Hydrodesulfurization of Thiophene and Benzothiophene to Butane and Ethylbenzene by a Homogeneous Iridium Complex

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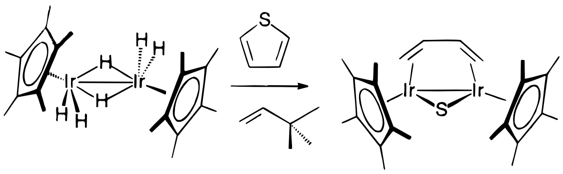
Reaction of the dimer $[Cp^*IrHCl]_2$ ($Cp^* = \eta^5$-C_5Me_5) in benzene solution with either thiophene or benzothiophene at 90 °C in the presence of H_2 gives the hydrogenolysis products $[Cp^*IrCl]_2(\mu$-$H)(\mu$-$SC_4H_9)$ (**1**) and $[Cp^*IrCl]_2(\mu$-$H)[\mu$-$S(C_6H_4)CH_2CH_3]$ (**2**), respectively, in high yields. Upon further thermolysis under H_2, the completely desulfurized products, butane and ethylbenzene, can be made. Complexes **1** and **2** were characterized by single-crystal X-ray diffraction. In the absence of H_2, reaction of $[Cp^*Ir\ HCl]_2$ with thiophene gives an additional trinuclear product $[Cp^*IrCl]_3(H)(SC_4H_6)$ (**3**), which was also structurally characterized.

Introduction

The hydroprocessing of crude oil is one of the largest scale chemical processes carried out in industry today. In this process, heteroatom impurities such as thiophenes, mercaptans, and quinolines are removed, making the oil amenable to further refining. Removal of the sulfur compounds, in particular, decreases the contributions to acid rain production upon fuel combustion and is also valuable in preventing catalyst poisoning both in the refinement process and in automobiles.[1] Because of both the environmental and economic rewards that can be achieved through the hydrodesulfurization (HDS) process, recent research has focused on trying to better understand the mechanism of HDS in hopes of designing more efficient catalysts.[2]

The difficulty in modeling HDS in solution lies greatly in the ability of a given system to cleave *both* carbon−sulfur bonds of various thiophenes. Mimicking the industrial process would require that both carbon−sulfur bonds be cleaved in a dihydrogen environment, affording the hydrogenated organic products plus adsorbed sulfur or H_2S. While many ring-opening oxidative additions of one of the C−S bonds of thiophene have been reported,[3] fewer examples of complete desulfurization to butanes, butenes, or metal alkyls have been reported.[4] In addition, there have been few reports of hydrodesulfurization of benzothiophene to ethylbenzene by well-defined homogeneous model systems.[5−7] In this work is presented a homogeneous model system which can desulfurize thiophene and benzothiophene to butane and ethylbenzene, respectively, in the presence of H_2.

Previously in our lab the dimeric species $[Cp^*IrH_3]_2$ was observed to cleave both C−S bonds of thiophene in the presence of a hydrogen acceptor (eq 1).[4a] Reaction of this butadiene complex with hydrogen yielded the desulfurized product *n*-butane. The ability of the dimeric species to completely remove a sulfur atom from thiophene led to our interest in finding a similar compound which did not require a hydrogen acceptor to generate the active species and could also desulfurize the more refractory thiophenes such as benzothiophene. This led us to explore the reactivity of the bis(μ-hydrido)-bis[chloro(pentamethylcyclopentadienyl)]iridium complex, first synthesized by Gill and Maitlis,[8] toward thiophenic molecules.



(1)

Results and Discussion

Heating a solution of $[Cp^*IrHCl]_2$ in benzene (90 °C, 3 h) with an excess of thiophene in the presence of 1 atm of H_2 afforded $[Cp^*IrCl]_2(\mu$-$H)(\mu$-$SC_4H_9)$ (**1**) (eq 2)

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1997.

(1) Topsøe, H.; Clausen, B. S.; Massoth, F. E. *Hydrotreating Catalysis*; Springer-Verlag: Berlin, 1996.

(2) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387−394. Rauchfuss, T. B. *Prog. Inorg. Chem.* **1991**, *39*, 259−329. Bianchini, C.; Meli, A. *J. Chem. Soc., Dalton Trans.* **1996**, 801−814.

(3) See, for example: (a) Selnau, H. E.; Merola, J. S. *Organometallics* **1993**, *12*, 1583−1591. (b) Garcia, J. J.; Mann, B. E.; Adams, H.; Bailey, N. A.; Maitlis, P. M. *J. Am. Chem. Soc.* **1995**, *117*, 2179−2186. (c) Buys, I. E.; Field, L. D.; Hambley, R. W.; McQueen, A. E. D. *J. Chem. Soc., Chem. Commun.* **1994**, 557−558. (d) Paneque, M.; Taboada, S.; Carmona, E. *Organometallics* **1996**, *15*, 2678−2679. (e) Jones, W. D.; Dong, L. *J. Am. Chem. Soc.* **1991**, *113*, 559−564. (f) Chen, J.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 199−204. (g) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Herrer, V.; Sanchez-Delgado, R. *J. Am. Chem. Soc.* **1993**, *115*, 2731−2742.

(4) Most examples come from polynuclear organometallic systems: (a) Jones, W. D.; Chin, R. M. *J. Am. Chem. Soc.* **1994**, *116*, 198−203. (b) Arce, A. J.; Arrojo, P.; Deeming, A. J.; De Sanctis, Y. *J. Chem. Soc., Dalton Trans.* **1992**, 2423−2424. (c) Riaz, U.; Curnow, O. J.; Curtis, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 1416−1417. (d) Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 2544−2552.

(5) Ogilvy, A. E.; Draganjac, M.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **1988**, *7*, 1171−1177.

(6) Desulfurization of benzothiophene to ethylbenzene was reported to occur by Bianchini *et al.*, but was found to be due to the presence of heterogeneous particles. See: Bianchini, C.; Herrera, V.; Jimenez, M. V.; Meli, A.; Sánchez-Delgado, R.; Vizza, F. *J. Am. Chem. Soc.* **1995**, *117*, 8567−8575.

(7) Bianchini, C.; Jiménez, M. V.; Mealli, C.; Meli, A.; Moneti, S.; Patinec, V.; Vizza, F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1706−1707.

(8) Gill, D. S.; Maitlis, P. M. *J. Organomet. Chem.* **1975**, *87*, 359−364.

S0276-7333(96)01010-2 CCC: $14.00

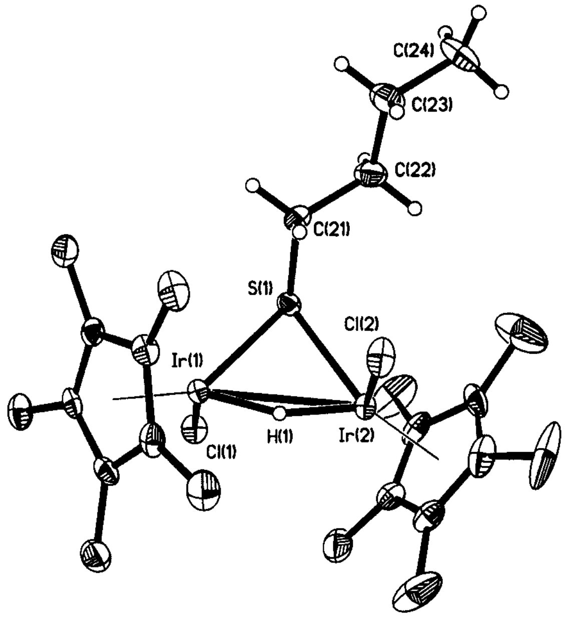
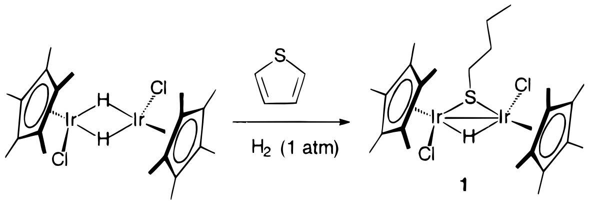


Figure 1. ORTEP drawing of $[Cp^*IrCl]_2(\mu\text{-}H)(\mu\text{-}SC_4H_9)$. Ellipsoids are shown at the 30% probability level. Hydrogen atoms are omitted from the Cp* ligand for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1

S(1)−C(21)	1.799(12)	Ir(2)−Cl(2)	2.404(3)
S(1)−Ir(2)	2.335(2)	C(21)−C(22)	1.53(2)
S(1)−Ir(1)	2.337(2)	C(22)−C(23)	1.53(2)
Ir(1)−Cl(1)	2.419(2)	C(23)−C(24)	1.55(2)
Ir(1)−Ir(2)	2.9041(4)		
C(21)−S(1)−Ir(2)	112.5(4)	S(1)−Ir(2)−Ir(1)	51.60(6)
C(21)−S(1)−Ir(1)	111.3(4)	Cl(2)−Ir(2)−Ir(1)	90.11(7)
Ir(2)−S(1)−Ir(1)	76.86(7)	C(22)−C(21)−S(1)	110.0(8)
S(1)−Ir(1)−Cl(1)	84.89(9)	C(23)−C(22)−C(21)	112.7(10)
S(1)−Ir(1)−Ir(2)	51.54(6)	C(22)−C(23)−C(24)	111.0(12)
Cl(1)−Ir(1)−Ir(2)	90.51(6)		

as a red crystalline solid in 80% isolated yield after purification. Under relatively mild conditions the thiophene molecule was ring opened and completely hydrogenated, having been transformed into a bridging *n*-butanethiolate ligand. No intermediates were observed while monitoring this reaction by ^1H NMR spectroscopy.



(2)

As is evident from the crystal structure of **1** (Figure 1), the Cp* and chlorine ligands are *trans* and the sulfur atom is pyramidal, rendering the complex with C_1 symmetry. Crystallographic data for **1** are listed in Tables 1 and 2. Carbon−carbon bond lengths of the butanethiolate moiety confirm that hydrogenation of thiophene is complete, with distances of 1.53(2), 1.53(2), and 1.55(2) Å for the $C_{21}-C_{22}$, $C_{22}-C_{23}$, and $C_{23}-C_{24}$ bonds, respectively, thus establishing their single-bond character. The bridging hydride ligand was located and refined. The solid state structure is consistent with the ^1H NMR data of the complex in solution.

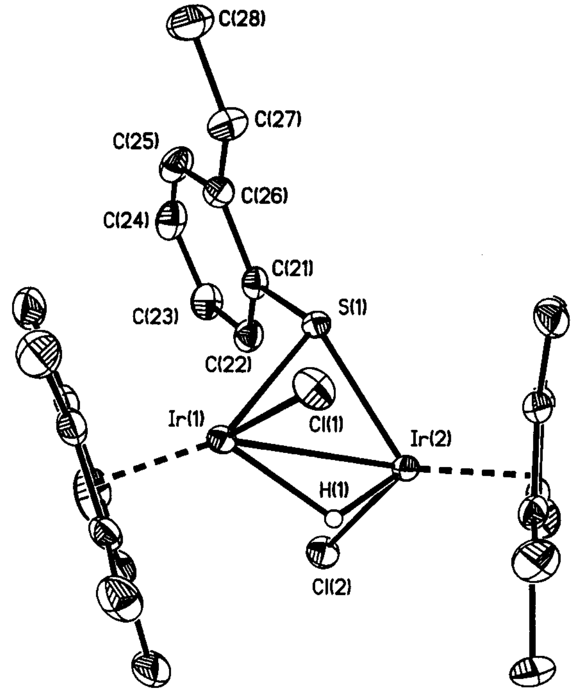
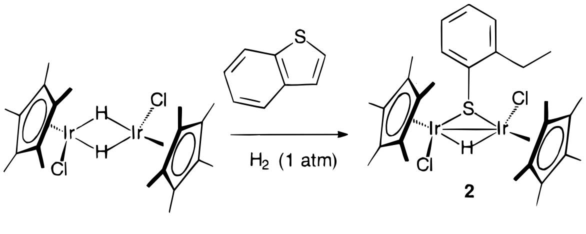


Figure 2. ORTEP drawing of $[Cp^*IrCl]_2(\mu\text{-}H)(\mu\text{-}S(C_6H_4)\text{-}C_2H_5)$. Ellipsoids are shown at the 30% probability level. Hydrogen atoms on the ligands have been omitted for clarity.

There are two singlets representing the magnetically inequivalent Cp* methyl groups. The α-CH_2 hydrogen atoms of the butanethiolate moiety are diastereotopic, appearing as multiplets at δ 3.36 and 2.05. A COSY spectrum shows coupling of the α-protons to broad multiplets in the region δ 1.5−1.9, which in turn couple to the terminal methyl group at δ 1.02. A hydride resonance is seen in the ^1H NMR spectrum at δ −15.54 in C_6D_6, similar to that seen in the spectrum of the isoelectronic complex $[\{Cp^*Ir\}_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2]$,[9] which has a hydride resonance at −13.73 in C_6D_6. Furthermore, the absence of an IR band in the 1800−2100 cm^{-1} range is consistent with a bridging hydride.[8]

The complex $[Cp^*IrHCl]_2$ was found to undergo a similar reaction with benzothiophene and H_2 (90 °C, 2 h), yielding the red crystalline species $[Cp^*IrCl]_2(\mu\text{-}H)(\mu\text{-}S(C_6H_4)CH_2CH_3)$ (**2**) in 85% isolated yield after purification (eq 3). Selective cleavage of the vinylic C−S bond is observed. Again, no intermediates were observed while monitoring the reaction by ^1H NMR spectroscopy. The X-ray crystal structure is shown in Figure 2, and the corresponding crystallographic data are given in Tables 2 and 3. The bridging hydride ligand was located and refined. The C_1 symmetry of complex **2** due to sulfur pyramidalization is similar to



(3)

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[9] White, C.; Oliver, A. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1973**, 1901−1907.

Table 2. Crystallographic Data for 1, 2, and 3

	1	2	3
	Crystal Parameters		
chemical formula	$C_{24}H_{40}Cl_2Ir_2S$	$C_{28}H_{40}Cl_2Ir_2S$	$C_{34}H_{52}Cl_3Ir_3S\cdot C_6H_5CH_3$
fw	815.92	863.96	1267.90
cryst syst	monoclinic	monoclinic	monoclinic
space group (No.)	*Cc* (9)	$P2_1/c$ (14)	$P2_1$ (4)
Z	4	4	2
a, Å	16.1874(5)	16.9397(7)	12.3172 (1)
b, Å	18.2180(6)	10.3584(4)	12.4859(2)
c, Å	9.2952(3)	16.7262(7)	14.6850(1)
β, deg	102.8200(10)	98.8880(10)	112.098(1)
vol, Å^3	2672.8(2)	2899.7(2)	2092.53(4)
ρ_{calc}, g cm^{-3}	2.028	1.979	2.012
cryst dimens, mm^3	0.50 × 0.30 × 0.10	0.24 × 0.30 × 0.08	0.50 × 0.10 × 0.20
temp, °C	−50	−50	−50
	Measurement of Intensity Data		
diffractometer	Siemens SMART	Siemens SMART	Siemens SMART
radiation	Mo, 0.710 73 Å	Mo, 0.710 73 Å	Mo, 0.710 73 Å
frame range/time, deg/s	0.3/10	0.3/10	0.3/30
2θ range, deg	3.4−56.0	4.6−56.5	3.4−56.0
data collected	$-21 \leq h \leq 21$, $-23 \leq k \leq 24$, $-8 \leq l \leq 12$	$-19 \leq h \leq 21$, $-7 \leq k\ 13$, $-21 \leq l \leq 20$	$-16 \leq h \leq 13$, $-10 \leq k\ 16$, $-17 \leq l \leq 19$
no. of data collected	8052	17 708	13 468
no. of unique data	3948	6851	8283
no. of obs data ($F_o > 4\sigma(F_o)$)	3711	5499	7629
agreement between equiv data (R_{int})	0.0346	0.0325	0.0336
no. of params varied	277	313	403
μ, mm^{-1}	10.235	9.440	9.785
abs corr	empirical (SADABS)	empirical (SADABS)	empirical (SADABS)
range of trans. factors	0.17−0.92	0.29−0.87	0.35−0.81
$R_1(F_o)$, $wR_2(F_o^2)$, ($F_o > 4\sigma(F_o)$)	0.0291, 0.0624	0.0323, 0.0585	0.0311, 0.0697
$R_1(F_o)$, $wR_2(F_o^2)$ (all data)	0.0321, 0.0638	0.0500, 0.0635	0.0359, 0.0714
goodness of fit	1.006	1.046	1.011

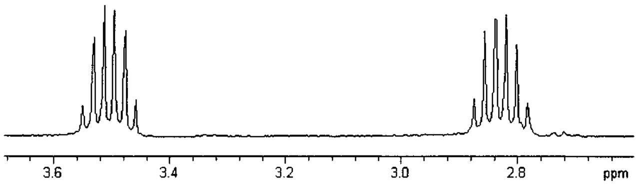

Figure 3. Selected region of the ^1H NMR spectrum of $[Cp^*IrCl]_2(\mu\text{-}H)(\mu\text{-}S(C_6H_4)C_2H_5)$ showing the methylene protons of the ethyl fragment.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 2

S(1)−C(21)	1.789(5)	C(21)−C(26)	1.409(7)
S(1)−Ir(2)	2.3449(12)	C(26)−C(25)	1.396(7)
S(1)−Ir(1)	2.3515(13)	C(26)−C(27)	1.518(7)
Ir(1)−Cl(1)	2.4153(13)	C(22)−C(23)	1.395(8)
Ir(1)−Ir(2)	2.9139(3)	C(23)−C(24)	1.368(8)
Ir(2)−Cl(2)	2.4101(13)	C(24)−C(25)	1.382(8)
C(21)−C(22)	1.383(7)	C(27)−C(28)	1.507(8)

C(21)−S(1)−Ir(2)	119.9(2)	C(22)−C(21)−S(1)	121.6(4)
C(21)−S(1)−Ir(1)	112.7(2)	C(26)−C(21)−S(1)	117.1(4)
Ir(2)−S(1)−Ir(1)	76.70(4)	C(25)−C(26)−C(21)	116.7(5)
S(1)−Ir(1)−Cl(1)	88.51(5)	C(25)−C(26)−C(27)	121.9(5)
S(1)−Ir(1)−Ir(2)	51.55(3)	C(21)−C(26)−C(27)	121.4(5)
Cl(1)−Ir(1)−Ir(2)	90.12(4)	C(21)−C(22)−C(23)	119.8(5)
S(1)−Ir(2)−Cl(2)	104.67(5)	C(24)−C(23)−C(22)	120.1(6)
S(1)−Ir(2)−Ir(1)	51.75(3)	C(23)−C(24)−C(25)	119.8(5)
Cl(2)−Ir(2)−Ir(1)	90.66(3)	C(24)−C(25)−C(26)	122.3(5)
C(22)−C(21)−C(26)	121.2(5)	C(28)−C(27)−C(26)	116.3(5)

that observed in **1** and can be observed in the ^1H NMR spectrum. Figure 3 shows the region of the ^1H NMR spectrum displaying the inequivalent methylene protons of the ethyl substituent of the phenyl ring. Two doublets of quartets (seen as apparent sextets due to overlap, $J = 7.6$ Hz) were found to resonate at δ 3.51 and 2.83 ppm, signifying the location of each proton in quite different environments, and demonstrating that inversion at sulfur is not rapid on the NMR time scale. The methyl group appears as a triplet at δ 1.42, and the hydride resonates at δ −15.62. No IR band in the 1800−2100 cm^{-1} region was observed, suggesting that the hydride is bridging.

No reaction took place when $[Cp^*IrHCl]_2$ was reacted with dibenzothiophene under similar reaction conditions (*vide supra*). Dibenzothiophene and alkyl-substituted dibenzothiophenes are representative of compounds that are most difficult to desulfurize under both heterogeneous and homogeneous reaction conditions.[10,11]

Reactions carried out with thiophene and benzothiophene in the absence of hydrogen also led to products **1** and **2**, but in much lower yields (2% and 33%, respectively, calculated by NMR). Apparently a hydrogen-activated species of $[Cp^*IrHCl]_2$ is not necessary to cleave the carbon−sulfur bond of either thiophene or benzothiophene. The reaction of $[Cp^*IrHCl]_2$ with thiophene in the absence of hydrogen also led to the new organometallic product $[Cp^*IrCl]_3(H)(SC_4H_6)$ (**3**) as the major isolated complex (32% crude yield). X-ray structural characterization of **3** revealed a trinuclear compound. An ORTEP drawing of **3** is provided in Figure 4, and the corresponding crystallographic data are given in Tables 2 and 4. The $Ir_2(\mu\text{-}H)(\mu\text{-}SR)$ core of the molecule is similar to that found in **1**. The η^3-allyl fragment of this complex aroused our curiosity in the mechanism of thiophene hydrogenation and brought about further investigation of the trinuclear complex. Heating a benzene solution of **3** at 90 °C for 24 h under

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(10) Myers, A. W.; Jones, W. D. *Organometallics* **1996**, *15*, 2905−2917 and references therein.

(11) Bianchini, C.; Jimenez, M. V.; Meli, A.; Moneti, S.; Vizza, F.; Herrera, V.; Sánchez-Delgado, R. *Organometallics* **1995**, *14*, 2342−2352 and references therein.

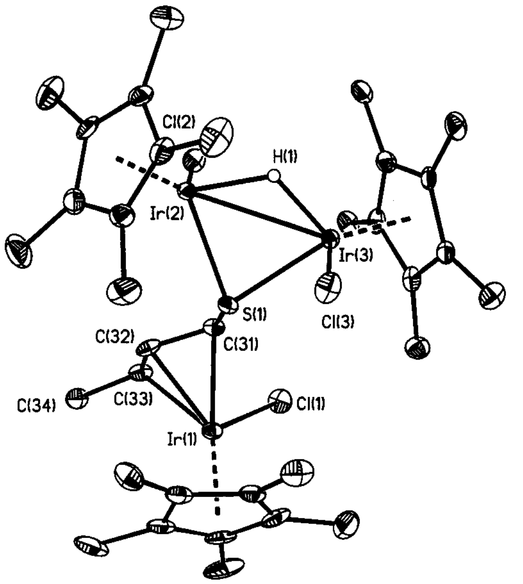


Figure 4. ORTEP drawing of the trinuclear species **3**. Ellipsoids are shown at the 30% probability level. Hydrogen atoms on the ligands are omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 3

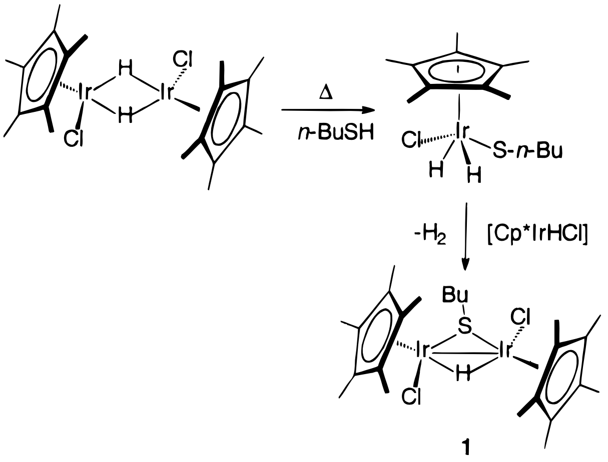
Ir(1)−C(32)	2.134(8)	Ir(3)−S(1)	2.340(2)
Ir(1)−C(31)	2.159(8)	Ir(3)−Cl(3)	2.415(2)
Ir(1)−C(33)	2.207(8)	S(1)−C(31)	1.790(9)
Ir(1)−Cl(1)	2.380(2)	C(31)−C(32)	1.429(12)
Ir(2)−S(1)	2.338(2)	C(32)−C(33)	1.425(11)
Ir(2)−Cl(2)	2.392(2)	C(33)−C(34)	1.497(12)
Ir(2)−Ir(3)	2.8859(4)		

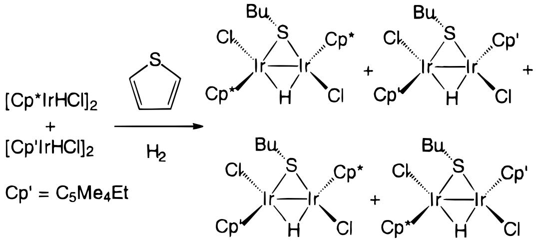
C(32)−Ir(1)−C(31)	38.9(3)	C(31)−S(1)−Ir(2)	113.6(3)
C(32)−Ir(1)−C(33)	38.3(3)	C(31)−S(1)−Ir(3)	114.6(3)
C(31)−Ir(1)−C(33)	67.7(3)	Ir(2)−S(1)−Ir(3)	76.18(6)
C(32)−Ir(1)−Cl(1)	104.9(3)	C(32)−C(31)−S(1)	115.3(7)
C(31)−Ir(1)−Cl(1)	87.4(2)	C(32)−C(31)−Ir(1)	69.6(5)
C(33)−Ir(1)−Cl(1)	84.6(3)	S(1)−C(31)−Ir(1)	117.3(4)
S(1)−Ir(2)−Cl(2)	92.45(8)	C(33)−C(32)−C(31)	117.0(9)
S(1)−Ir(2)−Ir(3)	51.94(5)	C(33)−C(32)−Ir(1)	73.6(5)
Cl(2)−Ir(2)−Ir(3)	89.86(6)	C(31)−C(32)−Ir(1)	71.5(5)
S(1)−Ir(3)−Cl(3)	83.72(8)	C(32)−C(33)−C(34)	118.3(9)
S(1)−Ir(3)−Ir(2)	51.87(5)	C(32)−C(33)−Ir(1)	68.1(5)
Cl(3)−Ir(3)−Ir(2)	89.98(6)	C(34)−C(33)−Ir(1)	122.2(6)

1 atm of H_2 did not lead to any new products, nor did heating a benzene solution of excess $[Cp^*IrHCl]_2$ with **3** at 90 °C for 20 h. Therefore it can be concluded that the trinuclear species **3** is not an intermediate in the formation of **1**.

The dimeric complex $[Cp^*IrHCl]_2$ does not readily dissociate into monomeric fragments. This was shown by heating a 1:1 mixture of $[Cp^*IrHCl]_2$ and $[(C_5Me_4Et)IrHCl]_2$ at 90 °C in C_6D_6 with no added substrates. Only 15% of the mixed species $[(C_5Me_4Et)(Cp^*)Ir_2H_2Cl_2]$ was observed after 3 h, a time scale comparable to what is required for reaction with thiophene and H_2. However, when a mixture of the Cp* and (C_5Me_4Et) starting materials was heated in the presence of thiophene at 90 °C, scrambling of the starting materials to a 1:2:1 ratio of pure Cp*, mixed Cp*(C_5Me_4Et), and pure (C_5Me_4Et) complexes was observed after 1.5 h. Consequently, cleavage of the dimers appears to be promoted by a reversible reaction with thiophene. Involvement of mononuclear iridium species in these reactions is further supported by the following experiment. When a mixture of $[(C_5Me_4Et)IrHCl]_2$ and $[Cp^*IrHCl]_2$ is heated in benzene at 90 °C in the presence of thiophene and hydrogen, all possible permutations of product **1** are seen in a 1:1:1:1 ratio (eq 4).

Scheme 1





(4)

$[Cp^*IrHCl]_2$ also reacts with 1-butanethiol in a fashion which we believe involves cleavage of the dimer. Reaction in benzene (90 °C, 30 h) affords **1** in quantitative yield (NMR yield) with the production of hydrogen gas. The proposed steps in this reaction pathway are given in Scheme 1. The dihydride thiolate chloride shown in Scheme 1 can be viewed as structurally similar to the known stable Ir(V) species Cp^*IrH_4[12] and Cp^*IrMe_4.[13] Additionally, $[Cp^*IrHCl]_2$ has been previously found to undergo oxidative additions producing monomeric Ir(V) complexes such as $Cp^*IrH_2Cl(SiR_3)$.[14] Further mention of related Ir(V) chemistry can be found in a recent theoretical treatment of a Cp* iridium complex, where oxidative addition producing Ir(V) over Ir(III) intermediates was favored in substrate activation.[15]

The fact that the trinuclear species **3** does not produce the hydrogenated complex **1** when heated under 1 atm of H_2 suggests that the hydrogenation of thiophene may be an *intramolecular* process rather than a process of hydrogenation of a butadiene thiolate ligand by an external metal complex. A proposed mechanism for the production of **1** is given in Scheme 2. Plots of product growth versus time for the reaction shown in eq 2 follow first-order kinetics.[16] Nearly identical rates were observed for runs using 0.5 and 1 atm of H_2, indicating

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[12] Gilbert, T. G.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3508−3516.

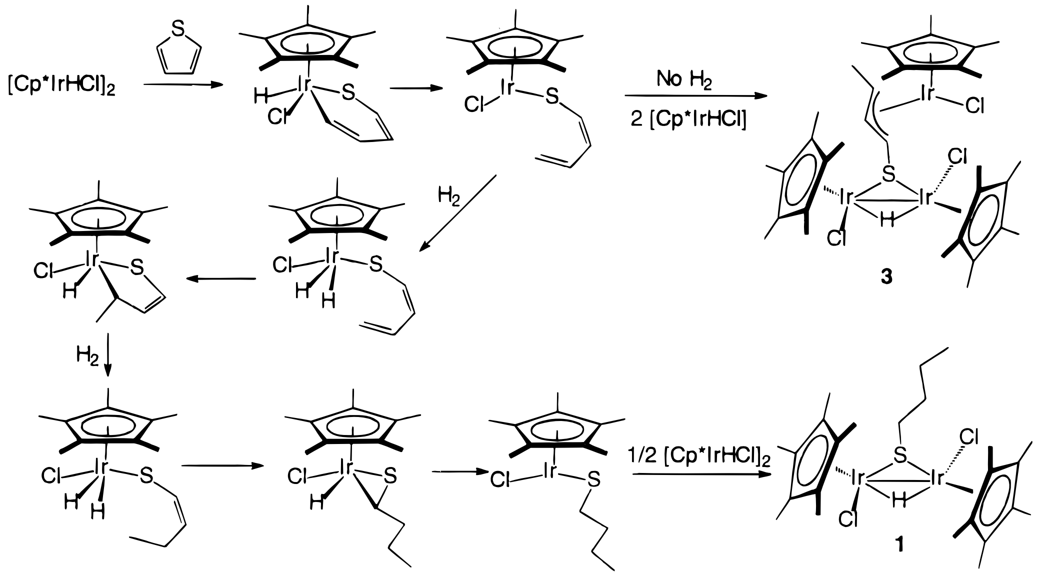
[13] Isobe, K.; Vàzquez de Miguel, A.; Nutton, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1984**, 929−933.

[14] Fernandez, M. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1984**, 2063−2066.

[15] Strout, D. L.; Zaric, S.; Niu, S.; Hall, M. B. *J. Am. Chem. Soc.* **1996**, *118*, 6068−6069.

[16] Data were fitted to the equation $C(t) = (C_0 - C_\infty)e^{-kt} + C_\infty$. At 1 atm of H_2, $k_{obs} = 0.004\ 96\ min^{-1}$, and at 0.5 atm of H_2, $k_{obs} = 0.004\ 15\ min^{-1}$.

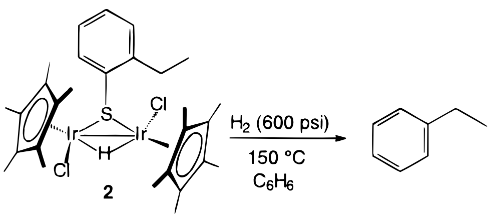
Scheme 2. Proposed Mechanism for the Formation of 1



that the reaction is first-order in $[Cp^*IrHCl]_2$ and zero-order in hydrogen concentration. This data implies that hydrogenation of thiophene is occurring after the rate-determining step, which is assumed to be carbon−sulfur bond cleavage. The hydrogenation of the double bonds of thiophene might then occur by a concerted four-center pathway, or by way of a coordination−insertion pathway where the vacant site would form by slippage of the Cp* ring to η^3-coordination or by migration of a hydride to the Cp* ring.[17]

Hydrogenation Experiments with 1 and 2

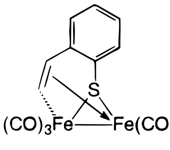
A benzene solution of complex **2** was heated at 150 °C for 16 h under 600 psi of H_2, yielding a dark red solution. Analysis of the solution by GC/MS and ^{1}H NMR spectroscopy reveals that the main organic product is ethylbenzene, formed in ~60% yield (eq 5).



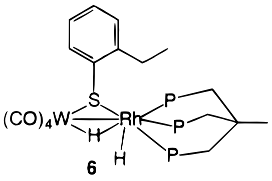
(5)

2-Ethylthiophenol and bis(2-ethylphenyl) disulfide were not detected in the reaction mixture. Lower yields of ethylbenzene were found when the reaction was carried out under 1 atm of H_2, although identification of an organometallic product, $[(Cp^*Ir)_3(\mu_3\text{-}S)_2](Cl)_2$[18,19] (18% crude yield), was possible.

The notion that the formation of a μ-thiolato bridge may be important in cleaving both carbon−sulfur bonds in thiophenes has been previously suggested,[4a] and this may be particularly important for the benzothiophene derivatives. Complexes **2**, **5**,[5] and **6**[7] have successfully yielded ethylbenzene under a dihydrogen atmosphere in homogeneous model systems, and all contain such thiolato bridges. Complexes **2** and **6** also have strikingly similar structural motifs with both complexes displaying an additional bridging hydride ligand.



5



6

The desulfurization of thiophene itself has been more successful with polynuclear model systems.[4b−d] When complex **1** is dissolved in THF-d_8 and heated to 145 °C under 600 psi of H_2, butane is produced in 30% yield, relative to starting material. Lower yields of the hydrogenolysis product of **1** relative to **2** may be due to the difficulty in quantifying the volatile gas produced. The NMR yield was determined by comparison to a known amount of standard added before the reaction (see experimental procedure for details). The production of butane was not suppressed when the reaction was repeated in the presence of a 2000-fold excess of elemental Hg, providing evidence that the desulfurization reaction is not due to the presence of heterogeneous particles in solution.[20] Higher temperatures are needed for the desulfurization reactions to take place, indicating that complexes **1** and **2** are thermally quite stable. NMR runs using 1 atm of H_2 only yielded the desulfurized products when temperatures near 150 °C were obtained. This work provides the first example of HDS of thiophene to *n*-butane via a well-defined 1-butanethiolate intermediate (eq 6). In contrast, earlier studies with $[Cp^*IrH_3]_2$ show that thiophene can be desulfurized to afford butane via a μ_2-η^4-butadiene complex (eq 1).[4a]

Removal of the butanethiolate moiety in **1** can be realized under mild conditions by the addition of H_2S. Heating a benzene solution of **1** at 90 °C for 15 h with excess H_2S (1 atm) yielded $[Cp^*IrCl]_2(\mu\text{-}SH)_2$ (**7**),[21] in

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[17] Jones, W. D.; Kuykendall, V. L.; Selmeczy, A. D. *Organometallics* **1991**, *10*, 1577−1586.

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[19] Nishioka, T.; Isobe, K. *Chem. Lett.* **1994**, 1661−1664.

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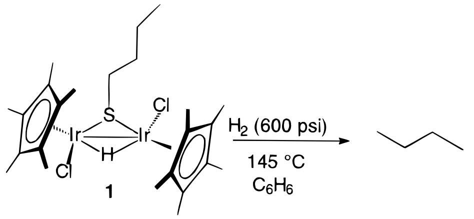
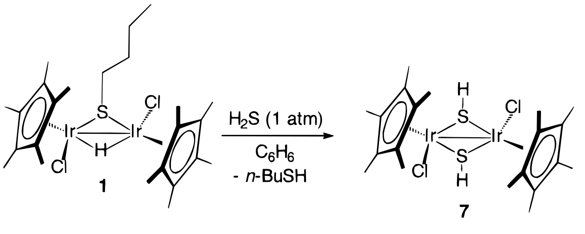


(6)

64% yield, along with *n*-butanethiol (eq 7). It is important to investigate the effects of H_2S gas on HDS



(7)

intermediates because H_2S is a noninnocent byproduct in the HDS process, and also because many industrial catalysts are based on sulfided phases whose structure and catalytic properties are modified by the presence of H_2S.[1,22] Here we report that a bridging butanethiolate moiety bound to two iridium centers can be removed by treatment with H_2S, producing 1-butanethiol, H_2, and complex **7**.

Conclusion

It was found that $[Cp^*IrHCl]_2$, in the presence of H_2, was able to completely desulfurize thiophene and benzothiophene to butane and ethylbenzene, respectively. Both hydrodesulfurization reactions proceed via organometallic intermediates containing bridging thiolate moieties, providing further evidence that cleavage of both carbon−sulfur bonds in various thiophenes may require the participation of more than one metal center with the capability to form a bridging thiolate intermediate. Topsøe, *et al.* have provided recent models for the heterogeneous reactive site in MoS_2 catalysts that are consistent with such a hypothesis.[1]

Experimental Section

General Procedures. All operations were performed under a nitrogen atmosphere unless otherwise stated. Benzene and THF were distilled from dark purple solutions of benzophenone ketyl. Neutral alumina was heated to 200 °C under vacuum for 2 days and stored under nitrogen. Thiophene (⩾99%) was purchased from Aldrich Chemical Co. and purified as previously reported.[23] Benzothiophene (99%) and hydrogen sulfide were purchased from Aldrich Chemical Co. and used without further purification. Ethylbenzene was purchased from Kodak Chemical Co. $[Cp^*IrHCl]_2$ was prepared as previously reported.[8] All C_5Me_4Et complexes were synthesized by procedures analogous to the preparation of the Cp* complexes. GC analyses were carried out on a Hewlett-Packard 5880 Series gas chromatograph, and GC/MS spectra were recorded on a Hewlett-Packard 5970 Series mass selective detector. A Siemens-SMART three-circle CCD diffractometer was used for X-ray crystal structure determination. Elemental analyses were obtained from Desert Analytics. All ^1H and ^{13}C spectra were recorded on a Bruker AMX400 NMR spectrometer, and all ^1H chemical shifts are reported relative to the residual proton resonance in the deuterated solvent. High-pressure reactions were performed with a Parr 4702 bomb equipped with a Teflon liner.

Preparation of $[Cp^*IrCl]_2(\mu\text{-}H)(\mu\text{-}SC_4H_9)$ (1). $[Cp^*IrHCl]_2$ (112 mg, 0.154 mmol) was dissolved in 3 mL of thiophene and 5 mL of benzene and placed in an ampule fitted with a Teflon valve. H_2 (1 atm) was added, and the solution was stirred at 90 °C for 3 h. All volatiles were then removed under vacuum, and the red residue was passed through a neutral alumina column using THF/benzene (1:1) as an eluant. The solvents were removed under vacuum, leaving **1** as a red solid (0.10 g, 80%). ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 3.36 (ddd, 1 H, α-CH), 2.10−2.01 (m, 1 H, α-CH), 1.89−1.70 (m, 2 H, β-CH$_2$), 1.75−1.50 (m, 2 H, γ-CH$_2$), 1.81 (s, 15 H, C_5Me_5), 1.73 (s, 15 H, C_5Me_5), 1.02 (t, 3 H, $J = 7.6$ Hz, Me), −15.54 (s, 1 H, IrH). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 25 °C): 90.58 (s, C_5Me_5), 89.79 (s, C_5Me_5), 34.13 (s, CH$_2$), 31.29 (s, CH$_2$), 22.64 (s, CH$_2$), 14.25 (s, CH$_3$), 9.95 (s, C_5Me_5), 9.76 (s, C_5Me_5). Anal. Calcd (found) for $C_{24}H_{40}Cl_2Ir_2S$: C, 35.33 (35.79); H, 4.94 (4.93).

Preparation of $[Cp^*IrCl]_2(\mu\text{-}H)(\mu\text{-}S(C_6H_4)CH_2CH_3)$ (2). $[Cp^*IrHCl]_2$ (100 mg, 0.14 mmol) and benzothiophene (290 mg, 2.16 mmol) were dissolved in benzene (13 mL) and placed in an ampule fitted with a Teflon valve. H_2 (1 atm) was added, and the solution was stirred at 90 °C for 2 h. All volatiles were removed under vacuum and the red residue was passed through a neutral alumina column using THF/benzene (9:1) as an eluant. The solvents were removed under vacuum, and excess benzothiophene was removed by sublimation under reduced pressure at room temperature, leaving **2** as a red solid (0.10 g, 85%). ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 8.89 (d, $J = 7.2$ Hz, 1 H), 7.12−7.01 (m, 3 H), 3.51 (sextet, $J = 7.6$ Hz, 1 H, α-CH), 2.83 (sextet, $J = 7.6$ Hz, 1 H, α-CH), 1.75 (s, 15 H, C_5Me_5), 1.48 (s, 15 H, C_5Me_5), 1.42 (t, $J = 7.6$ Hz, 3 H, Me), −15.62 (s, 1 H, IrH). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 25 °C): δ = 146.85 (s, C), 137.56 (s, C), 134.40 (br s, CH), 127.44 (s, CH), 127.33 (s, CH), 126.26 (s, CH), 91.45 (s, C_5Me_5), 89.94 (s, C_5Me_5), 28.07 (s, CH$_2$), 15.30 (s, Me), 9.61 (s, C_5Me_5), 8.85 (s, C_5Me_5). Anal. Calcd (found) for $C_{28}H_{40}Cl_2Ir_2S$: C, 38.92 (39.09); H, 4.67 (4.44).

Preparation of the Trinuclear Species 3. $[Cp^*IrHCl]_2$ (0.20 g, 0.27 mmol) was dissolved in 8 mL of thiophene and 8 mL of benzene and placed in an ampule fitted with a Teflon valve. The solution was stirred at 90 °C for 10 h. The volatiles were removed under vacuum, and the residue was passed through an alumina column using THF/benzene (1:1) as an eluant. The solvents were removed under vacuum, leaving crude product (32%). Trimer **3** was purified by dissolving the residue in the minimum amount of toluene and cooling to −30 °C overnight. The precipitate was collected and dried under vacuum, leaving a bright orange solid (25 mg, 8.1%). ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 4.48 (t, $J = 8.3$ Hz, 1 H, β-CH), 4.24 (d, $J = 8.0$ Hz, 1 H, α-CH), 3.82 (m, 1 H, γ-CH), 1.96 (s, 15 H, C_5Me_5), 1.85 (s, 15 H, C_5Me_5), 1.63 (s, 15 H, C_5Me_5), 1.28 (d, $J = 5.9$ Hz, 3 H, Me), −15.29 (s, 1 H, IrH). ^{13}C $\{^1H\}$NMR (100 MHz, C_6D_6, 25 °C): δ 92.91 (s, C_5Me_5), 90.53 (s, C_5Me_5), 90.10 (s, C_5Me_5), 85.36 (s, CH), 57.66 (s, CH), 53.30 (s, CH), 18.08 (s, Me), 10.22 (s, C_5Me_5), 10.04 (s, C_5Me_5), 8.88 (s, C_5Me_5). Anal. Calcd (found) for $C_{34}H_{52}Cl_3Ir_3S$: C, 35.70 (36.38); H, 4.58 (4.61).

$[(C_5Me_4Et)IrHCl]_2$. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 2.16 (q, $J = 7.8$ Hz, 4 H, CH$_2$), 1.66 (s, 12 H, CH$_3$), 1.52 (s, 12 H, CH$_3$), 0.82 (t, $J = 7.5$ Hz, 6 H, CH$_3$), −13.43 (s, 2 H, IrH).

$[(C_5Me_4Et)IrCl]_2(\mu\text{-}H)(\mu\text{-}SC_4H_9)$ (1′). ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 3.40 (ddd, 1 H), 2.43−2.31 (m, 4 H), 2.14−2.07 (m, 1 H), 2.02−1.95 (m, 2 H), 1.90−1.86 (m, 2 H) 1.85 (s, 3 H), 1.84 (s, 3 H), 1.82 (s, 3 H), 1.79 (s, 6 H), 1.78 (s, 3 H), 1.77 (s, 3H), 1.70 (s, 3 H), 1.63−1.51 (m, 2 H), 1.03 (t, $J = 7.44$ Hz, 3 H), 0.94 (t, $J = 7.44$ Hz, 3 H), 0.88 (t, $J = 7.82$ Hz, 3H), −15.51 (s, 1 H).

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Monitoring Exchange between [(C_5Me_4Et)IrHCl]$_2$ and [Cp*IrHCl]$_2$. [(C_5Me_4Et)IrHCl]$_2$ (7.3 mg, 0.01 mmol) and [Cp*IrHCl]$_2$ (7 mg, 0.01 mmol) were dissolved in 0.7 mL of C_6D_6 and heated at 90 °C. In the absence of thiophene, 15% of mixed species [(C_5Me_4Et)(Cp*)$Ir_2H_2Cl_2$] (hydride resonance at δ −13.46) was found to be present after 3 h. In the presence of 36 μL of thiophene, a 1:2:1 ratio (pure Cp*:mixed species: pure (C_5Me_4Et)) of products was found after 1.5 h.

Reaction of [(C_5Me_4Et)IrHCl]$_2$ and [Cp*IrHCl]$_2$ with Thiophene and H_2. [(C_5Me_4Et)IrHCl]$_2$ (41 mg, 0.05 mmol) and [Cp*IrHCl]$_2$ (39 mg, 0.05 mmol) were dissolved in 11 mL of C_6H_6 and 4.5 mL of thiophene. The solution was heated at 90 °C for 3 h under 1 atm of H_2. The solvents were then removed on a vacuum line, and the residue was analyzed for the different derivatives of **1** that were present. The exchange experiments can easily be analyzed by observing the hydride resonances in the ^{1}H NMR spectrum, with the mixed species showing hydride resonances that are intermediate between those of the two pure species (see eq 4). The pure Cp* complex shows a hydride resonance at δ −15.54, the two mixed Cp*Cp′ species show resonances at −15.53 and −15.52, and the resonance for the pure Cp′ complex appears at −15.51. All four products were found to be present in a 1:1:1:1 ratio.

Reaction of [Cp*IrHCl]$_2$ with 1-Butanethiol. Butanethiol (3.7 μL, 0.03 mmol) was added to a solution of [Cp*IrHCl]$_2$ (25 mg, 0.03 mmol) in C_6D_6 (0.7 mL) and heated at 90 °C for 30 h under 1 atm of H_2 to produce **1** in quantitative yield (NMR yield based on internal standard).

Hydrogenation of [Cp*IrCl]$_2$(μ-H)(μ-S(C_6H_4)CH_2CH_3). [Cp*IrCl]$_2$(μ-H)(μ-S(C_6H_4)CH_2CH_3) (39 mg, 0.045 mmol), benzene (0.9 mL), and undecane (2.96 mg) were placed in a Parr bomb lined with Teflon. The bomb was pressurized with 600 psi of H_2, and the solution was heated at 150 °C for 16 h. The flask was then depressurized, and the dark red solution was analyzed by GC, giving a yield of 57% for ethylbenzene formation. Ethylbenzene was also identified by GC/MS (*m*/*z* = 106, 91). The ^{1}H NMR spectrum of the above reaction run in C_6D_6 showed the resonances of ethylbenzene as compared to an authentic sample [δ 7.18−7.04 (m, 5 H), 2.44 (q, J = 7.6 Hz, 2 H), 1.07 (t, J = 7.6 Hz, 3 H)]. The production of ethylbenzene is also seen when the reaction is run at 1 atm of H_2: [Cp*IrCl]$_2$(μ-H)(μ-S(C_6H_4)CH_2CH_3) (17 mg, 0.02 mmol) was dissolved in 0.7 mL of benzene with added internal standard and heated at 150 °C under 1 atm of H_2 for 19.5 h. The solution was then decanted and analyzed by GC (25% yield of ethylbenzene). The solid which had precipitated ([(Cp*Ir)$_3$(μ_3-S)$_2$](Cl)$_2$) was rinsed with benzene and dried under vacuum (yield 4 mg, 18%)

Hydrogenation of [Cp*IrCl]$_2$(μ-H)(μ-SC_4H_9). [Cp*IrCl]$_2$(μ-H)(μ-SC_4H_9) (49 mg, 0.06 mmol), cyclohexane (2.73 mg), and THF-d_8 (0.9 mL) were placed in a Parr bomb lined with Teflon, and the bomb was charged with 600 psi of H_2. The vessel was heated at 145 °C for 7.5 h. The bomb was then cooled to −78 °C and the vessel depressurized. The solution was transferred to a prechilled flask, where it was then freeze−pump−thawed on a high vacuum line. The volatiles were vacuum transferred to an NMR tube, and the solution was analyzed for butane relative to cyclohexane. NMR yield of butane: 30%. When the reaction was repeated in the presence of a 2000-fold excess of elemental Hg, the production of butane was not suppressed.

Reaction of [Cp*IrCl]$_2$(μ-H)(μ-SC_4H_9) (1) with H_2S. **1** (50 mg, 0.06 mmol) and C_6Me_6 (9.1 mg, 0.056 mmol) were placed in an ampule fitted with a Teflon stopcock and dissolved in 20 mL of benzene. H_2S (1 atm) (**CAUTION!** *Poisonous gas!*) was added to the flask and the solution stirred at 90 °C for 15 h. The solvent was removed under vacuum and the yellow residue dissolved in $CDCl_3$. The NMR yield of [Cp*Ir(Cl)(SH)]$_2$ (**7**) was found to be 64% by comparison to the internal standard. *n*-Butanethiol was also observed in 96% yield by ^{1}H NMR spectroscopy when the reaction was monitored in C_6D_6 (δ 2.12, q, J = 7.5 Hz, 2 H; 1.27, quint, J = 6.3 Hz, 2 H; 1.13, sext, J = 7.5 Hz, 2 H; 1.04, t, J = 7.7 Hz, 1 H; 0.71, t, J = 7.4 Hz, 3 H).

X-ray Structural Determination of [Cp*IrCl]$_2$(μ-H)(μ-SC_4H_9) (1). Slow evaporation of an acetone solution of **1** produced orange plates. A single crystal of dimensions 0.50 × 0.30 × 0.10 mm^3 was mounted on a glass fiber with epoxy. Data were collected at −50 °C on a Siemens SMART CCD area detector system employing a 3 kW sealed-tube X-ray source operating at 1.5 kW. Over a period of 7 h, 1.3 hemispheres of data were collected, yielding 8052 total data after integration using SAINT (see Table 2). Laue symmetry revealed a monoclinic crystal system, and cell parameters were determined from 7095 reflections.[24] The space group was assigned as *Cc* on the basis of systematic absences and intensity statistics using XPREP, and the structure was solved using direct methods included in the SHELXTL 5.04 package. For a Z value of 4 there is one independent molecule within the asymmetric unit. In the final model, non-hydrogen atoms were refined anisotropically (full matrix on F^2), with hydrogens included in idealized locations. A bridging hydride ligand, located in a difference Fourier map, was included and refined isotropically. The Flack parameter value of 0.011 indicated the selection of the correct enantiomorph. The structure was refined to R_1 = 0.029 and wR_2 = 0.062.[25] Fractional coordinates and thermal parameters are given in the Supporting Information.

X-ray Structural Determination of [Cp*IrCl]$_2$(μ-H)[μ-S($C_6H_4CH_2CH_3$)] (2). Slow evaporation of an acetone solution of **2** produced small, orange plates. A single crystal of dimensions 0.24 × 0.30 × 0.08 mm^3 was mounted on a glass fiber with epoxy. Data were collected at −50 °C on a Siemens SMART CCD area detector system employing a 3 kW sealed-tube X-ray source operating at 1.5 kW. Over a period of 7 h, 1.3 hemispheres of data were collected, yielding 17 708 total data after integration using SAINT (see Table 2). Laue symmetry revealed a monoclinic crystal system, and cell parameters were determined from 8192 unique reflections.[24] The space group was assigned as $P2_1/c$ on the basis of systematic absences using XPREP, and the structure was solved using direct methods included in the SHELXTL 5.04 package. For a Z value of 4 there is one independent molecule within the asymmetric unit. In the final model, non-hydrogen atoms were refined anisotropically (full matrix on F^2), with hydrogens included in idealized locations. A bridging hydride ligand, located in a difference Fourier map, was included and refined isotropically. The structure was refined with final residuals of R_1 = 0.032 and wR_2 = 0.059.[25] Fractional coordinates and thermal parameters are given in the Supporting Information.

X-ray Structural Determination of [Cp*IrCl]$_3SC_4H_6$ (3). After recrystallization from toluene, the filtered solid was dissolved in acetone and orange plates were grown by slow evaporation. A single crystal of dimensions 0.50 × 0.10 × 0.20 mm^3 was mounted on a glass fiber with epoxy. Data were collected at −50 °C on a Siemens SMART CCD area detector system employing a 3 kW sealed-tube X-ray source operating at 1.5 kW. Over a period of 14 h, 1.3 hemispheres of data were collected, yielding 13 468 total data after integration using SAINT (see Table 2). Laue symmetry revealed a monoclinic crystal system, and cell parameters were determined from 8283 reflections.[24] The space group was assigned as $P2_1$ on the basis of systematic absences and intensity statistics using XPREP, and the structure was solved using direct methods included in the SHELXTL 5.04 package. For a Z value of 2 there is one independent molecule within the asymmetric unit,

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(24) It has been noted that the integration program SAINT produces cell constant errors that are unreasonably small, since systematic error is not included. More reasonable errors might be estimated at 10× the listed values.

(25) Using the SHELXTL 5.04 package, $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$, $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [f(\text{maximum of 0 or } F_o^2) + (1 - f)F_c^2]$.

and one toluene molecule was also located in the structure. In the final model, non-hydrogen atoms other than those found in toluene were refined anisotropically (full matrix on F^2), with hydrogens included in idealized locations. A bridging hydride ligand, located in a difference Fourier map, was included and refined isotropically. The Flack parameter value of 0.011 indicated the selection of the correct enantiomorph. The structure was refined with final residuals of $R_1 = 0.031$ and $wR_2 = 0.070$.[25] Fractional coordinates and thermal parameters are given in the Supporting Information.

Acknowledgment is made to the National Science Foundation (Grant CHE-9421727) for their support of this work. We also thank Dr. Rene Lachicotte for assistance with the crystal structure determinations.

Supporting Information Available: Tables of bond distances, angles, atomic coordinates, and thermal parameters for **1**, **2**, and **3** (18 pages). Ordering information is given on any current masthead page.

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