of additional dimolybdenum thiocyanato compounds.

In Figure 5 we present a plot of the $\delta \rightarrow \delta^*$ transition energies versus the first reduction potentials (not available for Mo$_2$Br$_4$-(PMe$_3$)$_4$ in CH$_2$Cl$_2$). There is a good linear relationship, especially for the reductions measured in THF. Because of the ease of reduction of Mo$_2$(NCS)$_4$(PMe$_3$)$_4$, we are exploring the possibility that a compound containing the [Mo$_2$(NCS)$_4$(PMe$_3$)$_4$]$^-$ ion may be obtainable.

It is clear from Table V that over the series of five Mo$_2$X$_4$-(PMe$_3$)$_4$ compounds, the Mo–Mo distance is essentially constant, despite the large variation in $E_{1/2}$ and $\delta \rightarrow \delta^*$ values. The conclusion we draw from the combined data is that the changes in X have little influence on the energy of the HOMO (δ orbital)

but, rather, they change the energy of the LUMO (δ^*). Our observations also support and extend the work of Gray et al.,[2] who suggested that the $\delta \rightarrow \delta^*$ transition borrows intensity from the lowest LMCT band. Whether this relationship is capable of quantitative expression, however, remains uncertain. No doubt, experimental data on additional Mo$_2$X$_4$(PMe$_3$)$_4$ compounds would be informative, and we are trying to prepare several of them, especially the Mo$_2$F$_4$(PMe$_3$)$_4$ molecule, which may be the most important one to have.

Supplementary Material Available: Full listings of bond distances and angles, anisotropic thermal parameters, and positional parameters including those of hydrogen atoms for Mo$_2$(NCS)$_4$(PMe$_3$)$_4$, a cell packing diagram for Mo$_2$(NCS)$_4$(PMe$_3$)$_4$, and a labeled PLUTO drawing for Mo$_2$(NCO)$_4$(PMe$_3$)$_4$ (11 pages); listings of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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A New Sulfur-Bridged Ir(I)–Ir(I) Compound and Its Conversion to a Compound Containing a Metal–Metal Bond. Crystal Structures of Ir$_2$(SPh)$_2$(COD)$_2$ and Ir$_2$Cl$_2$(μ_2-SPh)$_2$(COD)$_2$

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The thiolato-bridged dinuclear compound Ir$_2$(SPh)$_2$(COD)$_2$ (**1**) was obtained from the alkoxide-bridged analogue by ligand exchange. **1** crystallizes in the space group $P2_1/c$ with a = 11.249 (6) Å, b = 11.564 (5) Å, c = 19.568 (10) Å, β = 100.28 (5)°, and Z = 4. The dinuclear molecule consists of Ir atoms with square-planar coordination sharing a S···S edge. The Ir···Ir separation of 3.181 (1) Å agrees with the assumed absence of a bond. The dinuclear compound is nonrigid in solution. Upon oxidative addition of halogens (Br$_2$, I$_2$), the dimeric M–M-bonded compounds of Ir(II), Ir$_2$X$_2$(μ_2-SPh)$_2$(COD)$_2$, are obtained. Alternatively, the Br and I derivatives can be prepared by electrochemical reduction of Ir$_2$(μ_2-X)$_2$X$_2$(COD)$_2$ (X = Br, I), followed by oxidative addition of PhSSPh. The chloro analogue, **2**, was prepared by oxidative addition of PhSSPh to Ir$_2$Cl$_2$(COD)$_2$ and was structurally characterized. It crystallizes in the space group $P\bar{1}$ with a = 8.370 (2) Å, b = 12.155 (1) Å, c = 13.184 (2) Å, α = 94.33 (1)°, β = 97.63 (2)°, γ = 96.47 (1)°, and Z = 2. The molecules are M–M-bonded dimers consisting of edge-sharing square pyramids. The Ir–Ir bond length is 2.800 (1) Å. The ^{13}C and ^{1}H NMR spectra indicate that the solid-state structure is retained in solution. The phenyl rings of the thiolate bridges exhibit a syn relationship with respect to the four-membered [IrS]$_2$ core, and the mean planes of the phenyl rings are approximately perpendicular to the Ir–Ir vector. The average Ir–S bond length is 2.345 (2) Å. Other important bond lengths and angles are given in Table III.

Introduction

Diiridium(II) compounds containing iridium–iridium bonds are far fewer than the homologous dirhodium(II) compounds. Only a limited number of examples are known containing pyrazolate,[1] thiolato,[2] and other different bridging ligands.[3] There is only one example reported of a diiridium(II) compound with no bridging ligand supporting the iridium–iridium bond.[4]

We have recently found[5] that by reacting Ir$_2$(OMe)$_2$(COD)$_2$ with iodine a new Ir(II) complex, Ir$_2$(μ_2-I)$_2$I$_2$(COD)$_2$, was obtained, which we used as starting material for the synthesis of cluster compounds.

We report here the preparation of several thiolato-bridged iridium compounds and the crystal structures of Ir$_2$(SPh)$_2$(COD)$_2$ and Ir$_2$Cl$_2$(μ_2-SPh)$_2$(COD)$_2$.

Experimental Section

IrCl$_3$·3H$_2$O was purchased from Engelhard Industries and diphenyl disulfide from Aldrich Chemical Co. All manipulations were done under

dry nitrogen or argon. The solvents were of analytical grade and were distilled under nitrogen prior to use. Ir$_2$Cl$_2$(COD)$_2$[6] and Ir$_2$(OMe)$_2$-

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Table I. Crystallographic Details for $Ir_2(SPh)_2(COD)_2$ (**1**) and $Ir_2Cl_2(\mu_2\text{-}SPh)_2(COD)_2$ (**2**)

	1	2
formula	$C_{26}H_{34}S_2Ir_2$	$C_{26}H_{34}S_2Cl_2S_2Ir_2$
fw	819	890
space group	$P2_1/c$	$P\bar{1}$
syst abs	$h0l$: $l = 2n + 1$	none
	$0k0$: $k = 2n + 1$	
a, Å	11.249 (6)	8.370 (2)
b, Å	11.564 (5)	12.155 (1)
c, Å	19.568 (10)	13.184 (2)
α, deg		94.33 (1)
β, deg	100.28 (2)	97.63 (2)
γ, deg		96.47
V, Å^3	2505 (2)	1315.3 (7)
Z	4	2
d_{calcd}, g/cm^3	2.17	2.25
cryst size, mm	$0.1 \times 0.2 \times 0.3$	$0.1 \times 0.2 \times 0.2$
μ(Mo Kα), cm^{-1}	107.5	104.4
data collcn instrum	Enraf-Nonius CAD4	
radiation (monochromated in incident beam)	Mo Kα ($\lambda\bar{\alpha} = 0.710\,723$ Å)	
orientation reflcns: no.; range (2θ), deg	25; 15–32	25; 16–30
temp, °C	25	25
scan method	ω-2θ	ω-2θ
data collcn range (2θ), deg	4–45	4–50
no. of unique data, total no. with $R_o^2 > 3\sigma(F_o^2)$	2951, 2467	4617, 4009
no. of params refined	289	307
transmissn factors: max, min		99.9, 37.8%
R^a	0.031	0.028
R_w^b	0.042	0.045
quality-of-fit indicator^c	1.41	1.468
largest shift/esd, final cycle	0.03	0.16
largest peak, e/Å^3	0.798	0.835

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $1/\sigma^2(|F_o|)$. ^{c} Quality of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

$(COD)_2$[7] were prepared by literature procedures. The ^1H and ^{13}C NMR spectra were recorded with a Bruker AC200 spectrometer, operating at 200.132 and 50.323 MHz respectively. The electrochemical experiments were carried out in a three-electrode cell. The working and auxiliary electrodes were platinum disk and wire, respectively, and the reference electrode was a saturated calomel electrode electrically connected to the solution via a "salt bridge" containing a saturated solution of the sup-

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Table II. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	$B,^a$ Å^2
		Compound 1		
Ir(1)	0.08871 (3)	0.18672 (3)	0.33555 (2)	2.105 (8)
Ir(2)	0.23816 (4)	0.28040 (3)	0.47822 (2)	2.353 (8)
S(1)	0.0376 (2)	0.3057 (2)	0.4234 (1)	2.42 (5)
S(2)	0.2484 (2)	0.3196 (2)	0.3621 (1)	2.34 (5)
C(1)	-0.0781 (9)	0.2679 (9)	0.4697 (4)	2.9 (2)
C(2)	-0.152 (1)	0.358 (1)	0.4851 (5)	4.5 (3)
C(3)	-0.238 (1)	0.342 (1)	0.5267 (7)	7.5 (4)
C(4)	-0.265 (1)	0.228 (2)	0.5430 (7)	7.1 (4)
C(5)	-0.193 (1)	0.133 (1)	0.5267 (6)	5.3 (3)
C(6)	-0.099 (1)	0.1565 (9)	0.4907 (5)	3.8 (3)
C(7)	0.3841 (9)	0.2933 (8)	0.3308 (4)	2.6 (2)
C(8)	0.426 (1)	0.3849 (8)	0.2954 (5)	3.4 (2)
C(9)	0.535 (1)	0.371 (1)	0.2704 (5)	4.0 (3)
C(10)	0.603 (1)	0.270 (1)	0.2822 (6)	5.3 (3)
C(11)	0.558 (1)	0.179 (1)	0.3176 (6)	4.2 (3)
C(12)	0.453 (1)	0.1900 (9)	0.3435 (5)	3.5 (3)
C(13)	0.182 (1)	0.0758 (8)	0.2749 (5)	3.1 (2)
C(14)	0.1031 (9)	0.1498 (8)	0.2307 (4)	2.5 (2)
C(15)	-0.016 (1)	0.1066 (9)	0.1873 (5)	3.7 (2)
C(16)	-0.123 (1)	0.1258 (9)	0.2229 (5)	3.6 (2)
C(17)	-0.0869 (9)	0.1245 (8)	0.3019 (5)	3.0 (2)
C(18)	-0.0191 (9)	0.0366 (8)	0.3378 (5)	3.1 (2)
C(19)	0.024 (1)	-0.0699 (8)	0.3030 (5)	4.0 (3)
C(20)	0.150 (1)	-0.0530 (8)	0.2854 (6)	4.8 (3)
C(21)	0.410 (1)	0.206 (1)	0.5139 (6)	5.0 (3)
C(22)	0.421 (1)	0.329 (1)	0.5189 (5)	3.8 (3)
C(23)	0.431 (1)	0.399 (1)	0.5836 (6)	5.8 (3)
C(24)	0.331 (1)	0.374 (1)	0.6250 (6)	5.2 (3)
C(25)	0.202 (1)	0.2031 (9)	0.5711 (5)	3.9 (3)
C(26)	0.217 (1)	0.3254 (9)	0.5805 (5)	3.8 (3)
C(27)	0.294 (1)	0.112 (1)	0.5998 (6)	5.0 (3)
C(28)	0.417 (1)	0.133 (1)	0.5811 (7)	6.0 (3)
		Compound 2		
Ir(1)	0.08476 (3)	0.11689 (2)	0.23957 (2)	1.909 (5)
Ir(2)	0.09346 (3)	0.34791 (2)	0.24011 (2)	2.098 (5)
Cl(1)	0.2771 (2)	-0.0154 (1)	0.2087 (2)	3.42 (4)
Cl(2)	0.3056 (2)	0.4846 (2)	0.2011 (2)	3.79 (4)
S(1)	0.3046 (2)	0.2501 (1)	0.3064 (1)	2.19 (3)
S(2)	0.0982 (2)	0.2209 (1)	0.0955 (1)	2.28 (3)
C(1)	0.3692 (8)	0.2489 (6)	0.4417 (5)	2.4 (1)
C(2)	0.4398 (9)	0.1576 (7)	0.4705 (6)	3.6 (2)
C(3)	0.508 (1)	0.1520 (8)	0.5717 (7)	4.8 (2)
C(4)	0.499 (1)	0.241 (1)	0.6453 (7)	5.7 (2)
C(5)	0.429 (1)	0.3304 (9)	0.6162 (8)	7.6 (2)
C(6)	0.363 (1)	0.3363 (8)	0.5133 (8)	6.7 (2)
C(7)	0.2822 (8)	0.2391 (6)	0.0427 (5)	2.5 (1)
C(8)	0.314 (1)	0.3361 (8)	-0.0053 (5)	3.6 (2)
C(9)	0.451 (1)	0.3519 (7)	-0.0567 (6)	4.5 (2)
C(10)	0.554 (1)	0.2669 (8)	-0.0612 (6)	4.2 (2)
C(11)	0.522 (1)	0.1731 (8)	-0.0179 (6)	4.2 (2)
C(12)	0.383 (1)	0.1584 (7)	0.0365 (6)	3.6 (2)
C(13)	-0.0116 (9)	0.1016 (6)	0.3866 (5)	3.2 (1)
C(14)	0.0604 (8)	0.0082 (5)	0.3646 (5)	2.7 (1)
C(15)	-0.030 (1)	-0.1043 (7)	0.3272 (7)	4.2 (2)
C(16)	-0.088 (1)	-0.1230 (7)	0.2105 (7)	4.6 (2)
C(17)	-0.0890 (9)	-0.0196 (6)	0.1540 (6)	3.7 (2)
C(18)	-0.1751 (9)	0.0698 (7)	0.1821 (7)	3.7 (2)
C(19)	-0.2819 (9)	0.0590 (9)	0.2701 (8)	5.1 (2)
C(20)	-0.1988 (9)	0.1043 (8)	0.3752 (6)	4.3 (2)
C(21)	-0.020 (1)	0.3875 (7)	0.3798 (6)	3.8 (2)
C(22)	0.0910 (9)	0.4810 (6)	0.3637 (6)	3.2 (1)
C(23)	0.035 (1)	0.5840 (7)	0.3210 (7)	4.8 (2)
C(24)	-0.063 (1)	0.5647 (7)	0.2143 (8)	5.3 (2)
C(25)	-0.0620 (9)	0.4542 (6)	0.1556 (7)	3.9 (2)
C(26)	-0.1580 (9)	0.3566 (6)	0.1739 (6)	3.7 (2)
C(27)	-0.281 (1)	0.3504 (9)	0.2484 (8)	5.2 (2)
C(28)	-0.204 (1)	0.3930 (9)	0.3579 (8)	5.7 (2)

^{a} Values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3 + bc(\cos \alpha)B(2,3)]$.

porting electrolyte. Cyclic voltammograms were obtained with a programming function generator Model 305 from H.Q. Instruments were

Table III. Important Bond Distances (Å) and Bond Angles (deg) for $Ir_2(SPh)_2(COD)_2$ (1) and $Ir_2Cl_2(SPh)_2(COD)_2$ (2)

	1	2
Ir(1)–Ir(2)	3.181 (1)	2.800 (1)
Ir(1)–S(1)	2.352 (2)	2.338 (1)
Ir(1)–S(2)	2.351 (2)	2.367 (1)
Ir(2)–S(1)	2.337 (2)	2.349 (1)
Ir(2)–S(2)	2.341 (2)	2.368 (1)
Ir(1)–Cl(1)		2.450 (1)
Ir(2)–Cl(2)		2.426 (1)
Ir(1)–C(13)	2.142 (8)	2.225 (6)
Ir(1)–C(14)	2.130 (7)	2.211 (6)
Ir(1)–C(17)	2.095 (9)	2.194 (6)
Ir(1)–C(18)	2.123 (8)	2.186 (6)
Ir(2)–C(21)	2.177 (10)	2.209 (6)
Ir(2)–C(22)	2.144 (9)	2.205 (5)
Ir(2)–C(25)	2.130 (8)	2.209 (6)
Ir(2)–C(26)	2.121 (8)	2.202 (6)
S(1)–C(1)	1.768 (9)	1.795 (6)
S(2)–C(7)	1.769 (10)	1.772 (6)
C(13)–C(14)	1.410 (12)	1.430 (9)
C(17)–C(18)	1.385 (12)	1.411 (9)
C(21)–C(22)	1.430 (14)	1.374 (9)
C(25)–C(26)	1.433 (13)	1.423 (11)
Ir(1)–S(1)–Ir(2)	85.43 (8)	73.37 (4)
Ir(1)–S(2)–Ir(2)	85.38 (7)	72.51 (4)
S(1)–Ir(1)–S(2)	74.51 (7)	80.68 (5)
S(1)–Ir(2)–S(2)	74.99 (8)	80.42 (5)

Table IV. ^{13}C NMR Data

compd	δ(–CH)[a]	^1J(C–H), Hz	δ(–CH₂)[a]	^1J(C–H), Hz
$Ir_2Cl_2(COD)_2$	61.7	158	31.3	129.5
$Ir_2(OMe)_2(COD)_2$	56.4	152.2	31.4	126.5
$Ir_2(SPh)_2(COD)_2$	64.6	155.4	31.6	127.8
$Ir_2Cl_2(SPh)_2(COD)_2$	85.1		34.6	
	84.6	161	34.1	130
	82.1		30.8	
	81.9		30.4	
$Ir_2Br_2(SPh)_2(COD)_2$	82.7		34.1	
	82.6	160	33.5	130
	81.2		31.9	
	80.7		30.4	
$Ir_2I_2(SPh)_2(COD)_2$	79.2		34.1	
	79.1	158	33.7	129
	78.4		33.2	
	78.2		32.4	

[a] In $CDCl_3$; δ > 0 resonances downfield from TMS.

Figure 1. ORTEP view of 1.

connected to a Model 552 Amel potentiostat and a Riken Denshi F-35 X-Y recorder. The solvent was THF, which had been freshly distilled over Na–benzophenone. The supporting electrolyte, Bu_4NPF_6, was recrystallized from ethanol and dried at 80 °C under vacuum for 48 h. Controlled-potential electrolyses were carried out in a three-compartment cell separated by fritted glass. Working and auxiliary electrodes were of platinum mesh. A Model 552 Amel potentiostat was used for controlled-potential electrolysis. The charge transferred was calculated by recording intensity versus the electrolysis time and carrying out an integration. The system was calibrated against cobaltocene.

X-ray Crystallographic Procedures. The crystallographic work followed the general procedures that were described previously.[8] The crystal parameters and basic information corresponding to data collection and structure refinement for compounds **1** and **2** are given in Table I. Atomic coordinates are listed in Table II. Important bond distances and angles are given in Table III. In both structures the positions of the two iridium atoms were obtained from the three-dimensional Patterson map. The remaining atoms were located by using successive least-squares refinement and difference Fourier maps. The refinement converged at residuals of $R = 0.031$, $R_w = 0.042$ for **1** and $R = 0.028$, $R_w = 0.045$ for **2**.
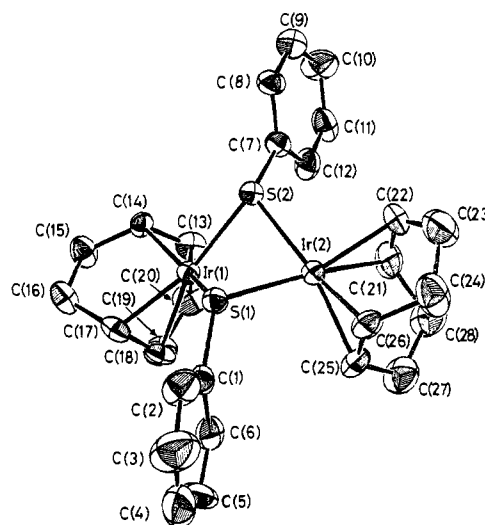
Synthesis of $Ir_2(SPh)_2(COD)_2$ (1). $Ir_2(OMe)_2(COD)_2$ (131 mg, 0.5 mmol) was dissolved in 8 mL of dichloromethane, and PhSH (0.05 mL, 0.5 mmol) was added with stirring. After 10 min the solution was evaporated to dryness. The resulting oil was dissolved in dichloromethane and chromatographed on a column (25 × 2 cm) packed with silica gel in hexane. Elution with dichloromethane yielded a yellow band, which after evaporation to dryness and further crystallization from dichloromethane–hexane gave yellow crystals of **1**. Yield: 120 mg, 70%.

Synthesis of $Ir_2Cl_2(\mu_2\text{-}SPh)_2(COD)_2$ (2). Diphenyl disulfide (92 mg, 0.42 mmol) was added to a solution of $Ir_2Cl_2(COD)_2$ (260 mg, 0.39 mmol) in 20 mL of dichloromethane. The solution, which immediately became deep red, was stirred for 1 h and then concentrated under reduced pressure. It was transferred to a chromatography column (2 × 20 cm) packed with silica gel in dichloromethane. The column was eluted with dichloromethane, and a small yellow band, identified as Ir_2-$(SPh)_2(COD)_2$, was collected. Further elution with the same solvent afforded a red band; this fraction was concentrated under reduced pressure to about 5 mL and then carefully layered with a large excess of hexane. Red crystals of **2** (175 mg, 50% yield) were collected after 2–3 days. Crystals suitable for X-ray crystallography were obtained by

(8) (a) Calculations were done on the VAX-11/780 computer at Department of Chemistry, Texas A&M University, College Station, TX, with the VAX-SPD software package. (b) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558. (c) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227. (d) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351.
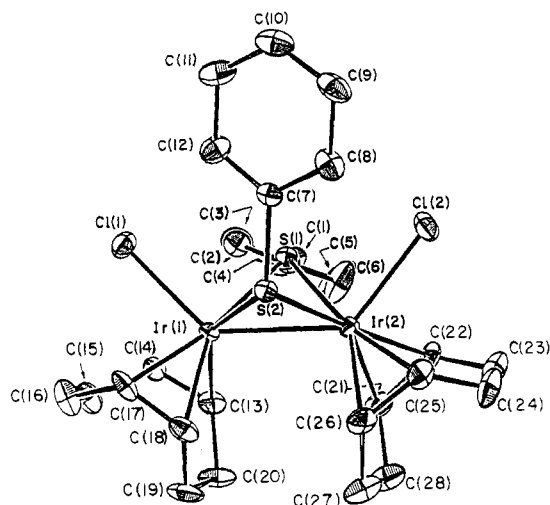
this procedure. Anal. Calcd for $C_{28}H_{34}S_2Cl_2Ir_2$: C, 37.8; H, 3.8. Found: C, 37.8; H, 3.8.

Synthesis of Compounds $Ir_2X_2(\mu_2\text{-}SPh)_2(COD)_2$ [X = Br (3), X = I (4)]. Method A. Oxidative Addition of Halogens to Compound 1. To a solution of $Ir_2(SPh)_2(COD)_2$ (163.7 mg, 0.2 mmol) in 10 mL of dichloromethane was added an equimolar amount of X_2 (X = Br, 3.15 mL of a 10.15 M Br_2 solution in CCl_4; X = I, 50.8 mg, 0.2 mmol). In both cases the solution turned immediately to a red-brown color. After 30 min of stirring, the solvent was removed, and the crude product was dissolved in 2 mL of dichloromethane and chromatographed on a column (25 × 2 cm) using silica gel in hexane as support. Elution with CH_2Cl_2 (X = Br) or CH_2Cl_2/hexane 1:1 (X = I) separated a red-brown (X = Br) or deep red (X = I) band, which was collected and evaporated to dryness. Recrystallization from CH_2Cl_2/hexane gave compounds **3** and **4** as crystalline solids. Yields: X = Br, 153 mg, 77%; X = I, 139 mg, 65%. Anal. Calcd for $C_{28}H_{34}S_2Br_2Ir_2$ (3): C, 34.3; H, 3.4. Found: C, 34.3; H, 3.4. Calcd for $C_{28}H_{34}S_2I_2Ir_2 \cdot 2CH_2Cl_2$ (4): C, 28.9; H, 3.1. Found: C, 28.8; H, 2.9. The existence of two solvent molecules in the lattice was confirmed by ^1H NMR.

Method B. Electrochemical Reduction of $Ir_2(\mu_2\text{-}X)_2X_2(COD)_2$ (X = Br, I). A solution of 43 mg (0.04 mmol) of $Ir_2(\mu_2\text{-}I)_2I_2(COD)_2$ in 15 mL of 0.15 M THF in Bu_4NPF_6 was placed in the cathodic compartment of the electrolytic cell, at room temperature. This solution was electrochemically reduced at −0.45 V vs SCE. During this process the solution, initially dark red, turns yellow. The electrolysis was considered completed when the current dropped below 1% of the initial intensity (about 45 min). Diphenyl disulfide (8.46 mg, 0.04 mmol) was added to this solution. After 15 min of stirring, the resulting purple solution was evaporated to dryness, and the residue was extracted several times with toluene. The extracts were evaporated to dryness and purified by chromatography on a column (25 × 2 cm) using silica gel in hexane as support. Elution with Cl_2CH_2 separated a deep red band, which was collected and evaporated to dryness. Recrystallization with Cl_2CH_2/hexane gave the pure product. Yield: 18%.

Figure 2. ORTEP view of **2**.

The homologous bromine compound can be prepared by an exactly analogous method. Yield: 14%.

^{13}C NMR spectral data for the four new compounds as well as the starting materials are presented in Table IV.

Results and Discussion

Molecular Structure of 1. Figure 1 shows a perspective view of **1** and also defines the atom-numbering scheme. The dinuclear unit is composed of two iridium atoms that have a square-planar arrangement Ir(COD)S$_2$; the two squares share an edge defined by the bridging S atoms. The phenyl rings of the thiolato bridges exhibit a syn configuration with respect to the four-membered [IrS]$_2$ core, and the mean planes of the phenyl rings are approximately perpendicular to the Ir–Ir vector. The average Ir–S bond length is 2.345 (7) Å. The Ir···Ir separation of 3.181 (1) Å is consistent with the expected repulsive interaction between the metal centers.

It is interesting to compare the molecular structure of **1** with that of the previously reported Ir$_2$Cl$_2$(COD)$_2$[9] in order to evaluate the structural differences resulting from the replacement of the soft sulfur bridges by the considerably harder chloride bridges. We find that the Ir–S bond length (2.345 (7) Å) is significantly shorter than the analogous Ir–Cl distance (2.401 4) Å), despite the fact that the covalent radius of S is about 0.05 Å larger than that of Cl. Also, the butterfly-shaped core is flattened out in the sulfur compound, resulting in a larger metal separation. We attribute this, tentatively, to a higher degree of π-bond character for the Ir–S bonds, thereby compensating, in part, for the electron deficiency of the Ir centers with respect to a rare-gas electron configuration.

The structure of the carbonyl analogue of **1**, Ir$_2$(SPh)$_2$(CO)$_2$, has been reported in a preliminary fashion, and a metal separation of 3.10 Å has been given.[2b] Additionally there is a pairwise stacking resulting in a second relatively short Ir–Ir distance (3.37 Å). This stacking, naturally, is not observed in **1** as the COD ligands prevent a close interaction between dimers. According to both ^{13}C and ^1H NMR spectra, compound **1** as well as Ir$_2$-Cl$_2$(COD)$_2$ are nonrigid in solution. Consequently only one type of olefinic carbon or proton is observed at room temperature. A plausible mechanism accounting for the simplicity of the spectra involves the inversion of the butterfly-shaped core.

Molecular Structure of 2. A perspective view of the molecular compound **2** is shown in Figure 2. Each Ir center exhibits a square-pyramidal coordination sphere with the COD and the thiolato ligands defining the square and the Cl atoms occupying the apical positions. The two square pyramids are united along a common basal edge defined by the sulfur atoms in such a way that the apical Cl atoms are cisoid. The average Ir–S bridging
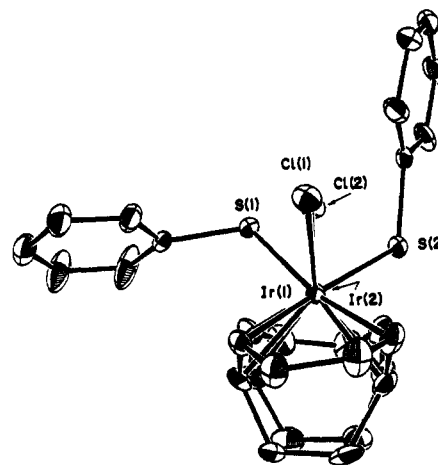
(9) Cotton, F. A.; Lahuerta, P.; Sanaú, M.; Schwotzer, W. *Inorg. Chim. Acta* **1986**, *120*, 153.

Figure 3. ORTEP view of **2** along the Ir–Ir axis.

bond length is 2.356 (14) Å, and the Ir–Cl distance is 2.44 (2) Å. The short Ir–Ir distance (2.800 (1) Å) indicates the existence of an Ir–Ir single bond. This leads to an 18-electron configuration at each metal center and agrees with the diamagnetic behavior of **2** in the NMR experiments. Interestingly the configuration of the phenyl substituents is anti with respect to the four-membered core; this is most clearly seen in the view along the M–M axis shown in Figure 3. All main features of configuration are retained in solution on the NMR time scale as the signals corresponding to the four inequivalent olefinic protons appear sharp and well separated in the chemical shift range 5.2–4.6 ppm. In the ^{13}C NMR spectrum there are four resonances between 81.9 and 85.1 ppm that can plausibly be assigned to the four magnetically inequivalent olefinic carbon atoms. Compounds **3** and **4** behave spectroscopically very similarly, indicating that they have essentially the same structure as **2**. The average ^{13}C chemical shift value for the olefinic carbons in **2–4**, 83.4, 81.8, and 78.7 ppm, decrease in going from the chloro to the iodo compound.

Chemical Reactions. The reaction of Ir$_2$(OMe)$_2$(COD)$_2$ with thiophenol, eq 1, gave **1** in high yield (>80%). The driving force for this reaction must be the greater strength of the Ir–S (soft

$$2MeOH \quad (1)$$
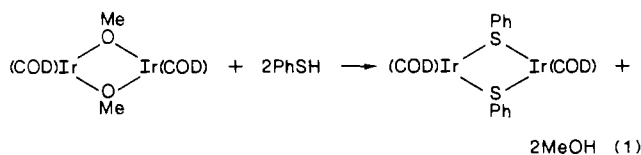
acid–soft base) bonds formed compared to the strength of the Ir–O bonds (soft acid–hard base) in the starting compound. The short Ir–S bond lengths found in the crystal structure of **1** support this idea. Compound **1** in solution is fairly reactive and air-sensitive. It undergoes oxidative addition of Br$_2$ or I$_2$ (eq 2), yielding

$$(2)$$

$$X_2 = Cl_2, Br_2, I_2$$
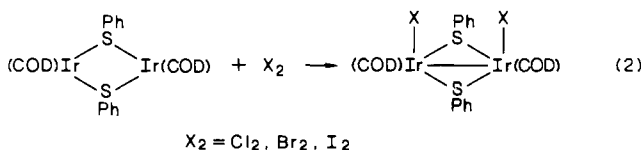
compounds **3** and **4**. Similar reactions but with different substrates have been described for other diiridium(I) compounds containing thiolato bridges.[2f,h] Compound **2** can be made not only by a similar reaction with Cl$_2$ but also by reacting Ir$_2$Cl$_2$(COD)$_2$ with diphenyl disulfide (eq 3). During the purification of **2** made by the latter
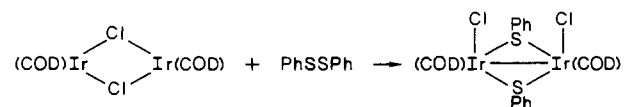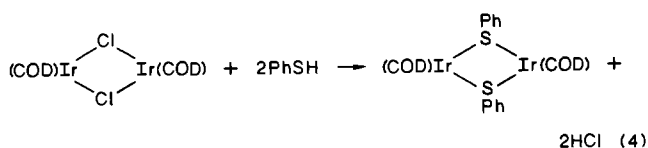

$$(3)$$

method, small amounts of **1** were separated from the reaction mixture. The origin of this compound is not obvious but it might

be produced by the action of small amounts of benzenethiol generated in solution by decomposition of diphenyl disulfide also (eq 4). It is interesting that in reaction 3 not only does oxidative addition occur but also migration of the preferred bridging ligands, PhS, occurs concomitantly.

Tris((trifluoromethyl)sulfonyl)methane, HC(SO₂CF₃)₃

Lutz Turowsky and Konrad Seppelt*

Tris((trifluoromethyl)sulfonyl)methane, HC(SO₂CF₃)₃, is prepared from CH₃MgBr and CF₃SO₂F. Known H₂C(SO₂CF₃)₂ is an intermediate. This novel material is a very strong C–H acid. Some derivatives, such as salts and halogen compounds, are described. The crystal structure of K⁺C(SO₂CF₃)₃⁻·H₂O is presented. Crystal data: $a = 605.91$ (6) pm, $b = 1398.77$ (8) pm, $c = 1605.60$ (13) pm, $Pc2_1b$, $Z = 4$.

Introduction

In search of extremely electronegative groups having carbon as the central atom we sought a way of preparing CH(SO₂CF₃)₃. One motive for this search was the potential for forming a stable xenon–carbon bond. Many other carbon ligands, such as C(CN)₃, C(NO₂)₃, CN, C₆F₅, or C(SO₂F)₃,[1] have failed to do this. The only unconfirmed report of macroscopic amounts of a Xe–C-bonded species is that of Xe(CF₃)₂,[2] which is supposed to be thermally quite unstable.

The success of preparing xenon–nitrogen bonds, first with the N(SO₂F)₂ ligand[3] and later and better with the N(SO₂CF₃)₂ ligand,[4] suggested C(SO₂CF₃)₃ as a possible candidate for a Xe–C-bonded ligand, even though C(SO₂F)₃ had failed to give a xenon–carbon bonded species.[5]

Results and Discussion

Our first attempts to prepare HC(SO₂CF₃)₃ were unsuccessful. Thus we have not been able to obtain the title compound by transfer of trifluoromethyl groups onto HC(SO₂OH)₃ or HC(SO₂F)₃.[5] We were also unable to oxidize the known HC(SCF₃)₃ molecule.[6] These negative findings led to the trifluoromethyl sulfonation of CH₂(SO₂CF₃)₂ or, in other words, stepwise trifluoromethyl sulfonation of methane. CH₂(SO₂CF₃)₂ is prepared from CH₃MgBr and CF₃SO₂F and is itself a quite strong CH acid.[7] In fact, with CH₃MgBr, 2 mol of CH₄ are formed, an indication of the existence of the C(SO₂CF₃)₃²⁻ dianion in solution.[7] This dianion is reacted with CF₃SO₂F to give C(SO₂CF₃)₃⁻ from which the title compound can be isolated. It is possible to

Table I. Atomic Coordinates of K⁺C(SO₂CF₃)₃⁻·H₂O (Except for Hydrogen Atoms)

	x	y	z
K	0.948 (4)	0.51710 (0)	0.39040 (8)
O	0.429 (2)	0.5388 (5)	0.8584 (4)
S1	0.1031 (3)	0.2433 (2)	0.46323 (7)
S2	0.0297 (2)	0.0645 (2)	0.36421 (7)
S3	0.1196 (2)	0.2502 (2)	0.28040 (7)
O1	0.0559 (8)	0.1789 (3)	0.5294 (3)
O11	−0.0002 (8)	0.3353 (3)	0.4610 (3)
O3	0.2030 (7)	0.1933 (4)	0.2138 (2)
O31	0.2246 (7)	0.3390 (3)	0.3020 (3)
O2	−0.0311 (7)	0.0393 (3)	0.2807 (2)
O21	−0.1008 (7)	0.0310 (3)	0.4325 (3)
C	0.0802 (9)	0.1840 (4)	0.3696 (3)
C1	0.407 (2)	0.2716 (5)	0.4768 (4)
F11	0.4428 (8)	0.3620 (3)	0.4648 (3)
F12	0.4654 (7)	0.2458 (4)	0.5522 (3)
F13	0.5276 (6)	0.2227 (4)	0.4242 (3)
C2	0.299 (1)	0.0067 (5)	0.3801 (4)
F21	0.3765 (6)	0.0289 (3)	0.4554 (2)
F22	0.4431 (6)	0.0365 (4)	0.3245 (3)
F23	0.2788 (7)	−0.0871 (3)	0.3760 (3)
C3	−0.1589 (9)	0.2874 (5)	0.2468 (4)
F31	−0.2435 (6)	0.3503 (4)	0.2996 (3)
F32	−0.2915 (6)	0.2143 (3)	0.2401 (3)
F33	−0.1444 (7)	0.3300 (3)	−0.1733 (2)

Table II. Selected Bond Distances in K⁺C(SO₂CF₃)₃⁻·H₂O (pm)[a]

C–S	169.3, 172.6, 172.7
S–O	143.0, 142.8, 143.5, 143.5, 143.7, 143.2
S–C(F)	189.5, 184.7, 184.2
C–F	130.1, 133.6
K···O(S)	257.9, 284.5, 284.8, 287.0, 297.6, 305.0
K···O(H)	294.7, 322.9
K···F(C)	325.3, 343.3, 378.3

[a] Estimated standard deviations 0.3–0.8 ppm.

circumvent the isolation of CH₂(SO₂CF₃)₂ by reacting CH₃MgBr and CF₃SO₂F in the appropriate ratio.

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