HDS Model Systems. 2,3-Dihydrothiophene as an Intermediate in the Homogeneous Hydrogenation of Thiophene to Tetrahydrothiophene at Iridium

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Thermolysis of the bis(thiophene) (T) dihydride $[(PPh_3)_2Ir(H)_2(\eta^1\text{-}SC_4H_4)_2]PF_6$ (**1**) in 1,2-dichloroethane at 80 °C gives the thioallyl complex $[(PPh_3)_2IrH(\eta^4\text{-}SC_4H_5)]PF_6$ (**2**) by a stereospecific endo migration of one of the coordinated hydrides. Reaction of the thioallyl complex with H_2 under mild conditions yields the bis(tetrahydrothiophene) (THT) dihydride $[(PPh_3)_2Ir(H)_2(\eta^1\text{-}SC_4H_8)_2]PF_6$ (**3**) plus the pentahydride $[\{(PPh_3)_2IrH\}_2(\mu^2\text{-}H)_3]PF_6$ (**4**); if the hydrogenation is carried out in the presence of excess T, complex **3** is obtained exclusively. Interaction of **2** with CO at room temperature produces the two novel isomeric derivatives $[(PPh_3)_2Ir(H)(CO)(\eta^2\text{-}C_5,S\text{-}SC_4H_5)]PF_6$ (**7**) and $[(PPh_3)_2Ir(H)(CO)(\eta^2\text{-}C_3,S\text{-}SC_4H_5)]PF_6$ (**8**) in a 5:1 ratio, which do not interconvert from −50 to +80 °C; longer reaction times (24 h, 25 °C) or higher temperatures (3 h, 50 °C) result in quantitative conversion of the complex to $[(PPh_3)_2Ir(CO)_3]PF_6$ with concomitant liberation of 2,5-dihydrothiophene (2,5-DHT) and 2,3-DHT in a 5:1 ratio. Reaction of **2** with 2,5-DHT under H_2 at 80 °C produces the new bis(2,5-DHT) dihydride complex $[(PPh_3)_2Ir(H)_2(\eta^1\text{-}2,5\text{-}SC_4H_6)_2]PF_6$ (**5**), whereas the analogous reaction with 2,3-DHT results in hydrogenation to yield the bis(THT) dihydride derivative **3**. Complex **5** and its 2,3-DHT analog $[(PPh_3)_2Ir(H)_2(\eta^1\text{-}2,3\text{-}SC_4H_6)_2]PF_6$ (**6**) may also be prepared by displacement of coordinated acetone in $[(PPh_3)_2Ir(H)_2(Me_2CO)_2]PF_6$ (**5**) by the appropriate ligand. Complex **5** does not react with H_2 at 80 °C, whereas **6** is readily transformed into **3** under analogous conditions. Interaction of **2** with syngas results in the production of **7** and **8**, together with free 2,5-DHT and 2,3-DHT, plus small amounts of $[(PPh_3)_2Ir(H)_2(CO)(\eta^1\text{-}SC_4H_8)]PF_6$ (**10**) and $[(PPh_3)_2Ir(H)_2(CO)_2]PF_6$ (**11**). These combined results clearly establish that only the 2,3-DHT isomer is an intermediate in the homogeneous hydrogenation of T to THT (via the isolated thioallyl (**2**) and hydrido-η^2-C,S (**8**) intermediates) with this Ir system, a result of relevance in connection with the HDS mechanisms. The THT complex **10** crystallizes in monoclinic space group $P2_1$ (No. 4) with a = 9.563(4) Å, b = 23.201(4) Å, c = 11.221(2) Å, β = 97.87° (2), Z = 2, and V = 2466.16 Å^3. The structure of the complex cation consists of a distorted octahedron with mutually *cis*-hydrides, *cis*-THT, and CO and *trans*-PPh_3 ligands.

Introduction

The coordination and reactivity of thiophenes on transition metal centers continues to attract considerable attention as model chemistry for the species and reactions that occur during heterogeneous hydrodesulfurization (HDS) of petroleum and other fossil fuels.[2] A variety of bonding modes of thiophene (T) have been identified in metal complexes and proposed as molecular analogues for the chemisorption of such sulfur heterocycles onto active metal sites in catalytic surfaces. These include η^1-S, η^2-C=C, η^4, and η^5, as well as some bridging modes in dinuclear or cluster compounds. Several of these bonding modes have been suggested to be associated with subsequent steps of the HDS process, e.g. hydrogenation,[3] hydrogenolysis,[4] or complete desulfurization.[5]

Another crucial point concerns the reactions of coordinated thiophene with metal hydrides. It is known that hydrogen easily adsorbs dissociatively on HDS-active metal sulfide surfaces; the formation of metal hydrides in such processes as well as their possible intervention as nucleophiles in HDS-related reactions has been discussed several times in the heterogeneous literature.[6] Some examples of this type of reactivity are also available in molecular chemistry: Angelici has shown that attack of H^- on $[(\eta^5\text{-T})Mn(CO)_3]^+$ yields a stable η^3,η^1S-allyl sulfide derivative $(\eta^3,\eta^1\text{S-T})Mn(CO)_3$ which upon protonation produces coordinated 2,3-DHT.[3a] In a related case also reported by Angelici, nucleophilic attack of H^- to $[CpRu(\eta^5\text{-T})]^+$ leads to C–S bond scission instead of hydroge-

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(2) (a) Angelici, R. J. *Coord. Chem. Rev.* **1990**, *105*, 61. (b) Rauchfuss, T. B. *Prog. Inorg. Chem.* **1991**, *39*, 259. (c) Sanchez-Delgado, R. A. *J. Mol. Catal.*, in press.

(3) (a) Lesch, D. A.; Richardson, J. W., Jr.; Jacobson, R. A.; Angelici, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 2901. (b) Rosini, G. P.; Jones, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 10767.

(4) (a) Spies, G. H.; Angelici, R. J. *Organometallics* **1987**, *6*, 1897. (b) Hachgenei, W.; Angelici, R. J. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 909. (c) Hachgenei, W.; Angelici, R. J. *J. Organomet. Chem.* **1988**, *355*, 359.

(5) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Herrera, V.; Sanchez-Delgado, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 2731.

(6) (a) Wambeke, L.; Jalowiecki, S.; Kasztelan, S.; Grimblot, J.; Bonnelle, J. P. *J. Catal.* **1988**, *109*, 320. (b) Kasztelan, S. *Langmuir* **1990**, *6*, 590. (c) Komatsu, T.; Hall, W. K. *J. Phys. Chem.* **1991**, *95*, 9966. (d) Lacroix, M.; Yuan, S.; Breysse, M.; Dorémieux-Morin, C.; Fraissard, J. *J. Catal.* **1992**, *138*, 409.

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nation.[4] More recently, Rosini and Jones have demonstrated that $ReH_3(PPh_3)_2$ (generated from $ReH_7(PPh_3)_2$ + 3,3-dimethyl-1-butene) reacts with thiophene by intramolecular endo attack of one of the hydrides to C(2), again generating a stable thioallyl complex $Re(H)_2(PPh_3)_2$-(η^3,η^1S-C_4H_5), presumably via an undetected η^4-T intermediate. Thermolysis of this thioallyl complex in the presence of PMe_3 results in complete hydrogenation to free tetrahydrothiophene (THT), whereas photolysis in presence of PMe_3 leads to C–S bond scission to yield coordinated 1-butenethiolate ligands.[3b]

We recently described the synthesis and characterization of a novel series of stable iridium complexes of general formula $[(PPh_3)_2Ir(H)_2(Th)_2]^+$ (Th = T, THT, benzothiophene BT, and dibenzothiophene DBT),[7] which opens the interesting possibility of studying the reactivity of these derivatives containing both hydrides and thiophenes on the same metal center. In this paper we report a thermally induced intramolecular hydride attack to an η^1-S bonded T ligand leading to complete hydrogenation to produce THT via a stable hydrido thioallyl complex. A detailed study of the reactivity of the various intermediates has also allowed us to establish the hydrogenation mechanism which proceeds only through Ir hydride complexes containing coordinated 2,3-DHT. Finally an X-ray structure determination of the complex $[(PPh_3)_2$-$Ir(H)_2(CO)(\eta^1$-S-THT) is reported.

Experimental Section

General Information. All reactions and manipulations were routinely performed under nitrogen, except where otherwise stated, by using Schlenk techniques. Reagent grade chemicals were used in the preparations of the complexes. Commercial thiophene (Aldrich, 99%) was purified as described in the literature.[8] Chloroform and 1,2-dichloroethane were purified by distillation from P_2O_5 under nitrogen, whereas tetrahydrofuran (THF) and diethyl ether from $LiAlH_4$. All other solvents were reagent grade and were used as received. Literature methods were used for the preparation of $[(PPh_3)_2Ir(COD)]PF_6$ (COD = 1,5-cyclooctadiene),[9] $[(PPh_3)_2Ir(H)_2(\eta^1$-$OCMe_2)_2]PF_6$,[10] $[(PPh_3)_2$-$Ir(H)_2(\eta^1$-$SC_4H_4)_2]PF_6$ (1),[7] $[(PPh_3)_2Ir(H)_2(\eta^1$-$SC_4H_8)_2]PF_6$ (3),[7] 2,5-dihydrothiophene,[11] and 2,3-dihydrothiophene ($CHCl_3$ solution).[12] The solid complexes were collected on sintered-glass frits and washed with appropriate solvents before being dried under a stream of nitrogen. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrophotometer using samples mulled in Nujol between KBr plates. $CDCl_3$ was dried over molecular sieves. ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded on either a Varian VXR 300 (299.94, 121.42, and 75.43 MHz, respectively) or a Bruker ACP 200 (200.13, 81.01, and 50.32 MHz, respectively) spectrometer. Chemical shifts are relative to residual ^1H resonances in the deuterated solvents (^1H NMR), to the deuterated solvent resonance ($^{13}C\{^1H\}$ NMR), or to external 85% H_3PO_4, with downfield values reported as positive ($^{31}P\{^1H\}$ NMR). Broadband and selective $^1H\{^{31}P\}$ NMR experiments were carried out on the Bruker ACP 200 instrument equipped with a 5-mm inverse probe and a BFX-5 amplifier device. In general, the assignment of the proton and carbon chemical shifts was done on the basis of ^1H,^1H 2D-COSY, ^{13}C DEPT, and ^1H,^{13}C 2D-HETCOR NMR experiments; these experiments were conducted on the Bruker ACP 200 instrument. The computer simulation of NMR spectra was carried out with a locally developed package containing the programs LAOCN3[13] and DAVINS,[14] running on a Compaq Deskpro 386/25 personal computer. The initial choices of shifts and coupling constants were refined by iterative least-squares calculations using experimental digitized spectra. The final parameters gave a satisfactory fit between experimental and calculated spectra, the agreement factor R being less than 1% in all cases. Conductivities were measured with an Orion Model 990101 conductance cell connected to a Model 101 conductivity meter. The conductivity data were obtained at sample concentrations of ca. 10^{-3} M in nitroethane solutions at room temperature. GC analyses were performed on a Shimadzu GC-14 A gas chromatograph equipped with a flame ionization detector and a 30-m (0.25-mm i.d.; 0.25-μm FT) SPB-1 Supelco fused silica capillary column. GC/MS analyses were performed on a Shimadzu QP 2000 apparatus equipped with a column identical to that used for GC analyses.

Synthesis of $[(PPh_3)_2Ir(D)_2(\eta^1$-$SC_4H_4)_2]PF_6$ (1-d_2). After adding T (0.3 mL, 3.7 mmol) to a solution of $[(PPh_3)_2Ir(COD)]$-PF_6 (0.20 g, 0.21 mmol) in CH_2Cl_2 (20 mL), deuterium was bubbled for 30 min during which time 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 1-d_2 as white crystals, which were washed with cold diethyl ether and dried in vacuo, yield 87%. IR: ν (Ir–D) 1587 cm^{-1}, ν (Ir–H)/ν (Ir–D) = 1.4.

Synthesis of $[(PPh_3)_2IrH(\eta^4$-$SC_4H_6)]PF_6$ (2). A solution of 1 (0.30 g, 0.29 mmol) in 1,2-dichloroethane (30 mL) was heated at 80 °C for ca. 30 min during which time the color gradually changed from light yellow to red orange. After removal of the solvent in vacuo, the orange crude product was recrystallized by addition of n-heptane to a concentrated THF solution to give orange microcrystals fo 2 in 80% yield. Anal. Calcd (found) for $C_{40}H_{36}F_6IrP_3S$: C, 50.68 (50.61); H, 3.83 (3.79); Ir, 20.28 (20.14); S, 3.38 (3.22). Λ_M = 83 cm^2 Ω^{-1} mol^{-1}. IR: (ν Ir–H) 2205 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C, 81.01 MHz): AM pattern; δ 13.8 (d, P_A), 2.8 (d, P_M), $J(P_AP_M)$ = 5.5 Hz.

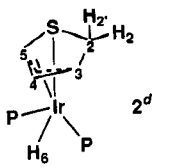
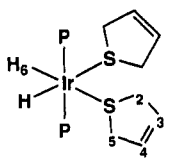
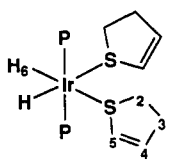
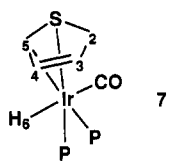
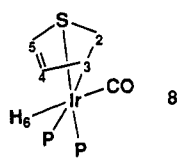
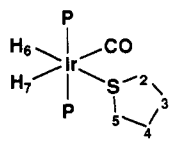
Synthesis of $[(PPh_3)_2IrD(\eta^4$-$SC_4H_4D)]PF_6$ (2-d_2). This synthesis proceeds as for 2 by using the bis-deuteride complex $[(PPh_3)_2Ir(D)_2(\eta^1$-$SC_4H_4)_2]PF_6$ (1-d_2). The orange product obtained was characterized by IR, $^{31}P\{^1H\}$, and ^1H NMR spectroscopy. The ^1H NMR spectrum was found to be analogous to that of 2 except for the absence of the resonances at δ 2.85 (H_2) and −21.04 (H_6) (see Table 1). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C, 81.01 MHz): AMX pattern (X = ^2D); δ 13.8 (m, P_A), 2.8 (m, P_M). IR: (ν Ir–D) 1590 cm^{-1}, ν (Ir–H)/ν (Ir–D) = 1.4.

Reaction of 1 with H_2. A light yellow solution of 1 (0.20 g, 0.19 mmol) in 1,2-dichloroethane (30 mL) was heated at 80 °C under a steady stream of hydrogen. After 2 h the resulting yellow solution was concentrated to dryness under vacuum to give a yellow solid which was washed with n-pentane. IR and multinuclear NMR spectroscopy showed the quantitative conversion of 1 to a 2:1 mixture of $[(PPh_3)_2Ir(H)_2(\eta^1$-$SC_4H_8)_2]PF_6$[7] (3) and $[\{(PPh_3)_2IrH\}_2(\mu^2$-$H)_3]PF_6$[15] (4). When the reaction was performed in the presence of T (20-fold excess), the isolated solid was shwon to contain 3 and 4 in a ratio of 5 to 1. The formation of 4 was almost completely suppressed by using a 100-fold excess of thiophene. No catalytic production of tetrahydrothiophene (THT) was observed even under a 30-atm hydrogen pressure. In a separate experiment, 4 did not react with T at 80 °C in 1,2-dichloroethane.

Reaction of 1 with THT. A solid sample of 1 (0.04 g, 0.04 mmol) was added to a $CDCl_3$ (0.7 mL) solution of THT (7 μL, 0.08 mmol) at room temperature. Analysis of the reaction mixture

(7) Sanchez-Delgado, R. A.; Herrera, V.; Bianchini, C.; Masi, D.; Mealli, C. *Inorg. Chem.* **1993**, *32*, 3766.
(8) Huckett, S. C.; Sauer, N. N.; Angelici, R. J. *Organometallics* **1987**, *6*, 591.
(9) Volger, H. C.; Vrieze, K.; Pratt, A. P. *J. Organomet. Chem.* **1968**, *14*, 429.
(10) Crabtree, R. H.; Hlatky, G. G.; Parnell, C. P.; Segmüller, B. E.; Uriarte, R. J. *Inorg. Chem.* **1984**, *23*, 354.
(11) Everhardus, R. H.; Gräfing, R.; Brandsma, L. *J. R. Neth. Chem. Soc.* **1976**, *95*, 153.
(12) Sauer, N. N.; Angelici, R. J.; Huang, Y. C. J.; Trahanovsky, W. S. *J. Org. Chem.* **1986**, *51*, 113.
(13) (a) Bothner-By, A. A.; Castellano, S. *QCPE* **1967**, *11*, 111. (b) Castellano, S.; Bothner-By, A. A. *J. Chem. Phys.* **1964**, *41*, 3863.
(14) Stephenson, D. S.; Binsch, G. *J. Magn. Reson.* **1980**, *37*, 395, 409.
(15) Crabtree, R. H.; Felkin, H.; Morris, G. E. *J. Organomet. Chem.* **1976**, *113*, C7.

Table 1. Selected NMR Spectral Data for the Complexes[a]

complex	^{1}H NMR assignt	^{1}H NMR δ (multiplicity, *J*)[b,c]	^{13}C{^{1}H} NMR assignt	^{13}C{^{1}H} NMR δ (multiplicity, *J*)[b]
 2[d]	H_4	6.59 (m, $^3J(H_4H_5)$ = 2.5, $^3J(H_4H_3)$ = 4.0)	C_4	92.0 (t, ^2J(CP) = 2.0)
	H_5	5.39 (m, $^4J(H_5H_3)$ = 1.5, $^4J(H_5H_2)$ = 1.5)	C_5	77.3 (d, ^2J(CP) = 15.3)
	$H_{2'}$	5.30 (ddd, $^2J(H_{2'}H_2)$ = 10.3)[e]	C_2	55.7 (dd, ^3J(CP) = 5.3, 2.7)
	H_3	3.44 (m, $^3J(H_3H_2)$ = 2.4)	C_3	49.8 (dd, ^2J(CP) = 29.2, 2.4)
	H_2	2.85 (m)		
	H_6	−21.03 (dd, $^2J(H_6P)$ = 23.0, 17.1)		
 5	H_3,H_4	5.34 (s)		
	H_2,H_5	3.20 (s)		
	H_6	−17.19 (t, $^2J(H_6P)$ = 17.3)		
 6	H_4	5.49 (dt, $^3J(H_4H_5)$ = 5.9, $^3J(H_4H_3)$ = 2.8)		
	H_5	5.03 (dt, $^4J(H_5H_3)$ = 2.2)		
	H_2	2.62 (t, $^3J(H_2H_3)$ = 8.2)		
	H_3	2.33 (m)		
	H_6	−17.25 (t, $^2J(H_6P)$ = 17.3)		
 7	H_4	6.38 (m, $^3J(H_4H_3)$ = 6.1, $^3J(H_4H_5)$ = 2.1)	C_3	142.6 (d, ^4J(CP) = 5.7)
	H_3	5.50 (m, $^3J(H_3H_{2'})$ = 2.6, $^3J(H_3H_2)$ = 2.6)	C_4	119.1 (d, ^3J(CP) = 6.4)
	H_5	4.60 (m, $^4J(H_5H_2)$ = 2.8, $^3J(H_5H_6)$ = 2.1)[f]	C_5	55.0 (dd, ^2J(CP) = 43.8, 3.0)
	H_2,$H_{2'}$	3.10 (m, $^2J(H_2H_{2'})$ = 19.3, $^4J(H_2H_4)$ = 2.3, $^4J(H_{2'}H_4)$ = 2.3)[g]	C_2	45.9 (br s)
	H_6	−10.87 (ddd, $^2J(H_6P)$ = 15.5, 12.9)		
 8	H_4	5.98 (m, $^3J(H_4H_5)$ = 6.3, $^3J(H_4H_3)$ = 2.5)	C_5	143.0 (d, ^3J(CP) = 5.0)
	H_5	5.42 (m, $^4J(H_5H_{2'})$ = 2.3, $^4J(H_5H_2)$ = 2.3)	C_4	119.3 (d, ^3J(CP) = 6.0)
	H_3	5.02 (m, $^3J(H_3H_2)$ = 2.5)[h]	C_3	55.7 (dd, ^2J(CP) = 43.5, 3.0)
	$H_{2'}$	2.85 (m, $^2J(H_{2'}H_2)$ = 18.4, $^4J(H_{2'}H_4)$ = 2.3)	C_2	45.5 (br s)
	H_2	2.20 (m, $^4J(H_2H_4)$ = 2.4)		
	H_6	−10.33 (dd, $^2J(H_6P)$ = 21.3, 11.7)		
 10	H_2,H_5	2.33 (m)		
	H_3, H_4	1.49 (m)		
	H_7	−8.60 (td, $^2J(H_7H_6)$ = 3.8, $^2J(H_7P)$ = 17.3)		
	H_6	−15.17 (brt, $^2J(H_6P)$ = 15.5)[i]		

[a] All spectra were recorded at room temperature in $CDCl_3$ solutions unless otherwise stated. [b] Chemical shifts are given in ppm and are relative either to residual ^{1}H resonances in the deuterated solvents (^{1}H NMR) or the deuterated solvent resonance (^{13}C{^{1}H} NMR). Key: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. Coupling constants (*J*) are in hertz. [c] The *J*(HH) values were determined on the basis of ^{1}H{^{31}P} NMR experiments. [d] The ^{13}C{^{1}H} NMR spectrum was recorded in CH_3COCH_3-d_6 at room temperature. [e] $^4J(H_2'P)$ = 14.8, 6.2. [f] Coupling of this proton to the phosphorus nuclei is shown by a comparison of the line widths of the signal in the ^{1}H ($w_{1/2}$ = 12 Hz) and ^{1}H{^{31}P} NMR spectra ($w_{1/2}$ = 6 Hz). [g] The ^{1}H{^{31}P} NMR spectrum has been properly computed. The H_2 and $H_{2'}$ hydrogens constitute the AB part of an ABDFHJ spin system (D, F, H, J = H_3, H_4, H_5, H_6). [h] Appreciable coupling of this proton to the phosphorus atoms is shown by a comparison between the ^{1}H ($w_{1/2}$ = 13 Hz) and ^{1}H{^{31}P} NMR spectra ($w_{1/2}$ = 6 Hz). [i] Small coupling to the H_2 and H_5 hydrogens was shown by a ^{1}H, ^{1}H 2D-COSY experiment but could not precisely be evaluated.

by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy showed quantitative conversion of **1** to **3**.

Reaction of 2 with H_2. An orange solution of **2** (0.10 g, 0.11 mmol) in 1,2-dichloroethane (20 mL) was heated at 80 °C under a steady stream of hydrogen for 2 h. The resulting yellow solution was concentrated to dryness under vacuum to yield a yellow residue which was characterized by IR and NMR spectroscopy as a mixture of **3** and **4** in a ca. 2:1 ratio. As in the above reaction, **3** formed quantitatively when a 100-fold excess of thiophene was added to the reaction mixture.

Reaction of 2 with H_2 in the Presence of 2,5-DHT. An orange solution of **2** (0.10 g, 0.11 mmol) and 2,5-DHT (0.19 g, 2.20 mmol) in 1,2-dichloroethane (20 mL) was heated at 80 °C under a steady stream of hydrogen. After 2 h, the resulting light yellow solution was sampled and analyzed by GC/MS which showed production of THT in an amount corresponding to that of coordinated SC_4H_5. The solution, concentrated to dryness under vacuum, yielded a pale yellow solid which was washed with *n*-pentane and characterized by IR and NMR spectroscopy as $[(PPh_3)_2Ir(H)_2(\eta^1\text{-}2,5\text{-}SC_4H_6)_2]PF_6$ (**5**) (see below).

Independent Synthesis of $[(PPh_3)_2Ir(H)_2(\eta^1\text{-}2,5\text{-}SC_4H_6)_2]PF_6$ (5). A solid sample of $[(PPh_3)_2Ir(H)_2(\eta^1\text{-}OCMe_2)_2]PF_6$ (0.20 g, 0.20 mmol) was added to $CHCl_3$ (15 mL) containing a 5-fold excess of 2,5-DHT (0.09 g, 1 mmol). After 15 min, diethyl ether was added until complete precipitation of **5** as white crystals, which were washed with cold diethyl ether and dried in vacuo, yield 75%. Anal. Calcd (found) for $C_{44}H_{44}F_6IrP_3S_2$: C, 51.01 (50.94); H, 4.28 (4.23); Ir, 18.55 (18.37); S, 6.19 (6.03). Λ_M = 81 $cm^2\ \Omega^{-1}\ mol^{-1}$. IR: (ν Ir–H) 2165 cm^{-1}. ^{31}P{^{1}H} NMR ($CDCl_3$, 20 °C, 81.01 MHz): A_2 pattern; δ 14.3. Compound **5** does not react with H_2 when heated at 80 °C in 1,2-dichloroethane.

Reaction of 2 with H_2 in the Presence of 2,3-DHT. An orange solution of **2** (0.10 g, 0.11 mmol) and 2,3-DHT (1.5 M solution in $CHCl_3$, 0.15 mL, 0.22 mmol) in 1,2-dichloroethane (20 mL) was heated at 80 °C under a steady stream of hydrogen. After 2 h, the resulting light yellow solution was concentrated to dryness under vacuum to give in quantitative yield a pale yellow solid, which was characterized by IR and NMR spectroscopy as **3**.

Synthesis of $[(PPh_3)_2Ir(H)_2(\eta^1\text{-}2,3\text{-}SC_4H_6)_2]PF_6$ (6). A solid sample of $[(PPh_3)_2Ir(H)_2(\eta^1\text{-}OCMe_2)_2]PF_6$ (0.20 g, 0.20 mmol) was added to $CHCl_3$ (20 mL) containing a 5-fold excess of 2,3-DHT (1.5 M solution in $CHCl_3$, 0.7 mL, 1 mmol). After 15 min, diethyl ether was added until complete precipitation of **6** as white crystals, which were washed with cold diethyl ether and dried in vacuo, yield 70%. Anal. Calcd (found) for $C_{44}H_{44}F_6IrP_3S_2$: C,

51.01 (50.83); H, 4.28 (4.28); Ir, 18.55 (18.40); S, 6.19 (6.07). Λ_M = 82 $cm^2\,\Omega^{-1}\,mol^{-1}$. IR: ($\nu$ Ir–H) 2180 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C, 81.01 MHz): A_2 pattern; δ 13.7.

Reaction of 6 with H_2. A solution of **6** (0.10 g, 0.10 mmol) in 1,2-dichloroethane (20 mL) was heated at 80 °C under a steady stream of hydrogen for 2 h. The resulting solution was concentrated to dryness under vacuum to yield **3** as a light yellow solid.

Reaction of 2 with CO. At Room Temperature. In a typical reaction, a stream of carbon monoxide was slowly bubbled through a $CDCl_3$ (2 mL) solution of **2** (40 mg, 0.04 mmol) at room temperature. After ca. 30 min, a sample (0.7 mL) of this solution was transferred into a 5-mm NMR tube. $^{31}P\{^1H\}$ and ^1H NMR spectra, immediately recorded, showed an almost complete conversion (>95%) of **2** to $[(PPh_3)_2IrH(CO)(\eta^2\text{-}C_5,S\text{-}SC_4H_5)]PF_6$ (**7**) and $[(PPh_3)_2IrH(CO)(\eta^2\text{-}C_3,S\text{-}SC_4H_5)]PF_6$ (**8**) in a ca. 5:1 ratio. Small amounts (<3%) of the known complex $[(PPh_3)_2Ir(CO)_3]PF_6$[16] (**9**) were also detected. For longer reaction times, the amounts of both **7** and **8** slowly decreased; complete disappearance occurred after ca. 24 h. Formed in their place were **9** and 2,5-DHT and 2,3-DHT in a ca. 5:1 ratio [^1H NMR: 2,5-isomer,[6] δ 5.83 (m, 2H), 3.71 (m, 4H); 2,3-isomer,[7] 6.11 (dt, 1H), 5.60 (dt, 1H), 3.20 (t, 2H), 2.71 (tt, 2H)]. The above reaction was carried out on a preparative scale. After elimination of the solvent in vacuo, the pale yellow residue was recrystallized from THF/*n*-heptane to give a 5:1 mixture of **7** and **8**. These products exhibit comparable solubility in most organic solvents and thus could not be separated from each other. Fortunately, **7** and **8** exhibit distinct NMR resonances and thus could be adequately characterized (see Table 1 for ^1H and $^{13}C\{^1H\}$ NMR data). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C, 81.01 MHz) for **7**: AM pattern; δ 9.2 (d, P_A), −1.1 (d, P_M), $J(P_AP_M)$ = 14.2 Hz. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C, 81.01 MHz) for **8**: AM pattern; δ 8.0 (d, P_A), 1.6 (d, P_M), $J(P_AP_M)$ = 18.5 Hz. IR: ν (Ir–H) 2124 (s); ν (CO) 2014 (vs), 1961 (s) cm^{-1}.

At 50 °C. In a typical reaction, a stock solution of **2** (240 mg, 0.24 mmol) and hexamethyldisiloxane (5 μL) as ^1H internal standard in $CDCl_3$ (6 mL) was heated at 50 °C under a slow stream of carbon monoxide. After ca. 30 min a 0.7-mL sample of the solution was transferred into an NMR tube. The $^{31}P\{^1H\}$ NMR spectrum showed the complete conversion of **2** to **7** (41%), **8** (8%), and **9** (51%). Both free 2,5- and 2,3-DHT in a ca. 5:1 ratio were also generated [^1H NMR]. The progress of the reaction was monitored by sampling the reaction mixture every ca. 30 min. Almost complete conversion (>90%) to **9** and the dihydrothiophene isomers was reached after ca. 3 h. It is noteworthy that the 5:1 ratio between **7** and **8** and between 2,5- and 2,3-DHT were found to be practically constant throughout the experiment. Identical results were obtained when a mixture of **7** and **8** was used in place of **2**. When the reaction was carried out for 3 h by using **2-d_2** in place of **2**, deuterium incorporation occurred only at the C_2,C_3 (2,3-isomer) and C_2,C_5 (2,5-isomer) carbon atoms, which suggests that no isomerization of 2,3- to 2,5-DHT occurs.

Reaction of 2 with H_2/CO. A stream of a 1:1 mixture of H_2/CO was slowly bubbled thorugh a $CDCl_3$ (2 mL) solution of **2** (40 mg, 0.04 mmol) at room temperature for ca. 1 h. A sample (0.7 mL) of the solution was transferred into a 5-mm NMR tube. $^{31}P\{^1H\}$ and ^1H NMR spectra showed the quantitative conversion of **2** to **7** (59%), **8** (12%), $[(PPh_3)_2Ir(H)_2(CO)(\eta^1\text{-}SC_4H_8)]PF_6$ (**10**) (10%) (see below) and $[(PPh_3)_2Ir(H)_2(CO)_2]PF_6$[16] (**11**) (19%). Formation of free 2,5- and 2,3-DHT in a ratio of approximately 5:1 was also observed (total amount of DHT isomers based on **2** ca. 16%, ^1H NMR integration). The above procedure can be scaled up. In this case $CHCl_3$ was employed as solvent. The mixture isolated by solvent evaporation exhibited approximately the same distribution of iridium complexes. For longer reaction times at room temperature, only a slow conversion of **7**, **8**, and **10** to **11** was observed. A faster and complete conversion to **11** was achieved by heating $CHCl_3$ (or $CDCl_3$) solutions of either a mixture of **7**, **8**, and **10** or a pure sample of **2** at 60 °C under a stream of H_2/CO for 3 h. In this case, free 2,5-DHT, 2,3-DHT, and THT were produced in a ratio of 71:15:14.

(16) Church, M. J.; Mays, M. J.; Simpson, R. N. F.; Stefanini, F. P. *J. Chem. Soc. (A)* **1970**, 2909.

Independent Synthesis of $[(PPh_3)_2Ir(H)_2(CO)(\eta^1\text{-}SC_4H_8)]PF_6$ (10). A stream of carbon monoxide was bubbled through a $CHCl_3$ (50 mL) solution of $[(PPh_3)_2Ir(H)_2(\eta^1\text{-}SC_4H_8)_2]PF_6$ (**3**) (0.20 g, 0.19 mmol) at room temperature. After ca. 30 min, removal of the solvent under vacuum gave a pure sample of **10** as a light yellow microcrystalline solid which was washed with *n*-pentane. Anal. Calcd (found) for $C_{41}H_{40}F_6IrOP_3S$: C, 50.25 (50.28); H, 4.11 (4.08); Ir, 19.61 (19.47); S, 3.27 (3.17). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C, 81.01 MHz): A_2 pattern; δ 9.6. IR: ν (Ir–H) 2212 (s), 2122 (s); ν (CO) 2026 (vs) cm^{-1}. Λ_M = 79 $cm^2\,\Omega^{-1}\,mol^{-1}$. Crystals suitable for an X-ray diffraction analysis of formula **10**·1.5$CHCl_3$ were obtained by slow concentration of the reaction mixture under nitrogen at room temperature. Anal. Calcd (found) for $C_{42.5}H_{41.5}Cl_{4.5}F_6IrOP_3S$: C, 44.04 (43.87); H, 3.61 (3.54); Ir, 16.58 (16.39); S, 2.77 (2.54).

Reaction of 10 with H_2/CO. Bubbling a 1:1 mixture of H_2/CO through a solution of **10** (0.10 g, 0.10 mmol) in $CHCl_3$ (10 mL) at 60 °C for 3 h, followed by removal of the solvent in vacuo, gave a product which was characterized by multinuclear NMR spectroscopy as a 7:3 mixture of **11** and **10**.

X-ray Data Collection and Structure Determination of **10**·1.5$CHCl_3$. A colorless crystal in a sealed capillary with its mother liquor was mounted on a standard goniometric head of an Enraf-Nonius CAD4 automatic diffractometer. The above procedure was necessary to avoid the loss of the crystallization solvent and thus the decay of the reflection intensities. The cell parameters were determined by least-squares refinement of the setting angles of 25 carefully centered reflections. As a general procedure, three standard reflections were collected every 2 h (no decay of intensities was observed in any case). Intensity data were corrected for Lorentz-polarization effects. Atomic scattering factors were those tabulated by Cromer and Waber[17] with anomalous dispersion corrections taken from ref 18. Absorption correction was applied via Ψ scan with transmission factors ranging between 54.21 and 99.97. All the calculations were carried out on a DIGITAL DEC 5000/200 computer by using the SHELX76 program.[19] The structure was solved by heavy atom techniques. Refinement was done by full-matrix least-squares calculations initially with isotropic thermal parameters. Anisotropic thermal parameters were used for iridium, phosphorus, and sulfur atoms. The phenyl rings were treated as rigid bodies of D_{6h} symmetry with C–C distances fixed at 1.39 Å and calculated hydrogen atom positions (C–H = 1.08 Å). Some disorder affects the C_4 atom. Double images were detected for this atom in ΔF maps and the respective positional parameters were refined by assuming population parameters of 0.5. Two molecules of $CHCl_3$ solvent were detected in the final stage of the refinement, and one of them was assigned a population factor of 0.5. The hydride ligands were not detected in the final ΔF map. A summary of crystal and intensity data is reported in Table 2. Selected bond distances and angles are given in Table 3.

Results and Discussion

Synthesis, Characterization, and Hydrogenation of $[(PPh_3)_2IrH(\eta^4\text{-}SC_4H_5)]PF_6$ (2). Heating a 1,2-dichloroethane solution of the bis-thiophene dihydride $[(PPh_3)_2Ir(H)_2(\eta^1\text{-}SC_4H_4)_2]PF_6$[7] (**1**) at 80 °C for 30 min results in the stoichiometric formation of the thioallyl complex $[(PPh_3)_2IrH(\eta^4\text{-}SC_4H_5)]PF_6$ (**2**) isolated as orange crystals, plus free T (GC/MS) (Scheme 1). No intermediate species was detected by *in situ* NMR experiments in the course of the reaction that, even though slowly, proceeds at room temperature.

The ^1H NMR spectrum of **2** contains a terminal hydride resonance at δ −21.03 coupled to two inequivalent phos-

(17) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.
(18) *International Tables of Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4.
(19) Sheldrick, G. M. *SHELX'76 Program for Crystal Structure Determinations*; University of Cambridge: Cambridge, England, 1976.

Scheme 1

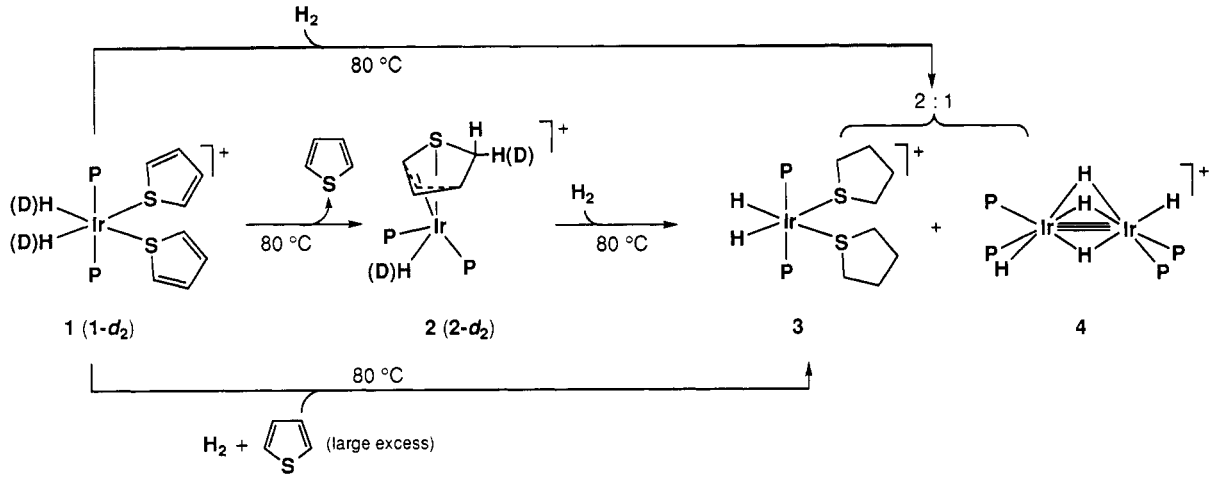


Table 2. Summary of Crystal Data for 10·1.5CHCl$_3$

formula	$C_{42.5}H_{41.5}Cl_{4.5}F_6Ir_1O_1P_3S_1$
fw	1159.02
cryst dimens, mm	0.35 × 0.20 × 0.10
cryst syst	monoclinic
space group	$P2_1$ (No. 4)
a, Å	9.563(4)
b, Å	23.201(4)
c, Å	11.221(2)
β, deg	97.87(2)
V, Å^3	2466.16
Z	2
ρ_{calc}, g cm^{-3}	1.56
μ(Mo Kα), cm^{-1}	31.31
radiation	graphite-monochromated Mo Kα, λ = 0.71069 Å
scan type	ω–2θ
2θ range, deg	5–50
scan width, deg	0.80 + 0.35(tan θ)
scan speed, deg min^{-1}	8.24
total no. of data	3697
no. of unique data, $I > 3\sigma(I)$	3318
no. of refined params	203
R	0.056
R_w	0.056

Table 3. Selected Bond Distances (Å) and Angles (deg) for 10·1.5CHCl$_3$

Ir1–P1	2.38(1)	C3–C4	1.53(3)
Ir1–P2	2.27(1)	C3–C4′	1.46(2)
Ir1–S1	2.479(5)	C5–O1	1.16(2)
Ir1–C5	1.88(2)	P1–C1,1	1.82(2)
S1–C1	1.83(2)	P1–C1,2	1.86(2)
S1–C4	1.87(2)	P1–C1,3	1.81(1)
S1–C4′	1.86(2)	P2–C1,4	1.84(2)
C1–C2	1.52(2)	P2–C1,5	1.87(2)
C2–C3	1.50(2)	P2–C1,6	1.80(2)
S1–Ir1–C5	100.3(5)	Ir1–C5–O1	172(1)
P1–Ir1–C5	96.7(7)	Ir1–S1–C1	116.9(6)
P1–Ir1–S1	103.6(3)	Ir1–S1–C4	116.4(6)
P1–Ir1–P2	161.1(4)	Ir1–S1–C4′	104.4(6)
P2–Ir1–C5	94.8(7)	C1–S1–C4	92.7(8)
P2–Ir1–S1	83.7(3)	C1–S1–C4′	76.5(9)

phorus nuclei, and five resonances between 6.59 and 2.85 ppm. Of these resonances, only the one at δ 5.30 shows appreciable coupling to two inequivalent phosphorus nuclei. Consistently, the $^{31}P\{^1H\}$ NMR spectrum shows an AM spin system with J(PP) = 5.5 Hz. A ^{13}C DEPT NMR experiment indicates the presence of one methylene carbon atom in the complex cation. Unambiguous assignment of all ^1H and ^{13}C resonances and coupling constants for **2** as labeled in Table 1 was made on the basis of $^1H,^1H$ 2D-COSY, $^1H,^{13}C$ 2D-HETCOR, and selective $^1H\{^{31}P\}$ NMR experiments. Comparison of the spectral data of **2** with those of known η^4-thioallyl complexes such as Mn(CO)$_3$(C$_4$H$_5$S),[3a,8] (η^4-C$_4$H$_5$S)ReH$_2$(PPh$_3$)$_2$,[3b] and [(η^6-C$_6$Me$_6$)Ru(η^4-C$_4$H$_5$S)]PF$_6$[20] shows a good correlation.

As previously shown by Jones for Re and by Rauchfuss for Ru, the conversion of thiophene to a thioallyl ligand occurs by migration of a hydride from the metal to thiophene coordinated in the η^4 fashion. Accordingly, it is reasonable to think of the **1** → **2** conversion as proceeding through a stepwise mechanism similar to the ones proposed by Jones and Rauchfuss. After a T ligand is lost from **1** in 1,2-dichloroethane solution, the remaining T ligand changes its bonding mode. Indeed, in poorly coordinating solvents, the resulting [(PPh$_3$)$_2$Ir(H)$_2$(η^1-*S*-SC$_4$H$_4$)]$^+$ system would be electronically unsaturated (16-e). In order to avoid an oversaturated electronic configuration, an η^4-bonding mode of T (18-e) would be more appropriate than an η^5-coordination (20-e); however, one cannot exclude the formation of an η^5-T intermediate, followed by rapid migration of a hydride from iridium to an α-carbon of the π-bound T (in this case, the oversaturation of the intermediate could be a driving force for the fast hydride migration). Since we cannot clearly discriminate between η^4 and η^5 hapticity of T, the intermediate will be considered from now on as containing a π-bound thiophene.

In order to establish the stereochemistry of hydride addition to π-bound thiophene, the isotopomer [(PPh$_3$)$_2$-Ir(D)$_2$(η^1-SC$_4$H$_4$)$_2$]PF$_6$ (**1-*d*$_2$**) was prepared and heated in 1,2-dichloroethane solution. As a result, the deuterium label was selectively found on the H$_2$ site of the thioallyl ligand to give [(PPh$_3$)$_2$IrD(η^4-SC$_4$H$_4$D)]PF$_6$ (**2-*d*$_2$**), which indicates a stereospecific endo migration of the hydride. This finding is consistent with previous reports by other workers.[3,8,20]

The thioallyl complex **2** in 1,2-dichloroethane solution reacts with a steady stream of H$_2$ at 80 °C for 2 h to give the bis-THT dihydride [(PPh$_3$)$_2$Ir(H)$_2$(η^1-SC$_4$H$_8$)$_2$]PF$_6$[7] (**3**) plus the pentahydride [{(PPh$_3$)$_2$IrH}$_2$(μ^2-H)$_3$]PF$_6$[15] (**4**) in a ratio of 2 to 1. The hydrogenation reaction slowly occurs also at room temperature (10% conversion of **2** in 6 h) with the same stoichiometry.

Compound **3** has recently been authenticated by an X-ray analysis.[7] The dimer **4** was prepared in 1976 by Crabtree by treatment of [(PPh$_3$)$_2$Ir(COD)]PF$_6$ in toluene

(20) Luo, S.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1992**, *114*, 8515.

with dihydrogen. We have found that replacement of toluene with any poorly coordinating solvent, including 1,2-dichloroethane, does not modify the course of the latter reaction.

An identical 3:4 ratio is obtained by a one-pot hydrogenation of 1 in 1,2-dichloroethane at 80 °C. In contrast, when the hydrogenation reaction of either 1 or 2 is carried out in the presence of a large excess of T, the bis-THT complex 3 is the only product of the reaction (Scheme 1), no catalytic production of THT being observed even for high pressures of H_2 (up to 30 atm). In a separate experiment, the dimer 4 was found to be fully stable when dissolved at 80 °C in 1,2-dichloroethane containing a large excess of T.

Analysis of all the above experimental evidence leads to the conclusion that the thioallyl ligand in 2 is hydrogenated (*vide infra*) to THT, which remains coordinated to iridium *via* the sulfur atom. As a result, a 16-electron and, thus, unstable species of the type $[(PPh_3)_2Ir(H_2)(SC_4H_8)]^+$ may form, which intermolecularly exchanges THT to give 3 and the unsaturated fragment $[(PPh_3)_2Ir(H)_2]^+$. The latter is appropriate to react with H_2 to yield 4.

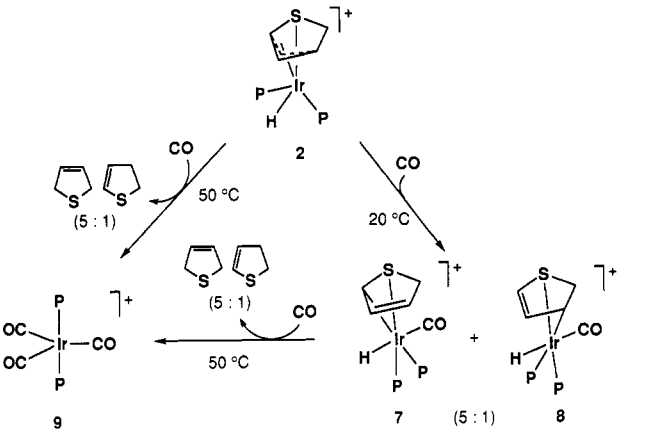
Within this mechanistic context, it is reasonable to have found that 2 is quantitatively converted to 3 only when the hydrogenation reaction is carried out in the presence of an excess of T. In fact, T is able to trap the "naked" dihydride fragment and then be converted to THT *via* thioallyl. In a formal sense, the hydrogenation reaction of T to THT is catalytic even though the reaction stops after only two cycles, due to the known much better bonding capability of the produced THT as compared to the T substrate[21] (addition of THT to a $CHCl_3$ solution of 1 also rapidly and quantitatively generates 3).

Reaction of $[(PPh_3)_2IrH(\eta^4\text{-}SC_4H_5)]PF_6$ (2) with CO at Room Temperature for 30 min. The hydrogenation of the thioallyl ligand to THT evidently implies the reaction of 2 with a molecule of H_2. Such a reaction pathway, in turn, necessarily requires that the hydride in 2 migrates from iridium to the η^4-SC_4H_5 ligand prior to reaction with H_2. Only in this way, in fact, the iridium(III) center is reduced to iridium(I) and, thus, becomes capable of oxidatively adding H_2. If one takes for granted that hydride migration precedes the oxidative addition of H_2, it remains to establish the regiochemistry of the migration process. Disregarding an unlikely nucleophilic attack on the central carbon atom of the allylic portion of the SC_4H_5 ligand, the hydride may migrate to either the C_3 or C_5 positions to yield 2,3-dihydrothiophene (2,3-DHT) and 2,5-dihydrothiophene (2,5-DHT), respectively.

In an attempt to elucidate this point which is of remarkable relevance for the HDS process, we reacted 2 with CO (steady stream) (Scheme 2). At room temperature, 2 is converted in 30 min to the pale yellow complexes $[(PPh_3)_2IrH(CO)(\eta^2\text{-}C_5,S\text{-}SC_4H_5)]PF_6$ (7) and $[(PPh_3)_2IrH(CO)(\eta^2\text{-}C_3,S\text{-}SC_4H_5)]PF_6$ (8) in an isomeric ratio of 5:1.

The structural assignments of 7 and 8 as labeled in Table 1 have been corroborated by a number of NMR experiments as well as their chemical behavior. At room temperature, the uptake of CO by 2 does not promote

Scheme 2



hydride migration as the two isomers still contain a terminal hydride ligand coupled to two inequivalent phosphorus nuclei (temperature-invariant $^{31}P\{^1H\}$ NMR AM spin systems). What changes is the bonding mode of the 6-e donor thioallyl SC_4H_5 ligand which adopts a 4-e donor η^2-*C,S* coordination *via* the C_5 and C_3 carbon atoms in 7 and 8, respectively. The η^3 to η^1 slippage of the allylic portion of the ligand is clearly shown by the ^{13}C chemical shifts of the carbon pairs C_3–C_4 in 7 and C_4–C_5 in 8, which are lowfield to the analogous resonances of the η^4-SC_4H_5 complex, and in the proper range for free olefins.

The experimental and computed $^1H\{^{31}P\}$ NMR spectra of the hydrogens of the SC_4H_5 moiety in the major isomer 7 are shown in Figure 1. Due to the close chemical shifts, the methylenic hydrogens H_2 and $H_{2'}$ give rise to a second-order spectrum which has satisfactorily been computed as the AB part of an ABDFHJ spin system (J = hydride ligand). Unlike in the case of 8, the hydride ligand is coupled even though weakly to H_5, *i.e.* the hydrogen atom of the σ-bonded carbon. In general, however, all spectral data of 7 and 8 show a good correlation with each other.

Slippages of allyl ligands from η^3 to η^1 hapticity are well-documented.[22] It is generally agreed that the steric preference is for η^1-allyl binding (two-electron donation), whereas the electronic preference is for η^3-binding (four-electron donation). In the case at hand, allyl hapticity is electronic in nature and modulated by the electron density at the iridium center that increases upon coordination fo the strong σ-donor CO molecule. Less obvious is why the reaction of 2 with CO produces two isomers, and particularly a larger amount of the complex in which the sulfur atom and the double bond of the C_4H_5S ligand are *trans* to each other. Most likely, a subtle combination of steric and electronic factors, including the smaller ring strain in the η^2-C_5,S-SC_4H_5 ligand and the way of attack of CO on the metal, is operational. What is definitely established is the fact that 7 and 8 do not interconvert in the temperature range from −50 to +80 °C in 1,2-dichloroethane solution under inert atmosphere.

To the best of our knowledge, the only metal complex with an SC_4H_5 ligand structurally similar to the one contained in 7 is the trinuclear $(\mu_2\text{-}H)Ru_3(CO)_9(\mu_3\text{-}1\text{-}4\text{-}\eta^4\text{-}SC_4H_5)$.[23] Interestingly (*vide infra*), this cluster was obtained by reacting $Ru_3(CO)_{12}$ with 2,5-DHT.

(21) (a) Benson, J. W.; Angelici, R. J. *Organometallics* **1993**, *12*, 680. (b) Benson, J. W.; Angelici, R. J. *Organometallics* **1992**, *11*, 922. (c) Choi, M.-G.; Angelici, R. J. *Inorg. Chem.* **1991**, *30*, 1417. (d) Choi, M.-G.; Angelici, R. J. *Organometallics* **1991**, *10*, 2436.

(22) (a) Larson, E. J.; Van Dort, P. C.; Lakanene, J. R.; O'Neill, D. W.; Pederson, L. M.; McCandless, J. J.; Silver, M. E.; Russo, S. O.; Huffman, J. C. *Organometallics* **1988**, *7*, 1183. (b) Erker, G.; Berg, K.; Augermund, K.; Krüger, C. *Organometallics* **1987**, *6*, 2620. (c) Siedle, A. R.; Newmark, R. A.; Brown-Wensley, K. A.; Skarjune, R. P.; Haddad, L. C.; Hodgson, K. O.; Roe, A. L. *Organometallics* **1988**, *7*, 2078.

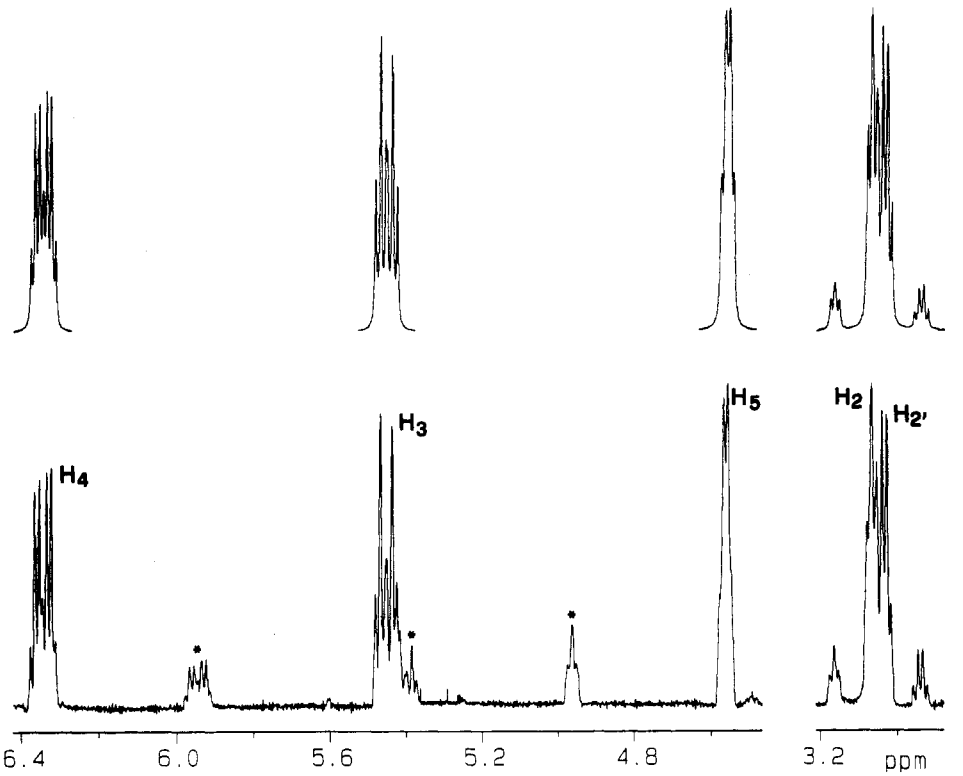


Figure 1. Experimental and computed (inset) $^1H\{^{31}P\}$ NMR spectra relative to the hydrogens of the SC_4H_5 moiety in **7**. Asterisks denote the H_4, H_5, and H_3 resonances of the isomer **8**.

Reaction of $[(PPh_3)_2IrH(\eta^4\text{-}SC_4H_5)]PF_6$ (2) with CO at Room Temperature for Times > 30 Min or at High Temperature. For a reaction time longer than 30 min, treatment of **2** in $CHCl_3$ with CO at room temperature results in its slow (24 h) and quantitative conversion, *via* **7** and **8**, to the known tricarbonyl $[(PPh_3)_2Ir(CO)_3]PF_6$[16] (**9**) and concomitant formation of free 2,5-DHT and 2,3-DHT in a ratio of 5 to 1. At 50 °C, the conversion of **2** to **9** *via* **7** and **8** is complete in 3 h and analogously produces 2,5-DHT and 2,3-DHT in a ratio of 5:1. Indeed, independent reactions showed that **7** and **8** (5:1 mixture) are precursors to 2,5-DHT and 2,3-DHT in the same ratio. Notably, the ratio between **7** and **8** during their disappearance as well as the ratio between free 2,5-DHT and 2,3-DHT in the course of their formation are invariant with time and temperature (in the range from 20 to 50 °C). Accordingly, this suggests that the two products are formed *via* two independent reactions and that there is no isomerization of 2,3-DHT to the thermodynamically more stable 2,5-isomer under our observational conditions. The lack of an isomerization process involving either of the DHT isomers was unambiguously demonstrated by deuterium labeling experiments, *i.e.* by reacting the isotopomer **2-d_2** with CO, deuterium incorporation occurs only on the C_2–C_3 and C_2–C_5 positions of the 2,3- and 2,5-isomers, respectively.

From a mechanistic viewpoint, the formation of 2,5-DHT and 2,3-DHT which, by the way, supports our structural assignment for **7** and **8**, respectively, may be seen as an ordinary ligand-promoted reductive elimination step. In this picture, after the first CO uptake, the formed DHT molecules remain coordinated to iridium *via* the sulfur atom and later would be displaced by CO of which there is a large excess in the reaction mixture. A related mechanism has already been proposed by Angelici for the stepwise hydrogenation of π-T to 2,3-DHT illustrated in Scheme 3.[3a] As is evident from inspection of Scheme 3, the isolation and characterization of the hydrido complexes with η^2-*C*,*S*-SC_4H_5 ligands described in this paper are of particular relevance as they represent the missing item in all the stepwise hydrogenation reactions of T to DHT so far reported.

Having found that the hydride in **2** is able to migrate from iridium to the terminal carbon atoms of the allyl portion of the SC_4H_5 ligand, one may conclude that an analogous step traverses the hydrogenation of T to THT shown in Scheme 1. In other words, it is reasonable to suggest that, like CO, H_2 initially promotes hydride migration and then reduces DHT to THT. It remains to establish whether the production of THT is preceded by formation of 2,5-DHT, 2,3-DHT, or both of them. The question is not of trivial relevance as hydrogenation of T to 2,3-DHT has been proposed as the initial step in the HDS of T.[24,25]

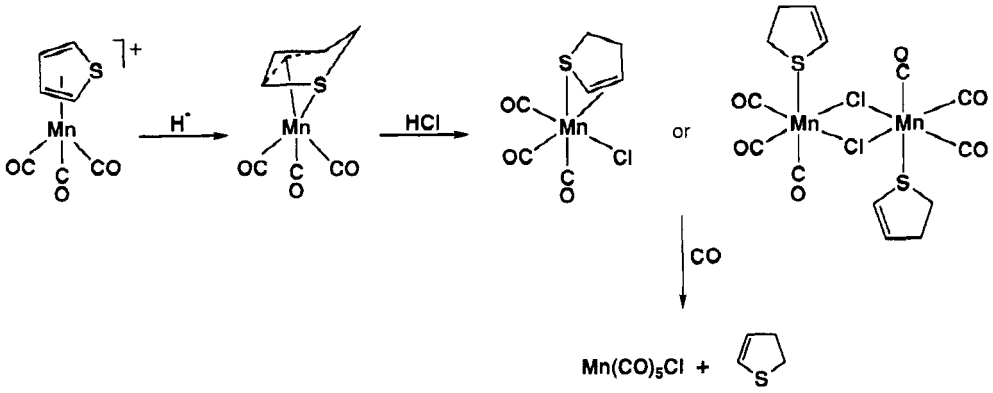
In order to gain further insight into this crucial point, pure samples of 2,5-DHT[11] and 2,3-DHT[12] have been prepared and reacted with the thioallyl complex **2** and H_2 under experimental conditions analogous to those of Scheme 1. As a result, only the 2,3-isomer was reduced to THT to give the bis-THT dihydride **3** thus suggesting its intermediacy in the hydrogenation of T to THT, whereas the 2,5-isomer simply stabilizes the $[(PPh_3)_2Ir(H)_2]^+$ fragment to form the novel bis(2,5-DHT) dihydride $[(PPh_3)_2Ir(H)_2(\eta^1\text{-}2,5\text{-}SC_4H_6)_2]PF_6$ (**5**) (Scheme 4). Consistently, the bis-2,5-DHT complex **5** prepared by an independent procedure does not react with H_2, whereas

(23) Choi, M.-G.; Daniels, L. M.; Angelici, R. J. *Inorg. Chem.* **1991**, *30*, 3647.

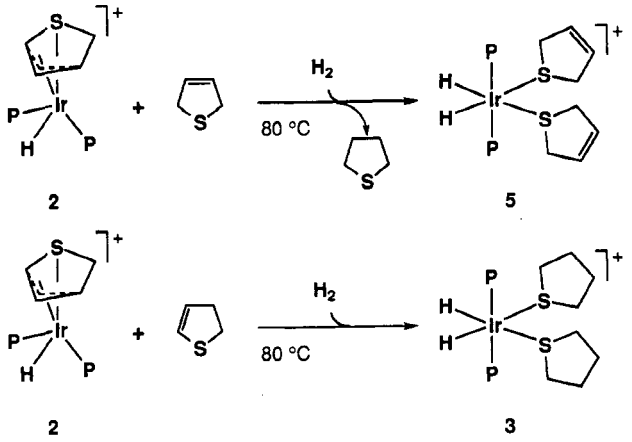
(24) (a) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387. (b) Markel, E. J.; Schrader, G. L.; Sauer, N. N.; Angelici, R. J. *J. Catal.* **1989**, *116*, 11. (c) Desikan, P.; Amberg, C. H. *Can. J. Chem.* **1964**, *42*, 843.

(25) Glavee, G. N.; Daniels, L. M.; Angelici, R. J. *Organometallics* **1989**, *8*, 1856.

Scheme 3



Scheme 4



the bis(2,3-DHT) analog $[(PPh_3)_2Ir(H)_2(\eta^1\text{-}2,3\text{-}SC_4H_6)_2]PF_6$ (**6**) is quantitatively hydrogenated to the bis-THT derivative (Scheme 5).

A detailed description of the $^{31}P\{^1H\}$ NMR and IR spectra of **5** and **6** is not necessary since they are quite comparable to those of the known, octahedral $[(PPh_3)_2Ir(H)_2(\eta^1\text{-}S\text{-}Th)_2]PF_6$ congeners (Th = T, THT, benzothiophene, dibenzothiophene).[7] In contrast, it is worth commenting on the ^1H NMR spectra. In the spectrum of the 2,5-DHT complex **5**, both the H_2,H_5 and H_3,H_4 sets of resonances are upfield compared to those (δ 3.76, 5.85, $CDCl_3$) in free 2,5-DHT (Table 1).[23] As previously suggested by Angelici, these unusual upfield shifts may be due to shielding of 2,5-DHT by the phenyl rings of the phosphines.[26a] Consistently, similar upfield shifts are observed for the 2,3-DHT derivative **6**.[26a] In the spectrum of the latter compound, two well-resolved resonances are seen for the two sets of methylene hydrogens, which indicates a rapid inversion of sulfur on the NMR time scale. This phenomenon has already been observed for $W(CO)_5$(2,3-DHT) for which an inversion barrier of 48.5 kJ/mol at T_c = 233 K was calculated.[26a] Rapid inversion at sulfur on the NMR time scale at room temperature evidently occurs also in the 2,5-DHT complex **5** as we observe a single resonance for the two sets of methylene hydrogens.[23]

The reactivity of 2,5-DHT and 2,3-DHT in homogeneous phase toward metal fragments has widely been investigated by Angelici.[23-26] In a series of elegant papers, this author showed that (i) 2,5-DHT coordinates to the metal centers *via* the sulfur atom and, in this sense, is a better ligand than T, which is consistent with our findings.[23] (ii) Complexed 2,3-DHT is hydrogenated to THT,[25,26b] whereas there is no report for an analogous reaction of the 2,5-isomer, which again is consistent with our observations.

Reaction of $[(PPh_3)_2IrH(\eta^4\text{-}SC_4H_5)]PF_6$ with Syngas. The capability of **2** to react with either CO or H_2 prompted us to investigate its reactivity toward a 1:1 mixture of the two gases.

Under analogous conditions to those used for the reactions with each single gas, treatment of **2** with syngas results in a reactivity pattern rather similar to the one originated by CO alone, although some peculiar aspects deserve a comment (Scheme 6).

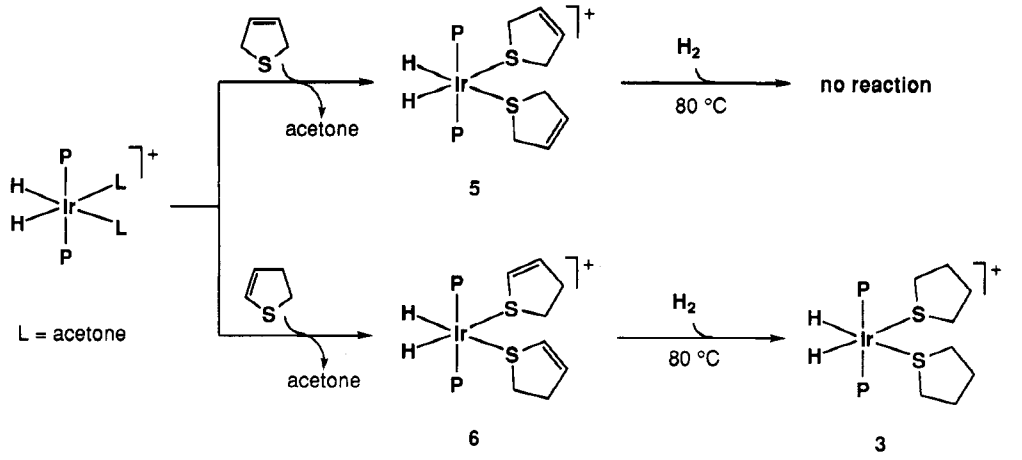
At room temperature, the prevailing reaction is the one between **2** and CO to give the monocarbonyls **7** and **8** as the major products (59 and 12% based on the starting complex, respectively). Hydrogenated products are also formed. In particular, one observes production of free 2,5-DHT and 2,3-DHT in a relative ratio of 5 to 1, of the new S-bonded THT complex $[(PPh_3)_2Ir(H)_2(CO)(\eta^1\text{-}SC_4H_8)]PF_6$ (**10**) (10%) and of $[(PPh_3)_2Ir(H)_2(CO)_2]PF_6$[16] (**11**). The overall amount of DHT isomers is comparable to that of **11**, thus suggesting that after CO has promoted the reductive elimination step in **7** and **8**, the resulting Ir(I) $[(PPh_3)_2Ir(CO)_2(DHT)]^+$ fragment reacts with H_2 yielding **11** and free DHT isomers. Alternatively, one may suggest that CO straightforwardly displaces DHT from $[(PPh_3)_2Ir(CO)_2(DHT)]^+$ to give the tricarbonyl **9**, which then is converted to **11** by reaction with H_2.[16] In this context it is important to stress the fact that **7** and **8** *do not* react with H_2 alone.

Formation (*ca.* 10%) of the (η^1-*S*-SC_4H_8) carbonyl **10** indicates that some **2** reacts with H_2 undergoing reduction of the SC_4H_5 ligand to THT. On the basis of the mechanistic considerations already reported, **10** may form by reaction of CO with the unsaturated $[(PPh_3)_2Ir(H)_2(THT)]^+$ fragment.

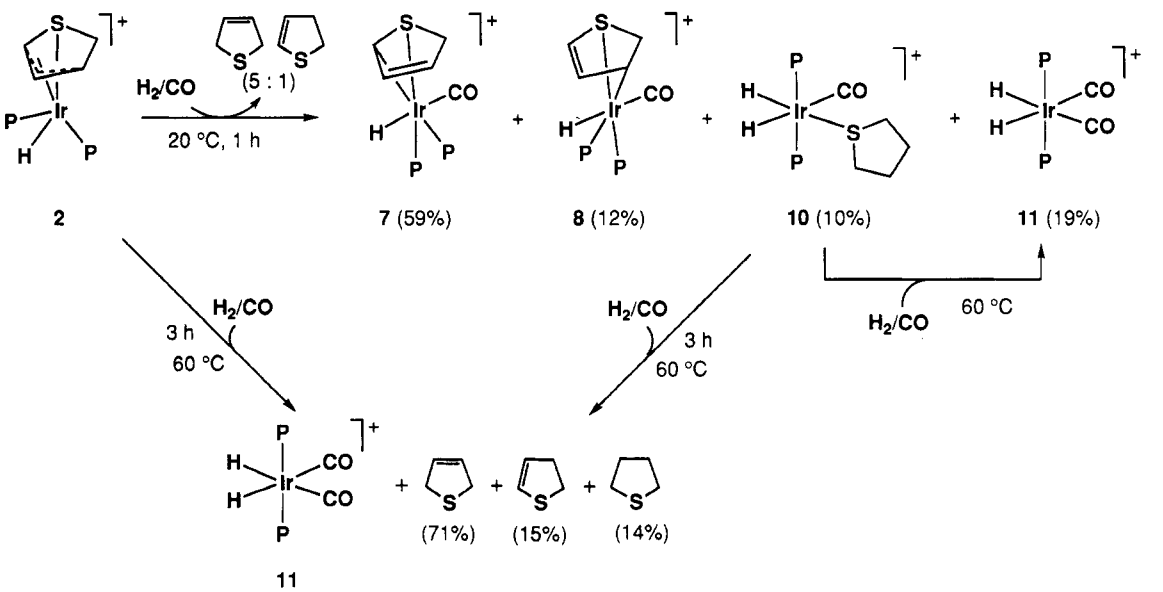
Compound **10** differs from all the known complexes containing thiophenic molecules coordinated to the $[(PPh_3)_2Ir(H)_2]^+$ system in the chemical and magnetic inequivalence of the two hydrides due to the different nature of the *trans* ligands. In fact, the hydride resonances appear as a triplet of doublets at δ −8.60 and a broad triplet at δ −15.17. The latter signal is assigned to the hydride *trans* to the THT ligand as it shows coupling to the H_2 and H_5 hydrogens of the THT ring (H_2 H_5, δ 2.33; H_3 H_4, δ 1.49). Two magnetically equivalent phosphorus nuclei and a terminal carbonyl ligand [ν (CO) 2026 cm^{-1}] complete the coordination sphere of the metal center.

(26) (a) Glavee, G. N.; Daniels, L. M.; Angelici, R. J. *Inorg. Chem.* **1989**, *28*, 1751. (b) Sauer, N. N.; Angelici, R. J. *Inorg. Chem.* **1987**, *26*, 2160.

Scheme 5



Scheme 6



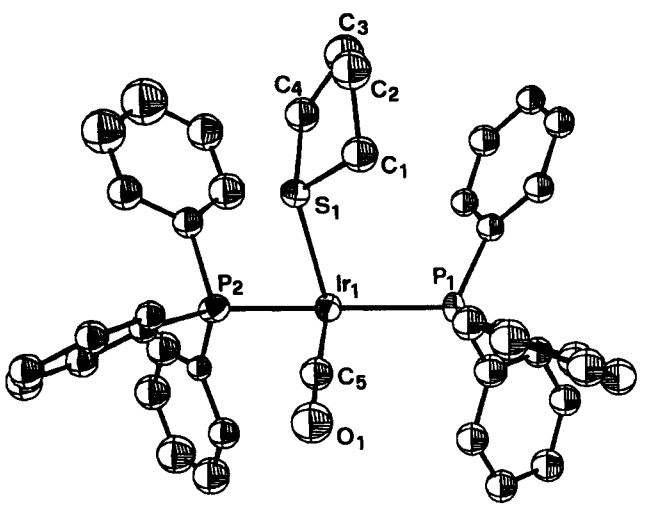


Figure 2. ORTEP drawing of the complex cation $[(PPh_3)_2Ir(H)_2(CO)(\eta^1\text{-}SC_4H_8)]^+$ in **10**·1.5$CHCl_3$. All of the hydrogen atoms are omitted for clarity.

An X-ray diffraction analysis has been carried out on **10**·1.5$CHCl_3$. Figure 2 shows an ORTEP view of the complex cation. Selected bond distances and angles are collected in Table 3. The coordination geometry around iridium consists of a distorted octahedron with mutually *cis*-hydrides, *cis*-sulfur (from THT) and carbon (from CO) atoms and *trans*-phosphines. The two phosphines are somewhat bent toward the smaller hydride ligands in order to minimize steric repulsions. The Ir–S distance (2.479 Å) is slightly longer than those found in the closely related bis(THT) complex $[(PPh_3)_2Ir(H)_2(SC_4H_8)_2]PF_6$ (2.446 and 2.457 Å).[7] Although some disorder was found in the C_4 atom of this structure, it is clear that the sulfur atom, as in all other structurally characterized η^1-S bonded T[2,7] or THT[7,27] complexes, adopts a pyramidal geometry corresponding to an approximate sp^3 hybridization. Accordingly, the sum of the angles around the sulfur atom (326° or 287°) is much less than the 360° required for a trigonal planar arrangement. All other strucutral parameters concerning the coordinated THT compare well with those found in other complexes containing this ligand.[27] All other features of this structure are normal.

When **2** in $CHCl_3$ is treated with syngas at 60 °C for 3 h, a stoichiometric reaction occurs which results in the

(27) See *eg.* (a) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1980**, *19*, 323. (b) El-Mehdawi, R.; Froczeck, F. R.; Roundhill, D. M. *Inorg. Chem.* **1986**, *25*, 1155. (c) Riley, D. P.; Oliver, J. D. *Inorg. Chem.* **1986**, *25*, 1825. (d) Gambarotta, S.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1988**, *27*, 99. (e) Clark, P. D.; Marchin, J. H.; Richardson, J. F.; Dowling, N. I.; Hyne, J. B. *Inorg. Chem.* **1988**, *27*, 3526. (f) Krogh-Jespersen, K.; Zhang, X.; Westbrook, J. D.; Fikar, R.; Nayak, K.; Kwik, W.-L.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1989**, *111*, 4082. (g) Arbuckle, B. W.; Bharadway, P. K.; Musker, K. *Inorg. Chem.* **1991**, *30*, 440.

conversion of all the metal into the dicarbonyl complex **11** and hydrogenation of the thioallyl ligand to 2,5-DHT, 2,3-DHT, and THT in a ratio of 71:15:14 (Scheme 6). An identical product distribution was observed by reacting the mixture obtained at room temperature with syngas at 60 °C for 3 h, which is consistent with the reactivity of each component of the mixture toward syngas at 60 °C.

In conclusion, the reactions of **2** with either H_2 or H_2/CO differ from each other in a significant decrease in the production of THT, and thus suggest that CO may be a poison for the HDS of thiophenic molecules. Also, it is worth mentioning that the reaction between the easily prepared thioallyl complex **2** and syngas may be exploited to prepare solutions of 2,5-DHT, 2,3-DHT, and THT of defined stoichiometry. This provides the chemist with a much simpler procedure to have available solutions of thiophene-derived molecules for comparative studies of their chemical reactivity.

Acknowledgment. Thanks are due to Mr. Dante Masi for collecting X-ray data. Financial support from CONICIT (Caracas) and the CNR (Rome) to V.H. for an exchange visit to ISSECC CNR (Florence) is gratefully acknowledged.

Supplementary Material Available: Final positional parameters and refined anisotropic and isotropic temperature factors for all non-hydrogen atoms (Table S1) and final positional parameters for hydrogen atoms for **10**·1.5$CHCl_3$ (Table S2) (3 pages). Ordering information is given on any current masthead page.

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