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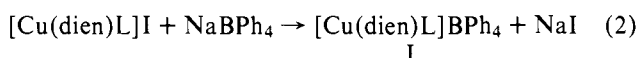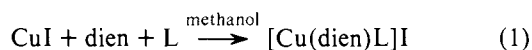Detroit, Michigan 48202*

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Interaction of an Aliphatic C–H Bond with Copper in a Norbornene(diethylenetriamine)copper(I) Cation Complex

Sir:

As would be predicted by all structural models, a diethyl-enetriamine ($H_2NCH_2CH_2N(H)CH_2CH_2NH_2$ or dien) complex of copper(I) has an open coordination site through which another ligand can be bound. In addition, the use of a polydentate ligand, such as dien, should prevent both the la-bility toward substitution and the tendency to disproportion-ation of copper(I).[1,2] For example, the complex [Cu(dien)-CO]BPh₄ is known as a thermally stable species.[2] We have now studied the binding of olefins to [Cu(dien)]⁺ and in one case have identified an expected and potentially significant Cu⁺–H–C bond.

A general method for preparing monomeric olefinic cationic complexes of copper(I)[3] can be given by the equations[4]

$$CuI + dien + L \xrightarrow{\text{methanol}} [Cu(dien)L]I \qquad (1)$$

$$[Cu(dien)L]I + NaBPh_4 \rightarrow [Cu(dien)L]BPh_4 + NaI \qquad (2)$$
$$I$$

where L = ethylene, norbornene, dimethyl maleate (DMM), and dimethyl fumarate (DMFu). The complex I can be re-covered as a white crystalline solid, the stability of which de-pends on the nature of the olefin.[5] The olefin can be displaced in every case by a molecule of CO or a molecule of $P(OC_2H_5)_3$.[4,5] In this paper we report the structure, as de-termined by x ray, for the complex in which the olefin is bicy-clo[2.2.1]hepta-2-ene. This particular complex has an unusual five-coordinate geometry and contains norbornene displaying a special bonding mode. Both these characteristics may be significant in understanding copper-photoassisted valence isomerization processes.[6]

Crystal Data. $C_{35}H_{43}BCuN_3$: mol wt, 580; orthorhombic; $a = 19.804 (3), b = 16.551 (2), c = 9.440 (1)$ Å; $Z = 4; d_{calcd} = 1.245$ g/cm³; μ (Cu Kα) = 11.6 cm⁻¹; space group $Pna2_1$ (from structural analysis). Diffraction intensities were mea-sured in the θ–2θ scan mode using Ni-filtered Cu Kα radiation on a Siemens on-line single-crystal diffractometer; 2463 in-dependent reflections ($6° < 2\theta < 120°$) were collected from a crystal of approximate dimensions $0.10 \times 0.24 \times 0.48$ mm, sealed in a glass capillary under nitrogen. The structure was solved by the heavy-atom method and refined by full-matrix least-squares technique[7] with anisotropic thermal parameters for all nonhydrogen atoms[8] to an R value of 4.8%, for 1525 independent data ($I > 2\sigma(I)$). The crystals are composed of discrete $[Cu(dien)(C_7H_{10})]^{+}$ [9] cations and BPh₄⁻ anions. A sketch of the macrocation is shown in Figure 1 and pertinent bond distances and angles are given in Table I. See the para-graph at the end of the paper regarding supplementary mate-rial.

The cation has no elements of symmetry. If the C=C bond is considered as occupying a single coordination site, the pol-yhedron about copper may be described as a slightly distorted trigonal bipyramid with the midpoint C(11)–C(12), N(1), and N(3) in the equatorial plane, N(2) and H(17) trans to each other in the axial positions. Besides the unusual coordination geometry for copper(I),[1] other chemically interesting struc-tural features of the cation are (i) the monomeric nature of the copper(I) complex[10] and (ii) the anchoring mode of the nor-bornene to the metal both through the olefinic C(11)–C(12) bond and the Cu–H–C interaction. A strong Cu–H(17) in-teraction can be established by the direct location of the in-teracting hydrogen.[8] The Cu–H distance (2.01 (15) Å) com-pares very well with the only very short Mo–H interactions known (2.15 and 1.93 Å),[11,12] all the other structurally iden-tified metal–H interactions being far weaker.[13] It was proposed that metal induced aliphatic C–H activation on coordinated olefins occurs through a metal–olefin interacting mode[14,15] which is exemplified by the copper-norbornene interaction in

Table I. Bond Distances (Angstroms) and Angles (Degrees) with Their Estimated Standard Deviations

Coordination sphere		
Cu–N(1) = 2.008 (6)	N(1)–Cu–N(3) = 105.6 (3)	A–Cu–N(2) = 108.2 (4)
Cu–N(2) = 2.252 (7)	N(1)–Cu–A[a] = 125.6 (4)	A–Cu–H(17) = 56 (5)
Cu–N(3) = 2.109 (8)	N(3)–Cu–A[a] = 128.4 (4)	N(2)–Cu–H(17) = 165 (5)
Cu–C(11) = 2.19 (1)	N(1)–Cu–N(2) = 83.3 (3)	C(11)–Cu–C(12) = 36.8 (5)
Cu–C(12) = 2.19 (1)	N(1)–Cu–H(17) = 106 (4)	C(17)–H(17)–Cu = 158 (17)
Cu–A[a] = 2.08 (1)	N(3)–Cu–N(2) = 81.5 (4)	
Cu–H(17) = 2.01 (15)	N(3)–Cu–H(17) = 107 (4)	
Cu–C(17) = 2.78 (1)		

Norbornlene ligand		
C(11)–C(12) = 1.38 (2)	C(16)–C(17) = 1.54 (2)	C(13)–C(14)–C(15) = 105.8 (7)
C(11)–C(16) = 1.37 (2)	C(13)–C(17) = 1.56 (2)	C(14)–C(15)–C(16) = 98.9 (8)
C(12)–C(13) = 1.39 (2)	C(11)–C(12)–C(13) = 109.3 (10)	C(15)–C(16)–C(11) = 103.5 (10)
C(13)–C(14) = 1.52 (1)	C(12)–C(13)–C(14) = 107.5 (12)	C(15)–C(16)–C(17) = 103.7 (11)
C(14)–C(15) = 1.53 (1)	C(12)–C(13)–C(17) = 100.3 (10)	C(11)–C(16)–C(17) = 104.2 (12)
C(15)–C(16) = 1.57 (1)	C(14)–C(13)–C(17) = 97.9 (10)	C(16)–C(17)–C(13) = 90.5 (12)
C(17)–H(17) = 0.81 (15)		

[a] A is the midpoint of C(11)–C(12).

Figure 1. A view of the molecular structure of $[Cu(dien)(C_7H_{10})]^+$, showing the atomic numbering scheme.

$[Cu(dien)(C_7H_{10})]^+$. A perturbation or polarization of the C–H bond by an electrophilic metal atom, like Cu^+, should be considered the earliest stage of a metal induced C–H activation.[16] This norbornene bonding mode, when applied to norbornadiene–copper(I) interaction, would help in describing the specific copper(I)–norbornadiene bonding which predisposes this olefin toward photoassisted valence isomerization processes.[6]

Both the results by Gagné et al.[1] and those here reported seem to suggest that the five coordination may play an unexpected role in molecular activation processes promoted by copper(I) complexes.

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Supplementary Material Available: The final atomic parameters, bond distances, and angles within the BPh₄⁻ anion and the diethylenetriamine ligand, and a complete listing of factor amplitudes (26 pages). Ordering information is given on any current masthead page.

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(5) All cited olefins gave isolable, rather thermally stable, microcrystalline complexes (yield in the range of 50–75%). Analytical data agree with the formulation given. For ethylene the stoichiometry was gas volumetrically controlled. Olefin can be replaced readily in the complex by CO and P(OC₂H₅)₃. Though stable in vacuo in the solid state, the complex containing ethylene loses it when in solution. The "practical" stability of the complex seems to increase along with the π acidity of the ligand, the greatest being found for L = DMM and DMFu. For these two complexes, which are yellow, the reaction with CO gives back the starting olefinic isomer. The IR spectra (Nujol) show that the CO groups (L = DMM and DMFu) are probably not directly involved in the coordination; in fact the absorptions due to these groups showed a shift to higher wave numbers of only 10–20 cm⁻¹ with respect to the free ligand: ν_{CO} (L = DMM) 1730 (br s), cm⁻; ν_{CO} (L = DMFu) 1740 (br s), cm⁻¹.
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Bromine Adsorbed on a Molecular Sieve: A Reagent for Selective Bromination

Sir:

In this communication we report a novel type of molecular sieve effect in which 5A zeolite crystals, saturated with bromine, are used as a reagent for the selective bromination of a terminal double bond. Although the novel adsorptive properties of molecular sieve zeolites have found widespread application in shape selective catalysis[1] and in separation processes,[2] previous applications in synthetic organic chemistry are limited to uses in esterification, ketalization, and other similar reactions as a means of selectively adsorbing the water which is formed during the reactions, in order to promote a favorable shift in the equilibrium.[3] Molecular sieves have also been used as carriers for KMnO₄ but in this application the sieve func-