

to reoxidize the CuCl produced.¹² The CuCl₂ reaction is of greater organic synthetic utility in that it is also effective with unbranched aldehydes and ketones. While MoCl₄(NCMe)₂ will chlorinate 2-methylcyclohexanone, we have not completed studies of this reaction or of the general scope of these Mo(IV)-induced oxidative chlorinations.

Previous synthetic routes to MoCl₃(NCMe)₃ include the reaction of Mo₂Cl₉³⁻ and MeCN⁶ as well as reduction of MoCl₄(NCMe)₂ with tetrakis(trimethylsilyl)hydrazine, [(Me₃Si)₂N]₂.⁷ The route described herein combines the advantages of reasonable yields and readily available starting materials. Furthermore, the THF complex MoCl₃(THF)₃ has proved useful as a Mo(III) starting material,⁴ and as such we felt it worthwhile to determine if the present chemistry could be utilized in the preparation of this compound. Indeed, if MoCl₃(NCMe)₃ is suspended in THF solvent and stirred for 1-2 days (ambient temperature), the result is high-yield conversion to MoCl₃(THF)₃ (the latter was identified by comparison of its IR spectrum to that of an authentic sample⁴). Overall, the sequence is as represented in eq 3. Additionally,

$$\text{MoCl}_5 \rightarrow \text{MoCl}_4(\text{NCMe})_2 \rightarrow \text{MoCl}_3(\text{NCMe})_3 \rightarrow \text{MoCl}_3(\text{THF})_3 \quad (3)$$

it should be mentioned that the yields of MoCl₃(THF)₃ are comparable to those obtained via the intermediacy of MoCl₄(THF)₂ and the workups are simplified since all byproducts are volatile and easily removed. The reactions reported here represent unusually mild conditions for the reduction of metal halide species. They are clearly useful in this molybdenum system, and we intend to determine if such reactions are generally applicable to high-valent-metal halide complexes. Additionally, efforts will be directed toward organic applications. Two immediate goals are further exploration of the scope and utility of the process (i.e., with what types of organic carbonyls it is operable) and the development of conditions for making the reaction catalytic in metal halide reagent.

Experimental Section

All manipulations were carried out under an inert atmosphere (argon or nitrogen) using either standard Schlenk techniques or a Vacuum Atmospheres Corp. glovebox. Acetonitrile was distilled from CaH₂ and ether was distilled from sodium benzophenone ketyl, both under nitrogen. Isobutyraldehyde (Aldrich) and propylene oxide (MCB) were stirred over 4Å molecular sieves and vacuum-distilled. Molybdenum pentachloride (Aldrich) was used as received and converted to MoCl₄(NCMe)₂ via the method of Dilworth.⁴ IR spectra were obtained on a Perkin-Elmer M1500 FTIR spectrophotometer and NMR spectra (200 MHz) on a Varian XL-200 FTNMR spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Tris(acetonitrile)trichloromolybdenum(III). Bis(acetonitrile)tetrachloromolybdenum(IV) (1.0 g, 3.13 mmol) was suspended in 20 mL of acetonitrile. A solution of isobutyraldehyde (0.57 mL, 6.26 mmol) in 20 mL of acetonitrile was then added to the suspension. The system was closed (to avoid loss of aldehyde) and immersed in a warm bath at ca. 50 °C. After being stirred for ca. 20 min, the brown suspension converted to a light yellow solution, at which time propylene oxide (0.28 mL, 4.0 mmol) was added to neutralize the HCl. After being stirred an additional few minutes, the solution was removed from the bath and stripped of dryness in vacuo. The greenish yellow residue was dissolved in a minimum volume of acetonitrile and ether added to the saturation point. Cooling resulted in precipitation of yellow MoCl₃(NCMe)₃·MeCN (0.64 g, 55%). Anal. Calcd for MoCl₃C₈H₁₂Cl₃: C, 26.22; H, 3.30; N, 15.29; Cl, 29.02. Found: C, 26.31; H, 3.24; N, 14.74; Cl, 29.71. IR (Nujol): 2312 m, 2280, s, 2275 m, 1028 m, br cm⁻¹.

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Registry No. MoCl₄(NCMe)₂, 19187-82-7; MoCl₃(NCMe)₃·MeCN, 102977-17-3; MoCl₃(THF)₃, 31355-55-2; Me₂CHCHO, 78-84-2.

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Effects of Mixed-Ligand Complexation on the Geometry of Copper(II) Complexes. X-ray Study of (Hexafluoroacetylacetonato)(acetylacetonato)copper(II)

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Cu(II) bis chelate complexes are normally found in a square planar or a tetrahedral environment.¹ Square-planar geometries are easily explained by crystal field theory. Distortions toward a tetrahedral environment are less common and are usually explained on the basis of steric and/or anion repulsions. Thus, we had very little expectation of any "surprises" when starting this structural study.² However, the previous studies do not include any examples of mixed-bidentate-ligand bis complexes. In this paper, we report the first study of this class of complex and find one completely unexpected result. Although the four oxygens and the Cu(II) are essentially square planar, the planes of the chelate rings form an angle of 163.5° with each other.

An ORTEP³ drawing is given in Figure 1. The bond lengths and angles are given in Tables I and II. Because the molecule has no imposed symmetry, four Cu-O distances and two O-Cu-O chelate "bite" angles were obtained. The average Cu-O bond length on the hfac side is 1.946 [5] Å. This difference is consistent with our earlier IR and ESR results.⁴ The Cu-O bond length on the acac side is shorter than the bond length in the nonmixed Cu(acac)₂ complex (1.921 [5] Å).⁷ This appears to be direct support for the trans effect model, as the stronger ligand (acac) has a shorter bond when across from a weaker ligand (hfac) than when across from another acac.

The atomic coordinates are given in Table III. Least-squares plane calculations indicated that the four oxygens are within ±0.062 Å of being square planar. The copper is displaced slightly (0.060 Å) from the plane. The surprising thing is that, in the solid state, the molecule as a unit is decidedly folded, the angle between the two chelates being 163.5°. As discussed by Maslen and Waters⁵ and by Robertson and Truter,⁶ a stepped (chair) type distortion is common in Cu(II) complexes. In Cu(II) acac type complexes, distortion angles ranging from 0 to 14° have been reported (see Table 6 of ref 6). All of these distortions are of the stepped type. A stepped type distortion still leaves the ligand planes parallel to each other and, thus, has only a small effect on inter-ring conjugation (see Figure 11 of ref 5). However, the large umbrella (boat) type distortion observed in the present complex is thought to be inconsistent with significant inter-ring conjugation. The extent of inter-ring conjugation in acac type complexes has been a controversial point in the literature.⁸ In a previous paper,⁹ we reported that molecular orbital calculations

- (1) Holm, R. H.; O'Conner, M. J. *Prog. Inorg. Chem.* 1971, 14, 241.
- (2) A green crystal of dimensions 0.2 × 0.2 × 0.06 mm was mounted on a Syntex P2₁ diffractometer equipped with a graphite monochromator. With Mo Kα (λ = 0.71069 Å) at room temperature, the crystal data were as follows: triclinic, P1̄, a = 8.775 (3) Å, b = 12.052 (4) Å, c = 6.978 (3) Å, α = 99.87 (3)°, β = 114.13 (3)°, γ = 90.70 (3)°, Z = 2, μ = 18.1 cm⁻¹, with no absorption correction applied. Data were collected for 1394 unique reflections up to a 2θ limit of 40.0° by the 2θ-θ scan technique in bisecting mode. The structure was solved by MULTAN.¹⁰ Full-matrix least-squares anisotropic (for all non-hydrogen atoms) refinement converged to R = 0.053. The final ΔF synthesis showed two peaks: 0.53/Å³ at one fluorine and 0.43 e/Å³ at the copper.
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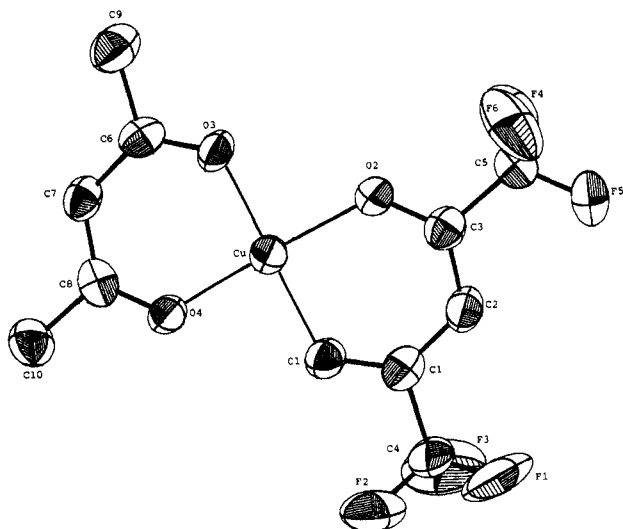


Figure 1. ORTEP plot of Cu(acac)(hfac).

Table I. Bond Lengths (Å) for Cu(acac)(hfac)^a

	hfac side	acac side	
Cu—O	1.948 (3)	1.884 (3)	
Cu—O	1.944 (4)	1.890 (4)	
C—O	1.256 (8)	1.248 (8)	
C—O	1.255 (7)	1.284 (7)	
C—CH	1.389 (8)	1.409 (8)	
C—CH	1.369 (8)	1.389 (8)	
C—CF ₃	1.526 (7)	1.503 (7)	C—CH ₃
C—CF ₃	1.529 (9)	1.484 (8)	C—CH ₃
C—H1	0.93 (3)	0.90 (4)	C—H2
C—F1	1.27 (1)	0.78 (5)	C—H3
C—F2	1.305 (7)	0.92 (4)	C—H4
C—F3	1.32 (1)	0.82 (4)	C—H5
C—F4	1.33 (1)	1.01 (5)	C—H6
C—F5	1.295 (7)	0.74 (3)	C—H7
C—F6	1.30 (1)	0.95 (3)	C—H8

^a Values in parentheses are estimated standard deviations.

Table II. Selected Bond Angles (deg) for Cu(acac)(hfac)^a

	hfac side	acac side
O—Cu—O	91.5 (1)	94.7 (1)
Cu—O—C	125.7 (3)	125.4 (3)
Cu—O—C	125.3 (3)	123.1 (3)
O—C—C	127.6 (5)	124.5 (4)
O—C—C	128.7 (6)	125.0 (5)
C—CH—C	121.3 (6)	124.1 (5)

^a Values in parentheses are estimated standard deviations.

indicated that there is delocalization over both rings in the symmetrical complexes and separate delocalized orbitals for each ligand in the mixed complexes. These calculations were carried out on assumed planar geometries and equal metal–ligand distances. Even under these restraints, the calculations predicted that the acac π system in the mixed complex was destabilized relative to the π system in the nonmixed complex. As an additional check on the above model, we now have calculated the total energies of both Cu(acac)₂ and Cu(acac)(hfac) in both the stepped and umbrella conformations with a 16° distortion. The same extended Hückel method was used as in ref 9. For Cu(acac)₂ the stepped form was more stable than the umbrella by 1.22 kcal/mol, but for Cu(acac)(hfac), the difference was only 0.56 kcal/mol. Although the absolute magnitudes of the energy differences are not expected to be quantitative, their relative values should be significant. Thus, the energy effect of the π delocalization in the mixed complex is only 46% that of the energy effect in the nonmixed. Apparently the energy barrier in the mixed complex is

Table III. Cu(acac)(hfac) Fractional Atomic Coordinates ($\times 10^4$)

	x	y	z
Cu	5357 (1)	9115 (1)	8037 (2)
F1	1076 (6)	6162 (6)	8074 (13)
F2	369 (6)	7771 (5)	7544 (9)
F3	298 (6)	6561 (5)	5019 (10)
F4	7377 (6)	5691 (4)	6667 (10)
F5	6168 (6)	4826 (4)	8064 (11)
F6	8223 (7)	6033 (4)	10018 (9)
O1	3237 (5)	8354 (4)	7606 (7)
O2	6424 (6)	7710 (4)	8250 (7)
O3	7330 (5)	9772 (4)	8075 (7)
O4	4258 (5)	10458 (4)	7828 (7)
C1	2964 (9)	7316 (7)	7511 (11)
C2	4081 (10)	6493 (6)	7683 (12)
C3	5707 (10)	6760 (6)	8035 (12)
C4	1173 (10)	6934 (8)	7094 (19)
C5	6874 (12)	5812 (7)	8245 (18)
C6	7472 (8)	10695 (7)	7550 (11)
C7	6221 (10)	11454 (6)	7060 (11)
C8	4704 (10)	11298 (6)	7204 (11)
C9	9093 (10)	11004 (6)	7437 (13)
C10	3458 (9)	12144 (6)	6644 (12)

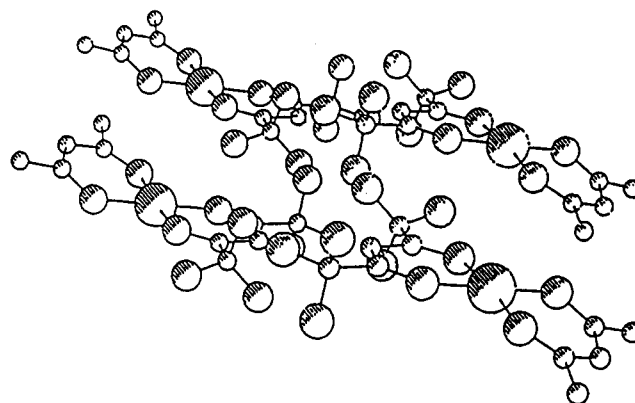


Figure 2. Cu(acac)(hfac) plot of contents of more than one unit cell with the *b* axis from left to right and the *c* axis down the page.

too small to be the geometry-determining factor. The observed umbrella (boat) type distortion could be due to nearest-neighbor interactions and/or crystal-packing effects. In our case, there are no intermolecular distances to copper less than 4.0 Å and no intermolecular distances to oxygens less than 3.5 Å. The primary interactions between neighboring molecules appear to be fluorine–hydrogen and fluorine–fluorine contacts. The shortest intermolecular contact, 2.99 (4) Å, is between a methyl hydrogen and fluorine and is not unusually short in view of the van der Waals radius for fluorine of 1.35 Å. It, therefore, appears that a crystal-packing explanation is more appropriate here. A packing diagram is given in Figure 2. There are two orientations of the molecule, one the inverse of the other. This packing allows the fluorines of one CF₃ group to occupy the space between the fluorines of a CF₃ group on the neighboring molecule. Fluorine F5 lies nearly in the plane of the hfac ring and is also the fluorine of closest intermolecular contact with a methyl hydrogen. This fluorine is as far as possible from its ring oxygen atom. The other two fluorines of this CF₃ group are equidistant from the plane of the hfac ring. The other CF₃ group is oriented so that the fluorines are staggered from the chelate ring and staggered from the fluorines of the first CF₃ group. The fluorine (F2) of this group closest to the plane of the ring is also closest to its ring oxygen (O—C—C—F trans to F5). One fluorine (F3) of this group is approximately normal to the hfac plane.

Thus, a consistent model emerges. The previous stepped or planar geometries are due to the two identical ligands having the same energies for their π systems, allowing maximum mixing of the two sets of orbitals. When the two ligands are different, the difference in their π energy levels limits the inter-ring conjugation.

There then would be a 50-50 chance of a boat or chair distortion depending on the more favorable crystal-packing conformation. We were, therefore, fortunate that our first structure of this type turned out to be of the boat form as the significance of the π interaction would have not been apparent if the chair geometry was found. These results suggest that mixed-ligand complexes should be useful templates for altering the aromatic chemistry of a particular ligand.

Registry No. Cu(acac)(hfac), 21429-77-6.

Supplementary Material Available: Tables of anisotropic thermal parameters and calculated hydrogen atom positions (2 pages). Ordering information is given on any current masthead page.

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Characterization of $[\text{Fe}_2(\text{CO})_6\text{B}_3\text{H}_6]^-$: A Comment on the Dynamic Structure of $\text{Fe}_2(\text{CO})_6\text{B}_3\text{H}_7$

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One of the interesting aspects of metal cluster chemistry is the positioning of skeletal endo hydrogens and their susceptibility toward fluxional processes on the cluster surface.² The association of metal and main-group fragments (e.g. borane) in a cluster environment can produce a significant effect on some or all of the skeletal protons.^{3,4} One simple chemical change that a hydrido cluster often readily undergoes is deprotonation. The action of removing an endo hydrogen can induce proton mobility among hydrogens remaining in the anion when such mobility required a greater activation energy in the conjugate acid. This is commonly the case in borane anions.⁵ Among the ferraboranes, examples of the lowering of the activation barrier for hydrogen scrambling are found in going from $\text{HFe}(\text{CO})_3\text{B}_5\text{H}_9$ to $[\text{HFe}(\text{C}-\text{O})_3\text{B}_5\text{H}_8]^-$,⁶ from $\text{HFe}_3(\text{CO})_9\text{BH}_4$ to $[\text{HFe}_3(\text{CO})_9\text{BH}_3]^-$,⁷ and from $\text{HFe}_4(\text{CO})_{12}\text{BH}_2$ ⁸ to $[\text{HFe}_4(\text{CO})_{12}\text{BH}]^-$.⁹ The latter two anions are distinct from the former one because they exhibit fluxionality between Fe-H-B and Fe-H-Fe hydrogens rather than simply between B-H-B hydrogens in different environments. $\text{Fe}_2(\text{CO})_6\text{B}_3\text{H}_7$ (II) has previously been characterized,^{10,11} but a

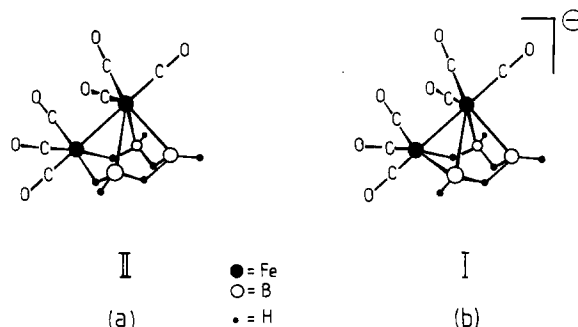
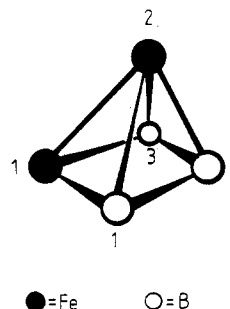


Figure 1. Structural representations of (a) $\text{Fe}_2(\text{CO})_6\text{B}_3\text{H}_7$ (II) and (b) $[\text{Fe}_2(\text{CO})_6\text{B}_3\text{H}_6]^-$ (I).

Chart I



study of its conjugate base $[\text{Fe}_2(\text{CO})_6\text{B}_3\text{H}_6]^-$ (I) is reported here for the first time. What made I seemingly unusual was the fact that, at room temperature and on the 300-MHz NMR time scale, it possessed a static structure, whereas II had been reported to be fluxional at the same temperature and on the 100-MHz time scale,¹⁰ i.e. the reverse trend for the conjugate ferraborane acid-base pairs mentioned above. The present work presents spectroscopic data and an analysis of I, along with a reanalysis of II. In addition, the Fenske-Hall quantum chemical approach is used to suggest reasons why II deprotonates via loss of an Fe-H-B rather than a B-H-B proton.

Experimental Section

General Methods. All manipulations were carried out under inert atmospheres by using standard techniques.¹² Hexane was dried over molecular sieves, degassed, and distilled from sodium/benzophenone; methanol was dried over molecular sieves and degassed before use; anhydrous diethyl ether (Fisher) was distilled from sodium/benzophenone. $[\text{PPN}]\text{Cl}$ (PPN = bis(triphenylphosphine)nitrogen(1+)) (Aldrich) was used as received.

¹¹B and ¹H FT NMR spectra were obtained on a Nicolet 300-MHz spectrometer; infrared spectra were recorded on a Perkin-Elmer 983 spectrometer. ¹¹B NMR shifts are reported with respect to $\text{BF}_3\cdot\text{Et}_2\text{O}$ ($\delta = 0$) and ¹H shifts, with respect to Me_4Si ($\delta = 0$).

Preparation of $[\text{I}]\text{PPN}$. I was formed as a byproduct during the preparation of $[\text{HFe}_3(\text{CO})_9\text{BH}_3]\text{PPN}$.⁷ I was readily separated from other anionic products of the reaction⁷ by selective protonation using 40% phosphoric acid followed by hexane extraction. The yellow-orange hexane extract containing II¹³ was transferred into a flask containing a solution of $[\text{PPN}]\text{Cl}$ dissolved in methanol. After 20 min of vigorous stirring, the color of the hexane layer diminished and the methanol layer turned dark red, indicating that deprotonation of II to I had occurred. II could be regenerated by treating I with H_3PO_4 . $[\text{I}]\text{PPN}$: ¹¹B NMR ($\text{CD}_3\text{C}(\text{O})\text{CD}_3$, 20 °C) $\delta +2.4$ (m, 1 B), $+8.6$ (m, 1 B), $+33.9$ (m, 1 B); ¹¹B{¹H} $J_{\text{BH}}(\text{Fe-H-B}) = 60$ Hz, $J_{\text{BH}}(\text{B-H-B}) < 40$ Hz, $J_{\text{BH}}(\text{term}) = 125$ Hz; ¹H NMR ($\text{CD}_3\text{C}(\text{O})\text{CD}_3$, 20 °C) $\delta 7.7-7.5$ (m, 30 H, PPN^+),

- (1) Laboratory experimental and spectroscopic work was carried out at the University of Notre Dame; calculational work was carried out at the University of New Hampshire.
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