 (2)	C(16)-C(17)-C(18)	120 (2)
Cu(2)-C(16)-C(15)	70 (2)	C(17)-C(18)-C(19)	135 (3)
Cu(2)-C(16)-C(17)	89 (1)	C(18)-C(19)-C(20)	126 (4)
C(15)-C(16)-C(17)	77 (2)	C(18)-C(19)-C(20*)	127 (4)

[a] A is the midpoint of C(9)-C(10). [b] B is the midpoint of C(15)-C(16).

intermolecular contact has been observed in either compound.

Acknowledgment. We thank CNR (Rome) for financial support.

Registry No. $[Cu(en)(CNC_6H_{11})_2](BPh_4)$, 71230-60-9; $[Cu(tmen)(CNC_6H_{11})_2](BPh_4)$, 71230-58-5; $[Cu(dien)(C_6H_{12})](BPh_4)$, 71230-56-3.

Supplementary Material Available: Table SI listing bond distances and angles in the BPh_4^- anions, Tables SII and SIII listing least-squares planes, Tables SIV and SV listing internal rotation angles, and a listing of observed and calculated structure factors for both compounds (47 pages). Ordering information is given on any current masthead page.

References and Notes

(1) F. H. Jardine, *Adv. Inorg. Chem. Radiochem.*, **17**, 115 (1975).

(2) A. Camus, N. Marsich, G. Nardin, and L. Randaccio, *Inorg. Chim. Acta*, **23**, 131 (1977).

(3) M. Pasquali, F. Marchetti, and C. Floriani, *Inorg. Chem.*, **17**, 1684 (1978).

(4) M. Pasquali, C. Floriani, A. Gaetani-Manfredotti, and A. Chiesi-Villa, *J. Am. Chem. Soc.*, **100**, 4918 (1978).

(5) M. Pasquali, C. Floriani, and A. Gaetani-Manfredotti, *J. Chem. Soc., Chem. Commun.*, 921 (1978).

(6) M. Pasquali, C. Floriani, and A. Gaetani-Manfredotti, *Inorg. Chem.*, submitted for publication.

(7) L. Malatesta and F. Bonati, "Isocyanide Complexes of Metals", Wiley, London, 1969; F. Bonati and G. Minghetti, *Inorg. Chim. Acta*, **9**, 95 (1974), and references cited therein.

(8) T. Saegusa, Y. Ito, and S. Tomita, *J. Am. Chem. Soc.*, **93**, 5656 (1971); T. Saegusa, Y. Ito, H. Kinoshita, and S. Tomita, *J. Org. Chem.*, **36**, 3316 (1971); *Bull. Chem. Soc. Jpn.*, **43**, 877 (1970); *J. Org. Chem.*, **35**, 670 (1970); T. Saegusa, I. Murase, and Y. Ito, *ibid.*, **36**, 2876 (1971); *Tetrahedron*, **27**, 3795 (1971).

(9) G. Banditelli, F. Bonati, and G. Minghetti, *Gazzetta*, **107**, 267 (1977).

(10) J. Bailey and M. J. Mays, *J. Organometl. Chem.*, **47**, 217 (1973), and references cited therein.

(11) P. J. Fisher, N. E. Taylor, and M. M. Harding, *J. Chem. Soc.*, 2303 (1960).

(12) W. Hoppe, *Acta Crystallogr., Sect. A*, **25**, 67 (1969).

(13) Data reduction, structure solution, and refinements were carried out on the CYBER 7600 computer of the Centro di Calcolo Universitario dell'Italia Nord-Orientale (Bologna) with the SHELX-76 system of crystallographic computer programs (G. Sheldrick, University of Cambridge, 1976).

(14) Neutral-atom scattering factors were taken from D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968), for nitrogen, carbon, and boron and from "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, p 99, for copper. Hydrogen atom scattering factors were taken from R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(15) Supplementary material.

(16) M. I. Bruce, *J. Organomet. Chem.*, **44**, 209 (1972).

(17) M. R. Churchill, B. G. DeBoer, F. J. Rotella, O. M. AbuSalah, and M. I. Bruce, *Inorg. Chem.*, **14**, 2051 (1975).

(18) R. R. Gagnê, J. L. Allison, R. S. Gall, and C. A. Koval, *J. Am. Chem. Soc.*, **99**, 7170 (1977).

(19) F. Klages, K. Mönkemeyer, and R. Heinle, *Chem. Ber.*, **85**, 109 (1952).

(20) S. Otsuka, K. Mori, and K. Yamagami, *J. Org. Chem.*, **31**, 4170 (1966).

(21) H. Irving and M. Jonason, *J. Chem. Soc.*, 2095 (1960).

(22) A. Sacco, *Gazzetta*, **85**, 989 (1955).

(23) F. A. Cotton and T. J. Marks, *J. Am. Chem. Soc.*, **92**, 5114 (1970).

(24) T. Tsuda, H. Habu, S. Horiguchi, and T. Saegusa, *J. Am. Chem. Soc.*, **96**, 5930 (1974).

(25) R. Nast and W. H. Lepel, *Chem. Ber.*, **102**, 3224 (1969).

(26) C. Kappenstein and R. P. Hugel, *Inorg. Chem.*, **16**, 250 (1977).

(27) J. H. Burns and W. H. Baldwin, *J. Organomet. Chem.*, **120**, 361 (1976).

(28) K. R. Mann, N. S. Lewis, R. M. Williams, H. B. Gray, and J. G. Gordon II, *Inorg. Chem.*, **17**, 828 (1978).

(29) M. Ahlgrên, R. Hämäläinen, and U. Turpeinen, *Cryst. Struct. Commun.*, **6**, 829 (1977).

(30) J. M. Williams, R. K. Brown, A. J. Schultz, G. D. Stucky, and S. D. Ittel, *J. Am. Chem. Soc.*, **100**, 7407 (1978).

(31) P. A. Kramer and C. Masters, *J. Chem. Soc., Dalton Trans.*, 849 (1975); D. H. Clague and C. Masters, *ibid.*, 858 (1975).