

quinone. Sulfite solutions for reactions with diazonium ions were prepared in acetic acid buffers, and the concentration of sulfite ion was calculated from the known pH of the buffer and pK of hydro-sulfite ion. All rates were studied over at least a tenfold range of concentrations of nucleophile, and many over a 100-fold range.

In the measurements of equilibrium constants, the change in absorbance of the cations at high and low concentrations of added nucleophile were measured to determine the extent of reaction of the cation at low nucleophile concentration. The equilibrium constants were calculated as described in the Results section.

Reaction of Benzenediazonium Ion with Diethylamine. Aqueous solutions of benzenediazonium ion and diethylamine, both at 0.03 M, were mixed in equal volumes. After several minutes, dilute

sodium hydroxide was added to the solution, and the product was extracted into ether. Evaporation of the ether at room temperature left a brownish oil. Gas chromatography on Carbowax at 210° showed a single peak which has retention time different from diethylamine, biphenyl, and azobenzene.

The nmr spectrum in carbon tetrachloride solution exhibited a triplet at δ 1.3, a quartet at 3.8, and a multiplet at 7.4, with relative intensities of 6:4:5, respectively. The ultraviolet spectrum of the oil showed strongly overlapping bands with maxima at 285 and 313 nm.

The kinetics of the reaction were followed by techniques analogous to those described above for reactions of other cations. The results are summarized in Table IV.

Cationic Olefin Complexes of Copper(I). Structure and Bonding in Group Ib Metal–Olefin Complexes

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Abstract: A variety of new structural types of cationic copper(I)–olefin complexes have been isolated and characterized. The nmr spectrum of the olefin changes with coordination to copper(I). An analysis of the chemical shifts indicates that the nature of the olefin–metal bond varies predictably with the number and the geometric arrangement of the coordinated C=C bonds. The bonding in olefin complexes of other group Ib metals is also discussed in the light of these results.

Olefin complexes of copper(I) salts are known for a variety of olefinic ligands, but these complexes, with few exceptions, have been limited to copper(I) halides.^{1–3} The presence of halide, however, limits the range of π -olefin structures possible, since it is extensively involved as a bridging ligand between copper(I) nuclei, and the resultant polynuclear copper(I) halide clusters often dominate the structures. Furthermore, copper(I) and nickel(0) are isoelectronic, yet despite the number of polyolefin complexes of nickel(0) that are extant, there are few isostructural analogs of copper(I) halide.^{2,4} Competition between halide ions and olefin or ligand sites on copper(I) is no doubt an important factor in determining the stability of these complexes.

Salts of copper(I) with noncoordinating anions are generally considered to be unstable due to the tendency of copper(I) to disproportionate to copper(II) and copper metal. We have found that benzene, a rather weak π ligand, provides sufficient stabilization of copper(I) to allow its isolation as a stable crystalline trifluoromethanesulfonate (triflate) salt **1**,⁵ which is an excellent reagent for the preparation of cationic olefin complexes of copper(I).

We wish to report a general method for the preparation and the properties of a wide variety of new structural types of copper(I)–olefin complexes. The use of the poorly coordinating triflate anion allows these cat-

ionic complexes to be readily soluble in organic solvents in contrast to other previously known complexes.^{6,7} Their unique solubility and stability thus enable structural studies to be carried out by nuclear magnetic resonance (nmr). For example, the olefin–metal bond is pictured in the Dewar–Chatt model as consisting of σ and π components, the relative contributions of which vary from one complex to another.⁸ Analysis of the changes in the olefin nmr spectra which occur on coordination can be employed to deduce factors which influence the contributions from σ and π components in a variety of olefin–copper(I) complexes. These results are compared with the bonding in other group Ib metal–olefin complexes involving silver(I) and gold(I).

Results and Discussion

Benzene–Copper(I) Triflate. A crystalline, air-sensitive complex of copper(I) triflate and benzene [(CuO-Tf)₂C₆H₆] can be isolated from the reaction of trifluoromethanesulfonic anhydride with copper(I) oxide in benzene. This colorless copper(I)–benzene complex is stable to about 100° when heated carefully in a sealed evacuated tube. Benzene is released quantitatively from **1** only when heated above 120°. Complex **1** probably has a structure with local C_{2h} symmetry about the benzene ring analogous to that found in the 1:1 benzene–AgClO₄ complex.⁹ One of the degenerate highest occupied molecular orbitals of benzene which

(1) E. O. Fischer and H. Werner, "Metal π -Complexes," Vol. I, Elsevier, Amsterdam, 1966; M. Herberhold *ibid.*, Vol. II, 1972.

(2) H. W. Quinn and J. H. Tsai, *Advan. Inorg. Radiochem.*, **12**, 217 (1969).

(3) S. E. Manahan, *Inorg. Chem.*, **5**, 2063 (1966).

(4) G. N. Schrauzer, *Advan. Organometal. Chem.*, **2**, 1 (1964).

(5) R. G. Salomon and J. K. Kochi, *J. Chem. Soc., Chem. Commun.*, 559 (1972).

(6) S. E. Manahan, *Inorg. Nucl. Chem. Lett.*, **3**, 383 (1967).

(7) B. W. Cook, R. G. J. Miller, and P. F. Todd, *J. Organometal. Chem.*, **19**, 421 (1969).

(8) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C79 (1951); J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(9) R. E. Rundle and J. H. Goring, *J. Amer. Chem. Soc.*, **72**, 5337 (1950).

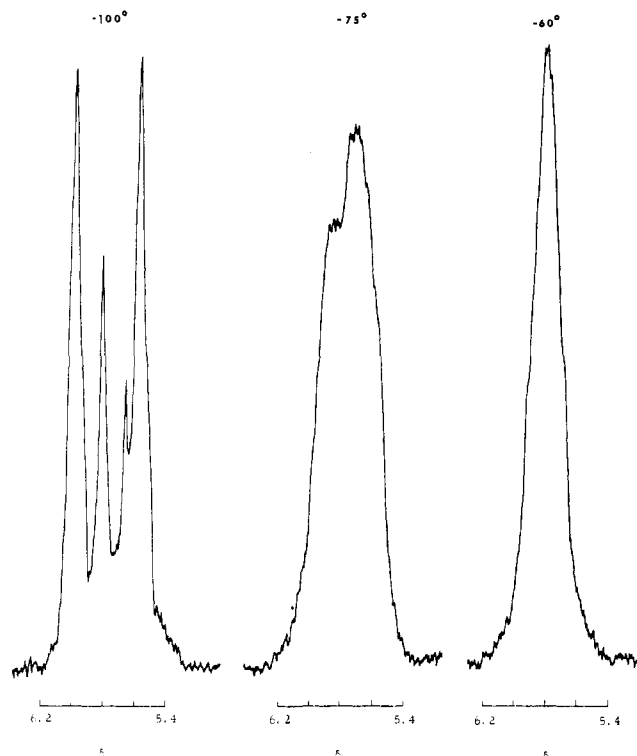
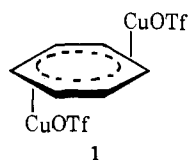


Figure 1. Proton magnetic resonance spectrum of cyclooctatetraene-copper(I) complex in solutions of a 1:1 mixture of acetone- d_6 and methanol- d_4 at various temperatures. At -100° , the minor resonances at δ 5.80 is due to the free cyclooctatetraene ligand and that at δ 5.66 is probably due to the 2:1 complex.



has a_g symmetry in the complex would be a major contributor to the bonding with copper(I) in such a structure.¹⁰

Olefin-Copper(I) Triflates. The weakly coordinated benzene is readily displaced from copper(I) in **1** by various olefins to form solutions of cationic olefin complexes in organic solvents (e.g., benzene, acetic acid, 2-butanone, and methanol). The nmr spectra of these complexes may be examined without isolation, or the crystalline Cu(I)-olefin complexes can be isolated from these solutions in fair to excellent yields (see Experimental Section).

The cationic Cu(I)-olefin complexes isolated in this manner usually differ in stoichiometry from the corresponding copper(I) halide-olefin complexes (Table I). These differences result from the competition of the strongly coordinating halides with the olefin for ligand sites on Cu(I), which is also reflected in the relatively high tendency of the olefin ligands in copper(I) halide complexes to dissociate. The structures of many of these new olefin complexes in solution can be deduced¹¹ from a consideration of their infrared (ir) and nmr

(10) We have recently been informed that a preliminary crystal structure of **1** indicates that the two copper nuclei are located on opposite faces of benzene largely in a meta relationship: M. B. Dines, private communication.

(11) Crystallographic structures are being determined independently.

Table I. Stoichiometries of Isolated Cationic Cu(I)-Olefin Complexes and the Corresponding Copper(I) Halide-Olefin Complexes

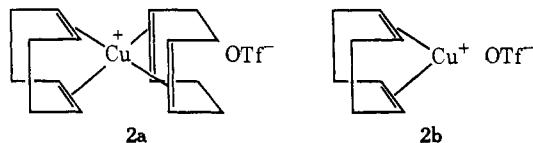
Complex	Coordinated olefin L	Stoichiometry	
		CuOTf · L _n	Cu · Cl · L _m
2a	1,5-Cyclooctadiene	CuL ₂ OTf	CuLCl ^a
2b	1,5-Cyclooctadiene	CuLOTf	CuLCl ^a
3	1,3,5,7-Cyclooctatetraene	CuLOTf	CuLCl ^a
4	<i>endo</i> -Dicyclopentadiene	CuL ₂ OTf	CuLCl ^a
5	Norbornylene	CuLOTf	
6a	(<i>E,E,E</i>)-1,5,9-Cyclododecatriene	CuLOTf	Cu ₂ LCl ₂ ^b
6b	(<i>Z,Z,Z</i>)-1,5,9-Cyclododecatriene	CuLOTf	
7	(<i>Z,E,E</i>)-1,5,9-Cyclododecatriene	CuLOTf	Cu ₂ LCl ₂ ^b
8	<i>trans</i> -Cyclooctene	CuL ₂ OTf	
9	1,3-Cyclooctadiene	CuLOTf	Cu ₃ LCl ₃ ^b
10	1,3,5-Cycloheptatriene	Cu ₂ L(OTf) ₂	

^a G. N. Schrauzer and S. Eichler, *Chem. Ber.*, **95**, 260 (1962).

^b H. L. Haight, J. R. Doyle, N. C. Baenziger, and G. F. Richards, *Inorg. Chem.*, **2**, 1301 (1963).

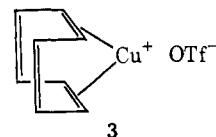
spectra, as well as the determination of the apparent molecular weights by vapor pressure osmometry (vpo).

1,5-Cyclooctadiene. Bis(1,5-cyclooctadiene)copper(I) triflate (**2**) is monomeric and undissociated in methanol solution by vpo measurements. All vinyl protons are equivalent in the nmr spectrum and only a single C=C stretching band is observed in its ir spectrum, similar to the corresponding perchlorate and fluoroborate complexes.^{6,7} These data suggest a symmetrical structure for **2** analogous to that of the isoelectronic Ni(0) complex in which 1,5-cyclooctadiene is a tetra-



hapto ligand.¹² In contrast, CuCl forms a 1:1 chlorobridged centrosymmetric dimeric complex with 1,5-cyclooctadiene.¹³ Upon heating **2a** in an evacuated sealed tube, it melts with loss of *one* diene ligand leaving the 1:1 cyclooctadiene-copper(I) triflate (**2b**), which crystallizes on cooling and remelts at 160–165° without further decomposition. The relatively facile replacement of one of the diene ligands on **2a** thus is clearly a contributing factor in the successful competition of halide ions for ligand sites on Cu(I).

Cyclooctatetraene. Vapor pressure osmometry indicates that 1,3,5,7-cyclooctatetraene-copper(I) triflate (**3**) is monomeric and undissociated in methanol solution. All protons are equivalent in the nmr spectrum of **3** at



room temperature but are resolved at -100° into non-equivalent resonances of equal area as shown in Figure 1. Moreover, the ir spectrum of this complex clearly

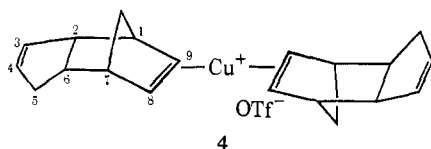
(12) (a) G. Wilke, *Angew. Chem.*, **72**, 581 (1960); (b) B. Bogdanović, M. Kröner, and G. Wilke, *Justus Liebigs Ann. Chem.*, **699**, 1 (1966); (c) J. Müller and P. Gösser, *Angew. Chem., Int. Ed. Engl.*, **6**, 364 (1967); (d) H. Dierks and H. Dietrich, *Z. Kristallogr., Kristallgeometrie, Kristallphys.*, **122**, 1 (1965). (e) K. Jonas, P. Heimbach, and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **7**, 949 (1968).

(13) J. H. van de Hende and W. C. Baird, *J. Amer. Chem. Soc.*, **85**, 1009 (1963).

indicates the presence of nonequivalent carbon-carbon double bonds. Thus, cyclooctatetraene exhibits a single C=C stretching frequency at 1635 cm^{-1} , whereas absorption bands occur at 1630 and 1520 cm^{-1} in complex **3** corresponding to free and π -complexed double bonds, respectively. These results suggest a structure for **3** in which cyclooctatetraene is bonded to copper(I) as a 1,2,5,6-tetrahapto ligand.¹⁴ A similar structure has been suggested for the analogous Ni(0) complex in solution.^{4,15} Interestingly, the nmr spectrum of the latter does not exhibit the equivalence of all protons at room temperature due to rapid exchange of cyclooctatetraene,^{12b} which characterizes the Cu(I) complex **3**.

Dicyclopentadiene. Infrared spectral data suggest that in the 1:1 complex of CuCl with *endo*-dicyclopentadiene, π -complexing occurs with the 8,9 double bond.^{2,7} Similar results are observed for the 1:2 complex (**4**) of CuOTf. The increased number of coordinated double bonds in **4** relative to its CuCl analog supports the hypothesis that competition between halide ions and olefin for copper(I) ligand sites is an important factor in the stability of these complexes.

In free dicyclopentadiene, $\nu_{\text{C}=\text{C}}$ at 1615 and 1570 cm^{-1} have been assigned to the double bonds in the cyclopentene and norbornene rings, respectively.⁷ In complex **4** the absorption band associated with the



double bond in the norbornene ring has been lowered to 1540 cm^{-1} by π -complexing. The nmr spectrum of **4** suggests an *exo* complexation of the 8,9 double bond. Thus, *endo*-dicyclopentadiene exhibits vinylic absorptions at δ 5.95 (2 H) and 5.45 (2 H). In complex **4** the ligand absorption at δ 5.95 is shifted to δ 5.4–5.5 while that at δ 5.45 is not shifted.¹⁶ Moreover, the C₁₀ methylene in dicyclopentadiene appears as two doublets ($J = 10\text{ Hz}$) centered at δ 1.25 and 1.45.¹⁷ In **4** the ligand absorption at δ 1.45 is shifted to δ 1.59 while the absorption at δ 1.25 is not shifted.

The *exo* complexation in **4** of dicyclopentadiene is noteworthy. *endo*-Dicyclopentadiene can act as a tetrahapto ligand, since the two C=C bonds are spatially situated in a manner similar to those of 1,5-cyclooctadiene. Indeed *endo*-dicyclopentadiene does act as a tri- or tetrahapto ligand in olefin complexes of a number of other transition metals.¹⁸ Yet, in spite of the advantages to complex stability which chelation

(14) For copper(I) halide complexes of cyclooctatetraene, see ref 2, and N. C. Baenziger, C. F. Richards, and J. R. Doyle, *Inorg. Chem.*, **3**, 1529 (1964).

(15) G. Wilke, *Angew. Chem.*, **75**, 10 (1963).

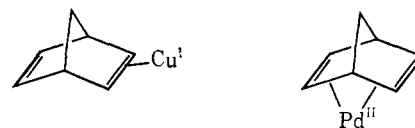
(16) Similar changes in the nmr chemical shifts of dicyclopentadiene upon complexation with AuCl have been interpreted analogously: R. Hüttel, H. Reinheimer, and H. Diel, *Chem. Ber.*, **99**, 462 (1966).

(17) The resonance at δ 1.25 is assigned to H₁₀(anti) (to the 8,9 C=C bond) and the resonance at δ 1.45 to H₁₀(syn), in analogy with the assignments established in norbornene in which H₇(anti) = δ 1.08 and H₇(syn) = δ 1.33: K. Tori, *et al.*, *Tetrahedron Lett.*, **9** (1966); cf. also B. Franzus, *et al.*, *J. Amer. Chem. Soc.*, **90**, 3721 (1968); A. P. Marchand and J. E. Rose, *ibid.*, **90**, 3724 (1968).

(18) (a) U. Belluco, B. Crociani, R. Pietropaolo, and P. Uguagliati, *Inorg. Chim. Acta, Rev.*, **3**, 19 (1969); (b) N. C. Baenziger, J. R. Doyle, G. F. Richards, and C. L. Carpenter, *Proc. Int. Conf. Coord. Chem.*, 6th Detroit, 131 (1961).

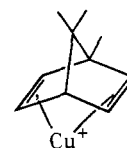
would confer, only one C=C bond is coordinated to Cu(I) or Au(I).^{2,16}

The spatial arrangement of the two C=C bonds in norbornadiene is also akin to that of 1,5-cyclooctadiene. However, only one C=C bond is complexed in the *exo* configuration in the 1:1 complexes of norbornadiene with cuprous halides.¹⁹ An *exo* bonded structure also pertains with Ag(I), Cu(II), and probably Au(I).^{16,20} With Pd(II), however, norbornadiene is bonded as a 2,3,5,6-tetrahapto (*endo*) ligand.²¹ This behavior of Cu(I), Ag(I), and Au(I) may reflect the difference



between these group Ib metals and other transition metals in their electronic requirements for olefin coordination.²²

It is noteworthy, however, that norbornadiene-type diolefins do undergo *endo* coordination with copper(I) triflate when *exo* coordination is discouraged by steric hindrance by methyl groups as in bornadiene²³ (*vide infra*).



A similar delicate balance between *exo* and *endo* coordination has been inferred from the course of catalytic deuteration with Pd(0). Thus, the Pd(0) mediated reaction of D₂ with norbornadiene yields almost exclusively *exo-cis*-5,6-dideuterionorbornylene presumably due to *exo* coordination of the Pd(0) catalyst. With *exo* coordination sterically inhibited in 7-*tert*-butylnorbornadiene, D₂ adds predominately *endo*.²⁴

Norbornylene. In methanol solutions, norbornylene-copper(I) triflate (**5**) is monomeric and undissociated. The contrasting stoichiometries between this complex and the *endo*-dicyclopentadiene complex **4** is curious in light of the structural similarity of the coordinated C=C double bonds of these ligands. This difference can be explained if both olefins form 2:1 complexes

(19) N. C. Baenziger, H. L. Haight, and J. R. Doyle, *Inorg. Chem.*, **3**, 1535 (1964).

(20) (a) N. C. Baenziger, H. L. Haight, R. Alexander, and J. R. Doyle, *ibid.*, **5**, 1399 (1966); (b) R. A. Zelonka and M. C. Baird, *J. Organometal. Chem.*, **33**, 267 (1971).

(21) (a) N. C. Baenziger, G. F. Richards, and J. R. Doyle, *Acta Crystallogr.*, **18**, 924 (1965); **14**, 303 (1961); (b) cf. also J. M. Harvilchuck, D. A. Aikens, and R. C. Murray, Jr., *Inorg. Chem.*, **8**, 539 (1969).

(22) (a) One difference between group Ib and transition metals is the relatively large contribution of olefin to metal electron donation in the group Ib metal-olefin bond. Additional stabilization in the group Ib complexes might result from homoconjugative donation of the "non-bonding" π electrons of the uncoordinated C=C bond in dicyclopentadiene and norbornadiene. Such an intramolecular "solvation" of the backside of the coordinated C=C bond is reasonable in light of the recently demonstrated stabilizing effect of intermolecular backside solvation in Ag(I)-olefin complexes: I. Rothberg, W. J. Krieg, and W. R. Sisco, *J. Org. Chem.*, **36**, 4076 (1971). (b) It has been suggested that stabilization of *exo*-monodentate coordination of norbornadiene by Ag(I) [and concomitant destabilization of coordination by a second Ag(I)] might be provided by homoconjugative charge delocalization by the second C=C bond: J. G. Traynham and J. R. Olechowski, *J. Amer. Chem. Soc.*, **81**, 571 (1959).

(23) H. C. Brown and J. H. Kawakami, *ibid.*, **92**, 201 (1970); H. C. Brown and K.-T. Liu, *ibid.*, **93**, 7335 (1971).

(24) W. C. Baird and J. H. Surrridge, *J. Org. Chem.*, **37**, 304 (1972).

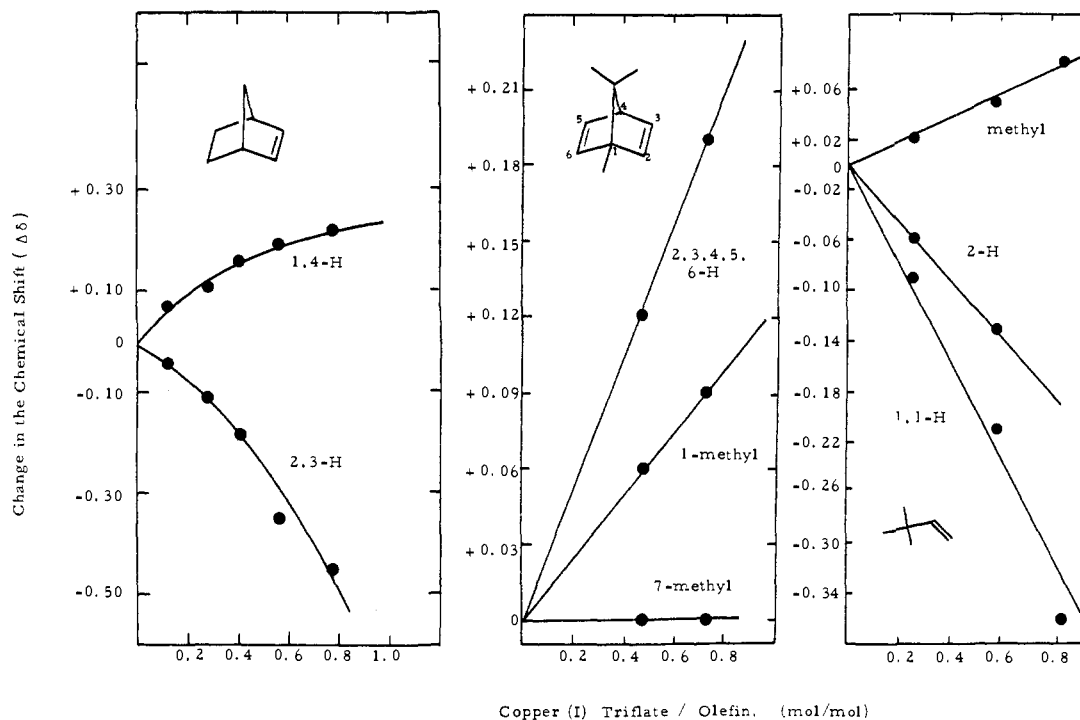
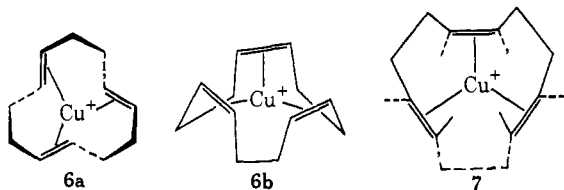


Figure 2. Variation of the change of chemical shift of various proton types due to olefin complexation with total copper(I) concentration relative to total olefin concentration in acetic-*d*, acid solution.

with CuOTf but that the second olefin ligand in each complex is bound more weakly than the first. The loss of the second ligand is dependent on its volatility, and would account for the reluctance of **5** to lose the second ligand and the apparent ease with which the 1:1 norbornylene-CuOTf complex is formed.²⁵ Further discussion of this point is deferred to the following section which deals with the nmr spectra of olefin-copper(I) complexes.

1,5,9-Cyclododecatriene. According to vapor pressure osmometric measurements, the *all-trans*-(*E,E,E*)-1,5,9-cyclododecatriene-copper(I) triflate (**6a**) is monomeric and undissociated in benzene solution. Furthermore, all vinyl protons are equivalent in the nmr spectrum of **6a**, as well as in the *all-cis*-(*Z,Z,Z*)-1,5,9-cyclododecatriene-copper(I) triflate (**6b**). Only a single C=C stretching band is observed in the infrared spectra of both **6a** and **6b**, and these results suggest symmetrical structures analogous to those of the isoelectronic Ni(0) complexes.^{12b,e,26}



The complexes **6a** and **6b** both exhibit extraordinary thermal stability and melt sharply without decomposition at 187–190 and 160–161°, respectively. The high solubilities of **6a** and **6b** in organic solvents (including

(25) In addition, the complexing power of *endo*-dicyclopentadiene might be enhanced relative to norbornylene due to homoconjugative stabilization.^{22b}

(26) H. Dietrich and H. Schmidt, *Naturwissenschaften*, **52**, 301 (1965).

benzene) are exceptional among polyene complexes of Cu(I) and are a reasonable consequence of the highly effective bonding between Cu(I) and the hexahapto ligands.

The 1:1 complex **7** isolated from (*Z,E,E*)-1,5,9-cyclododecatriene and copper(I) triflate also appears to involve all three double bonds. Although the nmr spectrum of **7** and the free ligand are not readily resolved, qualitatively the vinyl resonances of the triene are shifted downfield on complexation. Furthermore, the C=C stretching frequencies at 1670 and 1650 cm⁻¹ are shifted to 1620 and 1583 cm⁻¹ in **7**. A structure in which the π orbitals of all three C=C bonds are coplanar and in a trigonal array about Cu(I) can be readily accommodated.

trans-Cyclooctene. The 3:1 complex, tris(*trans*-cyclooctene)copper(I) triflate (**8**), exhibits only a single C=C stretching band in its ir spectrum. This suggests a symmetrical structure with three monoolefinic ligands coordinated to Cu(I) in a trigonal arrangement similar to that of the *all-trans*-cyclododecatriene complex. The exceptionally large number of volatile monoolefinic ligands coordinated to Cu(I) is unusual and relates to the strong complexing power of *trans*-cyclooctene as a result of the torsional C=C strain in this olefin. Complex **8** is extensively dissociated in methanol solution. For example, the "apparent" molecular weight of this complex measured by vapor pressure osmometry is 283, which corresponds to one-half of the calculated value, 543.²⁷

It is noteworthy that complexes **2**, **3**, **5**, and **6** can be washed repeatedly with pentane without any loss of olefin ligand. In contrast, copper(I) halide-olefin complexes readily lose coordinated olefin on prolonged

(27) The volatility of *trans*-cyclooctene complicates an accurate vpo measurement. It is also not clear from these measurements whether the olefin or triflate is dissociated from the complex.

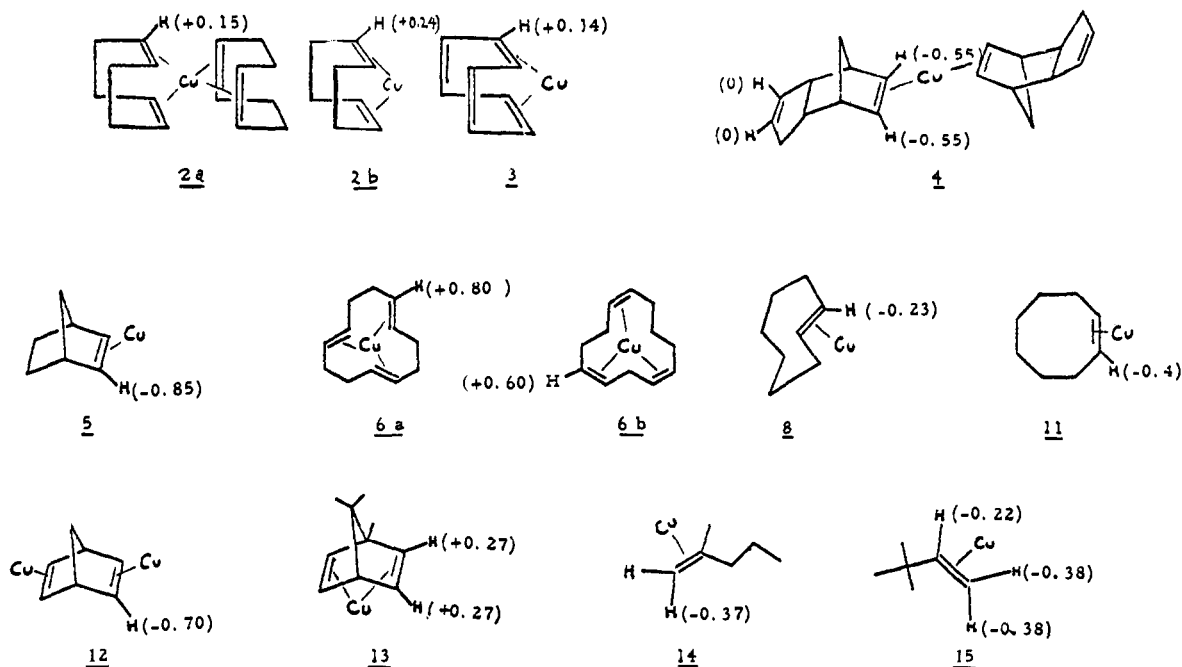


Figure 3. Proposed structures of CuOTf-olefin complexes in solution and the observed changes in the chemical shifts ($\Delta\delta_{\text{obsd}}$) of the vinyl protons on complexation. For convenience the anion is omitted in these structures. (The other *trans*-cyclooctene ligands are not included in 8.)

washing with organic solvents.²⁸ Thus, the high melting points and thermal stabilities shown by the CuOTf-olefin complexes (*vide supra*) are in sharp contrast to the low thermal stability of the corresponding olefin complexes derived from copper(I) halides (Table I, footnote b).

Nmr Studies of Olefin-Copper(I) Complexes in Solution. The nmr spectra of olefin-containing solutions varied with copper(I) concentration, but every spectrum contains only a single absorption due to a particular type of proton (Figure 2). These features can be understood in terms of rapid exchange between several different species in equilibrium with one another.²⁹⁻³¹ If $\Delta\delta_{\text{obsd}}$ is the change in chemical shift of a particular type of proton upon complexation, then for such a system at equilibrium

$$\Delta\delta_{\text{obsd}} = \delta_0 - \delta_{\text{obsd}} = (1 - X_0)\delta_0 - X_1\delta_1 - X_2\delta_2 \dots \quad (1)$$

where X_0 and δ_0 represent the fraction of olefin which is uncomplexed and the chemical shift of that form, respectively. X_n and δ_n have similar meanings for the various complexed olefin species present. In general, X_n and hence $\Delta\delta_{\text{obsd}}$ will be a complex function of the relative concentrations of olefin and copper(I). However, for the simplest case, namely, that involving only a single complexed species, eq 1 reduces to

$$\Delta\delta_{\text{obsd}} = (\delta_0 - \delta_1)X_1 \quad (2)$$

(28) (a) Norbornadiene complexes: E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 3178 (1959); (b) for the 1,5-cyclooctadiene-CuCl complex: G. M. Whitesides, G. L. Goe, and A. C. Cope, *J. Amer. Chem. Soc.*, 91, 2608 (1969).

(29) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, Chapter 10.

(30) Similar exchange has been noted previously, *e.g.*, for Ag(I): H. W. Quinn, J. S. McIntyre, and D. J. Peterson, *Can. J. Chem.*, 43, 2896 (1965); H. W. Quinn and R. L. Van Gilder, *ibid.*, 47, 4691 (1969).

(31) In these measurements, the value of $\Delta\delta_{\text{obsd}}$ is not necessarily equal to $\Delta\delta_{\text{max}}$; *e.g.*, see J. Solodar and J. P. Petrovich, *Inorg. Chem.*, 10, 395 (1971).

In general, if the formation constant of a particular complexed species of stoichiometry [(metal)_m(olefin)_n] is large and much greater than that of any other complex in the system, then in the presence of excess olefin

$$X_1 = \frac{n(M_{\text{total}})}{m(L_{\text{total}})}$$

$$\Delta\delta_{\text{obsd}} = \frac{n}{m}(\delta_0 - \delta_1)\frac{(M_{\text{total}})}{(L_{\text{total}})} \quad (3)$$

where (M_{total}) is the total concentration of the metal and (L_{total}) is the overall concentration of the olefin, *i.e.*, both free and complexed. Under these circumstances, the dependence of $\Delta\delta_{\text{obsd}}$ on the total equivalents of metal ion in the system relative to olefin will be linear (eq 3).

The linear dependence observed for neohexene and bornadiene in Figure 2 is presumptive evidence for the presence of only a single complexed species in rapid equilibrium with free olefin. We suggest that these species have structures 15 and 13, respectively (Figure 3).³² The nonlinear dependence of the chemical shift with the concentration of norbornylene shown in Figure 2 is consistent with a system involving several complexes in rapid equilibrium with free norbornylene suggested earlier (*vide supra*).³³

The nmr results presented in these studies are similar to those previously reported for the behavior of Cu(II) and Ag(I) toward olefin coordination in solution.^{20,30} Generally, only a single resonance was observed for each type of ligand proton, and $\Delta\delta_{\text{obsd}}$ increased with Cu(II) or Ag(I) concentration consistent

(32) Inhibition of exo complexation by steric hindrance due to methyl groups in bornadiene is also supported by the observation of a substantial shift of the methyl at C-1, but no shift of the C-7 methyl resonance upon coordination with Cu(I).

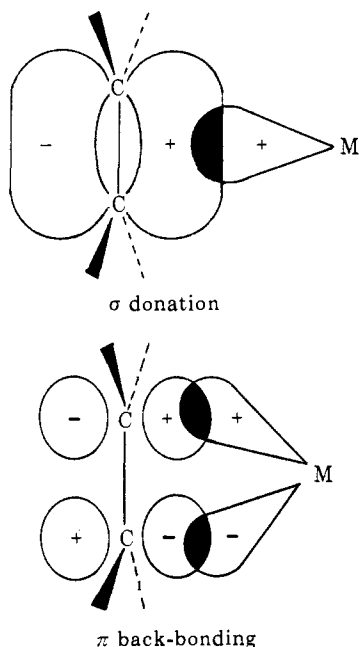
(33) With olefins containing the bicyclo[2.2.1]heptene skeleton, 2:1 as well as 1:1 complexes (*e.g.*, 4 and 5, respectively) are likely.

with exchange between free and coordinated olefin ligands which is rapid on the nmr time scale.³⁴

Extrapolation of the plots in Figure 2 to a 1:1 olefin: Cu(I) ratio provides the $\Delta\delta_{\text{obsd}}$ for the vinyl protons in complexes **15** and **13**. Similarly, $\Delta\delta_{\text{obsd}}$ were determined for the 1:1 complexes **11** and **14** and the 2:1 complex **12** listed in Figure 3. The $\Delta\delta_{\text{obsd}}$ indicated for the complexes **2**, **3**, **4**, **5**, **6a**, **6b**, and **8** were obtained by a similar procedure from the spectra of isolated complexes in acetone-*d*₆ solutions.

Bonding in Group Ib Metal-Olefin Complexes. Inspection of the $\Delta\delta_{\text{obsd}}$ for these complexes reveals a dichotomy between vinyl proton shifts in complexes of mono- and polydentate ligands. Thus, these shifts are negative for complexes **4**, **5**, **8**, **11**, **12**, **14**, and **15** of monodentate ligands while positive for complexes **2**, **3**, **6a**, **6b**, and **13** with polydentate ligands. We propose that this dichotomy arises from variations in the nature of the metal-olefin bond.

The transition metal-olefin coordinate bond according to the Dewar-Chatt model can be generally described as composed of σ and π components.⁸ The σ component involves overlapping of the occupied bonding π orbital of the olefin with a vacant σ -type metal orbital. The π component represents back-bonding and involves overlapping of the vacant antibonding π^* orbital of the olefin with a filled metal d



orbital. The relative contributions of these components may vary greatly from one complex to another. Since the magnetic shielding of protons at trigonal carbon atoms in olefins is directly proportional to π electron density at carbon,³⁰ the relative contributions of σ - and π -bonding in a particular metal-olefin complex would be reflected in the net shielding (or deshielding) of the vinyl protons accompanying complexation by the metal.² Thus, electron withdrawal from the double bond by σ -bonding results in deshielding, and electron donation to the double bond by π -bonding results in shielding of the vinyl protons upon complexation.³⁵

(34) See also R. Cramer, *J. Amer. Chem. Soc.*, **86**, 217 (1964); M. Orchin and P. J. Schmidt, *Inorg. Chim. Acta, Rev.*, **2**, 123 (1968).

(35) Shifts of the ir C=C stretching bands of olefins resulting from coordination with metals cannot be assumed to indicate specific changes

Olefin π complexation for most transition metals results in net shielding of vinyl protons³⁷ indicating a predominance of the π component. The olefin complexes of silver(I) which exhibit net deshielding of the vinyl protons constitute a glaring exception to this rule and indicate a predominance of the σ component.³⁰ Copper(I), in the same periodic group as silver(I), might be expected to behave similarly. However, the borderline behavior of the copper(I) complexes corresponds to a greater contribution of electron pair donation from metal d orbitals (*i.e.*, π component) to vacant olefin π^* orbitals. This trend follows the relative ease of oxidation of copper(I) and silver(I) to higher valence states, *i.e.*, the ease with which electrons can be promoted from d orbitals into the valency shell. It is also supported by the observation that olefin coordination by Cu(II) like Ag(I) always results in net deshielding of the vinyl protons,²⁰ since back-donation from Cu(II) into vacant π^* orbitals is not expected to contribute appreciably to bonding in Cu(II)-olefin complexes.

The observed dichotomy of vinyl proton shifts upon olefin complexation with copper(I) can be understood as the result of two factors. First, the σ component increases relative to the π component as the number of double bonds (σ donors) coordinated to the metal ion (π donor) increases.^{38a} Second, the σ component is subject to a trans effect which diminishes its magnitude. The first generalization accounts for the net shielding in complexes **5**, **11**, **12**, **14**, and **15** in which a single double bond is coordinated to each metal atom, and the net deshielding in complexes **2**, **3**, **6a**, **6b**, and **13** in which more than one double bond is coordinated to each metal atom. The second factor accounts for the net shielding in complexes **4** and **8**, in which the predominance of σ donors over π donors is overbalanced by the reduced effectiveness of the former due to their trans relationship in the complex.^{38b}

Further support for this model for bonding in the copper(I)-olefin complexes is provided by a consideration of the relative magnitudes of $\Delta\delta_{\text{obsd}}$ for the α and β vinyl protons of neohexene complex **15** and the related silver(I) fluoroborate complex (**16**) (Figure 3). The greater deshielding of the α than the β vinyl protons of **16** has been attributed to unsymmetrical positioning of the silver ion with respect to the trigonal carbon atoms.³⁰ The silver ion is pictured as being closer to the terminal carbon resulting in more effective π donation ("reshielding") to this end of the double bond, *i.e.*,

in the electron density of the C=C bond. Both removal of electron density by the metal from the π orbitals (σ component) and electron donation from the metal to the π^* orbitals (π component) of the C=C bond might result in shifts to lower frequencies due to weakening of the C=C bond. The conclusion³⁶ that shifts of $\nu_{\text{C=C}}$ to lower frequency indicate a decrease in the electron density of the C=C bond in CuClO₄ complexes with allyl alcohols is probably incorrect. Such a decrease in electron density should result in a decrease in shielding of the vinyl protons upon coordination. In fact, increased shielding was observed.

(36) Y. Ishino, T. Ogura, K. Noda, T. Hirashima, and O. Manabe, *Bull. Chem. Soc. Jap.*, **45**, 150 (1972).

(37) R. G. Kidd, "Characterization of Organometallic Compounds," M. Tsutsui, Ed., Wiley-Interscience, New York, N. Y., 1971, p 392 ff.

(38) (a) In other words, the share of the back-bonding from the metal to each double bond decreases as the number of coordinated double bonds increases. (b) This effect is again evident from comparison of $\Delta\delta_{\text{obsd}}$ for **2a** and **2b**. The greater ratio of deshielding σ donors to shielding π donors in **2a** vs. **2b** is overbalanced by the reduced effectiveness of the former due to the trans effect. Hence, the vinyl protons in **2a** are more shielded (or less deshielded) than those in **2b**.

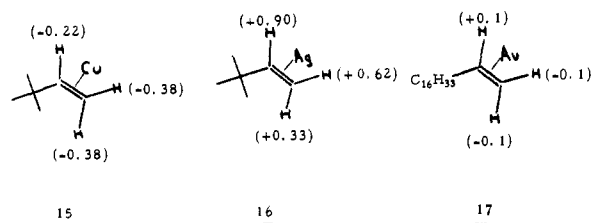


Figure 4. Chemical shift changes ($\Delta\delta_{\text{obsd}}$) of the vinyl protons upon complexation of neohexene and octadecene-1 with copper(I), silver(I), and gold(I). In these complexes, C-1 is designated as β and C-2 is α .

greater electron density at the less highly substituted carbon atom. While the net change in vinyl proton chemical shifts in **15** is opposite that in **16**, the greater shielding of the proton at the terminal compared to the substituted trigonal carbon atom of **15** is wholly consistent with the same unsymmetrical electron density distribution as in **16** (Figure 4). Shielding or deshielding of particular vinyl protons due to olefin complexation by gold(I) chloride^{1b,39} can also be understood in terms of a similar variation with structure of the nature of the metal-olefin bond. Gold(I) complexation of terminal olefins, exemplified by the octadecene-gold(I) chloride complex (**17**), results in shielding of the β protons and deshielding of the α protons. The shielding by the π component of the metal-olefin bond, thus, follows the order: Cu(I) > Au(I) > Ag(I), which is also that expected from the trend in the ionization potentials⁴⁰ of these ions [Cu(I), 20.29 eV; Au(I), 20.50 eV; and Ag(I), 21.49 eV].

There are other explanations for chemical shifts of vinyl protons upon complexation to metals. These models, however, cannot readily account for either the net deshielding⁴¹ frequently observed with Ag(I), Cu(I), Cu(II), and Au(I) or the variation from shielding to deshielding⁴² in a series of monoolefin complexes of Au(I) and the olefin-copper(I) complexes reported here.

Conclusion. A series of mono- and polyolefin complexes of copper(I) can be readily prepared from copper(I) triflate. As many as three monoolefinic ligands may coordinate with copper(I) in the most favorable cases (e.g., *trans*-cyclooctene). However, copper(I) usually coordinates significantly with only two monoolefinic ligands. In some cases, such as the sterically hindered *tert*-butylethylene, evidence for coordination by only one olefinic ligand can be detected by nmr.

The classification of Cu(I)-olefin complexes into monodentate and chelating polydentate structures provides a basis for interpreting the direction of changes in the nmr spectra (of the olefinic protons), which occur upon coordination. We have adduced evidence that the nature of the olefin-metal bond varies predictably with the number and geometric arrangement of coordinated C=C bonds and the identity of the metal in olefin complexes of the group Ib metals. It now seems possible that the direction of shifts of vinyl proton resonances upon coordination might be used as pre-

(39) R. Hüttel and H. Reinheimer, *Chem. Ber.*, **99**, 2778 (1966).

(40) H. Hosoya and S. Nagakura, *Bull. Chem. Soc. Jap.*, **37**, 249 (1964).

(41) M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3753 (1959); M. A. Bennett, L. Pratt, and G. Wilkinson, *ibid.*, 2037 (1961).

(42) J. C. Schug and R. J. Martin, *J. Phys. Chem.*, **66**, 1554 (1962).

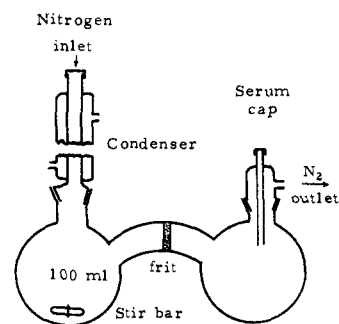


Figure 5. Reaction vessel for the preparation of copper(I) triflate.

sumptive evidence for or against chelate coordination of Cu(I) and Au(I) by polyolefins. For example, a decision in favor of the exo-monodentate structure over an endo-chelated bidentate structure seems warranted on the basis of the observed upfield shift of the vinyl proton nmr resonances of norbornadiene upon coordination with AuCl.^{16,39}

Further, new examples of the influence of anionic ligands on the stoichiometry of Cu(I)-olefin complexes have been accumulated and provide support for the proposition that strongly associating anionic ligands compete effectively with olefins for coordination sites on Cu(I). It might be anticipated from these observations that the dihalocuprate(I) complexes will exhibit little if any tendency to coordinate with olefins.

Experimental Section

Cuprous Triflate-Benzene Complex (1). The reaction vessel (Figure 5) consisted of two 100-ml, one neck, round-bottom flasks connected with a glass tube of 2-cm diameter in the middle of which was a medium porosity sintered glass disk. One of the flasks was charged with 2 g (14 mmol) of Cu₂O, 80 ml of dry benzene, and 5.5 g (19.5 mmol) of trifluoromethanesulfonic anhydride. A magnetic stirring bar was added and the flask fitted with a condenser which was connected through a gas outlet adapter to a mineral oil bubbler. The other flask was fitted with a gas inlet adapter which had a second inlet sealed off with a rubber serum cap. A slow stream of dry nitrogen was passed into the second flask and passed out of the first vessel through the condenser. The reaction mixture was gently refluxed with stirring for several hours until the red Cu₂O had dissolved and afforded a clear solution. The gas flow was reversed and the hot solution filtered into the second flask. Upon cooling to room temperature, a white complex crystallized from the solution. Reversal of the gas flow allowed back filtration and removal of the mother liquor. The product was washed with two 10-ml portions of fresh benzene, which were added with a hypodermic syringe through the serum cap. The washings were removed by filtration. The product was dried under a stream of dry nitrogen, yield 5.5 g (77%). The complex turns orange brown upon exposure to air and must be handled in an inert atmosphere.

Bis(1,5-cyclooctadiene)copper(I) Triflate (2). A solution of complex **1** (1.5 g) in 2-butanol (6 ml) was treated with 1,5-cyclooctadiene (3.6 ml). The resulting white crystalline precipitate was washed with benzene (2 × 5 ml) to yield 2.2 g (99%) of **2**: mp 157–165° dec; ν 1595 cm⁻¹; nmr δ 5.70 (8 H), 2.40 (16 H); ν λ_{max} 236 nm (ϵ 3060), 282 (1700); mol wt (methanol) 385 (calcd 429).

Anal. Calcd for C₁₈H₂₄CuF₃O₃S: C, 47.59; H, 5.64; Cu, 14.8. Found: C, 47.69; H, 5.75; Cu, 14.5.

1,3,5,7-Cyclooctatetraenecopper(I) Triflate (3). A solution of complex **1** (1.5 g) in 2-butanone (2.5 ml) was treated with 1,3,5,7-cyclooctatetraene (2 ml). The resulting solution was filtered, and addition of pentane resulted in precipitation of a light yellow crystalline complex which was washed with additional pentane (2 × 4 ml) to yield 1.4 g (86%) of **3**: mp 165–175° dec; ν 1630, 1520 cm⁻¹; nmr δ 5.89; (100 MHz in CD₃OD-acetone-*d*₆ (1:1) at -100°), 5.56 (4 H), 5.97 (4 H); ν λ_{max} 233 nm (ϵ 3600) 280 (2100); mol wt (methanol) 300 (calcd 317); 1,3,5,9-cyclooctatetraene 32% (calcd 33%).

Anal. Calcd for $C_9H_8CuF_3O_3S$: C, 34.13; H, 2.55; Cu, 20.0. Found: C, 33.70; H, 2.74; Cu, 19.5.

Bis(*endo*-dicyclopentadiene)copper(I) Triflate (4). A solution of complex **1** (0.80 g) in 2-butanone (1.4 ml) was treated with *endo*-dicyclopentadiene (1 ml). After a few minutes, a white crystalline product began to precipitate. A little pentane was added to induce further precipitation of product. The solid was washed with pentane (2×4 ml) to yield 0.71 g (54%) of **4**; ν 1615, 1540 cm^{-1} ; nmr δ 5.4 (2 H), 5.5 (2 H), 1.60 (1 H, d, $J = 10$ Hz); *endo*-dicyclopentadiene 50% (calcd 55%).

Anal. Calcd for $C_{21}H_{24}CuF_3O_3S$: Cu, 13.3. Found: Cu, 14.0.

(*E,E,E*)-1,5,9-Cyclododecatrienecopper(I) Triflate (6a). Complex **1** (0.50 g) was dissolved in a mixture of (*E,E,E*)-1,5,9-cyclododecatriene (0.5 g) and benzene (4 ml). The resulting solution was filtered. Addition of pentane resulted in precipitation of a white crystalline complex which was washed with additional pentane (2×4 ml) to yield 0.62 g (100%) of **6** as fine needles: mp 187–190°; ν 1600 cm^{-1} ; nmr δ 5.80 (6 H), 2.40 (12 H); $uv \lambda_{max}$ 240 nm (ϵ 2500), 280 (1500); mol wt (benzene) 366 (calcd 375).

Anal. Calcd for $C_{13}H_{18}CuF_3O_3S$: C, 41.65; H, 4.84; Cu, 16.9. Found: C, 41.75; H, 4.92; Cu, 16.8.

(*Z,Z,Z*)-1,5,9-Cyclododecatriene. A solution of 40 g of (*E,E,E*)-1,5,9-cyclododecatriene in CCl_4 (400 ml) was treated dropwise with a solution of bromine (144 g) in CCl_4 (500 ml) at 0° with mechanical stirring. Evaporation of solvent and excess bromine left crude hexabromide as a light yellow gum. The hexabromide in hot absolute ethanol (1 l.) was added in one portion to a solution of sodium ethoxide prepared from sodium metal (25.2 g) and absolute ethanol (1.2 l.). The mixture was stirred at 80° for 1 hr. After cooling to room temperature, the mixture was treated with water (720 ml) and extracted with pentane (3×700 ml). The combined organic extracts were washed with water (3×700 ml) and then saturated aqueous NaCl (700 ml). Removal of solvent by distillation and distillation of the residual oil under reduced pressure gave a mixture of 1,5,9- and 2,5,9-tribromo-(*Z,Z,Z*)-1,5,9-cyclododecatrienes as a light yellow oil, bp 145–154° (0.2 mm) (68 g). A solution of the tribromides in dry THF (250 ml) was added in one portion to a mixture of lithium metal (14.5 g), *tert*-butyl alcohol (72 ml), and dry THF (850 ml). After the exothermic reaction subsided, the mixture was boiled under reflux for an additional 3 hr with vigorous stirring. The excess lithium was then removed by filtration, and the mixture was treated with water and extracted with pentane (2.5 l.). The pentane extracts were washed with water (5×1.2 l.) and saturated aqueous NaCl (900 ml), and solvent was removed by distillation to give crude triene (28 g, 70% overall). The crude triene in pentane (100 ml) was extracted into a solution of 40 g of $AgNO_3$ in 100 ml of water. The aqueous extract was washed with an additional 50 ml of pentane. The compound organic washings were dried ($MgSO_4$) and concentrated to yield 13.2 g of impure oil which contained very little of the desired product. The aqueous extract was treated with 30% NH_3 in water (100 ml) and pentane (100 ml). The aqueous phase was extracted with an additional 100 ml of pentane. The combined organic extracts were washed with distilled water (2×50 ml) and dried ($MgSO_4$). The solvent was removed by rotary evaporation and the oily residue distilled under reduced pressure to give pure *Z,Z,Z* triene (13.5 g, 34% overall from the *E,E,E* triene) whose nmr and ir spectra were identical with those reported for the title compound.^{43a}

(*Z,Z,Z*)-1,5,9-Cyclododecatrienecopper(I) Triflate (6b). Complex **1** (1.5 g, 0.59 mmol) was dissolved in a solution of (*Z,Z,Z*)-1,5,9-cyclododecatriene (1.5 g, 0.93 mmol) in dry benzene (10 ml). Then 2 ml of pentane was added and the resulting mixture was placed in a refrigerator. After 24 hr, 0.4 g of crystalline olefin complex deposited from the solution. The mother liquor was separated and treated with more pentane and again refrigerated. After repetition of this procedure several times, a total of 1.9 g of nicely crystalline olefin complex (0.51 mmol, 86% yield) was collected and washed with pentane. The complex (**6b**) tends to oil out of benzene-pentane mixtures: mp 160–161°; ν 1585 cm^{-1} ; nmr (in CD_3CO_2D) δ 6.2 (6 H), 2.7 (12 H).

Anal. Calcd for $C_{13}H_{18}CuF_3O_3S$: C, 41.65; H, 4.84. Found: C, 41.78; H, 4.88.

(*Z,E,E*)-1,5,9-Cyclododecatrienecopper(I) Triflate (7). Complex **1** (0.93 g) was dissolved in a mixture of (*Z,E,E*)-1,5,9-cyclododecatriene (1 ml) and benzene (7 ml). Addition of pentane resulted in

precipitation of a white crystalline product which was washed with additional pentane (2×4 ml) to yield 1.2 g (100%) of **7**: ν 1620, 1583 cm^{-1} .

Anal. Calcd for $C_{13}H_{18}CuF_3O_3S$: C, 41.65; H, 4.84; Cu, 16.9. Found: C, 41.76; H, 4.70; Cu, 16.7.

1,3-Cyclooctadienecopper(I) Triflate (9). Complex **1** (0.82 g) was dissolved in a mixture of acetic acid (0.6 ml), benzene (1.4 ml), and 1,3-cyclooctadiene (1.4 ml). The solution was filtered, and pentane (2.8 ml) was added to the filtrate. A white powder precipitated which was washed with additional pentane (2×4 ml) to yield 0.63 g (70%) of very air-sensitive **9**: ν 1535 cm^{-1} ; 1,3-cyclooctadiene 31% (calcd 34%).

Anal. Calcd for $C_9H_{12}CuF_3O_3S$: Cu, 20.0. Found: Cu, 21.1.

1,3,5-Cycloheptatrienecopper(I) Triflate (10). A mixture of complex **1** (0.96 g), benzene (0.5 ml), and 1,3,5-cycloheptatriene (1 ml) was gently heated in a test tube which was sealed with a rubber serum cap. The resulting solution deposited a solid upon cooling to room temperature. After standing at room temperature for 15 hr, the product was collected and washed with pentane (2×4 ml) to yield 0.41 g (50%) of a yellow powdery very air-sensitive complex (**10**): ν 1635, 1530 cm^{-1} ; 1,3,5-cycloheptatriene 17% (calcd 18%). Complex **10** dissolves with decomposition in polar organic solvents at room temperature. However, a solution of **10** in acetone is stable at -80° . The vinyl proton absorptions in the nmr spectrum of **10** [δ 6.30 (2 H), 5.80 (2 H), 5.15 (2 H)] are similar to those of the free cycloheptatriene ligand [δ 6.55 (2 H), 6.15 (2 H), 5.30 (2 H)].

Anal. Calcd for $C_9H_8Cu_2F_6O_6S_2$: Cu, 24.6. Found: Cu, 23.4.

Norbornylenecopper(I) Triflate (5). A solution of complex **1** (0.95 g) in 2-butanone (0.9 ml) when treated with norbornylene (1.5 ml) and pentane (1 ml) deposited a white crystalline precipitate upon cooling to 0° and standing for 1 hr. The solid was washed with pentane (2×4 ml) to give a small yield of **5**: mp 184–187° dec; ν 1480 cm^{-1} ; nmr δ 5.15 (2 H), 3.05 (2 H); $uv \lambda_{max}$ 236 nm (ϵ 3400), 272 (2000); mol wt (methanol) 276 (calcd 307).

Anal. Calcd for $C_7H_{10}CuF_3O_3S$: C, 31.32; H, 3.29; Cu, 20.7. Found: C, 31.16; H, 3.38; Cu, 19.8.

Tris(*trans*-cyclooctene)copper(I) Triflate (8). A solution of complex **1** (0.58 g) in 2-butanone (2 ml) was treated with *trans*-cyclooctene^{43b} (0.9 ml). The resulting white crystalline precipitate was washed with pentane (2×4 ml) to yield 0.87 g (70%) of **8**: nmr δ 5.26 (6 H); ν 1570 cm^{-1} ; mol wt (methanol) 283 (at a concentration of 10.4 mg/g) (calcd 543).

Anal. Calcd for $C_{23}H_{42}CuF_3O_3S$: C, 55.28; H, 7.79; Cu, 11.7. Found: C, 55.16; H, 7.83; Cu, 11.8.

Thermal Decomposition of Benzenedicyclopentadiene (1). The benzene complex **1** (0.80 g) was carefully placed in the bottom of a glass tube (25 cm \times 8 mm), which had been sealed on one end, with the aid of a smaller tube (to avoid contamination of the upper portions of the tube with complex). The tube was then bent in the middle (90° angle) and sealed under reduced pressure (60 mm). The end containing the complex was slowly heated with an oil bath while the other end of the tube was cooled in a bath of liquid nitrogen. After about 30 min at 100°, the originally white complex yellowed slightly, but no volatile products of decomposition condensed in the cold end of the tube. Above 120°, however, the solid decomposed rapidly turning red-brown and evolving volatile material which condensed in the cold end of the tube. The solid did not melt up to 170°. The tube was sealed (constricted) in the middle and then brought to room temperature. The material which had condensed in the cool end liquefied upon warming to room temperature. The nmr spectrum of this liquid indicated that it was benzene [0.11 g (92%)].

Thermal Decomposition of Bis(1,5-cyclooctadiene)copper(I) Triflate (2). The 1,5-cyclooctadiene complex **2** (74 mg) was sealed into a bent tube under reduced pressure as for complex **1** above. Upon heating the end containing the complex at 160° with an oil bath, a clear colorless oil (14 mg) distilled into the other end of the tube which was cooled with an ice bath. In the hot end of the tube there remained a slightly yellow clear oil which crystallized upon cooling. The oil was shown to be 1,5-cyclooctadiene by its nmr spectrum. The solid exhibited a nmr spectrum different from that of **2**: δ 5.77 (4 H), 2.42 (8 H), and corresponded in composition to the 1:1 complex, 1,5-cyclooctadiene copper(I) triflate (**2a**).

Nmr Spectrum of Cyclooctenecopper(I) Triflate (11). Cyclooctene (40 mg, 0.3 mmol) and complex **1** (82 mg, 0.3 mmol of $CuOTf$) were dissolved in about 0.25 ml of acetone- d_6 containing a trace of TMS: δ 5.2 (2 H), 2.2 (4 H), 1.5 (8 H).

Nmr Spectra of Solutions of Olefins and Varying Amounts of CuO

(43) (a) R. G. Untch, D. J. Martin, *J. Amer. Chem. Soc.*, **87**, 3518 (1965); (b) E. Vedejs and P. L. Fuchs, *ibid.*, **93**, 4071 (1971).

Tf. Mixtures of various olefins and the complex **1** in varying relative amounts were dissolved in the acetic-*d*₄ acid containing a trace of TMS, and nmr spectra of these solutions were recorded. The mole ratio of Cu(I) to olefin was determined by comparison of appropriate integrated peak areas using the absorption due to benzene as an internal standard for estimation of CuOTf.

Elemental microanalysis was performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Analysis for copper(I) was performed by oxidation of a solution of ferric chloride and back titration with standard ceric solution. Melting points were measured in sealed capillary tubes. Nuclear magnetic resonance spectra were obtained on a Varian HA-100 or A-60 spectrometer. The spectrum of isolated complexes were obtained in dilute solution of acetone-*d*₆. Infrared spectra were recorded on a Perkin-Elmer 137G spectrometer. Molecular weights were measured with a Mechrolab 301A vapor pressure osmometer at 37°. Ultraviolet spectra were recorded with a Cary 14 spectrophotometer.

All reactions were conducted under a blanket of dry nitrogen. Benzene was freshly distilled from sodium benzophenone ketyl. Pentane was purified by stirring for 12 hr with concentrated sulfuric acid, then with 0.5 M potassium permanganate in 3 M sulfuric acid for 12 hr. It was washed successively with water and aqueous sodium bicarbonate and dried over anhydrous magnesium sulfate and finally with phosphorus pentoxide. It was fractionally distilled under nitrogen. All other solvents were reagent grade materials used without further purification.

Complexes were prepared in vessels sealed with an air tight rubber septum cap, and separated from the mother liquor by filtration through a sintered glass disk with the aid of a positive pressure of nitrogen. After washing, the complexes were dried under a stream of dry nitrogen in the same apparatus.

Acknowledgment. We wish to thank the National Science Foundation for generous financial assistance.

Insensitivity to Steric Hindrance of E2 Olefin-Forming Elimination Induced by Halide Ions in Aprotic Solvents¹

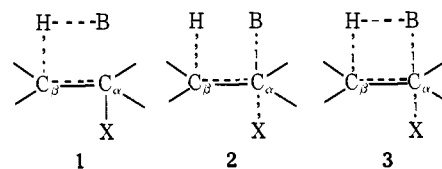
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Received July 13, 1972

Abstract: In olefin-forming elimination induced by chloride ion in acetone solution, cyclohexyl tosylate reacts only 12 times faster than 2,2-dimethylcyclohexyl tosylate. In the latter substrate, access to C_α is hindered by the methyl groups. The fact that they retard elimination by only one power of ten shows that, in the transition state, chloride ion does not interact with C_α in fashion geometrically similar to an S_N2 transition state. This is further evidence against the putative "E2C" mechanism of elimination.

In 1956 it was discovered that halide ions in acetone solution² and mercaptide ions in alcoholic solvents³ are surprisingly effective at bringing about olefin-forming elimination from secondary and tertiary alkyl halides and arenesulfonates. Noting that these rather weakly basic reagents are strong nucleophiles toward carbon, Winstein proposed transition states in which the base (nucleophile) interacts covalently with the α carbon of the substrate.² In most of his later publications on this subject,⁴⁻⁶ he was joined by Parker, and Parker has been the chief advocate of these views since Winstein's death.

The general idea of Winstein and Parker is that E2 reactions occur *via* transition states which represent various points in a spectrum between an "E2H" extreme (**1**) and an "E2C" extreme (**2**). They suggest that seldom is a real reaction adequately represented by either **1** or **2**; rather, most transition states have partial



association of the base (nucleophile) with both H_β and C_α, as in **3**, a larger degree of association with H_β implying less with C_α, and *vice versa*. Reactions induced by *tert*-butoxide ion are considered to lie close to the "E2H" extreme, and those induced by bromide ion to have a great deal of "E2C" character.

Parker's descriptions of the proposed "E2C" transition states vary in their implications as to the nature of interaction of base (nucleophile) with C_α. For example, he said in 1971:⁷ "The E2C transition state... has a rigorous stereochemical requirement that is reminiscent of that for the transition state of S_N2 substitution. Thus the base, B:, and leaving group, X, at sp²-hybridized C_α are colinear and at opposite corners of a trigonal bipyramid, anti to each other." Also, in 1968,⁸ some rate correlations were taken to "... support the concept of an E2C-like transition state, having much the same type of bonding and charge distribution between Y, C_α, and X, as is present in the concurrent S_N2 transition state." These statements depict the "E2C" and S_N2 transition states as very similar insofar as the interaction of base (nucleophile) and C_α are concerned.

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