Cationic Benzene and Olefin Complexes of Copper(I) Trifluoromethanesulphonate

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Summary The preparation and characterization of a labile benzene complex and a variety of structurally unique olefin complexes of copper(I) is described.

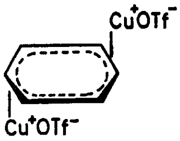
A CRYSTALLINE, air-sensitive complex $(CuOTf)_2C_6H_6$ (**1**), (OTf = trifluoromethanesulphonate), can be isolated from the reaction of trifluoromethanesulphonic anhydride with Cu^I oxide in benzene. This colourless complex is stable to about 100° when heated carefully in a sealed evacuated tube, and benzene is released quantitatively only above 120 °C. The complex (**1**) probably has a structure with local C_{2h} symmetry about the benzene ring analogous to that found in the 1:1 benzene–$AgClO_4$ complex.[1] It may be used to prepare various interesting and novel cationic olefin complexes of Cu^I, which differ dramatically in stoicheiometry, solubility, and stability from the well-known olefin complexes of Cu^I halides,[2] since the strongly co-ordinating halides compete with the olefin for the ligand sites on Cu^I.[3] The difference in stoicheiometries between halide and cationic complexes is shown by the 1:1 CuCl–cycloocta-1,5-diene complex which is a chloro-bridged dimer[4] and the monomeric 1:2 complex (**2**). Cu^I chloride forms a 1:1 complex with dicyclopentadiene and 2:1 complexes with both *Z,E,E*- and *E,E,E*-cyclododecatriene.[5,6] In contrast, we have isolated a 1:2 complex (**4**) with dicyclopentadiene and 1:1 complexes (**5**) and (**6**) with *Z,E,E*- and *E,E,E*-cyclododecatriene, respectively. All vinyl protons are equivalent in the n.m.r. spectrum of the cyclo-octa-1,5-diene complex (**2**). Only a single C=C stretching band is observed in the i.r. spectrum of (**2**) similar to the corresponding perchlorate and fluoroborate complexes.[3] Furthermore, all vinyl protons are equivalent in the n.m.r. spectrum of *E,E,E*-cyclododeca-1,5,9-triene complex (**6**) and only a single C–C stretching band is observed in its i.r. spectrum. The stoicheiometric composition as well as the n.m.r. and i.r. spectra suggest symmetrical structures for (**2**) and (**6**) analogous to those of the isoelectronic Ni^0 complexes.[7] The protons are all equivalent in the n.m.r. spectrum of the 1:1 cyclo-octatetraene complex (**3**) at room temperature, but are not magnetically equivalent at −100 °C. Moreover, the i.r. spectrum of this complex clearly indicates the presence of nonequivalent carbon–carbon double bonds.

TABLE

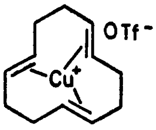
Cationic Copper(I)–*Olefin Complexes*

Complex	Co-ordinated Olefin L	Stoicheiometry $CuOTf{\cdot}L_n$	Mol. Wt. (Osmometry)
(2)	Cyclo-octa-1,5-diene	CuL_2OTf	385
(3)	Cyclo-octa-1,3,5,9-tetraene	CuLOTf	300
(4)	*endo*-Dicyclopentadiene	CuL_2OTf	
(5)	*Z,E,E*-Cyclododeca-1,5,9-triene	CuLOTf	
(6)	*E,E,E*-1,5,9-Cyclododecatriene	CuLOTf	366
(7)	Cyclo-octa-1,3-diene	CuLOTf	
(8)	Cyclohepta-1,3,5-triene	$Cu_2L(OTf)_2$	
(9)	Norbornylene	CuLOTf	276

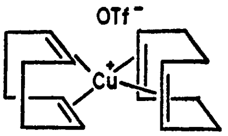
Thus, cyclo-octatetraene exhibits a single band at 1635 cm^{-1}, whereas absorption bands occur at 1630 cm^{-1} and 1520 cm^{-1} in complex (**3**). These observations are consistent with rapid exchange of cyclo-octatetraene in solution. I.r. spectral data suggest that in the dimeric 1:1 complex of CuCl with *endo*-dicyclopentadiene, π-complexing occurs with the 8,9-double bond.[3] Similar results are observed for the 1:2 complex (**4**) of CuOTf. In dicyclopentadiene, the bands at 1615 cm^{-1} and 1570 cm^{-1} have been assigned to the double bonds in the cyclopentene and norbornene rings, respectively. In complex (**4**) only the band at 1570 has been lowered to 1540 cm^{-1} by π-complexing.[8] The n.m.r. spectrum of (**4**) suggests an *exo* complexation of the 8,9-double bond. Thus, *endo*-dicyclopentadiene exhibits vinylic absorptions at δ 5·95 (2H) and 5·45 p.p.m. (2H). In complex (**4**) the ligand absorption at δ 5·95 is shifted to 5·4—5·5 p.pm. while that at 5·45 is not shifted. Moreover, the C-10 methylene in dicyclopentadiene appears as two doublets (J 10 Hz) centred at δ 1·25 and 1·45 p.p.m. In (**4**) the ligand absorption at δ 1·45 is shifted to 1·59 p.p.m. while the absorption at 1·25 is not shifted. The increased number of coordinated double bonds in (**4**) relative to its CuCl analogue supports the hypothesis that competition between halide ions and olefin for Cu^{I} ligand sites is an important factor in the stability of these complexes.



(1)



(6)



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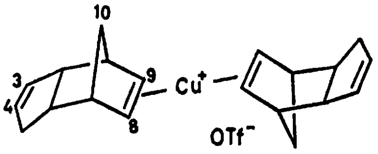

(4)

In contrast to the well-known insolubility of the olefin complexes of Cu^{I} halides, cationic olefin complexes containing CuOTf are readily soluble in polar organic solvents. Vapour pressure osmometric molecular weight determinations of the complexes (**2**), (**3**), (**6**), and (**9**) demonstrate the absence of appreciable dissociation in solution. Methanolic solutions of these complexes all exhibit two strong u.v. absorption bands, one at 233—241 nm (ϵ_{max} 2500—3600) and one at 272—282 nm (ϵ_{max} 1500—2100). The high m.p.s. and thermal stabilities shown by the CuOTf-olefin complexes are in sharp contrast to the low thermal stability of the olefin complexes derived from Cu^{I} halides.

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