Hydrodesulfurization of Thiophene to Butadiene and Butane by a Homogeneous Iridium Complex

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Abstract: Thermolysis of the dimer $[(C_5Me_5)IrH_3]_2$ in neat thiophene in the presence of *tert*-butylethylene at 60 °C gives the desulfurization cleavage product $[(C_5Me_5)Ir]_2(\mu\text{-}S)(\mu\text{-}1,2\text{-}\eta^2\text{-}3,4\text{-}\eta^2\text{-}C_4H_6)$. This butadiene complex crystallizes in monoclinic space group Cc (No. 9) with $a = 8.828(8)$ Å, $b = 14.132(3)$ Å, $c = 37.889(10)$ Å, $\beta = 96.76(5)°$, $Z = 8$, and $V = 4694.0(7.3)$ Å^3. Use of thiophene-d_4 gives a d_4 product in which deuterium appears at all positions of the coordinated butadiene. Reaction of the butadiene complex with CO produces free butadiene and the complex $[(C_5Me_5)Ir(CO)]_2(\mu\text{-}S)$. The dicarbonyl complex crystallizes in monoclinic space group $C2/c$ (No. 15) with $a = 11.404(5)$ Å, $b = 13.927(4)$ Å, $c = 14.047(3)$ Å, $\beta = 97.34(2)°$, $Z = 4$, and $V = 2212.8(2.1)$ Å^3. Reaction of the butadiene complex with H_2 produces butane.

Introduction

The reactions of thiophenes with homogeneous transition metals has been the subject of many recent studies as a means of modeling potential heterogeneous reactions that occur during the hydrodesulfurization (HDS) of petroleum. Several modes of thiophene binding have been identified, including both π- (η^5, η^4, or η^2) and σ- (S- or C-thienyl) complexation, with X-ray crystallographic studies providing details of the coordination.[1] Several models have been presented for the initial steps in thiophene (and benzothiophene) binding, including S-coordination,[2] η^4 or η^5 π-complexation,[3] or η^2-coordination.[4] Models have also been proposed for the subsequent steps in HDS, including S bonding followed by C–S cleavage,[5] π-complexation followed by C–S cleavage,[6] and π-complexation followed by nucleophilic attack.[7] In several cases, products have been produced in which the thiophene has been ring opened[8] or completely desulfurized with an iron carbonyl.[9] A report has recently been made of an iridium complex that inserts into thiophene and then produces

butadiene and butenethiol upon treatment with borohydride and acid.[10] Also of relevance to the present work, $Ru_3(CO)_{12}$ has been found to cleave both C–S bonds in 2-methylthiophene, giving a metallacyclobutadiene.[11]

In this paper, a binuclear polyhydride system was investigated for HDS activity. Earlier studies in our lab with mononuclear complexes had led only to the cleavage of a single thiophene C–S bond, suggesting that two metal centers might be required for cleavage of both C–S bonds. The dinuclear iridium complex $[(C_5Me_5)IrH_3]_2$ was chosen for study, as its chemistry was anticipated to be derivative of the $[(C_5Me_5)Rh]$ chemistry previously studied in our lab[5,12] and since it already contained the hydrogen needed for thiophene hydrogenolysis. The notion that polynuclear metal complexes might better model HDS catalysis has previously been suggested by the work of Curtis with a Mo_2-Co_2 sulfide cluster.[13] Indeed, the present studies show that the iridium dimer can facilitate both cleavage of the C–S bonds of thiophene and hydrogenation of the C_4 fragment to give butadiene or butane.

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Hydrodesulfurization of Thiophene by [(CH₅Me₅)IrH₃]₂

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Results

The synthesis of the dimer $[(C_5Me_5)IrH_3]_2$ (1) has been reported by Bergman for the reaction of $[(C_5Me_5)_2Ir_2H_3]^+$ with LiBH₄ in about 25% overall yield from $[(C_5Me_5)IrCl_2]_2$.[14] A more direct route to this dinuclear hexahydride complex has been developed involving the reduction of $[(C_5Me_5)IrCl_2]_2$ with LiAlH₄ in a 5% Et₂O/hexane solvent mixture. Following a methanol quench, product 1 is extracted from the residue and isolated in 50% yield. Under these conditions, only a trace (~7%) of the tetrahydride $(C_5Me_5)IrH_4$ is formed and is removed by washing with hexane. The structure of the hexahydride was proposed as $[(C_5Me_5)IrH_2]_2(\mu$-H$)_2$, as the ¹H NMR spectrum shows two broad hydride resonances in a 2:4 ratio at low temperature (–120 °C).[14]

Heating a solution of 1 in neat thiophene containing excess *tert*-butylethylene to 60 °C results in the formation of a green solution. Removal of the volatiles under vacuum followed by chromatography on neutral alumina allows isolation of a dark green product. The ¹H NMR spectrum of this material shows a large singlet for the C₅Me₅ ligands at δ 1.69 (30 H) and three multiplets at 1.34, 1.93, and 3.81 of area 2 H each. The product was formulated as $[(C_5Me_5)Ir]_2(\mu$-S$)(\mu$-1,2-η^2-3,4-η^2-C$_4$H$_6)$ (2) in which both the sulfide and the butadiene ligands bridge the two metal centers (eq 1). The isolated yield is 30% in neat
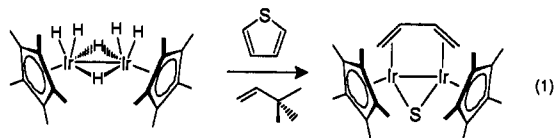
thiophene as solvent and somewhat smaller if cyclohexane is used as solvent. The hydrogenated olefin neohexane can be identified in the crude reaction mixture by GC–MS.

Proof of this formulation comes from the single crystal X-ray structural study carried out in accord with the parameters listed in Table 1. Examination of a light green plate revealed a monoclinic C-centered cell with eight molecules of dinuclear complex 2 per unit cell. The structure was solved in space group *Cc* with two independent molecules in the asymmetric unit. An ORTEP drawing of one of these is shown in Figure 1. The molecule contains a symmetrically bridging butadiene ligand in an s-cis configuration, with one double bond symmetrically coordinated to each metal center (d_{Ir-C} = 2.19–2.24 Å). The sulfur also symmetrically bridges the metal centers in the endo region of the butadiene ligand. The butadiene and Ir₂S planes are nearly coplanar, subtending an angle of only 12°. The Ir–Ir bond distance of 2.818(2) Å lies in the typical range for an Ir–Ir single bond (cf. 2.823 Å in $[(C_5Me_5)IrH]_2(\mu$-BH$_4)(\mu$-H$)$[14]), indicative of substantial metal–metal interaction. The sulfur-terminal carbon distances of >3 Å leave no doubt that both C–S bonds have been cleaved in 2. Fractional coordinates are listed in Table 2 and selected distances and angles are given in Table 3.

Complex 2 reacts with CO to give equal quantities of free butadiene and a new complex identified as $[(C_5Me_5)Ir(CO)]_2$-$(\mu$-S$)$ (3). 3 is produced in 70% NMR yield based upon internal cyclohexane standard and can be isolated in 44% yield as dark red crystals. The terminal CO ligands display an absorption at 1929 cm⁻¹ in the IR spectrum.

A single crystal X-ray structural study of 3 showed the molecule to crystallize in monoclinic space group *C2/c* with Z = 4, indicating that the molecule must sit on a 2-fold crystallographic axis. Patterson map solution and full anisotropic refinement led to the structure shown in Figure 2, displaying a trans relationship between the two CO ligands relative to the Ir₂S framework. These CO ligands are nearly perfectly perpendicular to the Ir₂S plane

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Table 1. Crystallographic Data for Compounds

|	$[(C_5Me_5)Ir]_2(\mu$-S$)(\mu$-C$_4$H$_6)$	$[(C_5Me_5)Ir]_2(\mu$-S$)(CO)_2$
	Crystal Parameters	
formula	Ir₂SC₂₄H₃₆	Ir₂SO₂C₂₂H₃₀
formula wt	741.05	742.98
cryst syst	monoclinic	monoclinic
space group (No.)	*Cc* (9)	*C2/c* (15)
Z	8	4
a, Å	8.828(8)	11.404(5)
b, Å	14.132(3)	13.927(4)
c, Å	37.889(10)	14.047(3)
β, deg	96.76(5)	97.34(2)
V, Å³	4694.0(7.3)	2212.8(2.1)
ρ_{calc}, g cm⁻³	2.10	2.23
cryst dimens, mm	0.60 × 0.26 × 0.05	0.22 × 0.19 × 0.11
T, °C	–20	–20
	Measurement of Intensity Data	
radiation (monochrome)	Mo, 0.710 73 Å (graphite)	Mo, 0.710 73 Å (graphite)
scan type	2θ/ω	2θ/ω
scan rate, deg/min	2–16.5	2–16.5
2θ range, deg	4–50	4–50
data collected	+*h*,+*k*,±*l*	+*h*,+*k*,±*l*
no. of data collected	4618	2147
no. of unique data $F^2 > 3\sigma(F^2)$	3572	1316
no. of params varied	280	123
μ, cm⁻¹	113.83	120.80
$R(F_o)$	0.0485	0.0369
$R_w(F_o)$	0.0536	0.0406
goodness of fit	1.87	1.27
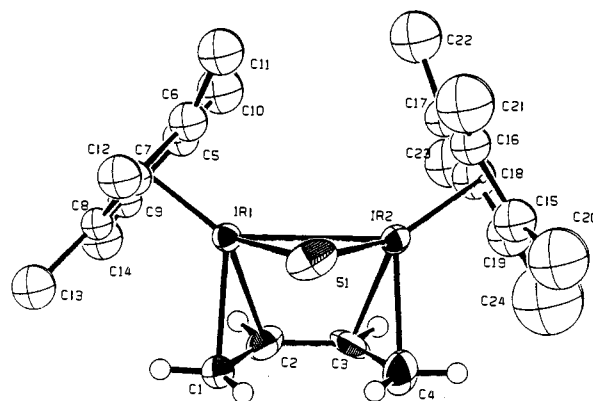
Figure 1. ORTEP drawing of $[(C_5Me_5)Ir]_2(\mu$-S$)(\mu$-1,2-η^2-3,4-η^2-C$_4$H$_6)$. Ellipsoids are shown at the 50% probability level.

(92.8°). The Ir–Ir distance of 2.734(1) Å is indicative of a strong metal–metal single bond interaction. Fractional coordinates are listed in Table 4 and selected distances and angles are given in Table 5.

A labeling study using thiophene-*d₄* was performed in order to confirm the origin of the butadiene ligand. Reaction of 1 with thiophene-*d₄* and *tert*-butylethylene at 60 °C leads to the formation of product 2-*d₄*, as determined by ²H NMR spectroscopy. Resonances are seen at δ 3.81, 1.93, and 1.34 in a 2:1:1 ratio, indicating that hydrogen has been incorporated into both the endo (δ 1.34) and exo (δ 1.93) terminal butadiene positions. That the product was actually 2-*d₄* and not a mixture of 2-*d₃* and 2-*d₅* was determined by displacement of the coordinated butadiene with CO and examination by GC–MS. The appearance of butadiene-*d₄* in the mass spectrum (*m/e* = 58) but no *d₃* or *d₅* product confirmed that the coordinated ligand was formed from the thiophene C₄D₄ framework plus two hydride ligands from the iridium. Unfortunately, these data do not distinguish between a 1:1 mixture of 1-*endo*-2,3,4-*endo*-C₄H₂D₄ + 1-*exo*-2,3,4-*exo*-C₄H₂D₄ or a single isomer, 1-*endo*-2,3,4-*exo*-C₄H₂D₄ (eq 2).

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(2)
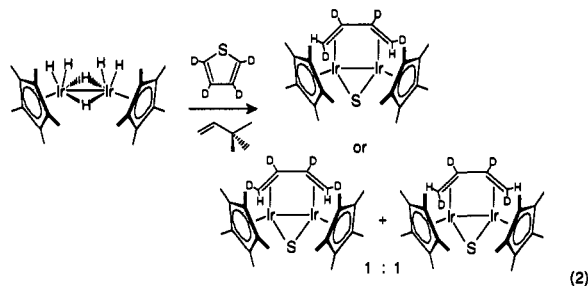
Reaction of **2** with hydrogen occurs at ≥1 atm and 60 °C. Butane can be observed by ¹H NMR spectroscopy, formed in up to 40% yield (GC). The fate of the iridium is uncertain, as multiple iridium products were formed based upon the large number of C₅Me₅ singlet resonances in the ¹H NMR spectrum of the residue. None of the cubane [(C₅Me₅)IrS]₄ was observed,[15] but a small quantity of the known[16] compound (C₅Me₅)IrH₄ could be identified. These reactions are summarized in Scheme 1.

Upon heating of **1** at 45 °C under vacuum, hydrogen is lost and a new complex characterized as [(C₅Me₅)IrH₂]₂ (**4**) is produced which can be isolated by chromatography on neutral alumina. This dimer reacts with PMe₃ to give 2 equiv of (C₅-Me₅)Ir(PMe₃)H₂.[17] At intermediate reaction times, the mono-PMe₃ adduct (C₅Me₅)₂Ir₂H₄(PMe₃) is observed prior to formation of (C₅Me₅)Ir(PMe₃)H₂. Complex **4** displays a singlet in the ¹H NMR spectrum at δ 1.82 for the C₅Me₅ groups and two broad hydrogen resonances at δ -1.08 and -20.23 (2 H each) for the hydride ligands, which are apparently fluxional.

Reaction of **4** with thiophene and *tert*-butylethylene at 25 °C for 24 h results in the formation of three species as determined by ¹H NMR spectroscopy following removal of the volatile reactants under vacuum and addition of C₆D₆. Decoupling experiments were used to determine the connectivity of the carbon chains associated with these resonances. The major species formed (**A**, 55%) shows two broad hydride resonances at δ -19.75 (1 H) and -16.57 (1 H) and four olefinic resonances (1 H each) at δ 9.31 (d, J = 10.5 Hz, H$_a$), 6.76 (ddd, J = 9.2, 7.0, 1.3 Hz, H$_c$), 6.65 (dd, J = 10.5, 7.0 Hz, H$_b$), and 5.62 (d, J = 9.2 Hz, 1 H$_d$), as well as two distinct C₅Me₅ resonances (δ 1.95 and 1.74, 15 H each). The second dinuclear species formed (**B**, 7%) shows a single sharp hydride resonance at δ -17.05 (1 H) and five coupled olefinic resonances (1 H each) at δ 8.10 (d, J = 5.7 Hz, H$_a$), 5.06 (t, J = 5.7 Hz, H$_b$), 3.21 (t, J = 5.2 Hz, H$_c$), 3.06 (ddd, J = 13.5, 5.2, 2.6 Hz, H$_d$), and 2.72 (dd, J = 13.1, 1.3 Hz, H$_{d'}$). Two distinct C₅Me₅ resonances are seen for this species also (δ 1.84 and 1.61, 15 H each). The third species (**C**, 38%) shows multiplets at δ 6.40 (μ, 1 H$_b$), 6.14 (dt, J = 9.2, 2.2 Hz, 1 H$_a$), 5.44 (m, 1 H$_c$), and 0.88 (m, 2 H$_{a,a'}$). A single C₅Me₅ resonance is seen at δ 1.88 (15 H), indicative of a mononuclear compound. A hydride doublet is also observed at δ -17.02 (J = 3.5 Hz, 1 H). Reasonable suggestions for the structures of these complexes are given in Scheme 2. Complex **A** would have two distinct hydride ligand resonances, two distinct C₅Me₅ resonances, and four olefinic multiplet resonances, as observed. Complex **B** would have one hydride ligand resonance, two downfield resonances for the uncoordinated olefin hydrogen atoms, and three upfield resonances for the metal-coordinated olefin hydrogen atoms.

Heating of this solution to 65 °C with monitoring by ¹H NMR spectroscopy shows the disappearance of **A** and the growth of **2**. Intermediate **B** is seen to increase to ~20% of the total and then decrease to zero over the course of the reaction (~12 h). The mononuclear species **C** rapidly disappears but is not believed to produce **2** as the yield of **2** more closely corresponds to the quantity of **A** initially present (Figure 3). A similar sequence of events
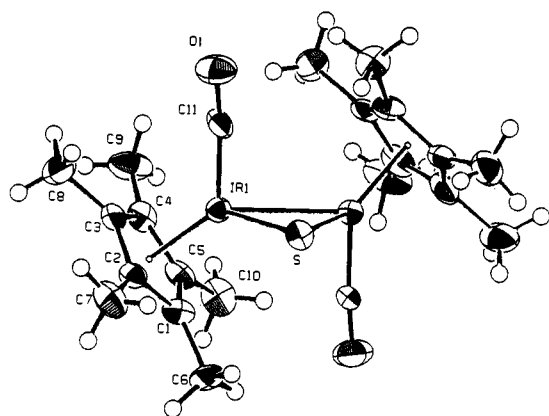
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Table 2. Positional Parameters and B(eq) for [(C₅Me₅)Ir]₂(μ-S)(μ-C₄H₆) (**2**)

atom	x	y	z	B_{eq} (Å²)
Ir(1)	0.5880	0.137 93(6)	0.1679	1.92(4)
Ir(2)	0.6193(1)	0.083 80(7)	0.097 52(4)	2.10(4)
Ir(3)	0.7736(1)	0.333 74(7)	0.906 17(4)	2.07(4)
Ir(4)	0.6720(1)	0.387 83(6)	0.835 76(4)	1.93(4)
S(1)	0.587(1)	0.2356(5)	0.1187(3)	4.1(4)
S(2)	0.721(1)	0.4851(5)	0.8846(3)	4.0(4)
C(1)	0.835(3)	0.177(2)	0.1796(8)	2.5(5)
C(2)	0.824(3)	0.078(2)	0.1677(8)	3(1)
C(3)	0.840(3)	0.051(2)	0.1320(9)	3(1)
C(4)	0.865(4)	0.120(2)	0.1029(9)	4(2)
C(5)	0.432(3)	0.046(2)	0.1913(8)	3.0(5)
C(6)	0.360(4)	0.131(2)	0.176(1)	3.5(6)
C(7)	0.436(3)	0.208(2)	0.1960(8)	2.8(5)
C(8)	0.543(3)	0.174(2)	0.2215(7)	2.3(5)
C(9)	0.544(3)	0.074(2)	0.2193(8)	2.6(5)
C(10)	0.386(4)	-0.054(2)	0.181(1)	4.9(8)
C(11)	0.221(4)	0.137(3)	0.154(1)	4.9(8)
C(12)	0.386(4)	0.310(2)	0.190(1)	4.4(7)
C(13)	0.640(4)	0.232(2)	0.249(1)	4.5(7)
C(14)	0.649(4)	0.007(2)	0.242(1)	4.1(6)
C(15)	0.588(4)	0.071(2)	0.042(1)	4.2(7)
C(16)	0.433(3)	0.078(2)	0.0549(9)	3.8(6)
C(17)	0.418(3)	-0.004(2)	0.0749(9)	3.4(6)
C(18)	0.560(4)	-0.054(2)	0.073(1)	4.4(7)
C(19)	0.653(4)	-0.012(2)	0.057(1)	4.7(7)
C(20)	0.628(6)	0.149(4)	0.016(2)	9(1)
C(21)	0.319(5)	0.150(3)	0.044(1)	8(1)
C(22)	0.277(4)	-0.042(3)	0.085(1)	6(1)
C(23)	0.577(4)	-0.155(3)	0.095(1)	5.7(9)
C(24)	0.799(7)	-0.049(5)	0.050(2)	12(2)
C(25)	1.013(3)	0.367(2)	0.902(1)	5(2)
C(26)	0.963(3)	0.299(2)	0.8723(7)	3(1)
C(27)	0.905(3)	0.327(2)	0.836(1)	4(2)
C(28)	0.906(3)	0.422(2)	0.8243(8)	3(1)
C(29)	0.594(4)	0.245(2)	0.929(1)	3.8(6)
C(30)	0.636(4)	0.324(2)	0.950(1)	4.7(7)
C(31)	0.798(4)	0.318(2)	0.962(1)	4.2(7)
C(32)	0.846(4)	0.237(2)	0.946(1)	4.5(7)
C(33)	0.731(3)	0.192(2)	0.9290(8)	2.9(5)
C(34)	0.444(5)	0.209(3)	0.917(1)	6(1)
C(35)	0.526(7)	0.400(4)	0.956(2)	11(2)
C(36)	0.877(6)	0.390(3)	0.988(1)	8(1)
C(37)	1.003(5)	0.199(4)	0.958(1)	8(1)
C(38)	0.737(4)	0.096(2)	0.910(1)	4.1(7)
C(39)	0.431(3)	0.382(2)	0.8279(9)	3.2(6)
C(40)	0.494(3)	0.295(2)	0.812(1)	3.6(6)
C(41)	0.581(3)	0.321(2)	0.7860(7)	2.1(4)
C(42)	0.574(3)	0.425(2)	0.7834(9)	3.5(6)
C(43)	0.488(3)	0.458(2)	0.8085(8)	2.6(5)
C(44)	0.322(4)	0.387(2)	0.853(1)	4.2(7)
C(45)	0.450(4)	0.197(2)	0.822(1)	4.3(7)
C(46)	0.665(4)	0.262(2)	0.762(1)	4.1(6)
C(47)	0.648(4)	0.478(2)	0.754(1)	4.6(7)
C(48)	0.446(4)	0.564(2)	0.814(1)	4.1(7)

is observed upon reaction of **1** with thiophene and *tert*-butylethylene at 60–65 °C, with resonances for **1** diminishing as those of **A**, **B**, and **C** grow in. These resonances eventually go away as those for **2** appear. Reaction of **4** with thiophene in the absence of *tert*-butylethylene results in the formation of only small amounts of **A** and **C** and substantial amounts of (C₅Me₅)-IrH₄.

Discussion

The reaction of **1** or **4** with thiophene occurs in the presence of the hydrogen acceptor *tert*-butylethylene to give the desulfurized adduct **2** in which both C–S bonds have been cleaved. Little reaction occurs in the absence of *tert*-butylethylene, and the highest yields of **2** are obtained if neat thiophene is used as solvent. In the absence of thiophene, **1** loses hydrogen slowly at 45 °C to give a species identified as [(C₅Me₅)IrH₂]₂. Presumably, this species must then undergo further loss of hydrogen in order to react with the thiophene since *tert*-butylethylene increases the yield of C–S cleavage product **2**.

Hydrodesulfurization of Thiophene by [(CH₅Me₅)IrH₃]₂

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Table 3. Selected Distances (Å) and Angles (deg) for **2**

	molecule 1		molecule 2
		Distances	
Ir(1)–Ir(2)	2.818(2)	Ir(3)–Ir(4)	2.818(2)
Ir(1)–S(1)	2.320(9)	Ir(3)–S(2)	2.317(7)
Ir(2)–S(1)	2.318(8)	Ir(4)–S(2)	2.304(9)
Ir(1)–C(1)	2.24(3)	Ir(3)–C(25)	2.19(3)
Ir(1)–C(2)	2.24(3)	Ir(3)–C(26)	2.27(3)
Ir(2)–C(3)	2.26(3)	Ir(4)–C(27)	2.22(3)
Ir(2)–C(4)	2.22(3)	Ir(4)–C(28)	2.21(3)
C(1)–C(2)	1.46(4)	C(25)–C(26)	1.50(5)
C(2)–C(3)	1.43(4)	C(26)–C(27)	1.46(4)
C(3)–C(4)	1.51(4)	C(27)–C(28)	1.42(4)
		Angles	
Ir(2)–Ir(1)–S(1)	52.5(2)	Ir(4)–Ir(3)–S(2)	52.2(2)
Ir(2)–Ir(1)–C(1)	93.0(7)	Ir(4)–Ir(3)–C(25)	94(1)
Ir(2)–Ir(1)–C(2)	72.6(8)	Ir(4)–Ir(3)–C(26)	72.3(7)
S(1)–Ir(1)–C(1)	85.6(7)	S(2)–Ir(3)–C(25)	85.6(8)
S(1)–Ir(1)–C(2)	97.7(8)	S(2)–Ir(3)–C(26)	97.3(8)
C(1)–Ir(1)–C(2)	38(1)	C(25)–Ir(3)–C(26)	39(1)
Ir(1)–Ir(2)–S(1)	52.6(2)	Ir(3)–Ir(4)–S(2)	52.6(2)
Ir(1)–Ir(2)–C(3)	71.5(8)	Ir(3)–Ir(4)–C(27)	72(1)
Ir(1)–Ir(2)–C(4)	93.0(9)	Ir(3)–Ir(4)–C(28)	92.6(7)
S(1)–Ir(2)–C(3)	97.0(7)	S(2)–Ir(4)–C(27)	98(1)
S(1)–Ir(2)–C(4)	84.8(9)	S(2)–Ir(4)–C(28)	86(1)
C(3)–Ir(2)–C(4)	39(1)	C(27)–Ir(4)–C(28)	37(1)
Ir(1)–S(1)–Ir(2)	74.8(2)	Ir(3)–S(2)–Ir(4)	75.1(2)
Ir(1)–C(1)–C(2)	71(1)	Ir(3)–C(25)–C(26)	73(1)
Ir(1)–C(2)–C(1)	71(2)	Ir(3)–C(26)–C(25)	67(2)
Ir(1)–C(2)–C(3)	108(2)	Ir(3)–C(26)–C(27)	106(2)
C(1)–C(2)–C(3)	123(3)	C(25)–C(26)–C(27)	124(3)
Ir(2)–C(3)–C(2)	108(2)	Ir(4)–C(27)–C(26)	109(2)
Ir(2)–C(3)–C(4)	69(2)	Ir(4)–C(27)–C(28)	71(2)
C(2)–C(3)–C(4)	124(3)	C(26)–C(27)–C(28)	123(3)
Ir(2)–C(4)–C(3)	72(2)	Ir(4)–C(28)–C(27)	72(2)

Table 4. Positional Parameters and *B*(eq) for [(C₅Me₅)Ir]₂(μ-S)(CO)₂ (**3**)

atom	*x*	*y*	*z*	B_{eq} (Å²)
Ir(1)	0.017 56(5)	0.164 66(4)	0.155 54(4)	2.17(2)
S	0	0.0297(3)	1/4	2.7(2)
O(1)	−0.2365(8)	0.1631(8)	0.0810(8)	4.6(5)
C(1)	0.217(1)	0.170(1)	0.152(1)	2.5(5)
C(2)	0.155(1)	0.135(1)	0.061(1)	2.6(6)
C(3)	0.077(1)	0.210(1)	0.023(1)	3.3(7)
C(4)	0.090(1)	0.290(1)	0.083(1)	2.9(6)
C(5)	0.178(1)	0.267(1)	0.161(1)	2.6(6)
C(6)	0.311(1)	0.115(1)	0.212(1)	3.3(6)
C(7)	0.177(1)	0.037(1)	0.017(1)	4.1(8)
C(8)	0.006(1)	0.205(1)	−0.079(1)	4.8(8)
C(9)	0.030(1)	0.386(1)	0.065(1)	4.9(9)
C(10)	0.225(1)	0.332(1)	0.243(1)	3.6(6)
C(11)	−0.139(1)	0.166(1)	0.114(1)	3.1(6)

Table 5. Selected Distances (Å) and Angles (deg) for **3**

		Distances	
Ir(1)–Ir(1)	2.734(1)	Ir(1)–C(11)	1.80(1)
Ir(1)–S	2.324(4)	O(1)–C(11)	1.15(1)
		Angles	
Ir(1)–Ir(1)–S	53.98(7)	Ir(1)–S–Ir(1)	72.0(1)
Ir(1)–Ir(1)–C(11)	92.8(4)	Ir(1)–C(11)–O(1)	174(1)
S–Ir(1)–C(11)	92.2(5)		

Scheme 1

Scheme 2

Figure 2. ORTEP drawing of [(C₅Me₅)Ir]₂(μ-S)(CO)₂. Ellipsoids are shown at the 50% probability level.

Scheme 2 shows a possible sequence that would lead to **2**, although this proposal must be regarded as speculative in light of the limited quantity of supporting evidence. The first steps form [(C₅Me₅)IrH]₂, which then reacts with thiophene by coordination and insertion into the C–S bond to give species **A**. The four low-field resonances of **A** are consistent with this structure, in which none of the olefinic carbons are bound to the metal and in which the hydride ligands lie in different environments. A similar C–S insertion adduct with a bridging sulfur is seen in Fe₂(CO)₆(SC₈H₆)[9a], [(C₅Me₅)Rh]₂(SC₄Me₄),[18] and Cp₂-Co₂(SC₄H₄).[19] Reductive elimination of this vinyl hydride intermediate leads to structure **B**, in which the terminal olefin of the butadienylthiolate ligand is bound to the second iridium. Note that this reductive elimination will result in a transfer of hydride ligand from the metal to the endo site of the butadiene. Insertion of the olefin adjacent to sulfur into the iridium–hydride bond

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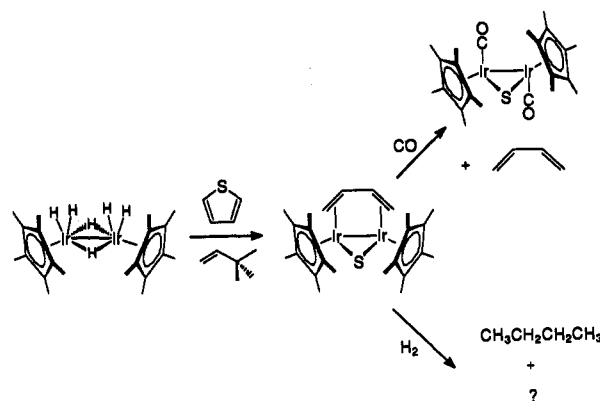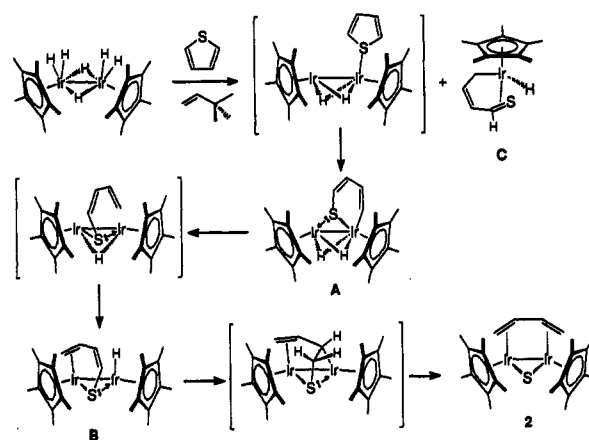
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leaves the iridium attached to the β-carbon. Finally, a β-elimination of the C–S bond leads directly to the formation of the butadiene complex **2** with one double bond bound to each metal center. Furthermore, this Ir–H insertion/C–S elimination sequence will regiospecifically introduce a hydrogen from the metal into the exo site of the butadiene ligand. This sequence predicts that the product of the deuterium labeling experiment described earlier will be the 1-*endo*-2,3,4-*exo*-C₄H₂D₄ butadiene isomer and is consistent with the experimental observations.
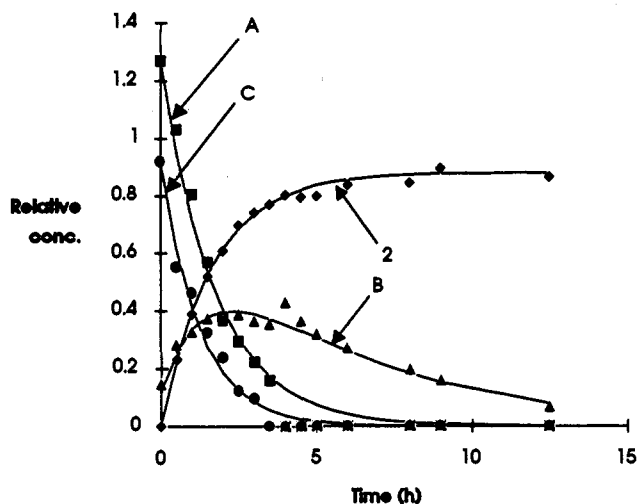
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Figure 3. Distribution of species in the reaction of [(C₅Me₅)IrH₂]₂ with thiophene and *tert*-butylethylene at 65 °C.

This mechanistic sequence involving C–S cleavage to give a butadiene thiolate followed by a second C–S hydrogenolysis is similar to that proposed in heterogeneous HDS systems by Kwart, Schuit, and Gates.[20] The fact that small amounts of butadiene have been observed while no tetrahydrothiophene has been produced has led to the conclusion that butadiene is an intermediate in HDS over molybdenum surfaces.[21] Also of relevance to the current study is the observation by Gellman, Neiman, and Somorjai of the formation of butadiene from thiophene over a Mo(100) crystal surface, which led them to conclude that butadiene is the primary product in HDS.[22] Kinetic studies of this system also led to the conclusion that a rate-limiting step was occurring prior to hydrogenation (the rates were independent of hydrogen pressure), and consequently thiophene adsorption or a reaction step leading to the species that is then hydrogenated to butadiene must be rate limiting. From our studies, the insertion of the iridium into the C–S bond could be just such a step, as intermediate A in Scheme 2 rapidly goes on to form **2** at 65 °C.

The displacement of the butadiene by CO leads to the simple substitution product, but the geometry of the dicarbonyl **3** is different from that of **2** in that the CO ligands are trans to one another relative to the Ir₂S framework, whereas the butadiene coordination was required to be cis. The reaction of **2** with hydrogen to give butane is not well understood mechanistically, but one can imagine a sequence in which one end of the olefin dissociates, allowing hydrogen to add to the vacant site on iridium, leading ultimately to hydrogenation of the diene by the usual insertion/reductive elimination reactions.

Conclusions

In summary, a binuclear homogeneous polyhydride complex has been used for the hydrodesulfurization of thiophene. An intermediate in which both thiophene C–S bonds are cleaved and butadiene is bound to the dinuclear unit in an η^2,η^2-fashion has been characterized. Butadiene can be either displaced with a ligand such as CO or further hydrogenated using H₂ to give butane. These observations support the notion that two metal centers may be required for the cleavage of both thiophenic C–S bonds.

Experimental Section

General. All operations and routine manipulations were performed under a nitrogen atmosphere, either on a high-vacuum line using modified Schlenk techniques or in a Vacuum Atmospheres Corporation Dri-lab. Tetrahydrofuran (THF), benzene, diethyl ether, and toluene were distilled

from dark purple solutions of benzophenone ketyl. Hexanes were stirred over concentrated H₂SO₄ overnight, washed with aqueous KMnO₄ and water, and then distilled from a dark purple solution of benzophenone ketyl. Benzene-d_6 and toluene-d_8 were distilled under vacuum from dark purple solutions of benzophenone ketyl and stored in ampules with Teflon-sealed vacuum line adapters. Neutral alumina was heated to 200 °C under vacuum for 2 days and stored under nitrogen. Trimethylphosphine was purchased from Strem and used as received. Methanol, lithium aluminum hydride (LAH), and 3,3-dimethyl-1-butene were purchased from Aldrich Chemical Co. and used as received. Thiophene, 99+%, was purchased from Aldrich Chemical Co. and purified as previously reported.[23] [(C₅Me₅)IrCl₂]₂[24] and thiophene-d_4[25] were prepared as previously described.

All ¹H, ¹³C, and ³¹P NMR spectra were recorded on a Bruker AMX400 NMR spectrometer. All chemical shifts are reported in ppm (δ) relative to tetramethylsilane, referenced to the chemical shifts of residual solvent resonances (¹H, ¹³C) or 85% H₃PO₄ (³¹P). GC analyses were done using a Hewlett-Packard 5710A gas chromatograph, and GC–MS spectra were recorded using a Hewlett-Packard 5890 Series II gas chromatograph and a Hewlett-Packard 5970 Series mass selective detector. An Enraf-Nonius CAD4 diffractometer was used for X-ray crystal structure determination. IR spectra were recorded on a Mattson Galaxy 6020 series FTIR. Elemental analyses were obtained from Desert Analytics.

Preparation of [(C₅Me₅)IrH₃]₂. [(C₅Me₅)IrCl₂]₂ (613 mg, 0.769 mmol) and LiAlH₄ (234 mg, 6.17 mmol) were added together in a 250-mL three-neck flask fitted with a rubber septum, a nitrogen inlet, and a gas bubbler, and 100 mL of 5% diethyl ether/hexanes was added. The resulting orange suspension was stirred for 20 h at room temperature. The resulting light green-gray mixture was cooled to 0 °C, and 9 mL of degassed methanol was added dropwise. After the addition of the methanol, the solution was warmed to room temperature and stirred for 40 min, by which time the solution had turned brown-black. The solvent was removed under vacuum and the residue extracted with 3 × 30 mL of benzene. The extracts were filtered through a frit packed with neutral alumina, and the resulting orange-red solution was collected. The benzene was removed under vacuum and the orange powder chromatographed on neutral alumina (activity V) using benzene as an eluant (2-cm × 15-cm column). A ¹H NMR spectrum in C₆D₆ showed a 14:1 ratio of [(C₅Me₅)IrH₃]₂:(C₅Me₅)IrH₄. The benzene was removed and the resulting orange powder washed with 6 × 1 mL of hexanes to remove any (C₅Me₅)IrH₄, giving pure [(C₅Me₅)IrH₃]₂ (226 mg, 47%). For (C₅Me₅)-IrH₄, ¹H NMR (C₆D₆): δ 1.98 (s, 15 H), –15.43 (s, 4 H). For [(C₅Me₅)IrH₃]₂, ¹H NMR (C₆D₆): δ 1.97 (s, 30 H), –14.77 (s, 6 H).

Preparation of [(C₅Me₅)IrH₂]₂. [(C₅Me₅)IrH₃]₂ (246 mg, 0.372 mmol) was dissolved in 2 mL of benzene and placed into a Schlenk tube. The benzene was removed under reduced pressure, and the resulting orange powder was heated between 40–45 °C for 6 days under a dynamic vacuum. A ¹H NMR spectrum of this solid showed an 85% conversion to [(C₅Me₅)IrH₂]₂. Chromatography of the black-red residue on a neutral alumina column using benzene as the eluant produced an orange band that was discarded and a second black-red band containing the product. The solvent was removed from this fraction under vacuum and the resulting black powder recrystallized by dissolving in toluene, layering the solution with hexane, and placing the solution in a –30 °C freezer overnight. The mother liquor was decanted, leaving black-red crystals of pure [(C₅Me₅)IrH₂]₂ (84 mg, 41%). ¹H NMR (400 MHz, toluene-d_8, 25 °C): δ 1.82 (s, 30 H), –1.08 (br s, 2 H), –20.23 (br s, 2 H). ¹H NMR (400 MHz, toluene-d_8, –70 °C) δ 1.79 (s, 30 H), –0.59 (br t, J = 6.2 Hz, 2 H), –19.98 (t, J = 6.2 Hz, 2 H). ¹³C{¹H} NMR (100 MHz, C₆D₆, 25 °C): δ 90.73 (s, C₅Me₅), 11.49 (s, C₅*Me₅*). IR(KBr): 2065 ($\nu_{Ir-H\ terminal}$), 1056 cm⁻¹ ($\nu_{Ir-H\ bridging}$). Anal. Calcd (found) for Ir₂C₂₀H₃₄: C, 36.46 (35.43); H, 5.20 (5.35).

Preparation of [(C₅Me₅)Ir]₂(μ-S)(μ-1,2-η^2-3,4-η^2-C₄H₆). [(C₅Me₅)-IrH₃]₂ (144 mg, 0.218 mmol) and 3,3-dimethyl-1-butene (2 mL, 15.5 mmol) were dissolved in 12 mL of thiophene and placed in an ampule fitted with a Teflon stopcock. The orange solution was heated at 60 °C for 30 h, by which time it had turned black. The thiophene and other volatiles were evaporated under vacuum to yield a black residue that was chromatographed on a neutral alumina column. Benzene was used to elute a red-brown band that was discarded. 10% THF/benzene was used to elute a second dark green band. Removal of the solvent under vacuum produced a residue that was recrystallized from a toluene/hexane solvent

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system at -30 °C. The resulting green powder that formed was washed with 3 × 1 mL of hexanes to give pure product (47 mg, 29%). ¹H NMR (400 MHz, C_6D_6, 25 °C): δ 3.81 (m, 2 H), 1.93 (br d, J = 8.5 Hz, 2 H), 1.69 (s, 30 H), 1.34 (br d, J = 7.0 Hz, 2 H). ¹³C{¹H} NMR (100 MHz, C_6D_6, 25 °C): δ 91.98 (s, C_5Me_5), 31.80 (s, C_2, C_3), 27.83 (s, C_1, C_4), 10.15 (s, C_5Me_5). Anal. Calcd (found) for $Ir_2SC_{24}H_{36}$: C, 38.90 (38.39); H, 4.90 (4.84); S, 4.33 (3.90).

Reaction of [(C5Me5)IrH3]2 with Thiophene-d_4 and 3,3-Dimethyl-1-butene. [(C5Me5)IrH3]2 (12 mg, 0.018 mmol) and 3,3-dimethyl-1-butene were dissolved in 0.5 mL of thiophene-d_4 and placed in a Teflon-capped resealable NMR tube. The solution was heated at 60 °C for 15 h. The volatiles were removed under reduced pressure, and 0.5 mL of C_6H_6 condensed into the NMR tube. The ²H NMR spectrum showed three resonances at δ 3.81 (2 D), 1.92 (1 D), and 1.33 (1 D), which matched with the resonances of **2** when the reaction was run using thiophene-d_0. The solvent was then removed from the NMR sample and the residue chromatographed through a pipet packed with 2 in. of neutral alumina. The first red band was eluted with benzene and the second green band eluted with 10% THF/benzene. The second band was collected and the solvent removed under reduced pressure. C_6H_6 (0.5 mL) was condensed into the NMR tube, and ¹H and ²H NMR spectra of **2-d_4** were recorded, showing no change in the resonances or their ratios compared with the crude product. CO (1 atm) was placed over the NMR sample, which was then heated at 60 °C for 16 h. The ²H NMR spectrum showed three resonances, corresponding to free butadiene in a 2:1:1 ratio. The presence of butadiene-d_4 was confirmed by GC–MS with a parent ion peak at m/e = 58. No other peaks corresponding to butadiene-d_1, -d_2, -d_3, -d_5, or -d_6 were observed.

Hydrogenation of [(C5Me5)Ir]2(μ-S)(μ-1,2-η^2-3,4-η^2-C4H6). [(C5Me5)Ir]2(μ-S)(μ-1,2-η^2-3,4-η^2-C4H6) (36 mg, 0.049 mmol) and cyclohexane (10 μL, 0.093 mmol, internal standard) were dissolved in 0.7 mL of benzene and loaded into a Parr bomb reactor. The reactor was pressurized to 500 psi with H_2 and heated at 60 °C for 2 days. The entire contents of the bomb were then expanded into an evacuated 6.8-L vessel. Gas samples which were withdrawn for GC analyses showed a 0.40 mole equivalent of butane produced per mole of starting metal complex. The ¹H NMR spectrum of the residue in C_6D_6 showed ~10% (C5Me5)IrH4 and no other identifiable organometallic products.

In a separate experiment, **2** (~3 mg) was dissolved in C_6D_6 (0.5 mL) and placed under 1 atm H_2 in an NMR tube. Heating of the sample to 60 °C for 36 h showed the formation of butane in 15% yield.

Carbonylation of [(C5Me5)Ir]2(μ-S)(μ-1,2-η^2-3,4-η^2-C4H6). [(C5Me5)-Ir]2(μ-S)(μ-1,2-η^2-3,4-η^2-C4H6) (9 mg, 0.012 mmol) and cyclohexane (5 μL, 0.046 mmol) were dissolved in 0.5 mL of C_6D_6 and placed into a Teflon-capped resealable NMR tube. CO (1 atm) was placed over the solution, and the sample was heated at 65 °C for 18 h. The ¹H NMR spectrum in C_6D_6 showed a 1:1 ratio of free butadiene:[(C5Me5)IrCO]2-(μ-S) in a 73% yield versus cyclohexane. The presence of butadiene was confirmed by GC–MS.

The experiment was repeated on a preparative scale, using 25 mg (0.034 mmol) of [(C5Me5)Ir]2(μ-S)(μ-1,2-η^2-3,4-η^2-C4H6) in 8 mL of benzene. The solution was heated at 60 °C for 9 h under a slow purge of CO, during which time the solution became yellow-brown. The solvent was removed under reduced pressure and the brown residue taken up in 1.5 mL of toluene. The suspension was cooled to -30 °C for 5 h and filtered, and the brown powder was washed with 2 × 1 mL of hexanes to give pure product (11 mg, 44%). ¹H NMR (400 MHz, C_6D_6, 25 °C): δ 1.88 (s, 30 H). ¹³C{¹H} NMR (100 MHz, C_6D_6, 25 °C): δ 177.33 (s, CO), 97.35 (s, C_5Me_5), 10.29 (s, C_5Me_5). IR (KBr): 1929 cm⁻¹. Anal. Calcd (found) for $Ir_2O_2SC_{22}H_{30}$: C, 35.56 (35.18); H, 4.07 (3.85).

Reaction of [(C5Me5)IrH2]2 with P(CH3)3. [(C5Me5)IrH2]2 (7 mg, 0.011 mmol) was dissolved in 0.5 mL of C_6D_6 and pipetted into an NMR tube equipped with a Teflon valve. P(CH3)3 (3 μL, 0.029 mmol) was then added to the solution. Within 5 min the solution changed color from dark red to orange. The ¹H NMR spectrum showed two products, [(C5-Me5)Ir]2(PMe3)H4 and (C5Me5)Ir(PMe3)H2, in a 9:1 ratio. After 20 min, the ratio had changed to 0.77:1. After 5 h, the only product remaining was (C5Me5)Ir(PMe3)H2. For [(C5Me5)Ir]2(PMe3)H4, ¹H NMR (400 MHz, C_6D_6, 25 °C): δ 2.31 (s, 15 H), 2.01 (d, J = 1.7 Hz, 15 H), 1.34 (d, J = 10 Hz, 9 H), -18.80 (d, J = 14 Hz, 4 H). ³¹P{¹H} NMR (162 MHz, C_6D_6, 25 °C): δ -43.83 (s).

Observation of Intermediates A and B. [(C5Me5)IrH2]2 (4 mg, 0.006 mmol) was dissolved in 0.3 mL of thiophene, and 0.1 mL of 3,3-dimethyl-1-butene was added to the solution. The solution was pipetted into an NMR tube fitted with a Teflon valve and allowed to sit at 22 °C in the dark for 24 h. The thiophene and other volatiles were removed under vacuum, and 0.5 mL of C_6D_6 was condensed into the NMR tube. The

¹H NMR spectrum showed mostly intermediate **A** and compound **C**. Very little of intermediate **B** was observed at this time. The NMR sample was then heated to 65 °C, and ¹H NMR spectra were recorded every 0.5 h. The ¹H NMR spectra showed the gradual disappearance of intermediate **A** along with the growth and decay of intermediate **B**. The growth of [(C5Me5)Ir]2(μ-S)(μ-1,2-η^2-3,4-η^2-C4H6) was also seen in the ¹H NMR spectra. Complex **C** was seen to go away quickly. The same intermediates were also observed in the reaction of [(C5Me5)IrH3]2 with thiophene and 3,3-dimethyl-1-butene at early reaction times (3–6 h) at 60 °C. Decoupling experiments were used to assign connectivities in **A**, **B**, and **C**. In assigning resonances, H_a refers to the proton attached to the carbon atom α to sulfur, H_b to the proton attached to the carbon atom β to sulfur, etc. For intermediate **A**, ¹H NMR (400 MHz, C_6D_6, 25 °C): δ 9.31 (d, J = 10.5 Hz, 1 H), 6.76 (ddd, J = 1.3, 7.0, 9.2 Hz, 1 H), 6.65 (dd, J = 10.5, 7.0 Hz, 1 H), 5.62 (d, J = 9.2 Hz, 1 H), 1.95 (s, 15 H), 1.74 (s, 15 H), -16.57 (br s, 1 H), -19.75 (br s, 1 H). For intermediate **B**, ¹H NMR (400 MHz, C_6D_6, 25 °C): δ 8.10 (d, J = 5.7 Hz, 1 H), 5.06 (t, J = 5.7 Hz, 1 H), 3.21 (t, J = 5.2 Hz, 1 H), 3.06 (ddd, J = 2.6, 5.2, 13.5, Hz, 1 H), 2.72 (dd, J = 1.3, 13.1 Hz, 1 H), 1.84 (s, 15 H), 1.61 (s, 15 H), -17.05 (d, J = 1.3 Hz, 1 H).

X-ray Structural Determination of [(C5Me5)Ir]2(μ-S)(μ-1,2-η^2-3,4-η^2-C4H6). A small, light green crystal of the complex was mounted on a glass fiber with epoxy and placed in the cold stream (-20 °C) of the diffractometer. Twenty-five reflections with values of χ between 5 and 70° were centered and used for cell determination. Data were collected in a C-centered monoclinic crystal system. Data reduction showed absences consistent with space group Cc with Z = 8, indicating the presence of two independent molecules within the asymmetric unit. The TEXSAN structure solution package was used for solution and refinement of the structure.[26] Solution of the Patterson map allowed placement of the iridium atoms, and use of the program DIRDIF allowed location of all remaining atoms. An absorption correction was applied following isotropic refinement with the program DIFABS. In the final model, hydrogens were placed in idealized positions and only the iridium, sulfur, and butadiene carbon atoms were refined anisotropically. (C1 was left isotropic as anisotropic refinement led to a nonpositive definite ellipsoid.) Data collection and refinement parameters are given in Table 1. Positional parameters are given in Table 2, and selected distances and angles are given in Table 3. The rather large thermal parameters for the C5Me5 methyl groups are interpreted in terms of a rotary thermal motion of the ring rather than disorder of the C5Me5 ring.¶

X-ray Structural Determination of [(C5Me5)IrCO]2(μ-S). A small, dark red crystal of the complex was mounted on a glass fiber with epoxy and placed in the cold stream (-20 °C) of the diffractometer. Twenty-five reflections with values of χ between 5 and 70° were centered and used for cell determination. Data were collected in a C-centered monoclinic crystal system, and data reduction showed absences consistent with space group $C2/c$ with Z = 4, indicating that the molecule must lie on a special position. Solution of the Patterson map allowed placement of the unique iridium atom, and use of the program DIRDIF allowed location of all remaining atoms. An absorption correction was applied following isotropic refinement with the program DIFABS. In the final model, hydrogens were placed in idealized positions, and all non-hydrogen atoms were refined anisotropically. Data collection and refinement parameters are given in Table 1. Positional parameters are given in Table 4, and selected distances and angles are given in Table 5.

Supplementary Material Available: X-ray characterization data for [(CH5Me5)Ir](μ-S)(μ-C4H6) and [(CH5Me5)Ir](μ-S)(CO)2, including tables of distances and angles, fractional atomic coordinates, thermal parameters, and least squares planes (24 pages); calculated and observed structure factors (35 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(26) $R_1 = \{\sum\|F_o\| - |F_c\|\}/\{\sum|F_o|\}$; $R_2 = [\sum w(|F_o| - |F_c|)^2]^{1/2}/\{\sum wF_o^2\}$, where $w = [\sigma^2(F_o) + (\rho F_o^2)^2]^{1/2}$ for the non-Poisson contribution weighting scheme. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. Source of scattering factors f_o, f', f'': Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.