were placed in idealized staggered tetrahedral positions by using the program HYDRO. Final refinement of the positions of all non-hydrogen atoms was carried out anisotropically with fixed hydrogen positions and thermal parameters ($B = 5.0$ Å^2). A final difference Fourier map showed a peak (1.2 e/Å^3) located near the octahedral hole where the hydride was expected to be located, but not in an ideal location. Table III contains the relevent bond distances and angles, and Table IV includes the positional parameters.

X-ray Structural Determination of $H_2Re(PEt_3)_3(PPh_2C_6H_4)$. Slow evaporation of a saturated benzene solution yielded large crystals. The orthorhombic space group was assigned as *Pcab*, and the correctness of this assignment was confirmed by successful solution of the Patterson map. Hydrogen atoms were placed in idealized positions on carbon atoms by using the program HYDRO. After a final anisotropic least-squares refinement of all non-hydrogen atoms, a final peak search revealed only two large peaks in the map near the rhenium atom in the equatorial plane in locations expected for the two hydride ligands. These atoms were placed in the structure, and their positions were refined while the thermal parameters were fixed ($B = 5.0$ Å^2). Table V contains the relevent bond distances and angles, and Table VI includes the positional parameters.

X-ray Structural Determination of $HRe(PPh_3)(DMPE)_2$. Slow evaporation of a saturated benzene solution yielded large crystals. The triclinic space group $P\bar{1}$ was assigned, and the correctness of this assignment was confirmed by successful solution of the Patterson map. A benzene of crystallization was located on a center of symmetry. Hydrogen atoms were placed in idealized positions on carbon atoms by using the program HYDRO. After a final anisotropic least-squares refinement of all non-hydrogen atoms a final peak search revealed only a large peak in the map near the rhenium atom in the octahedral hole. Final refinement was carried out anisotropically on all non-hydrogen atoms and isotropically on the hydride. Table VII contains the relevent bond distances and angles, and Table VIII includes the positional parameters.

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Registry No. **1**, 81368-84-5; **2a**, 108453-34-5; **2b**, 108453-35-6; **2c**, 108453-36-7; **2d**, 108453-37-8; **2e**, 108453-38-9; **2f**, 108453-39-0; **2g**, 108453-40-3; **2h**, 84756-10-5; $HRe(PPh_3)^2(CO)_3$, 25734-54-7; $H_2Re(PEt_3)_3(PPh_2C_6H_4)$, 108453-41-4; *trans*-$HRe(PPh_3)(DMPE)_2$, 108453-42-5; *cis*-$HRe(DMPE)_2(PPh_3 \cdot {}^1/_2C_6H_6$, 108509-40-6.

Supplementary Material Available: Listings of anisotropic thermal parameters, bond distances and angles, calculated fractional coordinates for $HRe(PMe_3)_5$, $HRe(PPh_3)_2(CNMe)_3$, $H_2Re(PEt_3)_3(PPh_2C_6H_4)$, and $HRe(PPh_3)(DMPE)_2$ (43 pages); listings of calculated and observed structure factors (112 pages). Ordering information is given on any current masthead page.

Bridged Ferrocenes. 13.[1] Preparation and Properties of Derivatives with β-Oxatrimethylene Bridges

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Ferrocene derivatives containing one β-oxatrimethylene and 0–2 trimethylene bridges were prepared. The X-ray crystallographic structures of all but the one containing two trimethylene bridges were determined. The X-ray crystallographic structures of 1,1′-trimethyleneferrocene (I), 1,1′-(β-thiatrimethylene)ferrocene (III), and the two bis(trimethylene)ferrocenes IV and VI were also determined. The reduction potentials of all of the (β-oxatrimethylene)ferrocenes and the (β-thiatrimethylene)ferrocene were newly measured and compared with the reduction potentials of the corresponding trimethyleneferrocenes that were remeasured. Evidence was found for an interaction between the iron atom and the oxygen atom of the bridge that is comparable to that suggested previously for the central methylene group of a trimethylene bridge, but not significantly greater.

Introduction

Simple alkyl substituents and homoannular trimethylene groups all cause the ferrocene derivative to be more easily oxidized by the same amount for each substituent (counting the homoannular trimethylene group as two substituents). On the other hand, a bridging trimethylene group makes the derivative more easily oxidized by a substantially smaller amount. Furthermore, the influence of the trimethylene bridge can be correlated with the iron-to-ring distance of each compound. Since the electron distribution around the iron atom is oblate and the oblateness increases with a decreased iron-to-ring distance, the effect of bridges on the reduction potentials was attributed[2] to an increased interaction of the iron atom with the central methylene of the bridge as the iron-to-ring distance decreases.

To test this hypothesis, we undertook the investigation of the properties of ferrocene derivatives containing central groups on the bridges that are expected to be more interactive with the iron atom than are methylene groups. The primary candidates for this investigation were the (β-oxotrimethylene)ferrocenes wherein the carbonyl group would most certainly be expected to be more interactive than the methylene. Spatial models indicate that the

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(1) Paper 12 of series: Hillman, M.; Austin, J. D. *Organometallics* **1985**, *3*, 316–320.

(2) Fujita, E.; Gordon, B.; Hillman, M.; Nagy, A. *J. Organomet. Chem.* **1981**, *218*, 105–114.

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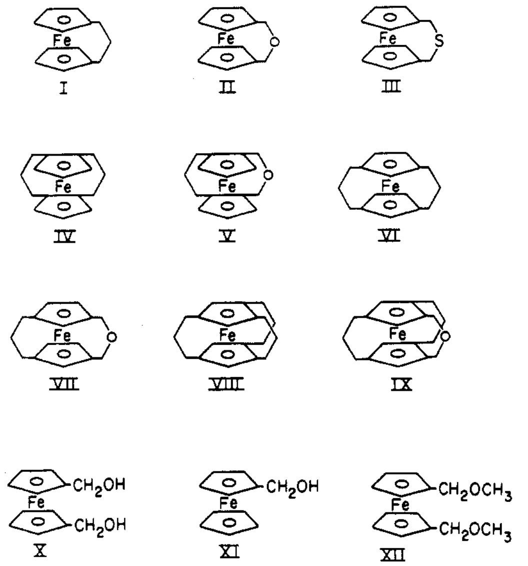

Figure 1. Compounds referred to in this paper.

primary mode of this interaction would be dipolar acceptance of electron density by $^+$C–O$^-$, which would result in higher reduction potentials than expected from nonbridged, differently interacting groups.

The single-bridged compound 1,1′-(β-oxotrimethylene)ferrocene was reported[3] as prepared in a nine-step synthesis from ferrocene. We considered this to be too tedious for the preparation of all of the compounds we envisaged studying and examined other, possibly shorter routes. None proved to be satisfactory. The original method also proved to be unsatisfactory because of the excessive reactivity of the bis(chloromethyl)ferrocene intermediates when trimethylene bridges are also present. We, therefore, decided to undertake a simpler approach, using the more readily obtainable (β-oxatrimethylene)ferrocenes. The interaction between the ether oxygen and the iron atom is expected to be smaller than that of the carbonyl but larger than that of the methylene; however, the direction of the interaction is not readily predictable. Because of its availability and because of a possibly greater interaction between sulfur and iron than oxygen and iron, III was also included in this investigation.

Experimental Section

The preparations of 1,1′-trimethyleneferrocene (I) (all structures are given in Figure 1), 1,1′:2,2′-bis(trimethylene)ferrocene (IV), 1,1′:3,3′-bis(trimethylene)ferrocene (VI), and 1,1′:2,2′:4,4′-tris(trimethylene)ferrocene (VIII) are described in the literature.[4] So are the preparations of 1,1′-(β-oxatrimethylene)ferrocene[5,6] (II) and 1,1′-(β-thiatrimethylene)ferrocene[7] (III). Crystals of compounds I through VII were grown by vapor diffusion from a methanol–water system. The X-ray data were collected on an Enraf-Nonius CAD4 diffractometer. When there was only one independent iron atom per unit cell, the iron atoms were located by using the Patterson method. Otherwise, they were located by using direct methods (MULTAN[8]). The other non-hydrogen atoms were located from difference Fourier maps, and the structures were refined by using SHELX.[9] The location of the hydrogen atoms were calculated after each least-squares iteration and assigned a distance of 100 pm from the carbon atom, in accordance with experience accumulated with bridged ferrocenes when the C–H distances were refined. The reduction potentials were determined in acetonitrile by cyclic voltammetry using an IBM EC 225 voltammetric analyzer equipped with a YEW Model 3022 A4 X-Y recorder. All measurements were made by using 1,1′-(α-oxatrimethylene)ferrocene as an internal standard. all NMR spectra were obtained in $DCCl_3$ on a Varian CFT-20 instrument (80 MHz). High-resolution mass spectrometry was performed by Dr. Charles Iden of State University of New York at Stony Brook.

General Procedure for the Preparation of the (β-Oxatrimethylene)ferrocenes. The appropriate bis(hydroxymethyl) derivative of the trimethyleneferrocene was prepared by reduction of the corresponding dicarboxylic acid or its dimethyl ester with $LiAlH_4$ in ether. The alcohol was purified by chromatography and, without further characterization, was refluxed with an equimolar amount of *p*-toluenesulfonyl chloride in dried benzene. In some instances the addition of an equimolar amount of pyridine improved the yield of the product. The cooled mixture was neutralized with solid Na_2CO_3. It was then evaporated to dryness and purified by chromatography on silica gel (unless otherwise noted).

1,1′-(β-Oxatrimethylene)ferrocene (II). Solid tosyl chloride (1.59 g) was added to refluxing 1,1′-bis(hydroxymethyl)ferrocene (1.00 g) in 50 mL of benzene. After 2 h the reaction mixture was cooled. The crude yield was 2.41 g. After two chromatograms, 0.54 g of a reasonably pure product was obtained: mp 145–146 °C (lit.[6] mp 147–148 °C); ^{1}H NMR δ 4.15 (8 H ring, slightly br s), 3.89 (4 H, CH_2 on O, s); mol wt (for ^{12}C, ^{1}H, ^{16}O, and ^{56}Fe, $C_{12}H_{12}OFe$) calcd 228.0237, obsd 228.0243.

1,1′-(β-Oxatrimethylene)-2,2′-trimethyleneferrocene (V). Tosyl chloride (0.27 g) in 10 mL of benzene was added to refluxing 1,1′-bis(hydroxymethyl-2,2′-trimethyleneferrocene (0.39 g) in 35 mL of benzene. The crude yield was 0.59 g. The yield after chromatography was 0.23 g: mp 242–242.5 °C (with sublimation), ^{1}H NMR δ 4.08, 4.06, 4.01, 3.99 (6 H, ring, complex m), 4.43, 4.27, 3.40, 3.24 (4 H, CH_2 on O, AB q), 1.58–2.18 (6 H, trimethylene CH_2, complex m); mol wt (for ^{12}C, ^{1} H, ^{16}O, and ^{56}Fe, $C_{15}H_{16}OFe$) calcd 268.0551, obsd 268.0552.

1,1′-(β-Oxatrimethylene)-3,3′-trimethyleneferrocene (VII). Tosyl chloride (0.20 g) was added to refluxing 1,1′-bis(hydroxymethyl)-3,3′-trimethyleneferrocene (0.29 g) in 25 mL of benzene. The crude yield was 0.53 g. The yield after chromatography was 0.093 g: mp 88–89 °C; ^{1}H NMR δ 4.11, 4.09 (2 H, 2,2′, d, J = 1.1 Hz), 4.03, 4.00 (4 H, 4,4′,5,5′, slightly br d, J = 2.3 Hz), 4.34, 4.18, 3.43, 3.27 (4 H, CH_2 on O, AB q), 1.25–2.26 (6 H, CH_2, complex m); mol wt (for ^{12}C, ^{1}H, ^{16}O, and ^{56}Fe, $C_{15}H_{16}OFe$) calcd 268.0551, obsd 268.0557. When 0.088 mL of pyridine was added to an experiment with 0.31 g of the alcohol and 0.21 g of sulfonyl chloride in 50 mL of benzene, the crude yield was 0.48 g, and the yield after chromatography was 0.15 g.

1,1′-(β-Oxatrimethylene)-2,2′:4,4′-bis(trimethylene)ferrocene (IX). Tosyl chloride (0.21 g) in 20 mL of benzene was added to 1,1′-bis(hydroxymethyl)-2,2′:4,4′-bis(trimethylene)ferrocene (0.33 g) in 50 mL of refluxing benzene. The crude yield was 0.52 g. The yield after chromatography was 0.04 g: mp 165–166 °C; ^{1}H NMR δ 3.98, 3.93, (4 H, ring, slightly br s), 4.19, 4.02, 3.41, 3.24 (4 H, CH_2 on O, AB q), 1.45–2.26 (12 H, CH_2, complex m); mol wt (for ^{12}C, ^{1}H, ^{16}O, and ^{56}Fe, $C_{18}H_{20}OFe$) calcd 308.0864, obsd 308.0861. The addition of pyridine to this preparation appeared to have a detrimental effect; no β-oxatrimethylene product was obtained.

Results and Discussion

The preparation of the new β-oxatrimethylene compounds was encumbered by increased difficulty and decreased yields as the number of trimethylene bridges increased. No attempt was made to optimize the yields. Still, sufficient material was obtained for further study.

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Table I. Crystal Data

	I	II	III	IV	V	VI	VII
mol. formula	$C_{13}H_{14}Fe$	$C_{12}H_{12}FeO$	$C_{12}H_{12}FeS$	$C_{16}H_{18}Fe$	$C_{15}H_{16}FeO$	$C_{16}H_{18}Fe$	$C_{15}H_{16}FeO$
mol wt	226.1	228.1	244.1	266.2	268.1	266.2	268.1
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$C2/c$	$C2/c$	$C2/c$
a, pm	749.3 (1)	743.5 (1)	1061.6 (2)	789.0 (1)	2557.6 (5)	2391.7 (5)	1404.9 (3)
b, pm	1008.7 (2)	1012.0 (2)	743.3 (1)	1216.5 (2)	788.7 (1)	909.8 (2)	747.6 (2)
c, pm	1370.4 (3)	1282.2 (2)	1300.6 (2)	1262.9 (1)	1195.3 (3)	2325.3 (3)	2292.7 (4)
α, deg	90	90	90	97.47 (1)	90	90	90
β, deg	96.72 (1)	96.55 (1)	94.13 (1)	100.97 (1)	105.67 (2)	94.82 (1)	102.74 (1)
γ, deg	90	90	90	90.21 (1)	90	90	90
V, nm^3	1.0287 (3)	0.9585 (3)	1.0236 (3)	1.1794 (3)	2.3215 (8)	5.042 (2)	2.3487 (9)
Z	4	4	4	4	8	16	8
ρ_{calcd}, g cm^{-3}	1.460	1.581	1.585	1.500	1.535	1.403	1.517
abs coeff, cm^{-1}	13.92	15.01	15.89	12.20	12.46	11.4	12.3
2θ range, deg	50	50	60	54.6	60	60	60
reflctns collected	1989	5990	5427	5834	7169	7659	3588
unique reflctns ($F > 3\sigma(F)$)	442	2559	1213	3255	2412	3414	2501
scan width	1.0 + 0.35 tan θ	1.0 + 0.35 tan θ	1.5 + 0.35 tan θ	1.5 + 0.35 tan θ	1.5 + 0.35 tan θ	1.0 + 0.35 tan θ	1.0 + 0.35 tan θ
$R(F) = \sum\lvert F_o - F_c\rvert/\sum\lvert F_o\rvert$	0.097	0.060	0.070	0.046	0.067	0.071	0.056
$R_w(F) = \sum\lvert F_o - F_c\rvert w^{1/2}/\sum\lvert F_o\rvert w^{1/2}$	0.097	0.060	0.063	0.047	0.079	0.080	0.062
$w = 1/(\sigma^2(F) + cF^2)$	$c = 0$	$c = 0$	$c = 0.0011$	$c = 0.0015$	$c = 0.058$	$c = 0.0101$	$c = 0.0015$
max shift/error	0.035	0.100	0.122	0.005	0.424	0.067	0.045
res electron dens, e nm^{-3}	705[b]	661	763	531	686[a]	811	724

[a] minimum − 1086 [b] minimum − 710

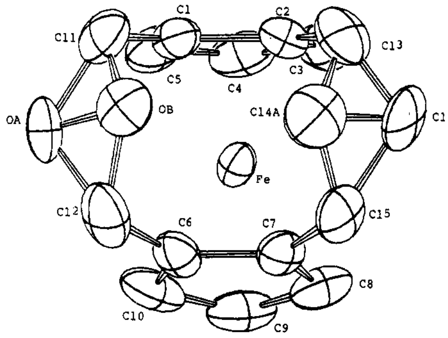


Figure 2. ORTEP diagram of 1,1′-(β-oxatrimethylene)-2,2′-trimethyleneferrocene, V.

An attempt was also made to prepare 1,1′-(β-oxatrimethylene)-3,3′:4,4′-bis(trimethylene)ferrocene from the corresponding diol, but none was obtained. The product that was observed appeared to be very unstable and did not have the characteristic AB quartet in the NMR spectrum.

Each new compound was characterized by high-resolution mass spectroscopy, by its NMR spectrum, and by X-ray crystal-structure determination when possible. The crystal data for the seven structures determined are given in Table I; the crystallographic coordinates of the atoms and the equivalent isotropic thermal parameters are given in Table II; selected molecular parameters are given in Table III. The ORTEP diagrams of V and VI are given in Figures 2 and 3, respectively, to illustrate the disorder observed. The ORTEP diagrams of the other compounds are given in the supplementary material since there is nothing special to learn from the pictures. The thermal parameters, the observed and calculated structure factors, bond distances and angles, and the equations for the least-squares planes of the cyclopentadienyl rings are given as supplementary material.

The number of diffraction peaks collected for I was limited by the apparent decomposition of the crystal while in the X-ray beam. It is not certain if the decomposition was caused by the beam since a crystal that had been mounted for collection of X-ray data decomposed or disappeared (evaporated?) over a period of 1 month while awaiting its turn on the diffractometer. A not-so-extensive decomposition was also observed in the X-ray data of compound II. The observed intensities of both compounds were corrected according to a periodically measured standard reflection. No correction was required for the other compounds.

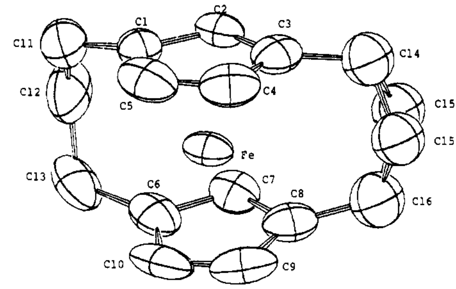


Figure 3. ORTEP diagram of 1,1′:3,3′-bis(trimethylene)ferrocene, VI.

If disorder exists in the crystal structure of a compound, then reliable coordinates cannot be obtained for the atoms of the bridge without further assumptions. Generally, the disorder observed in a bridge has virtually no effect on the coordinates of the remaining atoms. Among these seven compounds, disorder was observed for V and VI but not for the others. In these cases, it was assumed that the thermal parameters of the corresponding atoms in the disordered positions were equal and the occupancies were allowed to vary. The occupancies and thermal parameters were refined alternately with the additional constraint that the sum of the occupancies equals unity. For greater simplicity, only the isotropic thermal parameters were determined for the atoms of the bridges with disorder.

The disorder in V is difficult to explain. There are four different conformations of the oxygen and carbon atoms as symbolically illustrated in Figure 4. Since it was found not possible to differentiate the oxygen atom from the carbon of the β-methylene group on the basis of the observed electron densities, it is likely that the disorder not

Table II. Crystallographic Coordinates

atom	x/a	y/b	z/c	B, pm^2	atom	x/a	y/b	z/c	B, pm^2
				Compound I[a,f]					
Fe	0.9483 (7)	0.3163 (5)	0.6516 (3)	42 (1)	H2	0.972	0.082	0.752	
Cl	1.156 (4)	0.239 (3)	0.740 (2)	6 (1)	H3	0.938	0.070	0.565	
C2	1.036 (5)	0.141 (3)	0.708 (3)	6 (1)	H4	1.133	0.249	0.501	
C3	1.017 (5)	0.134 (3)	0.606 (2)	6 (1)	H5	1.307	0.362	0.654	
C4	1.122 (4)	0.228 (3)	0.571 (2)	5 (1)	H7	0.662	0.296	0.755	
C5	1.214 (4)	0.291 (4)	0.656 (2)	6 (1)	H8	0.602	0.314	0.565	
C6	0.861 (4)	0.452 (3)	0.744 (2)	5 (1)	H9	0.808	0.487	0.509	
C7	0.724 (4)	0.357 (3)	0.712 (2)	6 (1)	H10	0.989	0.578	0.655	
C8	0.691 (5)	0.368 (4)	0.608 (3)	8 (1)	H11A	0.863	0.492	0.888	
C9	0.800 (5)	0.459 (4)	0.578 (3)	7 (1)	H11B	1.041	0.545	0.841	
C10	0.896 (5)	0.507 (4)	0.658 (3)	8 (1)	H12A	1.123	0.397	0.953	
C11	0.956 (5)	0.469 (4)	0.844 (3)	7 (1)	H12B	0.973	0.291	0.905	
C12	1.062 (5)	0.360 (4)	0.890 (3)	9 (1)	H13A	1.306	0.352	0.842	
C13	1.202 (5)	0.290 (4)	0.843 (3)	9 (1)	H13B	1.239	0.212	0.885	
				Compound II[b,c,f]					
Fe	0.45487 (7)	0.71781 (5)	0.65777 (4)	250 (1)	O	0.5517 (5)	0.8514 (4)	0.9092 (2)	47 (1)
Cl	0.6647 (5)	0.7505 (4)	0.7555 (3)	31 (1)	H2	0.8186	0.8689	0.6553	
C2	0.7274 (5)	0.7973 (5)	0.6606 (3)	37 (1)	H3	0.6513	0.7362	0.4982	
C3	0.6366 (6)	0.7238 (5)	0.5741 (4)	42 (1)	H4	0.4443	0.5660	0.5741	
C4	0.5236 (6)	0.6313 (4)	0.6159 (4)	42 (1)	H5	0.4747	0.5909	0.7761	
C5	0.5393 (6)	0.6450 (4)	0.7267 (4)	36 (1)	H7	0.4978	1.0877	0.6603	
C6	0.3679 (5)	0.9494 (4)	0.7572 (3)	31 (1)	H8	0.2970	0.9861	0.5017	
C7	0.4075 (6)	1.0151 (4)	0.6639 (4)	36 (1)	H9	0.0971	0.8057	0.5721	
C8	0.2971 (6)	0.9598 (5)	0.5769 (3)	38 (1)	H10	0.1701	0.7950	0.7749	
C9	0.1880 (5)	0.8615 (5)	0.6155 (3)	37 (1)	H11A	0.7844	0.8895	0.8560	
C10	0.2286 (5)	0.8550 (4)	0.7268 (3)	35 (1)	H11B	0.7722	0.7437	0.9093	
C11	0.7055 (6)	0.8106 (5)	0.8622 (3)	42 (1)	H12A	0.3771	0.9976	0.9126	
C12	0.4663 (7)	0.9669 (5)	0.8650 (4)	47 (1)	H12B	0.5613	1.0362	0.8612	
				Compound III[b,c,f]					
Fe	0.6149 (1)	0.4790 (1)	0.81467 (9)	244 (3)	S	0.6747 (3)	0.5129 (4)	0.5513 (2)	60 (1)
Cl	0.7584 (7)	0.370 (1)	0.7431 (6)	29 (2)	H2	0.6179	0.170	0.7016	
C2	0.6655 (8)	0.239 (1)	0.7576 (7)	33 (2)	H3	0.5880	0.139	0.8932	
C3	0.6488 (9)	0.221 (1)	0.8615 (8)	42 (2)	H4	0.7434	0.358	0.9929	
C4	0.7340 (8)	0.341 (1)	0.9165 (7)	39 (2)	H5	0.8703	0.519	0.8587	
C5	0.8015 (7)	0.429 (1)	0.8432 (7)	38 (2)	H7	0.4078	0.479	0.6766	
C6	0.5558 (8)	0.673 (1)	0.7157 (7)	32 (2)	H8	0.3697	0.483	0.8709	
C7	0.4548 (7)	0.553 (1)	0.7312 (7)	35 (2)	H9	0.5295	0.703	0.9634	
C8	0.4352 (7)	0.554 (1)	0.8372 (7)	35 (2)	H10	0.6645	0.840	0.8235	
C9	0.5217 (7)	0.676 (1)	0.8879 (7)	31 (2)	H11A	0.8576	0.547	0.6618	
C10	0.5954 (7)	0.750 (1)	0.8111 (7)	32 (2)	H11B	0.8510	0.344	0.6128	
C11	0.8016 (9)	0.441 (1)	0.6452 (7)	47 (3)	H12A	0.5483	0.766	0.5665	
C12	0.6137 (9)	0.708 (1)	0.6147 (8)	52 (3)	H12B	0.6856	0.793	0.6297	
				Compound IV[b,c,f]					
Fe1	0.19827 (8)	−0.01130 (4)	0.83745 (5)	225 (2)	C30	0.8346 (6)	0.4729 (4)	0.6227 (4)	36 (1)
Fe2	0.69979 (8)	0.46932 (4)	0.83531 (5)	230 (2)	C31	0.8452 (7)	0.3458 (4)	0.6225 (5)	40 (1)
Cl	0.1657 (6)	−0.1629 (3)	0.7490 (4)	27 (1)	C32	0.6755 (7)	0.2913 (4)	0.6341 (4)	35 (1)
C2	0.3132 (6)	−0.1045 (3)	0.7290 (4)	27 (1)	H3	0.5454	−0.0401	0.8430	
C3	0.4312 (6)	−0.0802 (4)	0.8313 (4)	32 (1)	H4	0.4129	−0.1169	0.9916	
C4	0.3591 (7)	−0.1224 (4)	0.9127 (4)	35 (1)	H5	0.1159	−0.2121	0.8995	
C5	0.1956 (7)	−0.1743 (3)	0.8620 (4)	33 (1)	H8	0.3320	0.2033	0.8658	
C6	−0.0214 (6)	0.0535 (3)	0.7655 (4)	26 (1)	H9	0.1732	0.1474	1.0126	
C7	0.1273 (6)	0.1118 (3)	0.7471 (4)	27 (1)	H10	−0.0989	0.0311	0.9174	
C8	0.2224 (7)	0.1576 (3)	0.8518 (4)	31 (1)	H11A	0.0191	−0.1842	0.5949	
C9	0.1352 (7)	0.1271 (4)	0.9322 (4)	36 (1)	H11B	−0.0182	−0.2797	0.6680	
C10	−0.0133 (6)	0.0637 (3)	0.8803 (4)	30 (1)	H12A	−0.2624	−0.1745	0.6392	
C11	0.0019 (6)	−0.1984 (3)	0.6684 (4)	31 (1)	H12B	−0.1723	−0.1470	0.7677	
C12	−0.1600 (6)	−0.1388 (4)	0.6917 (4)	33 (1)	H13A	−0.2704	0.0155	0.6861	
C13	−0.1541 (6)	−0.0147 (4)	0.6808 (4)	31 (1)	H13B	−0.1284	−0.0069	0.6076	
C14	0.3357 (6)	−0.0659 (4)	0.6241 (4)	34 (1)	H14A	0.4435	−0.0984	0.6042	
C15	0.3500 (6)	0.0600 (4)	0.6283 (4)	35 (1)	H14B	0.2341	−0.0941	0.5666	
C16	0.1805 (6)	0.1186 (4)	0.6403 (4)	33 (1)	H15A	0.4418	0.0897	0.6918	
C17	0.6694 (6)	0.6003 (3)	0.7516 (4)	28 (1)	H15B	0.3833	0.0769	0.5595	
C18	0.8160 (6)	0.5368 (3)	0.7296 (4)	27 (1)	H16A	0.0864	0.0835	0.5808	
C19	0.9339 (6)	0.5371 (4)	0.8305 (4)	33 (1)	H16B	0.1955	0.1986	0.6324	
C20	0.8643 (7)	0.5990 (4)	0.9138 (4)	34 (1)	H19	1.0473	0.4996	0.8405	
C21	0.7026 (7)	0.6383 (3)	0.8661 (4)	33 (1)	H20	0.9194	0.6126	0.9927	
C22	0.4775 (6)	0.3877 (3)	0.7619 (4)	27 (1)	H21	0.6244	0.6851	0.9057	
C23	0.6243 (6)	0.3238 (3)	0.7422 (4)	28 (1)	H24	0.8278	0.2603	0.8568	
C24	0.7196 (7)	0.3033 (3)	0.8448 (4)	34 (1)	H25	0.6738	0.3535	1.0074	
C25	0.6352 (7)	0.3540 (4)	0.9274 (4)	36 (1)	H26	0.4028	0.4467	0.9151	
C26	0.4873 (6)	0.4050 (3)	0.8766 (4)	33 (1)	H27A	0.4909	0.6991	0.6751	
C27	0.5079 (6)	0.6174 (4)	0.6728 (4)	34 (1)	H27B	0.5234	0.5853	0.5984	
C28	0.3445 (6)	0.5644 (4)	0.6956 (4)	34 (1)	H28A	0.3348	0.5902	0.7726	
C29	0.3451 (6)	0.4365 (4)	0.6791 (4)	34 (1)	H28B	0.2422	0.5888	0.6453	

Table II (Continued)

atom	x/a	y/b	z/c	B, pm^2	atom	x/a	y/b	z/c	B, pm^2
H29A	0.3697	0.4113	0.6051		H31A	0.9375	0.3306	0.6845	
H29B	0.2281	0.4079	0.6837		H31B	0.8759	0.3122	0.5523	
H30A	0.7328	0.4880	0.5666		H32A	0.6880	0.2090	0.6237	
H30B	0.9427	0.5001	0.6029		H32B	0.5814	0.3125	0.5759	
Compound V^{c,d,f}									
Fe	0.08244 (2)	0.24266 (6)	0.04683 (4)	273 (2)	C10	0.9306 (3)	0.2493 (6)	0.6288 (5)	43 (1)
C1	0.8742 (2)	0.4283 (5)	0.3588 (4)	37 (1)	C11	0.8295 (3)	0.5144 (7)	0.3947 (6)	45 (3)
C2	0.8704 (2)	0.2734 (5)	0.2909 (4)	34 (1)	C12	0.8294 (2)	0.3459 (6)	0.5686 (4)	37 (2)
C3	0.9241 (3)	0.2311 (6)	0.2870 (5)	43 (1)	C13	0.8196 (2)	0.1714 (7)	0.2422 (4)	40 (2)
C4	0.9607 (2)	0.3535 (8)	0.3484 (4)	48 (1)	C14A	0.7884 (4)	0.135 (1)	0.325 (1)	35 (3)
C5	0.9308 (2)	0.4767 (6)	0.3936 (5)	44 (1)	C14B	0.8229 (4)	−0.000 (1)	0.2964 (9)	35 (3)
C6	0.8740 (2)	0.2238 (5)	0.5687 (4)	34 (1)	C15	0.8181 (3)	0.0079 (6)	0.4194 (6)	45 (3)
C7	0.8692 (2)	0.0735 (5)	0.5033 (4)	38 (1)	OA	0.8388 (8)	0.528 (2)	0.515 (1)	53 (9)
C8	0.9230 (2)	0.0055 (6)	0.5225 (5)	51 (1)	OB	0.7996 (2)	0.4007 (7)	0.4560 (5)	52 (3)
C9	0.9596 (2)	0.1128 (8)	0.6009 (4)	48 (1)					
Compound VI^{c,e,f}									
Fe1	0.91949 (4)	0.3147 (1)	0.92017 (4)	397 (2)	C28A	0.5575 (7)	0.620 (2)	0.3188 (7)	67 (3)
Fe2	0.67328 (3)	0.4315 (1)	0.34667 (4)	348 (2)	C28B	0.590 (1)	0.694 (3)	0.307 (1)	76 (6)
C1	0.8389 (3)	0.2611 (8)	0.9235 (3)	42 (2)	C29	0.5859 (4)	0.586 (1)	0.2657 (5)	69 (2)
C2	0.8476 (3)	0.3359 (8)	0.8711 (3)	45 (2)	C30	0.6937 (4)	0.191 (1)	0.4349 (4)	64 (3)
C3	0.8716 (3)	0.4755 (8)	0.8831 (4)	47 (2)	C31	0.6680 (4)	0.093 (1)	0.3907 (4)	65 (3)
C4	0.8754 (3)	0.489 (1)	0.9441 (4)	55 (2)	C32	0.6854 (5)	0.103 (1)	0.3317 (4)	67 (3)
C5	0.8548 (3)	0.362 (1)	0.9679 (4)	60 (2)	H2	0.8380	0.2953	0.8315	
C6	0.9562 (3)	0.1175 (9)	0.9182 (4)	52 (2)	H4	0.8905	0.577	0.9664	
C7	0.9624 (3)	0.1962 (8)	0.8660 (3)	46 (2)	H5	0.8518	0.344	1.0100	
C8	0.9899 (3)	0.3333 (9)	0.8796 (4)	50 (2)	H7	0.9496	0.1612	0.8263	
C9	1.0024 (3)	0.333 (1)	0.9401 (4)	61 (3)	H9	1.0223	0.413	0.9629	
C10	0.9829 (3)	0.203 (1)	0.9635 (4)	63 (3)	H10	0.9870	0.175	1.0052	
C11	0.8225 (4)	0.1020 (9)	0.9293 (4)	61 (3)	H11A	0.7835	0.0891	0.9107	
C12	0.8606 (4)	−0.0043 (9)	0.9019 (5)	71 (3)	H11B	0.8230	0.0780	0.9713	
C13	0.9210 (4)	−0.019 (1)	0.9250 (4)	66 (3)	H12A	0.8607	0.0249	0.8605	
C14	0.8963 (4)	0.578 (1)	0.8397 (4)	62 (2)	H12B	0.8433	−0.1039	0.9045	
C15A	0.9415 (6)	0.512 (2)	0.8053 (7)	64 (3)	H13A	0.9218	−0.042	0.9670	
C15B	0.956 (1)	0.577 (3)	0.842 (1)	64 (6)	H13B	0.9381	−0.102	0.9043	
C16	0.9950 (4)	0.456 (1)	0.8381 (4)	69 (2)	H18	0.5911	0.3710	0.4190	
C17	0.6355 (3)	0.5693 (8)	0.3975 (3)	45 (2)	H20	0.7636	0.454	0.4275	
C18	0.6280 (3)	0.4201 (9)	0.4152 (3)	46 (2)	H21	0.7120	0.6933	0.3953	
C19	0.6815 (3)	0.3535 (9)	0.4265 (3)	45 (2)	H23	0.5846	0.2743	0.2965	
C20	0.7220 (3)	0.466 (1)	0.4204 (4)	53 (2)	H25	0.7563	0.326	0.2814	
C21	0.6938 (3)	0.5970 (9)	0.4028 (4)	53 (2)	H26	0.7075	0.571	0.2513	
C22	0.6311 (4)	0.4664 (9)	0.2705 (3)	55 (2)	H30A	0.6802	0.161	0.4727	
C23	0.6218 (3)	0.3187 (8)	0.2903 (3)	48 (2)	H30B	0.7353	0.178	0.4361	
C24	0.6749 (3)	0.2469 (9)	0.2996 (3)	48 (2)	H31A	0.6757	−0.010	0.4044	
C25	0.7153 (4)	0.347 (1)	0.2819 (4)	61 (2)	H31B	0.6266	0.113	0.3883	
C26	0.6885 (4)	0.481 (1)	0.2649 (3)	63 (3)	H32A	0.7267	0.083	0.3339	
C27	0.5896 (4)	0.672 (1)	0.3726 (4)	69 (2)	H32B	0.6651	0.024	0.3085	
Compound VII^{b,c,f}									
Fe	0.60888 (4)	0.68225 (6)	0.36468 (2)	252 (1)	H2	0.7810	0.8364	0.4240	
C1	0.6350 (3)	0.9362 (5)	0.3870 (2)	31 (1)	H4	0.6088	0.7908	0.2497	
C2	0.7250 (3)	0.8451(5)	0.3886 (2)	30 (1)	H5	0.5150	0.9837	0.3113	
C3	0.7209 (3)	0.7685 (5)	0.3309 (2)	33 (1)	H7	0.7073	0.5203	0.4682	
C4	0.6313 (3)	0.8218 (5)	0.2930 (2)	35 (1)	H9	0.5177	0.3829	0.3053	
C5	0.5798 (3)	0.9261 (5)	0.3268 (2)	33 (1)	H10	0.4206	0.5754	0.3662	
C6	0.5551 (3)	0.5977 (5)	0.4333 (2)	34 (1)	H11A	0.5291	1.0396	0.4263	
C7	0.6488 (3)	0.5142 (5)	0.4344 (2)	33 (1)	H11B	0.6385	1.1134	0.4558	
C8	0.6438 (3)	0.4219 (5)	0.3791 (2)	37 (1)	H12A	0.5368	0.6751	0.5156	
C9	0.5446 (3)	0.4374 (5)	0.3453 (2)	39 (1)	H12B	0.4712	0.7901	0.4606	
C10	0.4913 (3)	0.5438 (6)	0.3789 (2)	37 (1)	H13A	0.7681	0.5912	0.2750	
C11	0.5993 (3)	1.0053 (5)	0.4400 (2)	35 (1)	H13B	0.8567	0.6992	0.3190	
C12	0.5368 (3)	0.7359 (6)	0.4767 (2)	39 (1)	H14A	0.8338	0.5189	0.4003	
C13	0.7933 (3)	0.6356 (6)	0.3167 (2)	43 (1)	H14B	0.8668	0.4027	0.3478	
C14	0.8126 (3)	0.4733 (6)	0.3584 (2)	42 (1)	H15A	0.7516	0.2390	0.3813	
C15	0.7268 (4)	0.3463 (6)	0.3565 (3)	44 (1)	H15B	0.7016	0.3090	0.3141	
O	0.6075 (2)	0.8771 (4)	0.4877 (1)	37 (1)					

[a] The thermal parameter for the iron atom is B_{eqv} and is divided by 10^3; the thermal parameters of the carbon atom is B_{iso} and is divided by 10^4. [b] The thermal parameters are B_{eqv}. [c] The thermal parameters are divided by 10^2 for the iron atom and 10^3 for the carbon atoms. [d] The thermal parameters for the iron atom and for C1–C10 are B_{eqv}. The thermal parameters for the other carbon atoms are B_{iso}. [e] The thermal parameters for the iron atom and for C1–C13, C17–C26, and C30–C32 are B_{eqv}. The thermal parameters for the other carbon atoms are B_{iso}. [f] $B_{eqv} = 8\pi^2(U_{11} + U_{22} + U_{33})/3$ and $B_{iso} = 8\pi^2 U_{iso}$.

only involves these four conformations but also configurations involving inversion of the entire molecule, i.e., the mirror images of XIIIa–d. XIIIb and XIIIc and their mirror images can alone account for the disorder observed, XIIIe, except that the occupancies (Table IV) determined for positions 1 and 2 of XIIIe are not equal while for positions 3 and 4 they are much more alike. It is necessary, therefore, to invoke the conformation XIIIa. This is considered an unlikely conformation because of steric interference between the oxygen and the methylene. How-

Table III. Selected Molecular Parameters[a]

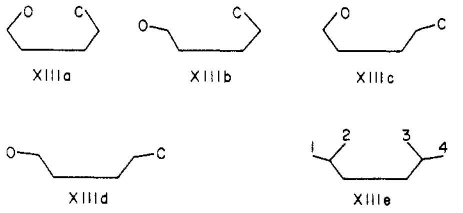
compd	I	II	III	IV	V	VI	VII	VIII
av C–C distance in Cp ring	138 (3)	142.5 (4)	141.0 (4)	142.5 (3)	142.6 (6)	141.8 (3)	142.9 (4)	138.5 (2)
av C–C–C angle in Cp ring	108 (2)	108.0 (2)	108.0 (4)	108.0 (2)	108.0 (4)	108.0 (3)	108.0 (3)	108.0 (1)
iron-to-ring distance	163.0 (3)	163.0 (1)	163.2 (5)	163.0 (1)	162.8 (6)	160.4 (2)	160.7 (3)	157.3 (2)
ring–ring tilt angle	7.4	11.9	6.0	13.1 (1)	15.0	9.6	12.8	2.5
ring–ring twist angle	0.4 (7)	1.3 (1)	2.4 (2)	1.1 (1)	0.3 (4)	1.2 (1)	0.8 (6)	
av α-C distance from ring plane	16 (3)	16 (1)	8.0 (8)	9.2 (3)	9.9 (8)	24 (1)	25 (1)	24 (1)
av α-C distance from trimethylene	16 (3)			9.2 (3)	10 (2)	24 (1)	23.2 (8)	24 (1)
av α-C distance from β-oxatrimethylene		16 (1)	8.0 (8)		10.2 (3)		27.4 (5)	
iron-to-heteroatom distance		324 (1)	353.7 (4)		325 (2)		317.8 (2)	
iron-to-β-carbon distance	331 (3)			331.2 (3)	330 (5)	324.4 (5)	329.2 (5)	322.6 (4)
carbon-to-heteroatom distance		141.5 (4)	182 (1)		148 (5)		143.8 (3)	
carbon–heteroatom–carbon angle		114.7 (4)	101.6 (5)		113 (3)		114.9 (3)	
carbon-to-β-carbon distance	146 (3)			153.6 (3)	150 (1)	148 (1)	153.0 (3)	154.6 (7)
carbon–β-carbon–carbon angle	123 (4)			113.1 (1)	111.8 (1)	119.7 (6)	116.4 (4)	115.9 (6)

[a] Distances in pm and angles in deg.

Table IV. Occupancies and Isotropic Thermal Factors of Central Atoms of Disordered Bridges

	occupanices	B_{iso},[b] pm^2
	Compound V	
OA[a]	0.239	53 (9)
OB	0.761	52 (3)
C14A	0.467	35 (3)
C14B	0.533	35 (3)
	Compound VI	
C15A	0.661	64 (3)
C15B	0.339	64 (6)

[a] Positions 1 and 2 are called OA and OB. Positions 3 and 4 are called C14A and C14B. [b] The thermal parameters are divided by 10^3.



XIIIa XIIIb XIIIc XIIId XIIIe

Figure 4. Symbolic representation of possible conformations of bridges of Compound V.

Table V. Correlation of Iron-to-Ring and Iron-to-Central Bridge Atom Distances

compd	Fe–ring dist, ppm	Fe–carbon dist, pm	Fe–oxygen dist, pm
I	163.0 (3)	331 (3)	
II	163.0 (1)		324 (1)
IV	163.0 (1)	331.2 (3)	
V	162.8 (6)	330 (5)	325 (2)
VI	160.4 (2)	324.4 (5)	
VII	160.7 (3)	329.2 (5)	317.8 (2)
VIII[11]	157.3 (2)	322.6 (4)	

Table VI. Reduction Potentials[a]

compd	ΔE,[b,c] mV	ΔE,[d] mV	ΔE,[f] mV
I	73		
II		76	
III		38[e]	
IV	142		
V		-7	
VI	82		
VII		72	
VIII	77		
IX		65	
X			-22
XI			-17
XII			-7

[a] The data are given as differences between the reduction potential of ferrocene and those of the compounds. [b] Compounds with central methylene groups on the bridges. [c] Remeasurement of reduction potentials reported in ref 2. [d] Compounds with central oxygen atoms on the bridges. [e] Central atom is sulfur. [f] Nonbridged compounds.

ever, the results indicate that some of XIIIa must exist and imply that there may be a stabilization of this conformation by an interaction between the oxygen and a hydrogen of the β-methylene.

In VI, disorder was observed in one of the trimethylene bridges but not in the other. A preliminary report[10] on a crystal structure determination of VI gives similar results but does not mention the disorder.

Except for II which, like I and III, has a rapidly flipping bridge on the NMR time scale, the β-oxatrimethylene bridge is characterized in the NMR spectra of V, VII, and IX by an AB quartet that arises from fixed methylene protons. For, in these compounds the nonflipping geminal protons are in different magnetic environments, one approximately in the plane of the cyclopentadienyl ring but slightly toward the iron atom and the other on the opposite side of the cyclopentadienyl ring and much further from the plane. If one assumes that the environments of the corresponding protons are the same for these three compounds, then the $\Delta\delta$ values observed would be indicative of the relative rates of flipping of the ether bridges. The rates of flipping by this criterion are thus found to increase in the order V ($\Delta\delta$ = 68.6 Hz), VII ($\Delta\delta$ = 59.4 Hz), and IX ($\Delta\delta$ = 48,8 Hz). These relative flipping rates are in accord with what is observed for the corresponding trimethylene-bridged compounds.

Suggestive evidence for an inverse correlation of the iron-to-ring distance and the interaction of the iron with the central atom of the bridge can be discerned in the crystal structures. This is shown in Table V in which it is evident that the iron-to-β-carbon distances and the iron-to-oxygen distances decrease as the iron-to-ring distances decrease. This interpretation is, of course, tentative since it is based on only three pieces of data that differ significantly from the others.

It is in the reduction potentials (the actual electrochemical experiment measures the potential for oxidation of the compounds; however, in accordance with tradition, the results are given for reduction reactions, in this case the inverse reaction, $Cp_2Fe^+ + e \rightarrow Cp_2Fe$) that the greatest effect of interaction of the oxygen atoms with the iron atoms is expected. These are given in Table VI. Except for the reduction potential of V, those for the (β-oxatrimethylene)ferrocenes appear to follow the same

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(10) Paul, I. *Chem. Commun.* **1966**, 377.

trends as those for the trimethyleneferrocenes. The potential and the crystal data obtained lend some support to the previous hypothesis that there is an interaction between the central atom of the bridge and the iron atom. However, the interaction of the iron with the oxygen is not convincingly different in strength from that with the central methylene group.

The reduction potential observed for V is considerably out of line with the others. However, if given only the data in this paper, it is also possible to conclude that the reduction potential for IV (the corresponding trimethylene derivative) is out of line with the others. The two discrepancies, though, are in opposite directions. We have no explanation to offer.

In order to ascertain that the small effects observed are not merely due to the contribution of the β-oxatrimethylene group to the reduction potential of ferrocene, reduction potentials were also determined for 1,1′-bis(hydroxymethyl)ferrocene (X), hydroxymethylferrocene (XI), and methoxymethylferrocene (XI). These groups were found to be electron-donating, in contrast to the oxygens on the bridges which could be considered to be mildly electron-withdrawing. This lends additional support to the contention that there is a special interaction through space for the oxygen atom of an ether bridge.

It is impossible to draw any significant conclusions from the results of only one (β-thiatrimethylene)ferrocene. However, if the above hypothesis is correct and the interaction is between the lone-pair electrons of the oxygen atom and the iron, then the interaction of the sulfur atom should be even stronger. The reduction potential of III does indicate a stronger electron donation for the sulfur atom, but to confirm this, comparison with other sulfur compounds is required. We must, however, leave this problem unsolved. No further work is planned.

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Supplementary Material Available: ORTEP diagrams for I–IV and VII and tables of bond distances and angles and anisotropic thermal parameters for I–VII, isotropic thermal parameters for I, V, and VI, and equations for least-squares planes (22 pages); listings of structure factors I–VII (70 pages). Ordering information is given on current masthead page.

Ortho Metalation of Pyridine at a Diiridium Center. Synthesis and Spectroscopic and Crystallographic Characterization of NC_5H_4- and *N,N′*-Di-*p*-tolylformamidinato-Bridged Complexes of Diiridium(II)

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The compound (COD)Ir(μ-form)$_2$Ir(OCOCF$_3$)$_2$(H$_2$O) (1) (COD = 1,5-cyclooctadiene; Hform = *N,N′*-di-*p*-tolylformamidine) thermally activates pyridine under mild conditions to afford the ortho-metalated derivative [Ir$_2$(μ-NC$_5$H$_4$)$_2$(μ-form)(py)$_4$]$^+$OCOCF$_3^-$ (3) in high yields. Metathesis with NaBPh$_4$ in MeCN affords [Ir$_2$(μ-NC$_5$H$_4$)$_2$(μ-form)(py)$_2$(MeCN)$_2$]$^+$BPh$_4^-$ (4). The cations in compounds 3 and 4 contain a singly bonded diiridium(II) core bridged by one form and two NC$_5$H$_4$ groups and bonded to two equatorial pyridine ligands. Axial pyridine (for 3) and MeCN (for 4) ligands complete the coordination sphere. Compound 4 crystallizes with two interstitial MeCN molecules. Crystal data: triclinic, space group $P\bar{1}$, a = 17.934 (5) Å, b = 18.397 (6) Å, c = 9.652 (1) Å, α = 97.09 (2)°, β = 97.67 (2)°, γ = 76.71 (2)°, V = 3057 (2) Å^3, d_{calcd} = 1.527 g·cm^{-3}, Z = 2, R = 0.0435 (R_w = 0.0518) for 4446 data having $F_o^2 > 3\sigma(F_o^2)$. The iridium–iridium distance, 2.517 (1) Å, is the shortest ever reported.

Introduction

We recently reported[1] that the oxidation of the formamidinato-bridged dimer of iridium(I) [Ir(form)(COD)]$_2$ [Hform = *N,N′*-di-*p*-tolylformamidine; COD = 1,5-cyclooctadiene) with AgOCOCF$_3$ results in the formation of the diiridium(I,III) compound (COD)Ir(μ-form)$_2$Ir(OCOCF$_3$)$_2$(H$_2$O) (1) containing a dative metal–metal bond. This result is in contrast with the reported[2] analogous reaction of the rhodium system, where the homogeneous-valence Rh(II) dimer Rh$_2$(μ-form)$_2$(μ-OCOCF$_3$)$_2$ is obtained in a number of adducts with different axial ligands. We also reported[1] that compound 1 easily exchanges its axially coordinated water molecule with neutral ligands and the pyridine adduct (COD)Ir(μ-form)$_2$Ir(OCOCF$_3$)$_2$py (2) was crystallographically characterized. During such a ligand exchange reaction we observed the formation of an orange powder along with the dark red crystals of compound 2.[1] We conjectured that such a material might be a homogeneous-valence iridium(II) dimer with bridging formamidinate and trifluoroacetate groups, analogous to the reported[2] rhodium complex. We therefore investigated the reaction between 1 and pyridine

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(2) Piraino, P.; Bruno, G.; Tresoldi, G.; Lo Schiavo, S.; Zanello, P. *Inorg. Chem.* 1987, *26*, 91.

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