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Reactions of CO, C_2H_4 and cyclic olefins with Cu^I-macrocyclic tridentate amine systems

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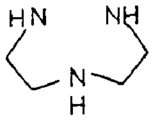
Abstract

Sixteen new cationic copper(I) complexes $[(\text{amine})\text{CuX}]^+$ (amine = 1,4,7-triazacyclononane or 1,4,7-trimethyl-1,4,7-triazacyclononane; X = carbon monoxide, ethylene, cyclohexene, cyclooctene, cyclohexyl isocyanide, 1,5-cyclooctadiene, norbornadiene and diphenylacetylene have been synthesized, and characterized by IR and ^{13}C NMR spectroscopy.

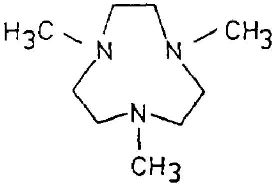
Introduction

Copper(I) complexes show a variety of coordination environments ranging in coordination number from 2 to 5. The number of ligands bound to the univalent metal seems to be influenced greatly by both the chemical nature of the ligands and the geometry they impose [1]. During recent years much interest has been focused in the chemistry of copper(I)-nitrogen donor-olefin complexes, because of their relevance to the proposed role of copper in the binding of the plant hormone ethylene to its receptor site [2,3,4]. The ethylene effect can also be induced by other gases such as carbon monoxide, acetylene, olefins, as well as by other structural analogues of ethylene, though their activities are lower [1–4]. Furthermore, the binding of unsaturated hydrocarbons to transition metals has occupied an important position in organometallic chemistry. For these reasons and others we have directed our efforts towards the syntheses of olefin–Cu^I complexes containing the small tridentate cyclic amines 1,4,7-triazacyclononane (L) and its trimethyl derivative (L′ as nitrogen donor ligands.

L ≙



L′ ≙



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These cyclic amines coordinate facially in an octahedron and form thermodynamically and kinetically stable complexes with almost all transition metals in various oxidation states [5].

In this paper we describe 16 new cationic copper(I) complexes, $[CuN_3X]^+$ where X is CO, C_2H_4 or mono- or di-olefins, and assign structures to them on the basis of their spectroscopic (IR and ^{31}C NMR) properties.

Experimental

The saturated macrocycles 1,4,7-triazacyclononane (L) [6*] and its *N*-methylated derivative *N,N′,N″*-trimethyl-1,4,7-triazacyclononane (L′) [7] were prepared by procedures described previously. All other starting materials were commercially available and were of reagent grade. All reactions were performed under argon (99.99%) in dried and deaerated solvents. Elemental analyses were performed by Beller Microanalytical Laboratory, Göttingen and by Microanalytical Laboratory, Ruhr-Universität Bochum, FRG. Copper was determined gravimetrically by using *N*-benzoylphenylhydroxylamine. Infrared spectra were recorded on a Beckman Acculab 10 instrument (KBr disks).

Proton decoupled ^{13}C NMR spectra were obtained at ambient temperature on a Bruker 250 WM spectrometer operating at 100.614 MHz. Chemical shifts are reported as δ vs. $SiMe_4$ with the solvent (acetone-d_6: δ 29.8 ppm, δ 206.5 ppm; dimethylsulfoxide-d_6: δ 39.7 ppm) as internal reference. In addition, off-resonance decoupled spectra were recorded to aid in assignment of pertinent carbon resonances. The assignments of the carbon resonances in the complexes were also helped by the use of the DEPT pulse sequence.

(Monocarbonyl)(1,4,7-triazacyclononane)copper(I) tetraphenylborate, $[(C_6H_{15}N_3)Cu(CO)][B(C_6H_5)_4]$

A mixture of copper(I) iodide (0.1 g, 0.7 mmol), sodium tetraphenylborate (0.34 g, 1 mmol) and 50 ml of dry methanol was stirred under a carbon monoxide atmosphere for 0.5 h. The ligand 1,4,7-triazacyclononane (0.7 ml of 1 *M* solution in methanol) was added dropwise with stirring, when a clear colorless solution was obtained. A white microcrystalline product precipitated out on cooling (yield: 0.13 g (33%)). Anal. Found: C, 68.2; H, 6.40; Cu, 11.3; N, 7.70. $C_{31}H_{35}BCuN_3O$ calcd.: C, 68.95; H, 6.53; Cu, 11.77; N, 7.78%.

(Monocarbonyl)(1,4,7-trimethyl-1,4,7-triazacyclononane)copper(I) tetraphenylborate, $[(C_9H_{21}N_3)Cu(CO)][B(C_6H_5)_4]$

The procedure described above was used to prepare the carbonyl complex of 1,4,7-trimethyl-1,4,7-triazacyclononane (yield: 0.1 g (24%)). Anal. Found: C, 70.2; H, 7.3; Cu, 10.3; N, 7.29. $C_{34}H_{41}BCuN_3O$ calcd.: C, 70.16; H, 7.09; Cu, 10.92; N, 7.22%.

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* Reference number with asterisk indicates a note in the list of references.

(Ethylene)(1,4,7-triazacyclononane)copper(I) tetraphenylborate, $[(C_6H_{15}N_3)Cu(C_2H_4)][B(C_6H_5)_4]$

A suspension of cuprous iodide (0.1 g, 0.7 mmol) and sodium tetraphenylborate (0.34 g, 1 mmol) in 50 ml of dry methanol was saturated with ethylene. When this saturation was complete (0.5 h), a methanol solution (1 ml) of the cyclic amine (0.1 g) was added slowly to give a clear solution, which on cooling afforded a white microcrystalline product (yield: 0.1 g (24%)). Anal. Found: C, 71.0; H, 7.12; N, 7.80; Cu, 11.9. $C_{32}H_{39}BCuN_3$ calcd.: C, 71.17; H, 7.27; Cu, 11.77; N, 7.78%.

(Ethylene)(1,4,7-trimethyl-1,4,7-triazacyclononane)copper(I) tetraphenylborate, $[(C_9H_{21}N_3)Cu(C_2H_4)][B(C_6H_5)_4]$

The analogous ethylene complex of the trimethyl derivative of the cyclic amine was prepared by the procedure described above (yield: 0.09 g (22%)). Anal. Found: C, 71.8; H, 7.85; Cu, 10.3; N, 7.20. $C_{35}H_{45}BCuN_3$ calcd.: C, 72.22; H, 7.79; Cu, 10.92; N, 7.23%.

(Cyclohexylisocyanide)(1,4,7-triazacyclononane)copper(I) tetraphenylborate, $[(C_6H_{15}N_3)Cu(C_6H_{11}CN)][B(C_6H_5)_4]$

To a stirred suspension of cuprous iodide (0.1 g, 0.7 mmol), sodium tetraphenylborate (0.34 g, 1 mmol) and cyclohexylisocyanide (0.14 g, 0.7 mmol) was added 0.1 g of the cyclic amine. The resulting colorless solution on standing gave white microcrystals, which were filtered off and stored under argon (yield: 0.15 g (34%)). Anal.

Table 1

Analytical data for the copper(I) complexes prepared from C_6H_{10}, C_8H_{14}, C_8H_{12}, C_7H_8 and $C_{14}H_{10}$

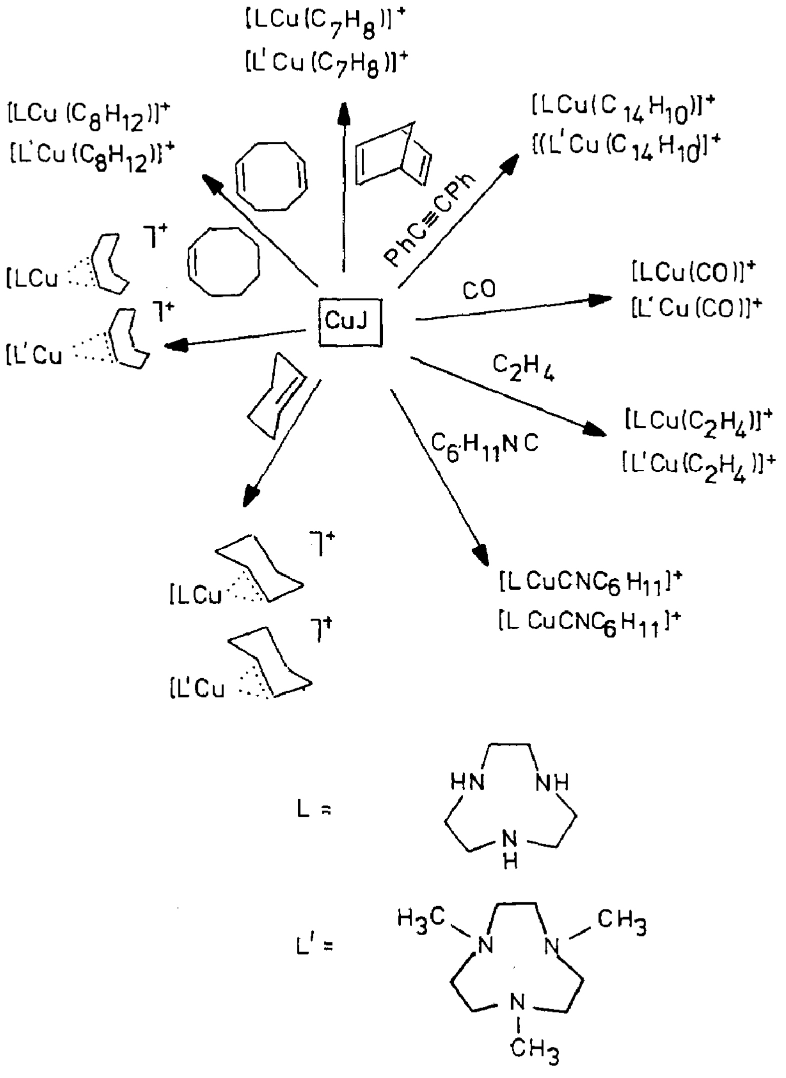
Empirical formula	Analysis (Found (calcd.) (%))			
	C	H	Cu	N
$C_{40}H_{52}BCuN_4$	74.0	9.0	9.10	8.70
	(72.44)	(7.90)	(9.58)	(8.45)
$C_{36}H_{45}BCuN_3$	72.0	7.60	9.80	7.20
	(72.78)	(7.63)	(10.68)	(7.11)
$C_{39}H_{51}BCuN_3$	75.4	8.50	9.20	6.30
	(73.75)	(8.09)	(10.00)	(6.62)
$C_{38}H_{49}BCuN_3$	71.43	7.78	9.96	6.61
	(73.36)	(7.93)	(10.21)	(6.75)
$C_{41}H_{55}BCuN_3$	75.27	8.76	9.88	6.40
	(74.14)	(8.34)	(9.57)	(6.33)
$C_{38}H_{47}BCuN_3$	71.8	7.38	10.11	6.71
	(73.60)	(7.63)	(10.25)	(6.78)
$C_{41}H_{53}BCuN_3$	73.1	8.20	9.30	6.40
	(74.37)	(8.06)	(9.60)	(6.35)
$C_{37}H_{43}BCuN_3$	72.67	7.05	10.20	7.03
	(73.56)	(7.17)	(10.52)	(6.96)
$C_{40}H_{49}BCuN_3$	74.82	7.79	10.1	6.83
	(74.35)	(7.64)	(9.83)	(6.50)
$C_{44}H_{45}BCuN_3$	75.60	6.68	9.43	6.02
	(76.57)	(6.57)	(9.21)	(6.09)
$C_{47}H_{51}BCuN_3$	76.3	6.91	8.82	5.68
	(77.09)	(7.01)	(8.68)	(5.74)

Found: C, 70.0; B, 7.60; Cu, 9.8; N, 8.80. $C_{37}H_{46}BCuN_4$ calcd.: C, 71.55; H, 7.46; Cu, 10.23; N, 9.02%.

Other copper(I) complexes were prepared similarly from cyclohexene (C_6H_{10}), cyclooctene (C_8H_{14}), 1,5-cyclooctadiene (C_8H_{12}), norbornadiene (C_7H_8), and diphenylacetylene ($C_{14}H_{10}$), the analytical data are gathered together in Table 1.

Results and discussion

Scheme 1 summarizes the synthetic routes to new copper(I) complexes containing the cyclic amines 1,4,7-triazacyclononane (tacn or L) and its *N*-methylated derivative (Me_3tacn or L′). Table 2 lists selected infrared spectral data, and Table 3 relevant ^{13}C NMR data for the new complexes.



Scheme 1

Table 2

Selected IR spectral data (KBr pellet) (L = 1,4,7-triazacyclononane; L′ = 1,4,7-trimethyl-1,4,7-triazacyclononane) m, medium; s, strong; w, weak

Compound	Frequencies [a] (cm^{-1})
$[LCu(CO)][B(C_6H_5)_4]$	(CO) 2030(m);
$[L'Cu(CO)][B(C_6H_5)_4]$	(CO) 2020(s)
$[LCu(C_2H_4)][B(C_6H_5)_4]$	(C=C) 1580(m)
$[L'Cu(C_2H_4)][B(C_6H_5)_4]$	(C=C) 1570(m)
$[LCu(C_6H_{11}CN)][B(C_6H_5)_4]$	(CN) 2120(m)
$[L'Cu(C_6H_{11}CN)][B(C_6H_5)_4]$	(CN) 2140(w)
$[LCu(C_6H_{10})][B(C_6H_5)_4]$	(C=C) 1580(m)
$[L'Cu(C_6H_{10})][B(C_6H_5)_4]$	(C=C) 1565(w)
$[LCu(C_8H_{14})][B(C_6H_5)_4]$	(C=C) 1570(w)
$[L'Cu(C_8H_{14})][B(C_6H_5)_4]$	(C=C) 1575(m)
$[LCu(C_8H_{12})][B(C_6H_5)_4]$	(C=C) 1560(w)
$[L'Cu(C_8H_{12})][B(C_6H_5)_4]$	(C=C) 1580(w)
$[LCu(C_7H_8)][B(C_6H_5)_4]$	(C=C) 1565(w)
$[L'Cu(C_7H_8)][B(C_6H_5)_4]$	(C=C) 1600(m)
$[LCu(C_{14}H_{10})][B(C_6H_5)_4]$	(C≡C) 1965(w) (C=C) 1580(w)
$[L'Cu(C_{14}H_{10})][B(C_6H_5)_4]$	(C≡C) 1920(w) (C=C) 1570(w)

[a] ν(BC): Three strong bands in the ranges 750–725, 740–715 and 720–690 cm^{-1}.

A carbon monoxide saturated methanolic suspension of CuI reacts with each of the cyclic amines to give a colorless solution. Addition of $Na[B(C_6H_5)_4]$ gave $[LCu(CO)][B(C_6H_5)_4]$ and $[L'Cu(CO)][B(C_6H_5)_4]$ as white crystalline solids. These carbonyls are stable to loss of carbon monoxide and dissolve sparingly in acetone, tetrahydrofuran, or dimethylsulfoxide without decomposition. On replacement of CuI with CuCl, the cationic $[LCu(CO)]^+$ species disproportionates as described earlier [8].

$$2[LCu(CO)]Cl \rightleftharpoons Cu^{II}L_2Cl_2 + Cu^0 + 2CO$$

In addition to the characteristic ν(BC) band (see Table 2) of the tetraphenylborate anion, the tacn complex shows a single sharp ν(CO) band at 2030 cm^{-1}, a value well within the range typically observed for $CuN_3(CO)$ species (2005–2080 cm^{-1}) [9]. This reduction of the CO stretching frequency (cf. that for free CO of

Table 3

^{13}C NMR spectra of amine-Cu^I-X cationic complexes

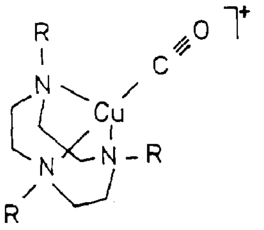
Compound	(^{13}C) [a] (ppm)
$[LCu(CO)][B(C_6H_5)_4]$	210 (CO), 137, 127, 122 (CH_{arom}), 52 (CH_2), 44 (CB)
$[L'Cu(CO)][B(C_6H_5)_4]$	210 (CO), 137, 127, 122 (CH_{arom}), 52 (CH_2), 44 (CB)
$[LCu(C_2H_4)][B(C_6H_5)_4]$	55, 51 (CH_2), 136, 125, 122 (CH_{arom}) 48 (CB)
$[L'Cu(C_2H_4)][B(C_6H_5)_4]$	55, 54 (CH_2), 136, 125, 122 (CH_{arom}) 48 (CB)
$[LCu(C_6H_{10})][B(C_6H_5)_4]$	54, 27, 26, 23 (CH_2), 128 (CH) 137, 126, 122 (CH_{arom}), 46 (CB)
$[LCu(C_8H_{14})][B(C_6H_5)_4]$	56, 27, 26, 25 (CH_2), 131 (CH) 137, 126, 122 (CH_{arom}), 46 (CB)
$[L'Cu(C_8H_{14})][B(C_6H_5)_4]$	56, 27, 26.5, 26 (CH_2), 131 (CH), 137, 126, 122 (CH_{arom}), 46 (CB)

[a] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$ (0.0 ppm).

2155 cm^{-1} [10]) can be attributed to the presence of both σ- and π-type bonding:

$$L\xrightarrow{\sigma}Cu\underset{\pi}{\overset{\sigma}{\rightleftharpoons}}CO$$

This results from the good symbiotic presence of the cyclic amines (L and L′) and carbon monoxide, on copper(I). With the 1,4,7-trimethyl-1,4,7-triazacyclononane compound the ν(CO) band is at 2020 cm^{-1}, as expected for an even stronger electron donor. The results reported here together with those in the literature [4,9], raise the possibility of ascribing the high stabilities of the isolated carbonyl complexes to (a) the highly basic nitrogen as donor atoms, (b) the macrocyclic nature of the ligands, and (c) the nature of the counterion, the highest stability being found for the $[B(C_6H_5)]^-$ anion. The cyclic amines act as tridentate ligands, and each donates six electrons to the d^{10} copper(I) ion; the carbonyl ligand donates two electrons, thereby completing the tetrahedral arrangement of donor ligands around the central atom and also completing the 18 outer-electron configuration of this atom.We propose the following tetrahedral structure for these cationic carbonyls.

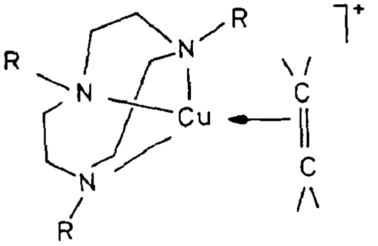


R = H or CH_3

The ^{13}C NMR spectra (Table 3) exhibit a resonance at 210 ppm, which is in the terminal carbonyl region [11], supporting the suggested structure. The fact that both carbonyl complexes exhibit δ(CO) at 210 ppm indicates once again [12] that the chemical shift of the carbonyl carbon atom is probably not an exact measure of transition metal → carbonyl π back-donation.

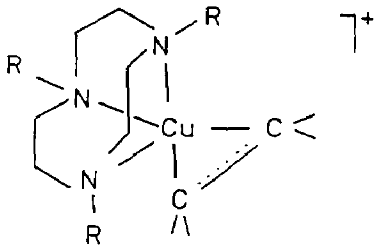
White crystalline $[LCu(C_2H_4)][B(C_6H_5)_4]$ and $[L'Cu(C_2H_4)][B(C_6H_5)_4]$ compounds were isolated from the reaction of CuI and L or L′ in methanol under an ethylene atmosphere. The completely dried colorless complexes are stable under argon for at least three days at room temperature. Ethylene exhibits a ν(C=C) stretching frequency at 1623 cm^{-1}, whereas the ethylenecopper(I) complexes with tacn and Me$_3$tacn show the stretching frequencies at 1580 and 1570 cm^{-1}, respectively. The (C=C) stretching frequency of free ethylene thus decreases 43–53 cm^{-1} with coordination to copper. The reported decrease in the stretching frequency for ethylene upon coordination is 40 cm^{-1} for $Ag(C_2H_4)^+$, 96 cm^{-1} for $[PdCl_2(C_2H_4)]_2$, 103 cm^{-1} for $[Rh(C_2H_4)Cl]_2$, 107 cm^{-1} for $[PtCl_2(C_2H_4)]$, 112 cm^{-1} for $Ni(C_2H_4)_3$, 120 cm^{-1} for $[Cu(NHPy_2)(C_2H_4)]^+$, 98–118 and 87–100 cm^{-1} for some other ethylenecopper(I) complexes [13,14,15].

The decrease in the C=C stretching frequency has been thought to correspond roughly to the increase in the π character of the double bond [16]. The decrease for our ethylenecopper(I) complexes is similar to that for the Ag^I complex, but smaller than those for the Ni^0, Pd^{II}, Pt^{II}, Rh^I and other reported Cu^I complexes. These results suggest that σ-bonding between Cu^I and coordinated ethylene is the dominant interaction and that the π-back bonding ability of Cu^I is poor relative to that of Ni^0. The ability of a d^{10} metal to π-back-bond decreases in the sequence Ni^0 > Cu$^{\text{I}}$ ≥ Ag$^{\text{I}}$. Thus the following structure, which allows predominant σ-type bonding, may be envisaged:



R = H or CH$_3$

^{13}C NMR spectra in solution at ambient temperature exhibit two resonances (Table 3), showing the inequivalence of the two ethylene carbons and suggesting the following trigonal bipyramidal structure for the ethylene complexes in solution containing two nitrogens and one carbon in the equatorial plane.



R = H or CH$_3$

The difference in the carbon chemical shifts decreases on going from 1,4,7-triazacyclononane ($\Delta\delta$ 4 ppm) to its trimethyl derivative ($\Delta\delta$ 1 ppm). In the ^{13}C NMR spectra of our compounds upfield shifts (shielding) of ca. 68–72 ppm are observed for the coordinated ethylene carbon resonances, relative to that of the free ethylene (123 ppm [18]). Salomon and Kochi [19g] found that olefins on coordination show larger upfield shifts of their carbons in (cyclic olefin)copper(I) CF_3SO_3 complexes, and concluded that this reflects the degree of Cu → olefin back-bonding; similar ^{13}C NMR investigations of bonded olefin-transition metal complexes have also been reported [19].This rationalization for the carbon-13 chemical shifts of carbon atoms bound to transition metal has been criticized [12]. According to the Dewar–Chatt–Duncanson model [17] in which the olefins were regarded σ-donors and π-acceptors, net shielding results from a preponderance of back donation of metal electron density to the olefin π^* orbital (π-bonding) over donation of olefin π-density to the metal (σ-bonding). The σ-donation of the nitrogens of the cyclic amines enhances the electron density on copper, thus promoting π-back-donation in the copper(I)–ethylene bonding. This demonstrates the contribution of π-back-donation to the copper–ethylene bonding, but does not have implications for the relative importance of π-back-donation compared with σ-donation, because the chemical shifts give no detailed information on π-bonding. In fact the σ-bonding contribution has been shown to predominate in copper–ethylene bonds [20].

The coordination of more, strongly basic amine to copper(I) may be more advantageous for stabilizing the ethylene complex than that of a pyridyl ligand [4(c)]. However, it must be emphasized that the weak back-donation from copper(I), as well as the σ-donation, is an important factor in stabilization of the ethylene complexes.

If, $C_6H_{11}NC$ is used instead of carbon monoxide or ethylene in the preparations, white solids $[LCu(C_6H_{11}NC)][BPh_4]$ and $[L'Cu(C_6H_{11}NC)][BPh_4]$ separate out after addition of $NaBPh_4$.The IR spectra exhibit one band (2140 cm^{-1} for L′ and 2120 cm^{-1} for L) in the $\nu(C{\equiv}N)$ region, as expected for a molecule of pseudotetrahedral arrangement of the four donor atoms: three nitrogens from the amine ligands and one carbon from the isocyanides. A similar structure has been established by X-ray analysis for the complex $[Cu(tmen)(CNC_6H_{11})_2][BPh_4]$ [21]. 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. The presence around the metal of basic σ-donor ligands (tacn or Me_3tacn) enhances the back-bonding by the metal, so that the ν(CN) stretching frequencies fall in a rather low range.

Similar reactions in the presence of cyclic olefins such as cyclohexene and cyclooctene afford the analogous complexes, $[(amine)Cu(C_6H_{10})][BPh_4]$ and $[(amine)Cu(C_8H_{14})][BPh_4]$. The C=C stretching frequencies of the coordinated monoolefins (Table 2) are rather low compared with those for the free monoolefins (cyclohexene: 1646 cm^{-1} [23], cyclooctene: 1648 cm^{-1} [23]), indicating a significant lengthening of the olefin bond upon coordination [24]. The ^{13}C NMR data are in accord with this picture and a single resonance is observed (Table 3) for two olefinic carbons of these cyclic olefins, showing their equivalence. Thus the analytical and spectroscopic data for each of the cyclic monoolefin complexes suggest formation of a five-coordinate cuprous cation, possibly with square pyramidal geometry, having two nitrogens and two carbons in the equatorial plane and the third nitrogen occupying the apical position, and with an uncoordinated tetraphenylborate anion. The structure could equally well be thought of as involving the amines acting as tridentate ligands, with the C=C of the monoolefin molecules completing the pseudotetrehedral coordination geometry around copper.

We have extended this investigation to other π-acid ligands by changing the cyclic monoolefins to cyclic diene species, viz. 1,5-cyclooctadiene (C_8H_{12}) and norbornadiene (C_7H_8). On the basis of the comparison of their spectral parameters with those complexes of known structures [25,26], we suggest that these complexes also contain 4-coordinate C=C bonded copper(I), as described before. The ^{13}C NMR spectra could not be obtained for these complexes because of their low stability in solutions.

CuI reacts with diphenylacetylene ($C_{14}H_{10}$) in the presence of the cyclic amines L and L′ to give the cations $[LCu(C_{14}H_{10})]^+$ and $[L'Cu(C_{14}H_{10})]^+$, which upon addition of $NaBPh_4$ yield the yellow tetraphenylborate salts. The absence of a ν(C=C) bond (Table 2) in the region of 2100–2200 cm^{-1} suggests that the acetylenic π-bond is directly coordinated to copper(I) ion, resulting in a decrease in the bond order. Because of decomposition of the products in solution, their ^{13}C NMR spectra could not be measured. The elemental analyses and IR data suggest that the disubstituted acetylene is coordinated to the $(N)_3Cu^I$-core via the acetylenic π-bond using two electron, three centre carbon–copper bonds.

In summary, we have demonstrated that the $Cu(N)_3{}^+$ cations (where N_3 denotes the macrocyclic tridentate ligands 1,4,7-triazacyclononane or its *N*-methylated derivative), a d^{10} 16-electron species, is capable of forming stable pseudotetrahedral complexes with carbon monoxide, ethylene and a few other olefins. Their stability may be ascribed to the macrocyclic nature of the amine ligands and to the weak

π-bonding ability of copper(I) together with the σ-bonding of the olefins. The findings also demonstrate the versatility of the ability of these tridentate *N*-donor ligands to form stable complexes with higher as well as lower oxidation states of metals [5,27*].

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