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Simultaneous Coordination of Hydrides and η^1-S Thiophenes Made Possible at Iridium

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The complexes $[IrH_2(\eta^1S\text{-}Th)_2(PPh_3)_2]PF_6$ (Th = thiophene (**2**), benzo[*b*]thiophene (**3**), dibenzothiophene (**4**) and tetrahydrothiophene (**5**)) have been synthesized in high yields by hydrogenation of $[Ir(COD)(PPh_3)_2]PF_6$ (COD = 1,5-cyclooctadiene) in the presence of the appropriate thiophene. The structures of **2** and **5** have been determined by X-ray diffraction. Crystal data: **2**, monoclinic, space group *C*2/*c*, with $a = 12.742$ (6) Å, $b = 17.078$ (4) Å, $c = 22.920$ (3) Å, $\beta = 93.33$ (2)°, $Z = 4$, and $R = 0.038$ ($R_w = 0.041$) for 2802 unique reflections; **5**, monoclinic, space group $P2_1/a$ with $a = 21.995$ (5) Å, $b = 19.428$ (3) Å, $c = 10.403$ (5) Å, $\beta = 100.59$ (2)°, $Z = 4$, and $R = 0.064$ ($R_w = 0.071$) for 4058 unique reflections. In both complexes the coordination geometry around the metal atom consists of a distorted octahedron with mutually *cis* S-bonded thiophenes, *cis* hydrides and *trans* triphenylphosphines. These structures can be considered as models for the initial chemisorption step in the hydrodesulfurization of thiophenes on solid catalysts.

Introduction

The interaction of thiophenes with transition metals continues to attract considerable interest as model chemistry for the hydrodesulfurization (HDS) reaction, which is one of the largest volume applications of transition metal catalysis.[1]

Two main types of HDS mechanisms have been proposed to occur on surfaces; one involves π coordination of the thiophene, either in the η^2 or the η^5 fashion,[2] prior to desulfurization, while the other involves cleavage of the C–S bonds of η^1-S-bonded thiophene.[3] During the last few years, a variety of coordination modes of thiophene on metal complexes have been authenticated.[4] The η^5-thiophene coordination has generally turned out to be the most stable one, and a number of well-characterized complexes of this type are now known. On the other hand, complexes containing η^1-S-bonded thiophenes continue to be elusive; the accumulated experimental evidence shows that this type of bonding is usually rather weak, resulting in very unstable or labile compounds.[4] This has precluded in most cases a proper characterization of the complexes and the study of the reactivity of the η^1S-bonded thiophene. The only structurally characterized compounds containing simple unchelated η^1-S-bonded thiophenes are $Cp^*(CO)_2Re(T)$ (T = thiophene),[5] $[Cp(CO)(PPh_3)Ru(2\text{-}Me\text{-}T)]BF_4$,[6] $[CpFe(CO)_2(\eta^1S\text{-}DBT)]$ (DBT = dibenzothiophene),[7] and $Cp^*IrCl_2(DBT)$;[8] other related complexes include $[(PPh_3)_2Ru(C_5H_4CH_2C_4H_3S)]^+$ in which the S-bonded thiophene is linked to a cyclopentadienyl ligand through a $\text{-}CH_2\text{-}$ group,[9] $[RuCl\{6\text{-}(thienyl)\text{-}2,2'\text{-}bipyridine\}_2]Cl$ which contains the thiophene moiety attached to a bipyridine framework,[10] and $RuCl_2\{(p\text{-}tolyl)_2P\text{-}DBT)\}_2$, in which dibenzothiophene is part of a chelating phosphine ligand.[11] A number of crystal structures of metal complexes containing tetrahydrothiophene (THT) ligands are available.[12]

Besides the activation of thiophenes by coordination to metal centers, it is crucial in the context of the HDS mechanism, to obtain information on how dissociation of hydrogen takes place on catalytic surfaces, and on the pathways through which such activated hydrogen combines with chemisorbed organosulfur compounds to yield the hydrodesulfurized products. Several proposals have been advanced in this respect for metal sulfide catalysts: (i) oxidative addition of dihydrogen to single or multiple metal centers to yield metal hydrides, which would then react with neighboring thiophenes; (ii) heterolytic activation of dihydrogen to yield a metal hydride plus a surface –SH group. Desulfurization of thiophenes may then take place by either hydride or proton attack to C═C and/or C—S bonds.[1–3]

With the aim of probing these important mechanistic aspects, we became interested in exploring the possibility of activating both dihydrogen and thiophenes on the same metal atom. Coordination of hydrides and thiophenes on one metal center would provide a particularly favorable situation for a hydride attack on coordinated thiophene to take place, if such a mechanism is of importance in connection with HDS.

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In 1986 some of us reported the reaction of [Rh(COD)-$(PPh_3)_2]PF_6$ (COD = 1,3-cyclooctadiene) with hydrogen and thiophene leading to the π-bonded derivative [(η^5-T)$Rh(PPh_3)_2]PF_6$.[13] In the same paper it was briefly mentioned that the analogous reaction with $[Ir(COD)(PPh_3)_2]PF_6$ (**1**) led to a product wrongly formulated then as [(η^5-T)$Ir(PPh_3)_2]PF_6$ (**1′**). We now report a more detailed account of the reactions of **1** with H_2 in the presence of thiophenes, which lead in fact to a novel series of very stable η^1S-bonded complexes $[IrH_2(\eta^1S\text{-}Th)_2(PPh_3)_2]PF_6$ [Th = T (**2**), which is the correct formulation for the complex previously described as **1′**,[13] BT, benzo[*b*]thiophene (**3**), DBT (**4**), THT (**5**)]; the X-ray structures of complexes **2** and **5** are also described. To the best of our knowledge, there are no previous examples of metal complexes containing more than one thiophene or both thiophene and hydride ligands on the same metal atom.

Experimental Section

All the reactions were carried out under dry nitrogen or argon using standard Schlenk techniques. Solvents were distilled from appropriate drying agents immediately prior to use. $[Ir(COD)(PPh_3)_2]PF_6$ was prepared by the method described in the literature.[14] Thiophene (Aldrich) was purified by a known procedure;[15] benzothiophene (Aldrich) was recrystallized from ethanol/water mixtures; $IrCl_3 \cdot 3H_2O$ (Johnson Matthey) and all other chemicals (Aldrich) were used without further purification. ^1H and ^{31}P NMR measurements were performed using a Bruker AM 300 instrument (300.134 and 121.496 MHz).

$[Ir(H)_2(\eta^1\text{-}Th)_2(PPh_3)_2]PF_6$[Th = T (2), BT (3), DBT (4), THT (5)]. In a typical experiment, to a solution of **1** (200 mg, 0.21 mmol) in CH_2Cl_2 (20 mL) was added thiophene (0.3 mL, 3.7 mmol), and hydrogen was then bubbled for 30 min during which the color of the solution changed from red to pale yellow. The volume of the resulting mixture was reduced to *ca.* 50% and diethyl ether was added until complete precipitation of **2** as white crystals, which were washed with cold CH_2Cl_2 and diethyl ether and dried *in vacuo.* (87% yield; ^{1}NMR (CD_2Cl_2, 243 K) 7.46 ppm (m, H_2-T), 6.98 ppm (m, H_3-T), 7.1 ppm (m, PPh_3)). Compounds **4** and **5** were prepared by the same method, using dibenzothiophene (230 mg, 1.24 mmol) (70% yield; ^1H NMR (CD_2Cl_2, 298 K) 7.90 ppm (m, H_2-DBT), 7.58 ppm (m, H_5-DBT), 7.2 ppm (m, PPh_3); white crystals) and tetrahydrothiophene (0.3 mL, 3.4 mmol) (85% yield, ^1H NMR (CD_2Cl_2, 298 K) 7.2 ppm (m, PPh_3), 2,77 ppm (br, H_2-THT), 1.91 ppm (m, H_3-THT); white crystals.). Complex **3** was best prepared by addition of a 10-fold excess of BT to $[Ir(H)_2(THF)_2(PPh_3)_2]PF_6$[14b] in THF solution at room temperature, followed by addition of diethyl ether (85% yield; ^1H NMR (CD_2Cl_2, 223 K) 6.36 ppm (d, *J*(H–H) = 15.8 Hz, H_2-BT), 6.93 ppm (d, *J*(H–H) = 5.5 Hz, H_3-BT), 7.3 (m, PPh_3).

Anal. Calcd for $C_{44}H_{40}F_6IrP_3S_2 \cdot 0.5CH_2Cl_2$ (**2**): C, 49.73; H, 3.82; S, 5.98. Found: C, 49.68; H, 3.92; S, 6.10. Calcd for $C_{52}H_{44}F_6IrP_3S_2$ (**3**): C, 55.15; H, 3.89; S, 5.67. Found: C, 54.96; H, 3.81; S, 5.77. Calcd for $C_{60}H_{48}F_6IrP_3S_2$ (**4**): C, 58.47; H, 3.90; S, 5.21. Found: C, 58.41; H, 3.81; S, 5.40. Calcd for $C_{44}H_{48}F_6IrP_3S_2$ (**5**): C, 50.80; H, 4.62; S, 6.18. Found: C, 50.63; H, 4.69; S, 6.09.

X-ray Diffraction Studies. Summary of crystal and intensity data for $[Ir(PPh_3)_2(H)_2(C_4H_4S)_2]PF_6 \cdot 0.5CH_2Cl_2$ (**2**) and $[Ir(PPh_3)_2(H)_2(C_4H_8S)_2]PF_6$ (**5**) are reported in Table I.

All X-ray measurements were performed at room temperature. The data were collected for compound **2** on a Enraf-Nonius CAD4 diffractometer and for compound **5** on a Philips PW1100 diffractometer. Unit cell dimensions were determined from the least-squares refinement of the angular settings of 25 carefully centered reflections for each compound. Three standard reflections, checked every 2 h, showed a significant decay only for compound **2** (ca. 10%). Intensity data were corrected for Lorentz–polarization effects. Atomic scattering factors were those reported by Cromer and Waber with anomalous dispersion correction taken from ref 16. Absorption correction was applied using the program DIFABS.[17] All the calculations were done on a DIGITAL DEC 5000/200 computer, by using the SHELX76 program. The structures were solved by the heavy atom technique. Some detailed procedures for each structure are reported below.

Table I. Summary of Crystal Data for $[Ir(PPh_3)_2(H)_2(C_4H_4S)_2]PF_6 \cdot 0.5CH_2Cl_2$ (**2**) and $[Ir(PPh_3)_2(H)_2(C_4H_8S)_2]PF_6$ (**5**)

	2	**5**
formula	$C_{44.5}H_{41}P_3S_2F_6Ir_1Cl_1$	$C_{44}H_{48}P_3S_2F_6Ir_1$
mol wt	1074.51	1040.11
cryst size, mm	0.37 × 0.32 × 0.17	0.50 × 0.40 × 0.37
cryst syst	monoclinic	monoclinic
space group	*C*2/*c* (No. 15)	$P2_1/a$ (No. 14)
a, Å	12.742(6)	21.995(5)
b, Å	17.078(4)	19.428(3)
c, Å	22.920(3)	10.403(5)
β, deg	93.33(2)	100.59(2)
V, Å^3	4979.15	4369.68
Z	4	4
d_{calc}, g cm^{-3}	1.43	1.58
μ(Cu Kα), cm^{-1}	30.04	82.24
radiation	Mo Kα, λ = 0.710 69 Å	Cu Kα, λ = 1.5418 Å
scan type	ω–2θ	ω–2θ
2θ range, deg	5–45	5–50
scan width, deg	0.7 + 0.35(tan θ)	0.8 + 0.15(tan θ)
scan speed, deg^{-1}	0.13	0.05
tot. no. of data	3491	4983
no. of unique data, $I \geq 3\sigma(I)$	2802	4058
no. of params	304	186
R	0.038	0.064
R_w	0.041	0.071
abs. cor, min–max	0.88–1.21	0.73–1.31

$[Ir(PPh_3)_2(H)_2(C_4H_4S)_2]PF_6 \cdot 0.5CH_2Cl_2$ (2). Both the complex cation and the PF_6^- anion have inner C_2 symmetry with the Ir and P(2) atoms lying on the 2-fold axis. In the last ΔF Fourier a peak attributable to the unique hydride ligand was detected and successfully refined at the late stage of the least-squares refinement. Also in this case, the initial cycles were performed by defining only isotropic thermal parameters. Finally the anisotropic parameters were introduced for all of the non-hydrogen atoms. The atoms of methylene chloride solvent molecule were assigned a population factor of 0.5. Crystallographic and other relevant data collection are reported in Table I. Atomic coordinates for all the non-hydrogen atoms are given in Table II.

$[Ir(PPh_3)_2(H)_2(C_4H_8S)_2]PF_6$ (5). Refinement was done by full-matrix least-squares calculations, initially with isotropic thermal parameters and finally with anisotropic thermal parameters for Ir, P, and S atoms. The phenyl rings were treated as rigid bodies of D_{6h} symmetry with C–C distances fixed at 1.395 Å and calculated hydrogen atom positions (C–H = 1.08 Å). None of the residual peaks detected in the Fourier map allowed us to localize the metal-coordinated hydride ligands. An attempt to locate the latter atoms with the program HYDEX could not be considered successful as the two atoms collapse into each other. Crystallographic and other relevant data collection are reported in Table I. Atomic coordinates for all the non-hydrogen atoms are given in Table III.

Results

Syntheses of $[IrH_2(\eta^1\text{-}Th)_2(PPh_3)_2]PF_6$ Complexes. The complex $[Ir(COD)(PPh_3)_2]PF_6$ (**1**) reacts rapidly with hydrogen in the presence of thiophenes, to form $[IrH_2(\eta^1\text{-}S\text{-}Th)_2(PPh_3)_2]PF_6$ [Th = T (**2**), BT (**3**), DBT (**4**), THT (**5**)] in good yields (eq 1).

$$[Ir(COD)(PPh_3)_2]^+ + 6H_2 + 2Th \rightarrow [IrH_2(\eta^1\text{-}S\text{-}Th)_2(PPh_3)_2]^+ + C_8H_{16} \quad (1)$$

In the case of BT, this direct method does not usually yield **3** in a pure form. A better synthetic procedure for this compound is the addition of excess BT to a THF solution of $[Ir(H)_2(THF)_2(PPh_3)_2]PF_6$, previously generated by hydrogenation of $[Ir(COD)(PPh_3)_2]PF_6$.[14b]

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Table II. Atomic Parameters for the Structure of $[Ir(PPh_3)_2(H)_2(C_4H_4S)_2]PF_6{\cdot}0.5CH_2Cl_2$[a]

atom	*x*	*y*	*z*	*U* or U_{eq}, Å^2
Ir	10000	287(1)	2500	33(0.2)*
H	11056(90)	−331(56)	2551(51)	108(36)
P1	9966(1)	142(1)	1491(1)	35(1)*
P2	10000	4414(2)	2500	54(2)*
S	8490(2)	1174(1)	2375(1)	45(1)*
C1	7494(7)	1131(5)	2845(4)	62(5)*
C2	7183(9)	1868(7)	2965(5)	84(7)*
C3	7794(8)	2448(6)	2727(5)	75(6)*
C4	8557(7)	2174(5)	2410(4)	57(5)*
C1,1	9583(5)	1007(4)	1064(3)	35(4)*
C2,1	10027(6)	1718(4)	1212(3)	46(5)*
C3,1	9788(7)	2387(5)	895(4)	57(5)*
C4,1	9065(7)	2351(5)	427(4)	59(5)*
C5,1	8632(7)	1651(6)	263(4)	62(5)*
C6,1	8875(7)	977(5)	580(4)	51(5)*
C1,2	9038(6)	−602(4)	1200(3)	41(4)*
C2,2	8040(7)	−612(5)	1382(4)	55(5)*
C3,2	7284(7)	−1124(5)	1136(4)	66(6)*
C4,2	7555(9)	−1626(7)	713(5)	79(6)*
C5,2	8586(9)	−1653(6)	533(5)	76(7)*
C6,2	9313(7)	−1118(5)	774(4)	55(5)*
C1,3	11218(6)	−149(4)	1208(3)	40(4)*
C2,3	11723(6)	−793(4)	1441(3)	49(4)*
C3,3	12695(7)	−1003(6)	1259(4)	64(5)*
C4,3	13172(7)	−588(6)	844(4)	64(5)*
C5,3	12678(7)	51(7)	610(5)	68(6)*
C6,3	11698(7)	278(5)	780(4)	54(5)*
F1	11234(4)	4402(4)	2437(3)	91(4)*
F2	9887(5)	3748(4)	2013(3)	98(5)*
F3	9861(7)	5039(7)	2009(4)	126(7)*
C5	6144(14)	1176(14)	1227(10)	82(13)*
Cl1	5636(6)	756(4)	587(3)	99(4)*
Cl2	5920(7)	2136(4)	1269(3)	140(5)*

[a] Thermal Parameters multiplied by 1000, coordinates by 10000. An asterisk denotes U_{eq}, defined as one-third of the trace of the orthogonalized thermal tensor.

Table III. Atomic Parameters for the Structure of $[Ir(PPh_3)_2(H)_2(C_4H_8S)_2]PF_6$[a]

atom	*x*	*y*	*z*	*U* or U_{eq}
Ir1	2446(1)	710(1)	3889(1)	23(1)*
P1	1456(1)	556(2)	4290(3)	27(2)*
P2	3494(1)	502(2)	4246(3)	22(2)*
P3	3235(2)	2653(2)	−929(4)	62(2)*
S1	2176(2)	691(2)	1500(3)	38(2)*
S2	2593(2)	1964(2)	3988(3)	39(2)*
C1	2772(6)	455(8)	562(15)	50(4)
C2	2544(8)	−122(10)	−280(18)	77(5)
C3	1868(6)	−195(8)	−444(14)	52(4)
C4	1700(8)	−38(9)	855(17)	69(5)
C5	2453(8)	2412(9)	2411(17)	71(5)
C6	2033(11)	2965(12)	2541(23)	109(7)
C7	1952(10)	3128(11)	3858(21)	98(6)
C8	2032(7)	2479(8)	4635(15)	55(4)
C1,1	819(3)	685(4)	2931(8)	34(3)
C2,1	812(3)	1297(4)	2226(8)	36(3)
C3,1	332(3)	1427(4)	1176(8)	59(4)
C4,1	−140(3)	946(4)	832(8)	64(4)
C5,1	−133(3)	335(4)	1537(8)	62(4)
C6,1	346(3)	204(4)	2587(8)	47(4)
C1,2	1221(3)	1060(5)	5593(7)	32(3)
C2,2	599(3)	1220(5)	5545(7)	44(4)
C3,2	413(3)	1547(5)	6602(7)	53(4)
C4,2	850(3)	1715(5)	7708(7)	60(4)
C5,2	1472(3)	1555(5)	7756(7)	58(4)
C6,2	1658(3)	1227(5)	6699(7)	48(4)
C1,3	1345(4)	−328(4)	4817(7)	34(3)
C2,3	1458(4)	−868(4)	4008(7)	45(4)
C3,3	1371(4)	−1547(4)	4371(7)	55(4)
C4,3	1172(4)	−1686(4)	5543(7)	56(4)
C5,3	1060(4)	−1146(4)	6352(7)	54(4)
C6,3	1146(4)	−467(4)	5988(7)	45(4)
C1,4	4049(3)	1173(4)	3995(6)	24(3)
C2,4	4571(3)	1316(4)	4941(6)	34(3)
C3,4	5005(3)	1795(4)	4683(6)	43(3)
C4,4	4918(3)	2132(4)	3478(6)	51(4)
C5,4	4396(3)	1989(4)	2532(6)	47(4)
C6,4	3962(3)	1510(4)	2791(6)	35(3)
C1,5	3731(3)	−234(4)	3340(9)	29(3)
C2,5	3359(3)	−820(4)	3148(9)	44(4)
C3,5	3529(3)	−1377(4)	2445(9)	57(4)
C4,5	4072(3)	−1348(4)	1934(9)	59(4)
C5,5	4445(3)	−762(4)	2127(9)	42(4)
C6,5	4274(3)	−205(4)	2829(9)	33(3)
C1,6	3765(4)	273(4)	5967(7)	28(3)
C2,6	4059(4)	−353(4)	6318(7)	38(3)
C3,6	4252(4)	−518(4)	7635(7)	61(4)
C4,6	4150(4)	−57(4)	8601(7)	68(5)
C5,6	3856(4)	570(4)	8250(7)	59(4)
C6,6	3664(4)	735(4)	6933(7)	37(3)
F1	3462(6)	3052(7)	412(13)	117(4)
F2	3340(6)	1989(7)	−136(14)	130(5)
F3	2538(7)	2665(9)	−589(17)	152(6)
F4	3041(8)	3310(9)	−1752(17)	159(6)
F5	3876(9)	2664(10)	−1243(19)	182(7)
F6	3024(7)	2242(8)	−2212(16)	150(5)

[a] Thermal Parameters multiplied by 1000, Coordinates by 10000. An asterisk denotes U_{eq}, defined as one-third of the trace of the orthogonalized thermal tensor.

Table IV. NMR Data (δ, ppm) for Compounds **2–5** in CD_2Cl_2

complex	^1H	^{31}P
2	−17.98 (t)[a]	13.30 (s)[b] 11.24 (s)[c]
3	−17.22 (t)[d]	13.64 (s)[e]
4	−17.27 (t)[f]	11.23 (s)
5	−17.08 (t)[g]	13.45 (s)

[a] J_{H-P} = 15.1 Hz; at 243 K. [b] At 243 K. [c] MAS spectrum of solid **2**. [d] J_{H-P} = 15 Hz; at 223 K. [e] At 223 K; δ 12.79 at 293 K. [f] J_{H-P} = 16.9 Hz. [g] J_{H-P} = 17.3 Hz.

Complexes **2–5** are air stable in the solid state. Relevant ^1H and $^{31}P\{^1H\}$ NMR data are contained in Table IV. The high-field ^1H NMR spectra display triplets (T_1 values at 298 K and 300 MHz in CD_2Cl_2 range from 200 ± 10 ms to 210 ± 10 ms), while the corresponding $^{31}P\{^1H\}$ spectra consist of singlets. These features indicate the presence of two equivalent hydrides coupled with two equivalent phosphines, corresponding to a stereochemistry involving mutually *trans* phosphines, and mutually *cis* pairs of hydride and Th ligands. This is in accord with the solid-state structures determined by X-ray diffraction (*vide infra*). It is interesting to note that all four complexes prefer to adopt the more sterically crowded stereochemistry containing two *cis* thiophenes rather than an all *trans* disposition of the six ligands, most probably as a result of the large *trans* effect typical of hydride ligands. The latter give rise to intense ν(Ir–H) bands in the region from 2220 to 2180 cm^{-1}.

The thiophene and benzothiophene derivatives **2** and **3** undergo rapid exchange of a Th ligand in solution even with a poorly coordinating solvent like CD_2Cl_2 to yield new species $[IrH_2(\eta^1\text{S-Th})(CD_2Cl_2)(PPh_3)_2]^+$ (Th = T, **2′**, Th = BT, **3′**) (eq 2).

$$\underset{\mathbf{2,\,3}}{[IrH_2(\eta^1\text{-Th})_2(PPh_3)_2]^+} \overset{CD_2Cl_2}{\rightleftharpoons} \underset{\mathbf{2',\,3'}}{[IrH_2(\eta^1\text{-Th})(CD_2Cl_2)(PPh_3)_2]^+} + T \qquad (2)$$

This causes broadening of the spectral features at room temperature, which resolve well at 243 K for **2** and 223 K for **3**, at which temperatures the equilibria are largely shifted to the left. In agreement with this, incremental addition of the corresponding Th ligand to CD_2Cl_2 solutions of **2**/**2′** or **3**/**3′** results in the enhancement of the intensity of the ^1H and ^{31}P spectra corresponding to **2** and **3**, respectively. Finally, if **2** is dissolved in a more strongly coordinating solvent like CD_3CN, the original spectra are no longer observed; instead, the high field ^1H spectrum

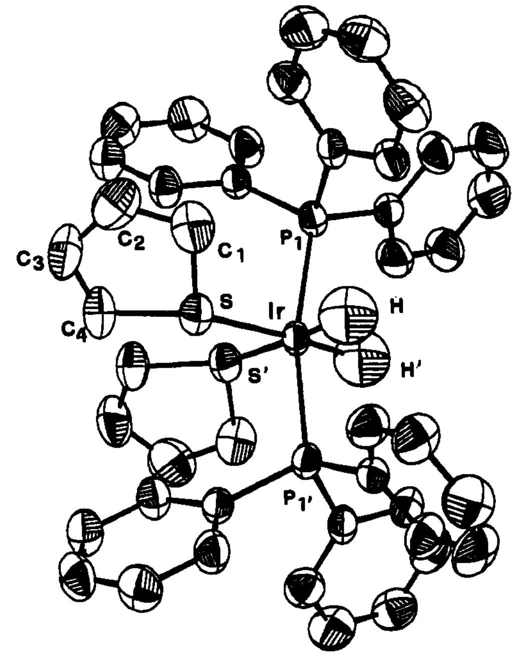

Figure 1. ORTEP drawing of the cation $[IrH2(\eta^1\text{-S-thiophene})_2(PPh_3)_2]^+$.

Table V. Selected Bond Distances (Å) and Angles (deg) for $[Ir(PPh_3)_2(H)_2(C_4H_4S)_2]PF_6 \cdot 0.5CH_2Cl_2$

	Distances		
Ir–P1	2.325(2)	C2–C3	1.39(2)
Ir–H	1.7(1)	C3–C4	1.33(1)
Ir–S	2.452(2)	P1–C1,1	1.821(7)
S–C1	1.71(1)	P1–C1,2	1.835(8)
S–C4	1.713(8)	P1–C1,3	1.825(8)
C1–C2	1.35(1)		
	Angles		
S–Ir–P1	88.86(7)	Ir–P1–C1,2	114.2(2)
H–Ir–P1	88.3(9)	Ir–P1–C1,3	104.0(3)
H–Ir–S	177(4)	S–C1–C2	109.0(8)
P1–Ir–P1′	167.8(1)	S–C4–C3	109.9(7)
H1–S–H1′	104(5)	C1–S–C4	92.8(4)
S–Ir–S′	103.7(1)	C1–C2–C3	114.0(9)
Ir–P1–C1,1	115.9(2)	C2–C3–C4	114.1(9)

shows a triplet at −20.56 ppm ($J_{H\text{-}P}$ = 17 Hz), and the ^{31}P spectrum consists of only a singlet at 19.14 ppm; these spectral changes are attributed to the complete conversion of **2** into $[IrH_2(NCCD_3)_2(PPh_3)_2]^+$ (eq 3); in agreement with this, free thiophene was detected by NMR (2 equiv) and by gas chromatography of the CD_3CN solution.

$$[IrH_2(\eta^1\text{-T})_2(PPh_3)_2]^+ \overset{CD_3CN}{\rightleftharpoons} [IrH_2(NCCD_3)_2(PPh_3)_2]^+ + 2T \quad (3)$$

No ligand exchange with CD_2Cl_2 was apparent at room temperature in the case of **4** or **5**, showing that DBT and THT are more basic than T or BT.

Discussion

Structures of $[IrH_2(\eta^1\text{-Th})_2(PPh_3)_2]PF_6$. The cations of **2** and **5** are shown in Figures 1 and 2, respectively. Selected bond distances and angles are collected in Tables V and VI. The coordination geometries around the metal atoms consist of distorted octahedra with *cis* sulfur atoms, *cis* hydrides and *trans* phosphines. The main distortion from the ideal octahedral geometry in both cases is the bending of the bulky phosphine ligands toward the small hydrides, in order to minimize steric repulsions. The Ir–S distances in **2** and **5** (2.452 and 2.457 Å, see Tables V and VI) are somewhat longer than those found in other η^1-S-bonded metal complexes of thiophenes, $Cp^*(CO)_2Re(T)$ (2.360 Å),[5a] $Cp^*(CO)_2Re(3\text{-MeBT})$ (2.356 Å),[5b] $[Cp(CO)(PPh_3)Ru(2\text{-Me-T})]BF_4$ (2.392 Å),[6] $[CpFe(CO)_2(\eta^1\text{-S-DBT})$ (2.289 Å),[7] $Cp^*IrCl_2(DBT)$ (2.375 Å),[8] $[(PPh_3)_2Ru(C_5H_4CH_2C_4H_3S)]^+$ (2.408 Å),[9] $[RuCl\{6\text{-(thienyl)-}2,2'\text{-bipyridine}\}_2]Cl$ (2.380 Å),[10] $RuCl_2\{(p\text{-tolyl})_2P(DBT)\}_2$ (2.343 and 2.402 Å),[11] and $Cp(PMe_3)Ru(2,5\text{-DHT})^+$ (2.330 Å).[19] The sulfur atoms in the structures of **2**, and **5** adopt a pyramidal geometry corresponding to an approximate sp^3 hybridization. Correspondingly, the sum of the angles around the S atoms [338° (**2**) and 324° (**5**)] are much less than the 360° required for a trigonal planar disposition. All the other structurally characterized η^1-S thiophene complexes[5–11] also contain pyramidal S atoms, although minor geometrical differences are observed from one complex to another.

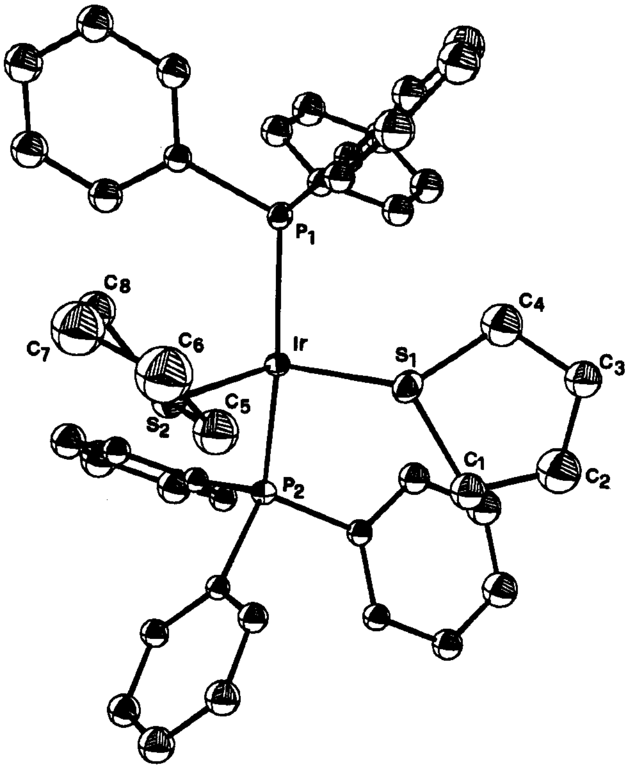

Figure 2. ORTEP drawing of the cation $[IrH_2(\eta^1\text{-S-tetrahydrothiophene})_2(PPh_3)_2]^+$.

Table VI. Selected Bond Distances (Å) and Angles (deg) for $[Ir(PPh_3)_2(H)_2(C_4H_8S)_2]PF_6$

	Distances		
Ir–P1	2.309(3)	S2–C8	1.81(2)
Ir–P2	2.303(3)	C1–C2	1.45(2)
Ir–S1	2.446(3)	C2–C3	1.47(2)
Ir–S2	2.457(3)	C3–C4	1.49(2)
S1–C1	1.83(2)	C5–C6	1.44(3)
S1–C4	1.81(2)	C6–C7	1.45(3)
S2–C5	1.83(2)	C7–C8	1.49(3)
	Angles		
P1–Ir–P2	153.7(1)	Ir–S2–C5	115.7(6)
S1–Ir–S2	93.6(1)	C5–S2–C8	93.3(8)
P1–Ir–S1	96.9(1)	S1–C1–C2	108(1)
P1–Ir–S2	104.0(1)	C1–C2–C3	112(1)
P2–Ir–S1	102.1(1)	C2–C3–C4	107(1)
P2–Ir–S2	92.7(1)	S1–C4–C3	106(1)
Ir–S1–C4	113.8(6)	S2–C5–C6	106(1)
Ir–S1–C1	118.7(5)	C5–C6–C7	116(2)
C1–S1–C4	91.6(7)	C6–C7–C8	108(2)
Ir–S2–C8	118(1)	S2–C8–C7	107(1)

The coordinated thiophene in **2** is essentially planar and only slightly distorted from its uncoordinated geometry. The S–C1

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[19] Sutherland, H. H.; Rawas, A. *Acta Crystallogr.* **1985**, *C41*, 929.

and S–C4 bonds of 1.71(1) and 1.713(8) Å are very close to the 1.714(1)-Å distance in free thiophene.[19] The C1–C2 (1.35(1) Å), C2–C3 (1.39(2) Å), and C3–C4 (1.33(1) Å) distances are a little shorter than the corresponding distances in free thiophene (1.370(2), 1.424(2), and 1.370(2) Å), but the alternate pattern of short–long–short bonds is maintained; similar effects have been observed for $Cp^*(CO)_2Re(T)$,[5a] $[Cp(CO)(PPh_3)Ru(2Me\text{-}T)]^+$,[6] and $[(PPh_3)_2Ru(C_5H_4CH_2C_4H_3S)]^+$.[9] Finally, the geometry of coordinated THT in **5** (Table III) compares well with those of other previously reported metal–THT complexes.[12]

Final Remarks in Relation to the HDS Mechanism. Adsorption of thiophenes to catalytic sites through the sulfur atom has been proposed as the first step in the HDS mechanism. Studies on thiophene adsorption on clean surfaces have shown that, depending on the coverage and the temperature, thiophene may be adsorbed parallel or perpendicular to the surface or tilted at an angle of approximately 40° from the surface.[20] The S-bonded complexes herein reported can be considered as good models for the latter situation. It is interesting to note that hydrides may coexist with thiophenes, even in the *cis* disposition which is favorable for attack to the sulfur ligand. This is probably related to the fact that iridium hydrides are among the strongest M–H bonds; this is clear, for instance, in Bergman's $(C_5Me_5)Ir(PMe_3)(alkyl)H$ complexes which do not reductively eliminate alkanes even above 100° C.[21] Angelici has also made an iridium hydride complex containing a C–S cleaved thiophene, which does not show any tendency towards H-transfer to the activated heterocycle.[22] In contrast, Rosini and Jones recently reported[23] that $ReH_3(PPh_3)_2$ (generated from $ReH_7(PPh_3)_2$ and 3,3-dimethyl-1-butene) reacts with thiophene by endo attack of one of the hydrides to C2, generating a stable thioallyl complex. It was suggested that the hydride attacks an η^4-T complex, but such intermediate could not be detected. Interestingly, thermolysis of the thioallyl compound in the presence of excess PMe_3 results in complete hydrogenation to free THT, whereas photolysis in presence of PMe_3 leads to C–S bond scission. Preliminary work on the reactivity of the complexes reported herein shows that hydride transfer to thiophene and benzothiophene leading to C═C bond hydrogenation can indeed be easily promoted; this will be the subject of future papers.

On a different line of thought, the facile displacement of coordinated thiophenes by solvent molecules in complexes **2** and **3** is suggestive of a different strategy for the removal of residual sulfur-containing aromatics from refined fuels in which the main organosulfur components are thiophenes and benzothiophenes. The reversible adsorption of such heteroaromatics on transition metal centers could be developed into a desulfurization process involving solvent extraction mediated by appropriate metal complexes.

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Supplementary Material Available: Tables of H-atom coordinates for **2** (Table S1) (1 page). Ordering information is given on any current masthead page.

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