Alkene and Carbon Monoxide Derivatives of Copper(I) and Silver(I) β-Diketonates

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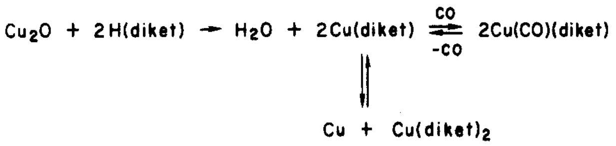
In the presence of CO or various alkenes and dienes, Cu_2O will react with certain partially fluorinated β-diketones (Hdiket) to form complexes of the type $[Cu(diket)]_nL_m$ (L = CO, alkene, or diene; n and m = 1 or 2). The complexes of CO or light olefins are unstable and subject to disproportionation, but nonvolatile alkenes and dienes form isolable compounds. Cyclooctatetraene (COT) forms a complex with the composition $Cu_2(COT)(hfacac)_2$ (Hhfacac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione), the structure of which was determined by single-crystal X-ray diffraction. The material crystallizes in the triclinic space group $P\bar{1}$ with a = 8.121 (2) Å, b = 9.555 (2) Å, c = 14.756 (3) Å, α = 86.67 (1)°, β = 76.45 (1)°, and Z = 2. A combination of direct methods and Fourier techniques were used in the structural analysis and full-matrix least-squares refinement with 340 variables has converged to final R values of R = 0.084 and R_w = 0.090 for 1914 reflections. The structure consists of a central cyclooctatetraene (COT) ring, one copper atom above the ring, a second copper atom below the ring, and a hexafluoroacetylacetonate (hfacac) group coordinated to each copper. Each of the copper atoms is disordered between two positions in a plane roughly perpendicular to the hfacac group to which it is coordinated. The two disorder positions are nearly equidistant from the hfacac oxygen atoms but are within bonding distance of opposite double bonds in the COT ligand. The geometry around the copper atoms is trigonal.

Introduction

In spite of the enormous amount of work devoted to copper(II) β-diketonate complexes there have been relatively few reports devoted to the corresponding Cu(I) complexes. Copper(I) acetylacetonate was first reported by Emmert and co-workers.[1] However, Nast has shown that work to be erroneous and that in the absence of stabilizing ligands, copper(I) acetylacetonate disproportionates to copper metal and the copper(II) compound.[2] These later workers were able to isolate and characterize a number of stable complexes containing ammonia, phosphines, and isonitriles as ligands.[3] Lewis' group extended this work to include silver(I) and gold(I) compounds,[4] and Carty and collaborators prepared a number of phosphine derivatives of copper(I) β-diketonates where the β-diketonate groups were fluorine substituted.[5]

There have been no reports thus far of carbon monoxide, alkene, or alkyne complexes of the copper(I) diketonates although a few silver(I) diketonate complexes with olefin ligands have been prepared,[6] and a larger number of other types of copper(I) complexes with unsaturated ligands are known.[7] The reaction of Cu_2O with various substituted sulfonic acids[8] or trifluoroacetic acid[9] in the presence of CO has proven to be an efficient route to copper(I) carbonyl complexes. Although the β-diketonates are in general weaker acids, it was thought that their chelating ability might allow the formation of isolable copper(I) carbonyl β-diketonate complexes. Such complexes could prove interesting since in the absence of any unusual interactions, the carbonyl group would be bound to a copper(I) moiety in which only two other coordination sites would be occupied and those by a ligand whose steric demands are not great.

Scheme I



$$Cu_2O + 2H(diket) \rightarrow H_2O + 2Cu(diket) \underset{-CO}{\overset{CO}{\rightleftharpoons}} 2Cu(CO)(diket)$$

$$2Cu(diket) \rightleftharpoons Cu + Cu(diket)_2$$

We have found that a number of partially fluorinated β-diketones will react with Cu_2O in the presence of CO to form solutions of the Cu(CO)(diketonate) complexes. These and similar reactions of alkenes and dienes are described here.

Results and Discussion

The reaction of the β-diketones with copper(I) oxide presumably proceeds through the formation of an unstable copper(I) diketonate which, in the absence of a stabilizing ligand such as carbon monoxide, will disproportionate to copper metal and the copper(II) diketonate. If carbon monoxide is present, it will react reversibly with the copper(I) complex to form the copper carbonyl β-diketonate derivative. Derivatives of hexafluoroacetylacetone, trifluoroacetylacetone, thenoyltrifluoroacetone, and (trifluoroacetyl)camphor have been prepared in this manner. If the properties of the β-diketonate anion are such that it is not capable of stabilizing the carbonyl adduct, as is the case with acetylacetonate and alkyl- and aryl-substituted acetylacetonates, the equilibrium will lie on the side of the unstable copper(I) β-diketonate which will disproportionate. Reducing the partial pressure of CO by applying vacuum or passing an inert gas such as N_2 or Ar through a solution containing the carbonyl adduct will also shift the equilibrium in favor of the unstable copper(I) β-diketonate. These reactions can be summarized in Scheme I. This scheme implies that copper(II) diketonates such as copper(II) hexafluoroacetylacetonate should be capable of reacting with copper metal in the presence of carbon monoxide to form the soluble carbonylcopper(I) derivative. This has indeed been found to be the case.

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[1] Emmert, B.; Gsottochneider, H.; Stanger, H. *Chem. Ber.* **1936**, *69*, 1319.

[2] Nast, R.; Mohr, R.; Schultze, C. *Chem. Ber.* **1963**, *96*, 2127.

[3] Nast, R.; Lepel, W.-H. *Chem. Ber.* **1969**, *102*, 3224.

[4] Gibson, D.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc. A* **1970**, 367.

[5] Anderson, W. A.; Carty, A. J.; Palenik, G. J.; Schreiber, G. *Can. J. Chem.* **1971**, *49*, 761.

[6] Partenheimer, W.; Johnson, E. H. *Inorg. Chem.* **1972**, *11*, 2840.

[7] Quin, H. W.; Tsai, J. H. *Adv. Inorg. Chem. Radiochem.* **1968**, *12*, 217. Jardine, F. H. *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 115 and references cited therein.

[8] Doyle, G. *Inorg. Chem.* **1983**, *22*, 2892.

[9] Scott, A. F.; Wilkening, L. L.; Rubin, B. *Inorg. Chem.* **1969**, *8*, 2533.

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Other synthetic methods such as the reaction of thallium(I) or silver(I) diketonates with copper(I) halides under CO can be useful for the preparation of the carbonyl complexes (eq 1), but these methods also fail for all but the fluorinated β-diketonates.

$$\mathrm{Tl(diket)} + \mathrm{CuX} + \mathrm{CO} \rightarrow \mathrm{Cu(CO)(diket)} + TlX \quad (1)$$

The CO stretching frequencies in the carbonyl β-diketonate complexes are generally observed as strong single bands at ~2100 cm^{-1}. Absorption measurements indicate only one CO is absorbed per copper. Reactions with phosphines, amines, and isonitriles show that the CO is very easily displaced by such ligands and derivatives of the type L_2Cu(diket) are formed. No mixed-ligand complexes containing CO have been observed even when less than stoichiometric amounts of the phosphine, amine or isonitrile are used.

The complexes derived from C_2 to C_4 olefins are nearly identical with the CO complex with regard to their methods of preparation, composition, chemical reactivity, and stability. Higher olefins react in a manner similar to the lower homologues but, presumably due to their lower volatility, the copper(I) β-diketonate complexes formed from then can often be isolated in a relatively pure form. For most simple olefins including styrene, 1-decene, cyclooctene, norbornene, and the like, the hexafluoroacetylacetonate complexes are isolated as yellow or greenish yellow oils or solids containing 1 mol of olefin per copper atom (see Table I). Depending on the particular olefin and β-diketonate groups, the complexes are more or less unstable with respect to air oxidation and disproportionation but are moisture insensitive. In general those complexes derived from hexafluoroacetylacetone are more stable than those prepared from trifluoroacetylacetone, thenoyltrifluoroacetone, and (trifluoroacetyl)camphor. In a few cases the complexes isolated appear to have 2 mol of olefin per copper. Surprisingly, all the complexes which have been prepared that have this stoichiometry are rather hindered systems containing either a hindered olefin such as α-pinene or a hindered β-diketonate group such as (trifluoroacetyl)camphor or both. Although copper is certainly capable of binding 2 mol of olefin, one would think that this would occur in sterically less crowded systems as well. The factors determining the number of olefin ligands coordinated to the copper are not fully understood at this time and are currently under investigation.

The reaction of dienes with Cu_2O and a sterically unhindered fluorinated β-diketone yields complexes with either one or two atoms of copper per diene depending on the particular diene chosen. Both 1,5-cyclooctadiene and 1,3-butadiene give complexes with the composition (diene)Cu(diket) whereas norbornadiene and isoprene appear to give complexes which analyze for (diene)$[\mathrm{Cu(diket)}]_2$. Since these pairs of olefins are structurally quite similar, it is somewhat surprising that they should form complexes with different compositions. The isoprene and butadiene complexes are very unstable; however, the cyclooctadiene and norbornadiene complexes are stable yellow solids which can be handled in air for short periods without decomposition. The complex $[(1,5\text{-COD})\mathrm{CuCl}]_2$ has been structurally characterized and shows the copper to be tetrahedrally coordinated with the cyclooctadiene asymmetrically bonding to the copper through both double bonds.[10] Attempts to solve the single-crystal X-ray structure of the (1,5-COD)Cu(hfacac) complex have only been partially successful thus far, and although it appears that the copper in this complex is strongly bound to one of the double bonds (Cu–X distance = 1.95 Å where *x* is the centriod of the double bond), there is a much weaker interaction with the other double bond (Cu–X distance = 2.34 Å).[11] The proton resonance shows only two broad signals (δ ~5.5 and 2.4) with a 1:2 ratio even at low temperatures. Although this is consistent with a chelated structure, it could also be the result of a fluxional process in which the copper is alternately bound to one of the two double bonds if the process has a low thermal barrier. With the bulky diketonate group derived from (trifluoroacetyl)camphor, [H(TAC)], 1,5-cyclooctadiene forms the complex $(\mathrm{COD})_2$Cu(TAC) with two molecules of the diene bound to each copper. This compound is the only complex formed even when an excess of Cu_2O and the diketone are present. In this case the diene can only function as a monodentate ligand although a fluxional behavior rendering the two double bonds equivalent is still probable. The NMR signals for the COD protons in this complex are very similar to the (COD)Cu(hfacac) complex (two broad signals at ~5.5 and 2.4 ppm in a 1:2 ratio) supporting a fluxional structure.

The range of compositions found for the copper(I) β-diketonate complexes formed from the cyclic dienes, including the COD complexes with a 2:1 and a 1:1 diene: copper ratio and the 1:2 norbornadiene complex, graphically illustrates the variations possible in copper(I) olefin complexes. Only one other nonbornadiene copper complex has been subject to X-ray crystal determination.[12] In this complex, $[(\mathrm{norbornadiene})\mathrm{CuCl}]_4$, the copper is trigonally coordinated to two chlorines and one of the double bonds on the norbornadiene. The other double bond remains uncoordinated, and norbornadiene behaves essentially as a monoolefin. We have been unable to prepare a norbornadiene complex with only one copper diketonate group even when a large excess of the diene is used.

Depending on the reaction conditions employed, one can prepare two different complexes from cyclooctatetraene: one with the compositions COTCu(hfacac) and another with the composition COT$[\mathrm{Cu(hfacac)}]_2$. A similar pair of complexes can also be prepared from trifluoroacetylacetone. All these complexes display a single resonance (δ ~5.7) for the COT protons in the NMR spectra over a fairly wide temperature range. For the 1:1 complexes this is almost certainly due to a fluxional process in which the copper coordination is averaged over the four double bonds. It could not be determined from the available data whether the copper is coordinated to one or two of the double bonds of the COT ligand. The same possibilities exist for the 2:1 complexes except that in this case we are dealing with two pairs of double bonds on the COT ligand. In order to determine the mode of coordination in this molecule, a single-crysal X-ray diffraction study was undertaken. The overall structure of the complete molecule, as determined, is shown in Figure 1. A view emphasizing the coordination about the copper atoms is given in Figure 2.

A large amount of disorder is present in the complex and is centered around the copper atoms and the trifluoromethyl groups. In each molecule there are two copper atoms, one above and one below the cyclooctatetraene ring. Each copper atom, in turn, is disordered between two

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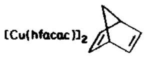
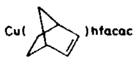
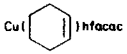
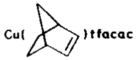
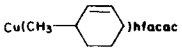
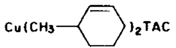
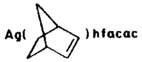
[10] van de Hende, J. H.; Baird, W. C., Jr. *J. Am. Chem. Soc.* **1963**, *85*, 1009.

[11] High-quality crystals of (1,5-COD)Cu(hfacac) could not be obtained. Bond distances quoted above are based on a model refined to an *R* value in the mid teens.

[12] Baenziger, N. C.; Haight, H. L.; Doyle, J. R. *Inorg. Chem.* **1964**, *3*, 1535.

[13] Ganis, P.; Lepore, U.; Paiaro, O. *J. Chem. Soc., Chem. Commun.* **1969**, 1054.

Table I. Preparation and Analyses of Cu and Ag Olefin Complexes

ligand (mmol)	β-diketone (mmol)	metal oxide (mmol)	solv	compd formed	elemental anal. calcd (found)			
					C	H	F	Cu
1,5-cyclooctadiene (COD) (9.0)	thenoyltrifluoroacetone (TTA) (14.0)	Cu_2O (9.0)	CH_2Cl_2	Cu(COD)TTA	48.89 (47.27)	4.07 (3.68)	8.15 (S) (8.32)	
1,5-cyclooctadiene (20.0)	hexafluoroacetylacetone (hfacac) (18.0)	Cu_2O (11.0)	$C_6H_5CH_3$	Cu(COD)hfacac	41.21 (41.27)	3.43 (3.59)	30.12 (30.30)	16.78 (16.56)
1,5-cyclooctadiene (20.0)	trifluoroacetylacetone (18.0)	Cu_2O (11.0)	CH_2Cl_2	Cu(COD)tfacac	48.07 (48.17)	4.93 (4.72)	17.56 (18.00)	19.58 (19.22)
bicyclo[2.2.1]hepta-2,5-diene (22.0)	hexafluoroacetylacetone (21.0)	Cu_2O (11.0)	CH_2Cl_2		32.20 (32.37)	1.59 (1.54)	36.00 (35.42)	20.00 (19.61)
bicyclo[2.2.1]-2-heptene (18.0)	hexafluoroacetylacetone (17.0)	Cu_2O (11.0)	CH_2Cl_2		39.48 (40.13)	3.02 (3.17)		
1,3,5,7-cyclooctatetraene (7.5)	trifluoroacetylacetone (7.1)	Cu_2O (4.0)	CH_2Cl_2	Cu(COT)tfacac	48.68 (48.83)	3.77 (3.91)		
1,3,5,7-cyclooctatetraene (3.6)	trifluoroacetylacetone (7.2)	Cu_2O (4.0)	CH_2Cl_2	$[Cu(tfacac)]_2COT$	40.21 (40.40)	2.98 (2.99)		
styrene (11.5)	hexafluoroacetylacetone (9.61)	Cu_2O (5.0)	CH_2Cl_2	$Cu(CH_2{=}CHC_6H_5)hfacac$	41.66 (41.86)	2.42 (2.52)	30.42 (30.89)	16.96 (16.76)
isoprene (15.0)	hexafluoroacetylacetone (7.3)	Cu_2O (4.0)	CH_2Cl_2	$[Cu(hfacac)]_2(CH_2{=}C(CH_3)\text{-}CH{=}CH_2)$	29.52 (29.61)	1.65 (1.39)		20.86 (20.91)
cyclohexene (27.0)	hexafluoroacetylacetone (12.0)	Cu_2O (7.0)	CH_2Cl_2		37.45 (38.02)	3.14 (3.48)		
bicyclo[2.2.1]-2-heptene (14.0)	trifluoroacetylacetone (13.0)	Cu_2O (6.5)	CH_2Cl_2		46.39 (46.02)	4.54 (4.29)		20.45 (20.81)
1,5-cyclooctadiene (4.5)	3-(trifluoroacetyl)-*d*-camphor (TAC) (4.0)	Cu_2O (2.0)	CH_2Cl_2	$Cu(COD)_2(TAC)$	63.79 (64.09)	7.21 (7.25)		
cyclooctene (COE) (9.07)	hexafluoroacetylacetone (9.0)	Cu_2O (4.6)	CH_2Cl_2	Cu(COE)hfacac	40.99 (40.76)	3.94 (3.91)		
1-decene (24.0)	hexafluoroacetylacetone (24.0)	Cu_2O (14.0)	CH_2Cl_2	$Cu(CH_2{=}CHC_8H_{17})hfacac$	43.85 (43.68)	5.15 (5.11)		
3-methylcyclohexene (15)	hexafluoroacetylacetone (9.0)	Cu_2O (5.0)	CH_2Cl_2		39.27 (40.72)	3.54 (3.98)		
1,3,5,7-cyclooctatetraene (7.5)	hexafluoroacetylacetone (7.2)	Cu_2O (4.0)	CH_2Cl_2	Cu(COT)hfacac	41.66 (41.82)	2.42 (2.56)	30.42 (30.61)	16.96 (17.05)
1,3,5,7-cyclooctatetraene (3.6)	hexafluoroacetylacetone (7.2)	Cu_2O (4.0)	CH_2Cl_2	$[Cu(hfacac)]_2COT$	33.50 (33.70)	1.56 (1.66)	35.33 (35.57)	19.69 (19.55)
(+)-α-pinene (7.5)	hexafluoroacetylacetone (7.4)	Cu_2O (4.0)	CH_2Cl_2	Cu(α-pinene)$_2$hfacac	55.25 (55.67)	6.08 (6.35)		
3-methylcyclohexene (8.0)	3-(trifluoroacetyl)-*d*-camphor (6.0)	Cu_2O (3.5)	CH_2Cl_2		62.01 (62.42)	7.55 (7.85)		
d,*l*-α-pinene (8.0)	3-(trifluoroacetyl)-*d*-camphor (6.0)	Cu_2O (3.5)	CH_2Cl_2	Cu(α-pinene)TAC mixed diastereomers	65.89 (66.04)	7.95 (7.30)		
diethyl maleate (300)	hexafluoroacetylacetone (20.0)	Cu_2O (10.0)	none	$Cu(C_2H_5OC({=}O)CH{=}CHC({=}O)\text{-}OC_2H_5)hfacac$	35.26 (35.04)	2.96 (2.86)		
4-methylstyrene (16)	hexafluoroacetylacetone (14)	Cu_2O (7.2)	CH_2Cl_2	$Cu(CH_3C_6H_4CH{=}CH_2)hfacac$	43.25 (42.82)	2.85 (2.82)		16.34 (16.70)
1-decene (4.4)	hexafluoroacetylacetone (4.3)	Ag_2O (2.2)	CH_2Cl_2	$Ag(CH_2{=}CHC_8H_{17})hfacac$	39.55 (40.81)	4.61 (4.89)		
1,5-cyclooctadiene (1.12)	hexafluoroacetylacetone (1.12)	Ag_2O (0.56)	CH_2Cl_2	Ag(COD)hfacac	36.88 (36.71)	3.07 (3.43)		
bicyclo[2.2.1]-2-heptene (4.4)	hexafluoroacetylacetone (4.3)	Ag_2O (2.2)	CH_2Cl_2		35.21 (34.46)	2.69 (2.80)		
cyclooctene (8.64)	hexafluoroacetylacetone (8.64)	Ag_2O (4.37)	CH_2Cl_2	Ag(COE)hfacac	36.70 (36.42)	3.53 (3.71)		

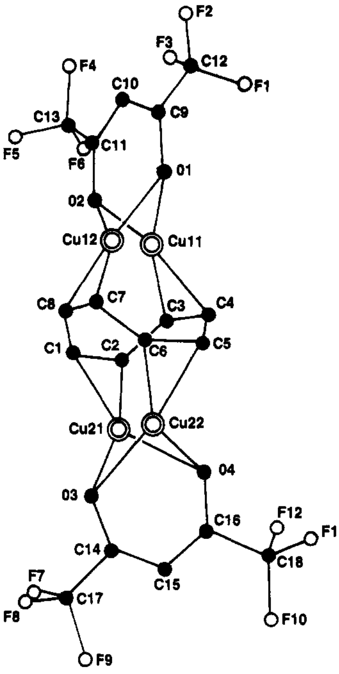


Figure 1. Structure of COT(Cu hfacac)$_2$.

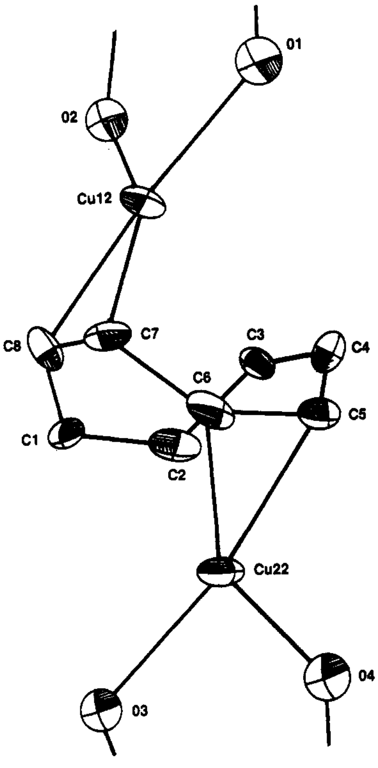


Figure 2. ORTEP diagram of COT(Cu hfacac)$_2$ showing coordination of copper atoms.

nearly equivalent positions. Thus, in any given molecule, there is one copper atom at either the Cu(21) or the Cu(22) position. Cu(11) and C(12) are separated by 1.02 Å and Cu(21) and Cu(22) by 1.16 Å.

The coordination around the four different copper positions is nearly identical. Each copper is bonded to two oxygen atoms of a hfacac group with the Cu–O distances ranging from 1.918 (9) to 2.093 (9) Å. In addition, each copper atom is coordinated with one double bond of the COT ring. The distances from each position to the center of the nearest double bond are as follows: Cu(11) to C1–C2, 1.910 (8) Å; Cu(12) to C5–C6, 1.937 (8) Å; Cu(21) to C3–C4, 1.911 (8) Å; Cu(22) to C7–C8, 1.896 (9) Å. The average distance from any given copper position to the opposite double bond of the COT ring is 2.64 Å, a distance too long for considerable interaction to be occurring. Thus, while a copper atom is bonded to the same hfacac group at either of its two possible locations, the two positions are within bonding distance of alternate double bonds of the COT ring. This is in contrast to the previously reported structure of Cu_2Cl_2(cyclooctadiene)$_2$.[10] In this molecule, each copper atom occupies only one position where it is unsymmetrically coordinated to both double bonds of a COD ring. The distances to the centers of the bonds are 2.05 and 2.22 Å. The Cu thus exhibits tetrahedral geometry in the COD complex, while it is trigonal in the current complex. The least-squares planes through each Cu atom, the two coordinating oxygen atoms, and the centroid of the nearest double bond demonstrate the planarity of the Cu coordination. The CuO_2CX planes do not quite coincide with the planes of the hfacac ligand however. The average angle between the CuO_2CX planes and the hfacac planes is approximately 27°. The reason Cu adopts this particular type of geometry is not at all clear. It is also not clear if one can predict the structure of other polyolefin complexes based on that determined for this COT complex. On the basis of complexes prepared in this work and those previously reported, it appears that copper(I) will form either monodentate or bidentate complexes with either a trigonal or tetrahedral structure with polyolefins in an almost unpredictable fashion since there is apparently little energetic difference between trigonal and tetrahedral coordination for soft ligands. Indeed, in the complex Cu_2Cl_2(cyclooctene)$_3$, one copper atom is bound to one cyclooctene and two chlorine atoms in a trigonal fashion while the other is coordinated to the two chlorines and two cyclooctene molecules in a tetrahedral arrangement.[12]

The cyclooctatetraene ring is in the boat conformation with alternating single (1.47 Å) and double (1.33 Å) bonds. The two hfacac molecules are only slightly distorted from planarity with an angle between the two planes of 101°. The fluorine atoms of the trifluoromethyl groups are disordered in a cone around the carbon atom due to rotation about the C–C bonds.

It is interesting to note that although several copper(I) aromatic complexes have been characterized,[14-17] many of which are quite stable and easily formed, the copper(I) diketonate complexes show no tendency to form complexes with aromatic hydrocarbons. If there is any tendency at all to form such compounds by interaction of the aromatics with the copper(I) β-diketonate species, it must be very weak and is not detectable under the conditions employed. Indeed, benzene or toluene can be effectively used as solvents for the preparation of the olefin complexes. The addition of large amounts of benzene to solutions of Cu(CO)hfacac shows no decrease in the intensity of the CO absorption other than that due to simple dilution.

In addition to those reported by Partenheimer and Johnson,[6] we have prepared a number of other silver(I) diketonate olefin complexes. We have found that the formation of the silver derivatives very closely parallels that of the copper analogues and in all cases the composition of the silver complexes is identical with the copper species. In general the silver complexes which can be isolated are white crystalline compounds with stabilities similar to the copper complexes. The loss of the olefin

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(14) Dines, M. B. *Inorg. Chem.* **1972**, *11*, 2949.

(15) Turner, R. W.; Amma, E. L. *J. Am. Chem. Soc.* **1963**, *85*, 4046; **1966**, *88*, 1877.

(16) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 1889.

(17) Rodesiler, P. R.; Amma, E. L. *J. Chem. Soc., Chem. Commun.* **1974**, 599.

Table II. Crystal and Experimental Data

mol formula	$Cu_2C_{18}H_{10}F_{12}O_4$
fw	645.3
cryst class	triclinic
space group	$P\bar{1}$
a	8.121 (2)
b	9.555 (2)
c	14.756 (3)
α, deg	86.67 (1)
β, deg	76.45 (1)
γ, deg	88.63 (1)
vol, Å^3	1111 (1)
Z	2
ρ_{calcd}, g cm^{-3}	1.93
$F(000)$	316
μ(Mo Kα), cm^{-1}	20.40
cryst size, mm	0.20 × 0.15 × 0.15
max 2θ, deg	50
scan technique	ω-2θ
scan speed, deg/min	variable (2-13)
scan width, deg	1.00 + 0.35 tan θ
unique data	3943
obsd data	1915
function minimized	$\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2$
R	0.084
R_w	0.090

Table III. Table of Positional Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B, A^2
Cu11	0.2410 (2)	0.7664 (2)	0.4030 (1)	4.10 (4)
Cu12	0.1618 (5)	0.8402 (4)	0.4374 (2)	4.56 (9)
Cu21	0.2253 (4)	0.6228 (3)	0.6806 (2)	4.32 (7)
Cu22	0.3399 (3)	0.6964 (3)	0.6709 (1)	4.17 (5)
C1	0.415 (1)	0.676 (1)	0.4649 (6)	4.1 (2)
C2	0.283 (1)	0.589 (1)	0.4782 (6)	4.4 (3)
C3	0.152 (1)	0.564 (1)	0.5633 (7)	4.9 (3)
C4	0.052 (1)	0.663 (1)	0.6079 (7)	5.1 (3)
C5	0.050 (1)	0.812 (1)	0.5775 (7)	5.1 (3)
C6	0.183 (2)	0.899 (1)	0.5652 (7)	5.7 (3)
C7	0.352 (1)	0.859 (1)	0.5814 (7)	4.9 (3)
C8	0.451 (1)	0.763 (1)	0.5366 (7)	4.3 (2)
C9	0.264 (1)	0.987 (1)	0.2599 (6)	4.1 (2)
C10	0.126 (1)	0.938 (1)	0.2317 (6)	3.3 (2)
C11	0.020 (1)	0.837 (1)	0.2812 (6)	3.4 (2)
C12	0.373 (1)	1.104 (1)	0.2023 (8)	6.2 (3)
C13	−0.129 (1)	0.797 (1)	0.2439 (7)	4.9 (3)
C14	0.425 (1)	0.514 (1)	0.8074 (6)	3.6 (2)
C15	0.318 (1)	0.578 (1)	0.8788 (6)	4.0 (2)
C16	0.197 (1)	0.6756 (9)	0.8670 (6)	3.6 (2)
C17	0.555 (2)	0.409 (2)	0.8274 (7)	6.8 (4)
C18	0.081 (2)	0.736 (1)	0.9556 (8)	7.2 (4)
O1	0.3154 (8)	0.9462 (7)	0.3320 (5)	4.9 (2)
O2	0.0304 (8)	0.7677 (7)	0.3543 (4)	4.7 (2)
O3	0.435 (1)	0.5320 (7)	0.7216 (4)	5.2 (2)
O4	0.166 (1)	0.7221 (8)	0.7932 (5)	6.6 (2)
F1A	0.355 (1)	1.214 (1)	0.2608 (8)	6.0*
F2A	0.535 (1)	1.067 (1)	0.1830 (8)	6.0*
F3A	0.333 (1)	1.140 (1)	0.1287 (8)	6.0*
F4A	0.138 (1)	0.140 (1)	0.8381 (8)	6.0*
F5A	0.137 (1)	0.329 (1)	0.7746 (8)	6.0*
F6A	0.276 (1)	0.170 (1)	0.6920 (8)	6.0*
F7A	0.572 (2)	0.405 (1)	0.9107 (9)	6.0*
F8A	0.713 (2)	0.455 (1)	0.7687 (9)	6.0*
F9A	0.516 (2)	0.276 (1)	0.8074 (9)	6.0*
F10A	−0.084 (2)	0.681 (1)	0.9577 (9)	6.0*
F11A	0.067 (2)	0.870 (1)	0.9469 (9)	6.0*
F12A	0.117 (2)	0.691 (1)	1.0325 (9)	6.0*
F1B	0.309 (2)	1.219 (2)	0.211 (1)	6.0*
F2B	0.523 (2)	1.111 (2)	0.214 (1)	6.0*
F3B	0.379 (2)	1.077 (2)	0.102 (1)	6.0*
F4B	0.171 (2)	0.100 (2)	0.816 (1)	6.0*
F5B	0.086 (2)	0.349 (2)	0.781 (1)	6.0*
F6B	0.260 (2)	0.223 (2)	0.687 (1)	6.0*
F7B	0.503 (3)	0.357 (2)	0.928 (1)	6.0*
F8B	0.695 (3)	0.453 (2)	0.825 (1)	6.0*
F9B	0.578 (3)	0.303 (2)	0.777 (1)	6.0*
F10B	0.058 (3)	0.636 (2)	1.026 (1)	6.0*
F11B	−0.048 (3)	0.782 (2)	0.952 (1)	6.0*
F12B	0.174 (3)	0.842 (2)	0.980 (1)	6.0*
F1C	0.273 (6)	1.194 (5)	0.165 (3)	6.0*
F2C	0.476 (6)	1.061 (5)	0.136 (3)	6.0*
F3C	0.464 (6)	1.167 (5)	0.241 (3)	6.0*
F4C	0.278 (6)	0.121 (5)	0.709 (3)	6.0*
F5C	0.132 (6)	0.167 (5)	0.840 (3)	6.0*
F6C	0.180 (6)	0.335 (5)	0.733 (3)	6.0*
F7C	0.638 (3)	0.483 (3)	0.893 (2)	6.0*
F8C	0.681 (3)	0.381 (3)	0.768 (2)	6.0*
F9C	0.485 (3)	0.311 (3)	0.881 (2)	6.0*
F10C	−0.007 (3)	0.860 (3)	0.935 (2)	6.0*
F11C	0.178 (3)	0.763 (3)	1.020 (2)	6.0*
F12C	−0.027 (3)	0.660 (3)	1.004 (2)	6.0*
H1	0.488	0.688	0.402	5.0*
H2	0.279	0.533	0.423	5.0*
H3	0.144	0.466	0.591	5.0*
H4	−0.038	0.632	0.666	5.0*
H5	−0.058	0.853	0.564	5.0*
H6	0.171	0.994	0.541	5.0*
H7	0.392	0.907	0.629	5.0*
H8	0.563	0.745	0.554	5.0*
H10	0.875	0.027	0.832	5.0*
H15	0.666	0.471	0.049	5.0*

[a] Atoms with an asterisk were assigned isotropic temperature factors. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

ligand in the case of the silver complexes results in the formation of a silver(I) β-diketonate which in general are quite stable. Since the silver(I) β-diketonates are not subject to disproportionation as are the copper complexes, the loss of the ligands does not result in the deposition of the metal. The formation of the silver olefin complexes can therefore be described by 2 and 3. Since the Ag(I)-(diket) complexes are fairly stable, they can be prepared independently and the olefin complexes can then be produced by the simple addition of the olefin to the performed diketonate complex.

$$Ag_2O + 2H(diket) \rightarrow H_2O + 2Ag(diket) \tag{2}$$

$$Ag(diket) + RCH{=}CHR' \rightarrow Ag(RCH{=}CHR')(diket) \tag{3}$$

Although the chemistry of the silver olefin β-diketonate complexes closely parallels that of the copper analogues, there is no evidence for the formation of a carbon monoxide complex in the case of silver. Evidently for these β-diketonate complexes, the olefin derivatives of silver are much more stable than the carbon monoxide species whereas for copper the CO and olefin derivatives are of comparable stability.

Experimental Section

General Data. All reagents and solvents were purchased from commercial sources and were used without further purification. All reactions were either carried out in a nitrogen-filled glovebox or in standard glassware under a nitrogen atmosphere.

Analyses. Elemental analyses were carried out by Analytical and Information Division, Exxon Research and Engineering Co., and by Galbraith Laboratories Inc., Knoxville, TN. Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer, and NMR spectra were obtained on a Varian 360L.

Preparation of Solutions of Cu(CO)hfacac. A three-necked flask containing a suspension of 7.5 g (52.5 mmol) of Cu_2O in 75 mL of THF was fitted with a pressure-equalized dropping funnel, a gas dispersion tube, and a nitrogen bubbler. Carbon monoxide was passed through the suspension at a rapid rate while a solution of 21 g (101 mmol) of hexafluoroacetylacetone in 25 mL of THF was added over a 30-min period through the dropping funnel. After the addition, the mixture was allowed to react for an additional 30 min while the CO flow was maintained. The solution was then filtered under CO to remove the excess Cu_2O. The resulting yellow to green solution of Cu(CO)(hfacac) is stable indefinitely if stored under a CO atmosphere.

Table IV. Major Bond Lengths (Å) for $Cu_2(COT)(hfacac)_2$[a]

	Cu-O		
Cu11-O1	1.990 (8)	Cu21-O3	2.093 (9)
Cu11-O2	2.004 (8)	Cu21-O4	1.918 (9)
Cu12-O1	1.992 (8)	Cu22-O3	1.925 (9)
Cu12-O2	1.967 (8)	Cu22-O4	2.038 (9)
	Cu-COT		
Cu11-X1[b]	1.910 (8)	Cu21-X2	1.911 (8)
Cu12-X3	1.937 (8)	Cu22-X4	1.896 (9)
	COT		
C1-C2	1.34 (1)	C5-C6	1.35 (1)
C2-C3	1.46 (1)	C6-C7	1.49 (1)
C3-C4	1.33 (1)	C7-C8	1.31 (1)
C4-C5	1.47 (1)	C8-C1	1.47 (1)
	hfacac		
O1-C9	1.27 (1)	O3-C14	1.25 (1)
C9-C10	1.38 (1)	C14-C15	1.36 (1)
C9-C12	1.53 (1)	C14-C17	1.51 (1)
C10-C11	1.37 (1)	C15-C16	1.377 (7)
C11-C13	1.51 (1)	C16-C18	1.556 (7)
O2-C11	1.25 (1)	O4-C16	1.230 (9)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] X_1, X_2, X_3, and X_4 are the centers of gravity of the C1-C2, C3-C4, C5-C6, and C7-C8 bonds, respectively.

Table V. Major Bond Angles (deg) for $Cu_2(COT)(hfacac)_2$[a]

	Cu		
O1-Cu11-O2	91.2 (3)	O3-Cu21-O4	90.6 (3)
O1-Cu11-X_1	133.3 (4)	O3-Cu21-X_2	128.3 (4)
O2-Cu11-X_1	134.7 (4)	O4-Cu21-X_2	140.8 (4)
O1-Cu12-O2	92.2 (3)	O3-Cu22-O4	92.1 (3)
O1-Cu12-X_3	131.8 (4)	O3-Cu22-X_4	134.9 (4)
O2-Cu12-X_3	133.2 (4)	O4-Cu22-X_4	132.4 (4)
	COT		
C2-C1-C8	124.5 (8)	C4-C5-C6	125.1 (7)
C1-C2-C3	127.2 (7)	C5-C6-C7	124.9 (6)
C2-C3-C4	124.9 (8)	C6-C7-C8	124.4 (7)
C3-C4-C5	125.8 (7)	C7-C8-C1	126.9 (1)
	hfacac		
Cu11-O1-C9	121.9 (7)	Cu21-O3-C14	116.8 (8)
Cu12-O1-C9	120.1 (6)	Cu22-O3-C14	120.9 (8)
Cu11-O2-C11	121.6 (7)	Cu21-O4-C16	122.6 (8)
Cu12-O2-C11	119.7 (6)	Cu22-O4-C16	119.6 (7)
O1-C9-C10	127.5 (8)	O3-C14-C15	129.0 (9)
O1-C9-C12	112.1 (7)	O3-C14-C17	111.0 (9)
C10-C9-C12	120.4 (7)	C15-C14-C17	120.0 (7)
C9-C10-C11	123.4 (7)	C14-C15-C16	123.9 (6)
O2-C11-C10	129.0 (7)	O4-C16-C15	127.5 (6)
O2-C11-C13	113.0 (8)	O4-C16-C18	114.2 (6)
C10-C11-C13	118.0 (7)	C15-C16-C18	118.3 (4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Solutions of Cu(olefin)hfacac Complexes. Solutions of a number of complexes formed from gaseous olefins and diolefins can be prepared in a manner exactly analogous to that used for the preparation of the carbonyl complex. Olefins which form such complexes include ethylene, propylene, 1-butene, 2-butene (either cis or trans), and 1,3-butadiene.

Preparation of Olefin Derivatives of Copper(I) and Silver(I) β-Diketonates. The general conditions for the preparation of the olefin complexes are given in Table I. All reactions were carried out at room temperature under a nitrogen atmosphere. The preparation of Cu(COD)hfacac is typical and is given below.

Preparation of Cu(COD)hfacac. A suspension of 1.43 g (10.0 mmol) of Cu_2O in 75 mL of tetrahydrofuran was stirred with 2.16 g (20.0 mmol) of 1,5-cyclooctadiene in a 250-mL flask under nitrogen. A solution of 4.16 g (20.0 mmol) of hexafluoroacetylacetone in 50 mL of THF was added dropwise over a 30-min period. The red Cu_2O gradually dissolved forming a clear yellow solution. This solution was then filtered to remove the small amount of solid material, and the solvent was then removed on a rotary evaporator. Solid Cu(COD)hfacac remained as a bright yellow crystalline residue. This was purified by recrystallization from hexane.

Crystal Structure of $Cu_2(COT)(hfacac)_2$. A light yellow crystal was mounted in random orientation on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. Accurate cell dimensions were determined by a least-squares fit of 25 diffractometer-measured 2θ values.

One-half sphere of data with $2\theta \leq 50°$ were measured as described in Table II and corrected for Lorentz and polarization effects and for absorption by using an empirical ψ-scan technique. All data with $|F_o|^2 \geq 2\sigma(F_o^2)$ were judged observed and were used in structure analysis and refinement. Three check reflections monitored periodically throughout data collection showed no decline in intensity with time. All calculations were performed by using the Enraf-Nonius SDP programs on a PDP 11/60 computer.

The structure was solved by using the program MULTAN and subsequent Fourier difference synthesis. Each copper atom was disordered, and each was initially entered at two positions with multiplicities of 0.5. Following anisotropic refinement of the copper atoms, the COT ring, and the carbon and oxygen atoms of the hfacac molecules, a difference map was calculated. It revealed that the electron density of the fluorine atoms was smeared out and they were entered in the three principle staggered conformations. In further cycles of refinement, the occupancy factors of the Cu atoms and of the three sets of resolved F atoms (with temperature factors fixed at 6.5 $Å^{-1}$) were allowed to vary. The occupancy factors refined to approximately 0.67 and 0.33 for Cu1, 0.55 and 0.45 for Cu2, 0.54, 0.32, and 0.14 for the F's of the one hfacac, and 0.47, 0.30, and 0.23 for the F's of the second hfacac. Hydrogen atoms were located in a subsequent difference Fourier map. They were assigned temperature factors of 5 $Å^{-1}$ and were not allowed to vary. Final cycles of refinement with occupancy factors fixed as above, and fixed isotropic temperature factors for F and H converged to $R = 0.084$ and $R_w = 0.091$. A final difference map displayed a maximum intensity of 0.65 e/$Å^3$.

Table II contains a summary of the crystal and experimental data. Final atomic coordinates are given in Table III and major bond distances and angles in Tables IV and V, respectively.

Registry No. Cu(COD)TTA, 95345-02-1; Cu(COD)hfacac, 86233-74-1; Cu(COD)tfacac, 95345-03-2; $[Cu(hfacac)]_2(B)$ (B = norbornadiene), 95345-04-3; Cu(B)hfacac (B = norbornene), 95345-05-4; Cu(COT)tfacac, 95362-66-6; $[Cu(tfacac)]_2COT$, 95387-20-5; $Cu(CH_2{=}CHC_6H_5)hfacac$, 95345-06-5; $[Cu(hfacac)]_2(CH_2{=}C(CH_3)CH{=}CH_2)$, 95345-07-6; Cu(hfacac)(B) (B = cyclohexene), 95345-08-7; Cu(B)tfacac (B = norbornene), 95345-09-8; $Cu(COD)_2(TAC)$, 95362-67-7; Cu(COE)hfacac, 95345-10-1; $Cu(CH_2{=}CHC_8H_{17})hfacac$, 95345-11-2; Cu(B)hfacac (B = 3-methylcyclohexene), 95345-12-3; Cu(COT)hfacac, 95345-13-4; $[Cu(hfacac)]_2COT$, 95345-14-5; Cu(α-pinene)$_2$hfacac, 95345-15-6; $Cu(B)_2TAC$ (B = 3-methylcyclohexene), 95345-16-7; Cu(α-pinene)TAC (isomer 1), 95462-06-9; Cu(α-pinene)TAC (isomer 2), 95345-17-8; $Cu(C_2H_5OC(O)CH{=}CHC(O)OC_2H_5)hfacac$, 95345-18-9; $Cu(CH_3C_6H_4CH{=}CH_2)hfacac$, 95345-19-0; $Ag(CH_2{=}CHC_8H_{17})hfacac$, 95345-20-3; Ag(COD)hfacac, 38892-25-0; Ag(B)hfacac (B = norbornene), 95362-68-8; Ag(COE)hfacac, 39015-19-5; Cu(CO)(hfacac), 95345-21-4; Cu(CO)(tfacac), 95345-22-5; Cu(CO)(TTA), 95345-23-6; Cu(CO)(TAC), 95345-24-7; COD, 111-78-4; COT, 629-20-9; COE, 931-88-4; TTA, 326-91-0; TAC, 51800-98-7; hfacac, 1522-22-1; tfacac, 367-57-7; Cu_2O, 1317-39-1; Ag_2O, 20667-12-3; $CH_2{=}CHC_6H_5$, 100-42-5; $CH_2{=}C(CH_3)CH{=}CH_2$, 78-79-5; $CH_2{=}CHC_8H_{17}$, 872-05-9; $C_2H_5OC(O)CH{=}CHC(O)OC_2H_5$, 141-05-9; 4-$CH_3C_6H_4CH{=}CH_2$, 622-97-9; norbornadiene, 121-46-0; norbornene, 498-66-8; cyclohexene, 110-83-8; 3-methylcyclohexene, 591-48-0; (+)-α-pinene, 7785-70-8; *d*,*l*-α-pinene, 2437-95-8.

Supplementary Material Available: Tables of anisotropic temperature factors, bond distances and angles, and observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.