sidered here the steric constraints within the gold complex are essentially identical with those of the bromide. An alternative electronic explanation for the quite angular arrangement has been developed on the basis of a molecular orbital study of transition-metal basicity which we plan to publish elsewhere. We believe that the observed structure is a consequence of the reverse polarity of the iron–gold bond. The $(\eta^3\text{-}C_3H_5)Fe(CO)_3^-$ anion is acting as a Lewis base and the $AuP(C_6H_5)_3^+$ cation as the Lewis acid. The electrons of the resulting donor–acceptor bond are located primarily on the iron atom and are primarily of d character. Since d orbitals have a multinodal structure they show little stereochemical activity when compared to orbitals with high s and p character. Since the electrons of the Fe–Au bond are not stereochemically active, the angles to the neighboring CO ligands are acute. The low angles are thus a direct consequence of the transition-metal basicity and do not reflect any direct interaction between the gold atom and the CO ligands. In the bromide derivative, I, the electrons of the Fe–Br bond are located primarily on the Br^- donor atom, while the acceptor orbital on the Fe moiety is of high s and p character and is thus stereochemically active.

The concept that the effective hybridization of a central atom, and thus its geometry, is dependent upon the nature of the substituents is certainly not a new one and many standard textbook examples are known in main-group chemistry. This concept, however, has not been routinely applied to transition-metal complexes. We believe the effect of the substituents is particularly important in molecules with polar metal–metal bonds as well as in other metal–Lewis acid adducts in which acute angles to cis ligands are found. The assignment of geometry has been most often discussed in terms of the stereochemical activity of the hydride ligand;[19] but the stereochemical consequences of polar bonds between two different metals are often even more dramatic. For example,[20] in the C_{3v} molecule $Co(CO)_4H$, the average angle between the hydride and the three cis CO ligands is 80°, which is far from the ideal value of 90°. In the analogous gold complex[21] $Co(CO)_4AuP(C_6H_5)_3$ the cis angles are only 77°.

In summary, we propose that the distinctly different coordination geometries of the gold and bromide complexes are directly due to the reversed polarity of the iron–gold bond as compared to the iron–bromide bond. We believe that this phenomenon can be observed in a wide range of compounds and that it deserves further investigation.

Registry No. I, 12192-46-0; II, 73891-25-5; III, 12288-77-6; IV, 73891-24-4; $AuPPh_3Cl$, 14243-64-2.

Supplementary Material Available: Listings of structure factor amplitudes and positional and thermal parameters for the hydrogens of $(\eta^3\text{-}C_3H_5)Fe(CO)_3Br$ and $(\eta^3\text{-}C_3H_5)Fe(CO)_3AuP(C_6H_5)_3$ (16 pages). Ordering information is given on any current masthead page.

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Reactions of Coordinated Molecules. 26. Crystal and Molecular Structure of $[\eta^5\text{-}C_5H_5(OC)Fe(CH_3CO)(i\text{-}C_3H_7CO)]BF_2$: A Metalla-β-diketonate Complex of Boron

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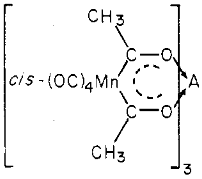
The complex $[\eta^5\text{-}C_5H_5(OC)Fe(CH_3CO)(i\text{-}C_3H_7CO)]BF_2$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 8.0972$ (11) Å, $b = 11.548$ (2) Å, $c = 15.393$ (3) Å, $\beta = 111.77$ (1)°, $V = 1337$ Å^3, $Z = 4$, and ρ(calcd) = 1.550 g cm^{-3} for mol wt 311.92. Diffraction data (2θ out to 60°) were collected with a four-circle diffractometer using Nb-filtered Mo Kα radiation. The structure was refined by using the full-matrix least-squares procedure, and the resulting discrepancy indices were $R = 4.8\%$ and $R_w = 3.3\%$ for 3891 independent reflections. The boron atom acts as the central coordinating atom with the BF_2 moiety being bonded to the ferra-β-diketonate ligand through the two oxygen atoms of the metallachelate ring. The atoms comprising the backbone of the metallachelate ring are not coplanar, and the chelate ring adopts a boat-shaped structure. This complex is the second example of a nonplanar, metalla-β-diketonate ring structure, and this nonplanar ring conformation is attributed to the relief of internal angle strain within the metallachelate ring due to the bonding preferences imposed by the metalla and the central coordinating atoms.

Introduction

The discovery of the metalla-β-diketonate molecules initiated a study of the coordination chemistry and the organic condensation chemistry of these complexes. The elucidation of the molecular structures of these metalla molecules is an important aspect of this continuing investigation.

The structures of three metallaacetylacetonate complexes, **1–3**, have been determined previously by X-ray crystallography.[2-4] Complex **1** is the neutral tris(metallaacetylacetonate) complex of Al(III) where the metalla moiety is the *cis*-$Mn(CO)_4$ group, and the complexes **2** and **3** are neutral metallaacetylacetonate molecules where the metalla moiety is the analogous rhenium fragment. In **1** and **2** the metallaacetyl-



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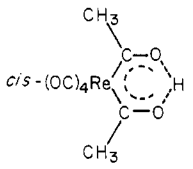

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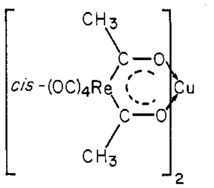

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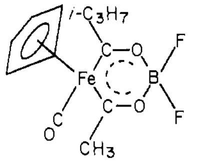
acetonate ligands are structurally similar to the acetylacetonate (acac) ligand regarding ligand planarity, intraligand C–O distances, and the O–O "bite" distance.

However, in **3** each rhenaacetylacetonate ligand ring adopts a distinct boat-shaped structure, even though the intraligand bond distances, the O–O "bite" distance, and the bonding geometry about the copper atom are the same in **3** as in **2** and in $Cu(acac)_2$. The overall molecular shape of **3** has a "chaise longue chair" appearance since the molecule possesses an inversion center. The nonplanar conformation of **3** was attributed either to long-range Cu–CO(axial) interactions or to angle strain within the metallaacetylacetonate ligand ring.

When the ferra-β-diketone, $[\eta^5\text{-}C_5H_5(OC)Fe(CH_3CO)(i\text{-}C_3H_7CO)]H$, is treated with BF_3, the condensation product obtained is $[\eta^5\text{-}C_5H_5(OC)Fe(CH_3CO)(i\text{-}C_3H_7CO)]BF_2$, **4**.



4

This air-stable complex and its (ferraacetylacetonato)boron difluoride analogue show two carbonyl stretching vibrations in the solution-phase IR spectra.[5] The relative intensities of these bands vary with a change in the solvent polarity which is a strong indication that geometrical isomers are present. The X-ray structure of **4** was undertaken to resolve this question of possible isomerism and to provide the first structural data for the ferra-β-diketonate ligand and for the metalla-β-diketonate complexes of boron. Complex **4** represents the second metalla-β-diketonate complex which has a nonplanar, boat-shaped ligand ring, and the nonplanarity of the ligand ring is now attributed primarily to internal angle strain within the six-membered chelate ring.

Experimental Section

Collection of X-ray Diffraction Data. Yellow crystals of **4** were prepared by using a literature preparation followed by crystallization from an ether solution at −20 °C.[5] Preliminary precession and cone-axis photographs indicated $2/m$ Laue symmetry and revealed the systematic absences $0k0$ for k odd and $h0l$ for l odd which identified the space group as $P2_1/c$. Cell parameters were determined by a least-squares fit of 2θ, ω, and χ diffractometer settings for 15 reflections in the range $47° < 2\theta < 52°$ as measured at both $\pm 2\theta$ with Mo $K\alpha_1$ radiation ($\lambda = 0.70926$ Å). Values for a, b, c, and β, respectively, at 20 °C are 8.0972 (11) Å, 11.548 (2) Å, 15.393 (3) Å, and 111.77 (1)°. The calculated volume of the cell is 1337 Å^3. With $Z = 4$ and a molecular weight of 311.92 the calculated density is 1.550 g cm^{-3}.

Intensity data were collected from a freshly grown crystal measuring 0.2 mm × 0.3 mm × 0.4 mm which was mounted with the longest dimension parallel to the ϕ axis of the four-circle automated Picker diffractometer. The control software used for the Picker FACS-I system has been reported previously.[6] A total of 8684 reflections were measured ($\pm h, \pm k, \pm l$ for $0° < 2\theta < 30°$ and $\pm hkl$, $\pm h\bar{k}\bar{l}$ for $30° < 2\theta < 60°$) by using Mo Kα radiation and θ–2θ step scans. The step size was 0.03° with the number of steps adjusted to cover the full scan range for each reflection and with background counts for 20 s at the ends of each scan. Zr–Y balanced filters were used below 12° 2θ, and a Nb filter was used above 12°. Five monitor reflections, used for scaling, showed a 4% decline in intensity in the course of 376 h of X-ray exposure. The scaling procedure provides a correction for this decline. Absorption corrections were calculated with ORABS[7] using a linear absorption coefficient of 11.47 cm^{-1} and a Gaussian grid of 8 × 8 × 8; maximum, minimum, and average transmission factors were 0.833, 0.746, and 0.800. Symmetry-related reflections were averaged to give 3891 independent structure factors with all but 177 greater than zero.

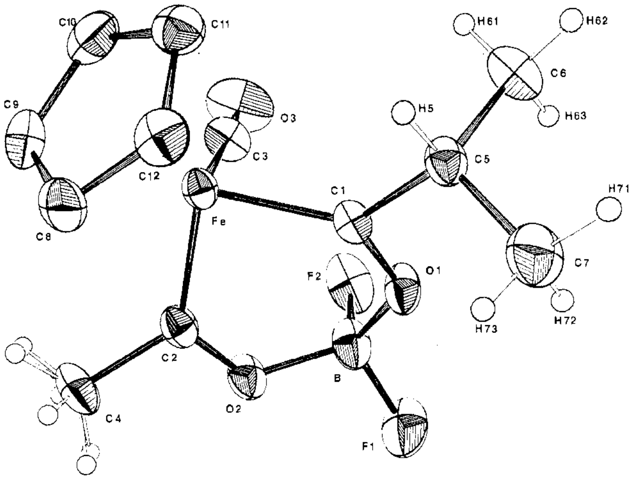


Figure 1. An ORTEP view of **4** (ellipsoids at 30% probability) from below the chelate ring showing the atomic numbering scheme.

A sharpened Patterson function indicated the Fe position which provided phases for a difference synthesis that revealed the remaining atoms. After preliminary least-squares refinement, a second difference synthesis showed peaks at expected H atom positions. A ring of electron density around the C(4) methyl carbon was taken to indicate rotational disorder and the H atoms of the disordered methyl group were approximated by six equally spaced half-atoms tetrahedrally located 1.0 Å from the carbon position.

The final refinement of all atoms (except the disordered H atoms) was carried out with all heavy atoms anisotropic and all H atoms isotropic. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma(F_o)$. The variance, σ^2, was based on counting statistics and included the usual instability term (2.0% in this case) as described previously.[8] Atomic scattering factors for the neutral atoms were those tabulated by Cromer and Mann[9] except for hydrogen where Stewart's values[10] were used. The anomalous dispersion factors used for all atoms except hydrogen were those given by Cromer and Liberman.[11] The final R factor was 0.048; the weighted R factor, $R_w = \{[\sum w(|F_o| - |F_c|)^2]/\sum w|F_o|^2\}^{1/2}$, was 0.033, both calculated with all 3891 reflections. The maximum shift to error ratio for the atomic parameters in the final cycle was 0.15, and the standard error of an observation of unit weight was 2.4. The maximum and minimum electron densities on the final difference map were 0.47 e Å^{-3} near Fe and −0.28 e Å^{-3} near F(1). The atomic parameters are displayed in Table I. The values shown were used before rounding to calculate the final structure factors.[12]

Except as noted, calculations were carried out with the X-ray 67 programs[13] as implemented and updated on the Vanderbilt Sigma 7 computer.

Results and Discussion

The crystal structure consists of discrete monomeric molecular units of $[\eta^5\text{-}C_5H_5(OC)Fe(CH_3CO)(i\text{-}C_3H_7CO)]BF_2$, **4**. The atomic numbering scheme and a view of the molecule from below the chelate ring are shown in Figure 1. There are no abnormally short intermolecular contacts. The inter-

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Table I. Final Positional and Thermal Parameters[a] (with Esd's) for $[\eta^5\text{-}C_5H_5(OC)Fe(CH_3CO)(i\text{-}C_3H_7CO)]BF_2$

atom	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	0.125 23 (3)	0.217 56 (2)	0.146 54 (2)	2.90 (1)	3.18 (1)	2.63 (1)	0.39 (1)	1.28 (1)	0.07 (1)
F(1)	−0.354 20 (16)	−0.005 27 (11)	0.104 02 (11)	4.65 (6)	5.17 (7)	12.42 (10)	−0.80 (5)	2.90 (6)	2.14 (7)
F(2)	−0.186 29 (17)	0.084 08 (10)	0.237 52 (9)	7.60 (8)	6.22 (7)	7.68 (8)	1.83 (6)	5.14 (6)	3.09 (6)
O(1)	−0.242 16 (15)	0.175 48 (10)	0.094 88 (9)	3.06 (5)	3.64 (6)	5.95 (8)	0.60 (4)	1.88 (5)	1.72 (5)
O(2)	−0.053 73 (16)	0.005 71 (10)	0.140 17 (9)	4.32 (6)	2.99 (5)	6.61 (8)	0.60 (5)	2.43 (6)	1.11 (5)
O(3)	0.113 65 (26)	0.231 71 (14)	0.331 41 (10)	12.05 (13)	7.07 (9)	3.82 (7)	−0.14 (8)	4.28 (8)	0.00 (6)
B	−0.211 02 (32)	0.064 39 (20)	0.146 57 (20)	4.31 (11)	3.70 (10)	7.40 (16)	0.66 (9)	2.98 (11)	2.03 (10)
C(1)	−0.119 06 (22)	0.243 22 (13)	0.089 72 (11)	3.33 (7)	2.96 (7)	3.13 (7)	0.57 (5)	1.60 (6)	0.46 (6)
C(2)	0.085 82 (23)	0.058 67 (15)	0.138 13 (11)	3.70 (8)	3.54 (8)	3.27 (8)	0.94 (6)	1.25 (7)	0.42 (6)
C(3)	0.112 90 (26)	0.223 25 (16)	0.257 52 (13)	5.34 (10)	3.87 (9)	3.31 (8)	0.49 (7)	1.86 (7)	0.50 (7)
C(4)	0.213 87 (28)	−0.032 27 (17)	0.130 70 (15)	5.86 (11)	4.10 (10)	7.16 (13)	2.07 (8)	3.24 (10)	0.41 (9)
C(5)	−0.206 52 (24)	0.351 55 (15)	0.035 90 (12)	3.43 (8)	3.05 (8)	4.02 (8)	0.57 (6)	1.43 (7)	0.93 (6)
C(6)	−0.271 40 (41)	0.425 36 (22)	0.098 93 (20)	6.48 (14)	3.67 (11)	6.05 (14)	1.29 (10)	2.89 (12)	0.24 (10)
C(7)	−0.357 78 (41)	0.323 07 (25)	−0.055 42 (18)	6.50 (15)	5.06 (13)	4.67 (12)	1.75 (12)	0.31 (11)	0.99 (10)
C(8)	0.301 24 (28)	0.215 33 (20)	0.072 92 (16)	4.60 (10)	4.98 (10)	5.62 (11)	−0.20 (9)	3.55 (9)	−0.80 (9)
C(9)	0.401 62 (28)	0.223 28 (22)	0.168 71 (17)	2.98 (9)	6.24 (12)	5.97 (13)	0.27 (9)	1.85 (9)	0.24 (11)
C(10)	0.352 51 (28)	0.325 83 (21)	0.201 13 (17)	3.89 (10)	6.15 (12)	4.70 (11)	−1.50 (9)	1.41 (9)	−1.08 (10)
C(11)	0.223 77 (28)	0.381 86 (18)	0.126 14 (14)	4.60 (10)	3.74 (9)	4.85 (10)	−0.66 (8)	2.61 (9)	−0.27 (8)
C(12)	0.192 32 (29)	0.313 55 (18)	0.046 88 (15)	4.49 (10)	4.88 (11)	3.71 (9)	−0.41 (8)	2.45 (8)	0.24 (8)
atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
H(411)[b]	0.1571	0.0802	0.0714	7.07	H(63)	−0.3586 (29)	0.3854 (18)	0.1150 (14)	6.54 (61)
H(421)	0.3244	0.0041	0.1279	7.07	H(71)	−0.4372 (34)	0.2751 (21)	−0.0416 (7)	7.39 (74)
H(431)	0.2484	−0.0869	0.1854	7.07	H(72)	−0.4099 (26)	0.3955 (17)	−0.0877 (13)	5.69 (48)
H(412)	0.2382	−0.0218	0.0711	7.07	H(73)	−0.3030 (40)	0.2834 (23)	−0.0929 (19)	9.95 (88)
H(422)	0.3295	−0.0284	0.1851	7.07	H(8)	0.3064 (25)	0.1561 (17)	0.0335 (13)	5.35 (49)
H(432)	0.1622	−0.1128	0.1285	7.07	H(9)	0.4874 (29)	0.1721 (18)	0.2066 (15)	6.55 (59)
H(5)	−0.1151 (21)	0.3944 (13)	0.0225 (10)	3.23 (35)	H(10)	0.3934 (25)	0.3499 (18)	0.2631 (14)	5.93 (53)
H(61)	−0.1812 (32)	0.4402 (20)	0.1589 (18)	8.22 (74)	H(11)	0.1678 (24)	0.4503 (16)	0.1291 (12)	5.07 (48)
H(62)	−0.3086 (27)	0.4952 (19)	0.0725 (15)	6.36 (57)	H(12)	0.1157 (22)	0.3278 (14)	−0.0099 (12)	3.59 (41)

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [b] Hydrogen atom positions are denoted by a number which refers to the carbon atom to which it is bonded and to the number of hydrogen atoms which are bonded to that atom when more than one such atom is present. The hydrogen atoms denoted by a three-digit number are given a weight of 0.5.

Table II. Interatomic Distances (in Å, with Esd's) for $[\eta^5\text{-}C_5H_5(OC)Fe(CH_3CO)(i\text{-}C_3H_7CO)]BF_2$

Fe–C(1)	1.867 (2)	C(2)–C(4)	1.509 (3)
Fe–C(2)	1.859 (2)	C(5)–C(6)	1.524 (4)
Fe–C(3)	1.749 (2)	C(5)–C(7)	1.517 (3)
Fe–C(8)	2.124 (3)	C(8)–C(9)	1.395 (3)
Fe–C(9)	2.135 (2)	C(9)–C(10)	1.398 (3)
Fe–C(10)	2.123 (2)	C(10)–C(11)	1.396 (3)
Fe–C(11)	2.127 (2)	C(11)–C(12)	1.397 (3)
Fe–C(12)	2.120 (2)	C(8)–C(12)	1.401 (3)
C(1)–O(1)	1.291 (2)	B–O(1)	1.480 (3)
C(2)–O(2)	1.297 (2)	B–O(2)	1.477 (3)
C(3)–O(3)	1.139 (3)	B–F(1)	1.363 (2)
C(1)–C(5)	1.523 (2)	B–F(2)	1.358 (3)

Table III. Interatomic Angles (in Deg, with Esd's) for $[\eta^5\text{-}C_5H_5(OC)Fe(CH_3CO)(i\text{-}C_3H_7CO)]BF_2$

C(1)–Fe–C(2)	89.94 (7)	C(2)–Fe–C(3)	92.0 (1)
Fe–C(1)–O(1)	125.7 (1)	Fe–C(1)–C(5)	125.7 (1)
Fe–C(2)–O(2)	127.3 (2)	Fe–C(2)–C(4)	126.0 (2)
Fe–C(3)–O(3)	175.6 (2)	C(4)–C(2)–O(2)	107.7 (2)
C(1)–O(1)–B	125.1 (2)	C(5)–C(1)–O(1)	108.5 (1)
C(2)–O(2)–B	124.5 (2)	C(1)–C(5)–C(6)	108.2 (2)
O(1)–B–O(2)	110.0 (2)	C(1)–C(5)–C(7)	112.2 (2)
F(1)–B–F(2)	111.5 (2)	C(6)–C(5)–C(7)	111.2 (2)
F(1)–B–O(1)	108.0 (2)	C(8)–C(9)–C(10)	107.6 (2)
F(1)–B–O(2)	107.3 (2)	C(9)–C(10)–C(11)	108.8 (2)
F(2)–B–O(1)	109.9 (2)	C(10)–C(11)–C(12)	107.3 (2)
F(2)–B–O(2)	110.2 (2)	C(11)–C(12)–C(8)	108.4 (2)
C(1)–Fe–C(3)	91.0 (1)	C(12)–C(8)–C(9)	107.9 (2)

molecular H(11)···F(2) distance of 2.533 (18) Å is the shortest such contact distance observed in **4**, and this distance represents a normal van der Waals contact although this distance may be systematically elongated from the actual internuclear separation. Interatomic distances and angles are compiled in Tables II and III, respectively, and selected least-squares plane data are listed in Table IV.

The geometry about the iron atom resembles a "three-legged piano stool" with the angles between the monodentate ligands being close to 90°. The apical position is occupied by the η^5-C_5H_5 ligand. This ligand has idealized D_{5h} symmetry, and the (η^5-C_5H_5)Fe moiety has the usual structural features.[14] The five carbon atoms [C(8)–C(12)] which form the ring are essentially coplanar (plane VI, maximum atomic deviation is 0.0029 Å), and the ring C–C distances range from 1.395 (3) to 1.401 (3) Å and have a weighted-mean value of 1.397 (3) Å. The Fe–C(η^5-C_5H_5) distances range from 2.120 (2) to 2.135 (2) Å, and the distance from the Fe atom to the plane of the η^5-C_5H_5 ligand is 1.763 Å.

The values of the Fe–C(3) and the carbonyl C(3)–O(3) distances of 1.749 (2) and 1.139 (3) Å, respectively, are very similar to the corresponding values observed for the symmetry-equivalent Fe–CO(terminal) groups of *trans*-[η^5-$C_5H_5Fe(CO)_2]_2$ (where the Fe–C distances are 1.748 (6) Å and the C–O distances are 1.157 (7) Å).[15] The Fe–C(3)–O(3) angle of 175.6 (2) Å is within the accepted range for linear, terminally coordinated carbonyl ligands.

The methyl and isopropyl groups are bonded to the ferra-β-diketonate ring via C(sp^2)–C(sp^3) single bonds These distances are 1.509 (3) Å [C(2)–C(4)] and 1.523 (2) Å [C(1)–C(5)], respectively.

The two intrachelate ring iron–carbon distances of 1.867 (2) and 1.859 (2) Å are not significantly different within a 2σ limit. These distances indicate Fe–C(sp^2) bonds which are between bond orders 1.0 and 2.0.[16] The best determined Fe–C(sp^3) distance is 2.0977 (23) Å in η^5-$C_5H_5Fe(CO)_2$-$[C_4H_7(CN)_4]$; the vinylic Fe–C(sp^2) bond distance of unit bond

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Table IV. Least-Squares Planes[a] and Atomic Deviations from the Planes

atom	dev, Å	atom	dev, Å
Plane I: $-0.1095I + 0.2439J + 0.9636K = 2.080$			
C(1)[b]	0.0028	Fe	0.532
C(2)[b]	−0.0028	B	0.401
O(1)[b]	−0.0031	F(1)	−0.280
O(2)[b]	0.0031	F(2)	1.744
		C(4)	−0.479
		C(5)	−0.389
Plane II: $-0.2594I + 0.1444J + 0.9549K = 2.164$			
Fe[b]	0.1532	B	0.606
C(1)[b]	−0.1504	F(1)	0.147
C(2)[b]	−0.1575	F(2)	1.963
O(1)[b]	0.0744	C(4)	−0.690
O(2)[b]	0.0803	C(5)	−0.600
Plane III: $0.3014I + 0.4685J + 0.8305K = 1.323$			
B[b]	0	F(1)	−1.158
O(1)[b]	0	F(2)	1.089
O(2)[b]	0	C(1)	0.613
		C(2)	0.605
Plane IV: $-0.4398I + 0.005\,43J + 0.8981K = 1.817$			
Fe[b]	0	C(4)	−0.575
C(1)[b]	0	C(5)	−0.508
C(2)[b]	0	O(1)	0.514
		O(2)	0.527
Plane V: $-0.5276I + 0.8052J - 0.2708K = 1.375$			
B[b]	0	Fe	−0.013
F(1)[b]	0	C(1)	1.318
F(2)[b]	0	C(2)	−1.315
		C(3)	−0.004
		O(1)	1.210
		O(2)	−1.212
Plane VI: $-0.8501I - 0.4897J + 0.1936K = -2.734$			
C(8)[b]	0.0026	Fe	1.763
C(9)[b]	−0.0029		
C(10)[b]	0.0021		
C(11)[b]	−0.0005		
C(12)[b]	−0.0014		

[a] The equations of the planes are expressed as $PI + QJ + RK = S$ in orthogonal angstrom space. See text for the angles of intersecting planes. [b] Atoms used in calculating the planes.

order is estimated to be 2.09 (1) Å as found in $(\eta^5\text{-}C_5H_5)Fe_2(CO)_5(CH{=}CHCOCH_3)$;[17] the vinylic Fe—C(sp^2) distance in $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2C_4H_4$ is 1.987 (5) Å; the best Fe—C(acyl) distance is 1.9596 (30) Å in $[\eta^5\text{-}C_5H_4C_6H_6CO]Fe_2(CO)_5$; and, the Fe—σ-alkynyl distance is 1.920 (6) Å in $\eta^5\text{-}C_5H_5Fe(CO)_2(\sigma\text{-}C{\equiv}CPh)$. The Fe—C(acyl) distances of 4 are significantly shorter than all of the above Fe—C distances, even though many of these distances should reflect some degree of multiple bonding, also.

The two acyl C–O distances of 1.291 (2) and 1.297 (2) Å within the ferrachelate ring are not significantly different with a 2σ limit. These distances also indicate some degree of multiple bonding, and, although they are slightly longer than the average values obtained for the corresponding bond distances in the complexes **1**, **2**, and **3** of 1.251 (9), 1.27 (2), and 1.245 (6) Å, respectively, these distances in **4** are very close to the average acyl C–O distance of 1.304 (2) Å observed in the organic β-diketonate complex (benzoylacetonato)boron difluoride.[18]

The comparison of the structural parameters of the BF_2 portion of the molecule of **4** and the (benzoylacetonato)boron difluoride complex is particularly interesting. For these two molecules, the B–O, B–F, and O–B–O bond distances and angles agree to within 0.011 Å and 1.4° or better, and the O–O "bite" distances differ by only 0.034 Å. Therefore, the structural parameters associated with the BF_2 moiety in both the metalla- and the nonmetalla-β-diketonate complexes are very similar and are essentially determined by the bonding preference of the BF_2 group. This structural influence from the nature of the central coordinating atom is observed in the complexes **1**–**3**, also.

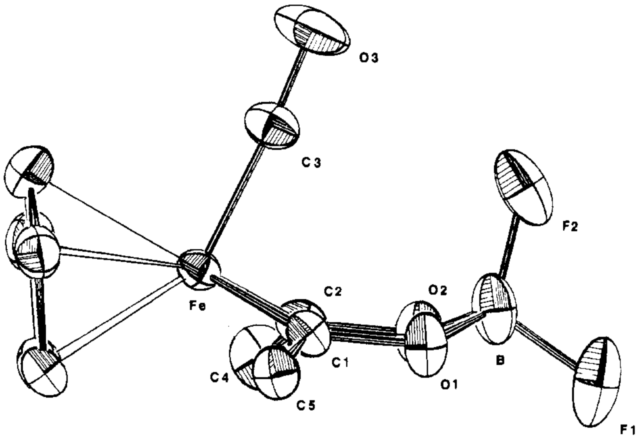
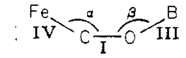


Figure 2. An ORTEP view of **4** (ellipsoids at 30% probability) showing the boat-shaped structure of the ferrachelate ring.

Figure 2 is a side view of **4** showing the distinct nonplanarity of the atoms comprising the ferra-β-diketonate ring. The six-membered chelate ring adopts a boat-shaped structure as shown below from the intersections of planes III and IV with plane I (see Table IV). The Fe and B atoms are displaced



by 0.53 and 0.40 Å, respectively, from plane I, and the values of the angles α and β are 156.2 and 151.8°, respectively. The rhenaacetylacetonate chelate rings of the copper complex **3** have a similar boat-shaped structure, and the values of α and β in **3** are 145.1 and 142.8°, respectively.[4] In both complexes, slightly more bending is observed at the acyl carbon atoms than at the acyl oxygen atoms. The (benzoylacetonato)boron difluoride complex has crystallographically imposed mirror symmetry although the out-of-plane thermal vibrations may indicate some slight nonplanar distortion <0.2 Å).[18]

Since the metallaacetylacetonate chelate rings of **1** and **2** were essentially planar, the boat-shaped structure of the rhenachelate ring of **3** was attributed to either very weak Cu–axial carbonyl bonding interactions or a deformation caused by the presence of considerable angle strain within the chelate ring. In **4** an intramolecular bonding interaction between the $\eta^5\text{-}C_5H_5(OC)Fe$ and the BF_2 moieties is not expected or observed, so the nonplanar distortion of the ferrachelate ring of **4** is attributed to the relief of angle strain within the chelate ring. Perhaps the additional bending of ca. 9° at α and β observed in **3** is due to very weak Cu–CO interactions.

The internal angle strain within the planar chelate ring arises when the requirement that the sum of the internal angles of the chelate ring must total to 720° while imposing the structural bonding preferences of both the metalla and the central coordinating atoms. The sum of the internal angles of the metallachelate rings of **1**, **3**, and **4** are 720, 679, and 702°, respectively. These values also indicate that the boat-shaped distortion of the rhenachelate ring of **3** is more pronounced than is the similar distortion of the ferrachelate ring of **4** (which is consistent with an additional bending force being present in **3**). Molecular models reveal that the displacement of the iron atom from a planar chelate ring structure imposes a slight rotation about the Fe–C(1) and Fe–C(2) bonds which displaces the two alkyl substituents to the opposite side of plane

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I. This effect explains the relative positions of the Fe, C(4), and C(5) atoms, and the same effect is observed in complex **3**, also. A crude molecular model reveals that a structure having a planar chelate ring can be formed only with imposing considerable ring strain and that the shortest intramolecular contact distance between the iron and boron portions of the molecule is a F···H (C_5H_5) contact of ca. 3.1 Å.

The second geometrical isomer observed for **4** in solution is, presumably, the other boat isomer where the η^5-C_5H_5 ligand and the fluorine atom are in closest proximity. Although a chair conformation is possible, also, there has been no evidence of such a structure for metalla-β-diketonate chelate rings.

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Supplementary Material Available: Structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

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Ambidentate Character of Dimethyl Sulfoxide in Adducts of Tetrakis(propionato)- and Tetrakis(trifluoroacetato)dirhodium(II)

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Dimethyl sulfoxide forms 2:1 adducts with rhodium(II) carboxylates to give compounds having the general formula $Rh_2(O_2CR)_4(Me_2SO)_2$. The structures of two compounds of this type have been determined by using single-crystal X-ray diffraction techniques, and the results reveal that oxygen or sulfur atom coordination of Me_2SO to $Rh_2(O_2CR)_4$ is dependent on the nature of the carboxylate R group substituent. Compound **1**, $Rh_2(O_2CC_2H_5)_4(Me_2SO)_2$, crystallizes as orange prisms in the space group $P2_1/n$ with four molecules in a cell of dimensions $a = 9.057$ (2) Å, $b = 15.709$ (4) Å, $c = 18.164$ (2) Å, and $\beta = 101.62$ (1)°. The structure was refined by using 3244 data with $I > 3\sigma(I)$ to an R_1 value of 0.045. There is no crystallographically imposed symmetry on the dinuclear unit; four propionate groups bridge the rhodium atoms, and two Me_2SO molecules are coordinated through their sulfur atoms in the axial positions just as in the corresponding acetate complex whose structure has been previously determined. The Rh–Rh bond length is 2.407 (1) Å with an average Rh–S distance of 2.449 (1) Å. Compound **2**, $Rh_2(O_2CCF_3)_4(Me_2SO)_2$, crystallizes as dark blue needles in the space group $P\bar{1}$ with one formula weight in a cell with $a = 8.621$ (2) Å, $b = 9.500$ (2) Å, $c = 8.766$ (2) Å, $\alpha = 112.68$ (1)°, $\beta = 110.99$ (2)°, and $\gamma = 87.83$ (2)°. A total of 1984 reflections with $I > 3\sigma(I)$ were used to refine the structure to a final R_1 value of 0.042. The structure consists of a dirhodium(II) moiety with a Rh–Rh bond length of 2.419 (1) Å bridged by four trifluoroacetate groups and two axial oxygen-bonded Me_2SO molecules with a Rh–O distance of 2.236 (3) Å. A crystallographic inversion center is located at the midpoint of the Rh–Rh bond. The observed ν_{SO} values in the infrared spectra for these compounds are in accord with long-established spectroscopic criteria for O- and S-bonded metal–sulfoxide complexes.

Introduction

A considerable amount of work has now been reported on the chemical and structural properties of complexes of Rh_2^{4+}, especially those with bridging carboxylato ligands.[1] These have the general formula $Rh_2(O_2CR)_4L_2$, where the L groups are monodentate ligands bound in each of the axial positions. One of these compounds, whose structure we recently reported,[1] is $Rh_2(O_2CCH_3)_4(Me_2SO)_2$, and it was found that the dimethyl sulfoxide (Me_2SO) ligands are attached to the rhodium atoms through their sulfur atoms. This is consistent with the inference made on the basis of spectral data ($\nu_{SO} = 1086\ cm^{-1}$) by Johnson, Hunt, and Neumann in 1963 when they reported the compound for the first time.[2]

The characteristic ligand properties of Me_2SO and other sulfoxides were first reported, with extensive documentation, about 20 years ago.[3,4] The ambidentate character of Me_2SO was explicitly noted, and the utility of infrared spectra in distinguishing between O- and S-bonded ligands was discussed and illustrated. It was shown that, for most of the transition-metal ions and main-group acceptors, coordination occurs through the oxygen atoms of Me_2SO and other sulfoxides but that, for Pd^{II} and Pt^{II}, coordination through the sulfur atom was indicated by an upward shift of ν_{SO}. These correlations were subsequently confirmed by X-ray crystallography.[5-7]

This paper reports the structures of two 2:1 adducts of rhodium(II) carboxylates with Me_2SO. Compound **1**, $Rh_2(O_2CC_2H_5)_4(Me_2SO)_2$, was first prepared and characterized by Mal'kova and Shafranskii.[8] Their results suggest that the complex is quite analogous to the corresponding acetate compound.[1,2] The interaction of Me_2SO with $Rh_2(O_2CCF_3)_4$ was reported several years ago by Kitchens and Bear[9] to produce a blue solution (neat Me_2SO) which, upon removal of excess Me_2SO, gave them a "green tar-like substance" that they regarded as "not a true adduct as in the case of rhodium(II) acetate". Kitchens and Bear noted that this product is most

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