^{31}P NMR ($CDCl_3$) δ –5.69 ($^1J_{PW}$ = 198 Hz); ^{13}C NMR ($CDCl_3$) δ 17.26 (CH_3), 26.11 (CH_2), 27.44 (PCH_2), 131.16 (:CH), 149.4 (:C–), 201.1 (CO), 204.4 (CO); IR (decaline) ν(CO) 2010 (m), 1905 (m), 1870 (s) cm^{-1}; mass spectrum (250 °C), *m/e* (relative intensity), 560 (M, 50), 532 (M – CO, 6), 504 (M – 2CO, 20), 476 (M – 3CO, 25), 448 (M – 4CO, 100). Anal. Calcd for $C_{19}H_{22}O_4P_2W$: C, 40.71; H, 3.93; P, 11.07. Found: C, 40.80; H, 4.03; P, 11.10.

{η^1(P),η^1(P′)-1,3-Bis[5,6-dimethyl-2,3-bis(methoxycarbonyl)-7-phosphanorbornadien-7-yl]propane}tetracarbonyltungsten (24). The same procedure as for **15** was used for compound **23**. Compound **24** was recovered in 22% yield: mp, decomposition; ^1H NMR (C_6D_6) δ 1.85 (CH_3), 1.23 (CH_2), 1.91 ($^2J_{HP}$ = 1.5 Hz, PCH_2), 3.43 (OCH_3), 3.50 (CH); ^{31}P NMR ($CDCl_3$) δ 216.13 ($^1J_{PW}$ = 225 Hz); ^{13}C NMR ($CDCl_3$) δ 15.75 (CH_3), 19.93 (CCH_2), 33.50 (PCH_2), 52.34 (OCH_3), 60.88 (CH), 138.43 (:CH), 145.28 (:C–), 165.45 (COO), 200.53 ($^2J_{CP}$ = 7.3 Hz, CO), 203.43 (CO); IR (decaline) ν(CO) 2015 (s), 1938 (s), 1903 (s), 1865 (s) cm^{-1}; mass spectrum (250 °C), *m/e* (relative intensity), 844 (M, 38). Anal. Calcd for $C_{31}H_{34}O_{12}P_2W$: C, 44.07; H, 4.03; P, 7.34. Found: C, 43.85; H, 3.88; P, 7.18.

[η^1(P),η^1(P′)-1,3-Bis(2,3-diphenylphosphiren-1-yl)propane]tetracarbonyltungsten (25). The same procedure as for **19** was used for compound **24**. Compound **25** was recovered in 14% yield: mp, decomposition; ^1H NMR ($CDCl_3$) δ 1.7–2 (CH_2); ^{31}P NMR ($CDCl_3$) δ –158.0 ($^1J_{PW}$ = 244 Hz); IR (decaline) ν(CO) 2010 (m), 1905 (m), 1890 (m), 1870 (s) cm^{-1}; mass spectrum (250 °C), *m/e* (relative intensity) 756 (M, 10), 672 (M – 3CO, 25), 644 (M – 4CO, 38). Anal. Calcd for $C_{35}H_{26}O_4P_2W$: C, 55.55; H, 3.44; P, 8.20. Found: C, 55.51; H, 3.37; P, 8.00.

[η^1(P),η^1(P′)-1,2-Bis(3,4-dimethylphospholyl)ethane]nickel Dichloride (26). A mixture of compound **3** (1.5 g, 6 mmol) and $NiCl_2$ (0.78 g, 6 mmol) in toluene (10 mL) and EtOH (10 mL) was heated at 70 °C for 3 h. Compound **26** was recovered by crystallization in $CHCl_3$ in 92% yield: mp, decomposition; ^1H NMR ($CDCl_3$) δ 2.02 ($^4J_{HH}$ = 0.72 Hz, CH_3), 2.20 (CH_2), 6.48 (:CH); ^{31}P NMR (CD_3OD) δ 67.69; ^{13}C NMR (CD_3OD) δ 18.40 (CH_3), 27.79 (CH_2P), 123.70 (:CH), 155.44 (:C–); mass spectrum (200 °C), *m/e* (relative intensity) 250 (M – $NiCl_2$, 100). Anal. Calcd for $C_{14}H_{20}Cl_2PNi$: C, 44.33; H, 5.28. Found: C, 44.89; H, 5.53.

Registry No. **2**, 106232-17-1; **3**, 106250-08-2; **4**, 106232-18-2; **5**, 106232-19-3; **6**, 67918-40-5; **8**, 106232-20-6; **9**, 106232-21-7; **10**, 106232-02-4; **11**, 106232-03-5; **12** (isomer 1), 106232-04-6; **12** (isomer 2), 106293-89-4; **13**, 106232-05-7; **14**, 106232-06-8; **15**, 106232-07-9; **17a**, 106293-85-0; **17b**, 106232-16-0; **18a**, 106232-08-0; **18b**, 106293-86-1; **19**, 106232-09-1; **20a**, 106232-10-4; **20b**, 106293-87-2; **20c**, 106293-88-3; **21**, 106232-11-5; **22**, 106232-12-6; **23**, 106250-07-1; **24**, 106232-13-7; **25**, 106232-14-8; **26**, 106232-15-9; Li, 7439-93-2; $ClCH_2Cl$, 75-09-2; $Cl(CH_2)_2Cl$, 107-06-2; $Cl(CH_2)_3Cl$, 142-28-9; $Cl(CH_2)_4Cl$, 110-56-5; S_8, 10544-50-0; $W(CO)_2THF$, 36477-75-5; $W(CO)_6$, 14040-11-0; HCl, 7647-01-0; $(Et)_2NPHCH_2CH_2PHN(Et)_2$, 106232-23-9; 1-phenyl-3,4-dimethylphosphole, 30540-36-4; dimethyl acetylene dicarboxylate, 762-42-5; tolan, 501-65-5; cyclooctene, 931-88-4; 1,2-bis[5,6-dimethyl-2,3-bis(methoxycarbonyl)-7-phophanorbornadien-7-yl]ethane, 106232-22-8; methanol, 67-56-1; diethylamine, 109-89-7; 1,3-bis[5,6-dimethyl-2,3-bis(methoxycarbonyl)-7-phosphanorbornadien-7-yl]propane, 106232-24-0.

(η-Thiophene)$Mn(CO)_3^+$ as a Model for Thiophene Reactivity on Hydrodesulfurization Catalysts

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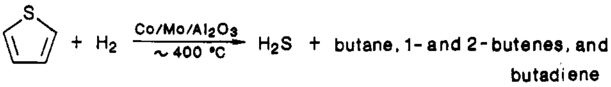
As a model for surface hydride transfer to thiophene π-bonded to a hydrodesulfurization (HDS) catalyst, $HFe(CO)_4^-$ was reacted with (η-thiophene)$Mn(CO)_3^+$ (**1**) to give the product (η^4-thiophene·H)$Mn(CO)_3$ (**3a**) in which H^- added to the 2-position of the thiophene ligand. The analogous reaction with $DFe(CO)_4^-$ shows that D^- adds to both the exo and endo sides of the thiophene ring. The (η-2-methylthiophene)$Mn(CO)_3^+$ complex **4** adds H^- from $HFe(CO)_4^-$ (or BH_4^-) at the non-methylated carbon, C_5, adjacent to the sulfur to give (η^4-2-methylthiophene·H)$Mn(CO)_3$ (**5**). These results are discussed in terms of the observed reactivity of methyl-substituted thiophenes in the HDS process. A hydride (H^-) is abstracted from **3a** and **5** when reacted with Ph_3C^+ to give **1** and **4**, respectively. Deuterium studies show that only the exo H^- (or D^-) is abstracted from **3a**.

Introduction

Hydrodesulfurization (HDS), the catalytic removal of sulfur from crude oil and coal liquids over a sulfided-cobalt-promoted molybdenum catalyst, has been studied extensively because of its widespread commercial use.[2] The HDS reaction of thiophene, an example of an organosulfur compound which is desulfurized with substantial difficulty, is shown in eq 1. Even for thiophene, which has been the subject of numerous investigations, most aspects of the mechanism are still being debated.[3] The initial mode of interaction of thiophene with the catalyst surface as well as the desulfurization pathway are areas which remain unclear.



(1)

Of several proposed binding modes, π-bonding of the aromatic π-system of thiophene with a metal site on the catalyst surface is supported by recent investigations. Benziger et al.[4] examined adsorption and desulfurization of thiophene on clean and sulfided Ni(111) surfaces by using reflection–adsorption infrared spectroscopy (RAIS). Their data suggested that the thiophene ring adsorbs parallel or nearly parallel to the nickel surface at 273 K.

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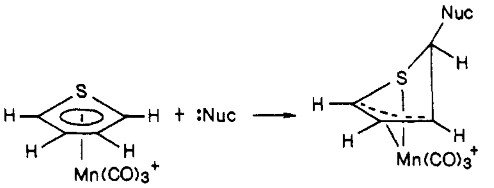
Low-energy electron diffraction (LEED) studies by Edwards and co-workers[5] have been interpreted to mean that the thiophene ring binds parallel to the metal surface, in agreement with Benziger's results. The interaction of the π-system of thiophene with the catalyst surface should be maximal for this flat bonding mode, as in the case of benzene and alkylbenzenes.[6] The adsorption of benzenes and thiophenes on a cobalt–molybdenum catalyst were examined by Zdrazil[7] and found to be quite similar, therefore, providing additional support for parallel bonding of thiophene on the catalyst surface. Cowley[8] proposed π-adsorbed thiophene on the basis of deuterium exchange studies and desulfurization products. Hydrogenation studies of benzene, benzothiophene, and other aromatic substrates by Gates and co-workers[9] also point to a planar π-bonded structure on the catalyst surface.

The pathway for the desulfurization of thiophene once it is adsorbed to the catalyst is also controversial. Carbon–sulfur bond cleavage prior to hydrogenation of the carbon–carbon double bonds[10] is supported by Desikan and Amberg,[11] who have observed butadiene among the HDS products in their reactor studies. However, recent kinetic studies by Devanneaux and Maurin[12] support the importance of hydrogenated thiophenes as intermediates in the HDS process. This latter pathway is further supported by the observations of Moldavski,[13] Zdrazil,[14] and Kemball,[15] who all detected tetrahydrothiophene among the products of thiophene HDS.

Because of the conflicting results of these and other studies done by using heterogeneous catalysts, our group has chosen to explore possible HDS mechanisms by examining the reactivity of transition-metal complexes with π-thiophene ligands in an attempt to model reactions that might occur on HDS catalyst surfaces. Several π-thiophene complexes are known,[16] but few investigations of their reactivity have been reported.[17] Spies and Angelici recently reported[18] that the π-bound thiophene ring of $[(\eta\text{-}C_4H_4S)Ru(\eta\text{-}C_5H_5)]BF_4$ is activated toward base-promoted exchange of the protons at the 2- and 5-positions with deuterium. This result supports the involvement of π-bonded thiophene in deuterium exchange on HDS catalysts, where facile 2,5-exchange is also observed.[8,19]

The π-thiophene ring has also been shown to be activated toward reactions with nucleophiles (eq 2).[17] Thus, H^-, CN^-, and $P(n\text{-}Bu)_3$ all add to the 2-position of the thiophene ring in $[Mn(CO)_3(\eta\text{-}C_4H_4S)]SO_3CF_3$. This type of reaction is important since it breaks the aromaticity of the thiophene ring that is probably a major barrier in the catalytic HDS process.[14] The hydride addition reaction is particularly significant because hydridic species have been proposed to be present on the surface of the HDS catalyst.[17,20] Presumably on a flat catalyst surface, hydride addition to π-bound thiophene could only occur on the side of the ring coordinated to the metal. However, at a step or kink on the surface, addition could occur on the distal face of the thiophene ring. In this paper we describe deuterium studies that establish the stereochemistry of hydride addition to π-bound thiophene.



(2)

While thiophene is commonly used as a model for HDS studies, petroleum feeds contain primarily substituted thiophenes.[21] Several heterogeneous reactor studies using substituted thiophenes have been reported. Desikan and Amberg[11] examined the relative reactivities of 2- and 3-methylthiophenes over a supported Co–Mo catalyst. The 3-methylthiophene was found to undergo higher conversion than 2-methylthiophene. Obolentsev and co-workers compared 2-octyl-, 2,5-dibutyl-, and 2,5-diethylthiophenes and noted only small differences in their reactivities.[22] Zdrazil,[7b] in an extensive series of competitive HDS experiments of mono-, di-, and trisubstituted thiophenes at 300–450 °C, observed an increase in reactivity with increasing substitution of the thiophene. Like Desikan and Amberg, he noticed only a slightly higher reactivity for 3-methylthiophene relative to 2-methylthiophene. These results suggest that substituted thiophenes are also bound flat on the catalyst surface rather than the frequently proposed S-bound mode.[10,23]

In our earlier studies,[17] hydride addition to π-bound thiophene followed by protonation with HCl was suggested as a model for the initial steps in the HDS process. In the present work, we report studies of hydride addition to methyl-substituted thiophenes in cationic manganese tricarbonyl complexes to determine the effect of these groups on the reactivity of the π-thiophene ring and to compare this reactivity with that observed for substituted thiophenes on HDS catalysts.

Experimental Section

General Procedures. ^1H and ^{13}C NMR spectra were obtained on a Nicolet NT-300 spectrometer using deuteriated solvents as internal locks. All ^1H NMR chemical shifts were referenced to internal $(CH_3)_4Si$. ^2H NMR spectra were obtained on a Bruker WM-300 spectrometer, using the proton signal of the solvent as an internal lock and $CDCl_3$ at 7.26 ppm as the internal reference. ^2H NMR spectra were obtained by using a 9° flip angle, 16K data points, and a 4-s acquisition time. Electron-ionization mass spectra

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Table I. IR and ^{1}H NMR Spectral Data for the Complexes

compound	IR	^{1}H NMR^a
$Mn(CO)_3(SC_4H_4{\cdot}H)$ (**3a**)	2021 (s), 1944 (vs), 1928 (vs)^g	6.02 s^5, 5.66 s^4, 3.67 d$^{2\,b}$, 3.26 d$^{1\,b}$, 3.18 s$^{3\,h}$
$[Mn(CO)_3$(thiophene)$]SO_3CF_3$ (**1**)	2080 (s), 2020 (s)^f	6.90 s^6, 6.77 s$^{7\,i}$
$Mn(CO)_3$(2-methylthiophene·H) (**5**)^d	2021 (s), 1942 (vs), 1929 (vs)^g	5.52 s^3, 3.66 d$^{2\,c}$, 3.40 d$^{1\,c}$, 2.93 s^4, 2.78$^{9\,h}$
$[Mn(CO)_3$(2-methylthiophene)$]SO_3CF_3$ (**4**)	2059 (s), 2020 (s)^e	6.68 s^3, 6.66 s^4, 6.51 s^5, 2.56 s$^{9\,i}$
$[Mn(CO)_3$(2,5-dimethylthiophene)$]SO_3CF_3$ (**6**)	2040 (s), 2015 (s)^e	6.40 s^6, 2.59 s$^{9\,i}$

[a] Numerical superscripts indicate the following assignments: 1, H_{exo}; 2, H_{endo}; 3, H_3; 4; H_4; 5, H_5; 6, H_3H_4; 7, H_2H_5; 8, H_4H_5; 9, CH_3. [b] $J_{Hexo,Hendo}$ = 9.4 Hz. [c] $^2J_{Hexo,Hendo}$ = 9.0 Hz. [d] δ (^{13}C) 91.75, 89.20, 57.55, 47.63, 18.14 (CD_2Cl_2). [e] CH_2Cl_2. [f] CH_3NO_2. [g] Hexanes. [h] $CDCl_3$. [i] CD_3NO_2.

Table II. Results of Deuteride Addition Reactions According to Eq 3

expt	deuteride source	solvent(s)	% endo D, **3b (endo)**	% exo D, **3b(exo)**	% deuteriated product
1	$PPN[DFe(CO)_4]$	CH_2Cl_2	30	70	18.2
2	$PPN[DFe(CO)_4]$	CD_2Cl_2	34	66	21.9
3	$PPN[DFe(CO)_4]$	$ClCH_2H_2Cl$	36	64	19.2
4	$PPN[DFe(CO)_4]$	CH_2Cl_2	34	66	4.0^a
5	$NaBD_4$	H_2O/CH_2Cl_2	22	78	34.8
6	$NaBD_4$	H_2O/CH_2Cl_2	24	76	90.2

[a] In this case neither the glassware used to synthesize the $PPN[DFe(CO)_4]$ nor that used in the reaction of 1 and $PPN[DFe(CO)_4]$ were treated with D_2O as described in the Experimental Section.

(EIMS) were run on a Finnigan 4000 spectrometer. Fast atom bombardment (FAB) spectra were run on a Kratos MS-50 mass spectrometer. Elemental analyses were performed by Galbraith Laboratories Inc. Infrared spectra were obtained by using a Perkin-Elmer 681 spectrophotometer and were calibrated by using the 1944 cm^{-1} peak of polystyrene. All reactions were performed under N_2 in reagent grade solvents. Methylene chloride (CH_2Cl_2) and hexanes were dried over CaH_2 and distilled. The solvents were stored over 4-Å molecular sieves and purged with N_2 prior to use. Commercial thiophene was stirred with $AgNO_3$ (0.01 g/mL) for 24 h, decanted, and then distilled. Reagent grade 2-methyl- and 2,5-dimethylthiophene, NaOD (40 wt % solution in D_2O), and CH_3OD (99.5%) were purchased from Aldrich and were used without further purification. The $NaBD_4$ (D purity 94.0%) was purchased from Alfa Products. The complexes $PPN[HFe(CO)_4]$,[24] $Mn(CO)_5OSO_2CF_3$,[17] and $[Mn(CO)_3(SC_4H_4)]SO_3CF_3$[17] (**1**) were prepared by literature methods.

$PPN[DFe(CO)_4]$ (2). A modification of the synthesis reported by Ford[25] was used. All glassware that came in contact with this compound were dried for 72 h at 350 °C, cooled in a desiccator, rinsed twice with D_2O, and flamed out under vacuum before use.[26] Both NaOD and CH_3OD were purged with N_2 and measured by using syringes that had been rinsed with D_2O. An N_2 atmosphere was maintained over treated reaction vessels and solutions at all times. For a typical preparation, NaOD (2.0 mL, 40% in D_2O) and CH_3OD (6.0 mL) were syringed into a 100-mL round-bottom Schlenk flask and stirred for 15 min. Then $Fe(CO)_5$ (0.50 mL, 3.7 mmol) was added under an N_2 flush. The solution was stirred for 1 h. Then, [PPN]Cl (2.1 g, 3.6 mmol) was added, followed by CH_3OD (8.0 mL). The solution was stirred an additional 25 min and then filtered. The light tan solid $PPN[DFe(CO)_4]$ was then washed with CH_3OD and dried in vacuo: yield 2.6 g (>99%). The product was stored under N_2 in the freezer for up to 3 months until use.

Reaction of $[Mn(CO)_3(SC_4H_4)]SO_3CF_3$ (1) with 2. To a suspension of **1** (1.21 g, 3.25 mmol) in CH_2Cl_2 (7 mL) was added **2** (2.30 g, 3.25 mmol). After being stirred for 30 min, the mixture was evaporated to dryness. The residue was extracted with hexanes, and the combined extracts were evaporated to dryness to give a brown oil containing **3** (a mixture of both $Mn(CO)_3(SC_4H_4{\cdot}H)$ (**3a**) and $Mn(CO)_3(SC_4H_4{\cdot}D)$ (**3b**) and small amounts (<5%) of iron-containing side products;[17] yield 0.23 g (32%). The product **3** was identified by its IR and ^{1}H NMR spectra (Table I). Mass spectral analysis showed that 18.2% of **3** was **3b**; the relatively low deuterium incorporation into **3** is presumed to be due to a kinetic isotope effect that results in faster H^- transfer to **1** from the $HFe(CO)_4^-$ impurity than D^- transfer from $DFe(CO)_4^-$.

This reaction was also performed by using either CD_2Cl_2 (experiment 2, Table II) or dichloroethane (experiment 3) as the solvent instead of CH_2Cl_2. There was no reaction of uncoordinated thiophene with $PPN[HFe(CO)_4]$ under these conditions.

Reaction of 1 with $NaBD_4$. To a solution of **1** (1.00 g, 2.69 mmol) in H_2O (30 mL) was added CH_2Cl_2 (20 mL). Then $NaBD_4$ (0.124 g, 2.96 mmol) was added slowly under an N_2 flush. The mixture was stirred for 30 min, and the layers were separated. The H_2O layer was washed twice with CH_2Cl_2 (2 × 10 mL). The CH_2Cl_2 extracts were dried over Na_2SO_4 and evaporated to dryness, giving an orange-brown oil, **3**. Mass spectral analysis showed that 90.2% of **3** was **3b**.

Reaction of 3 with $[Ph_3C]BF_4$. To a solution of a mixture of **3a** (9.8%) and **3b** (90.2%) (0.087 g, 0.39 mmol) in CH_2Cl_2 (4 mL) was added $[Ph_3C]BF_4$ (0.13 g, 0.39 mmol). The mixture was stirred for 20 min. The resulting yellow precipitate was filtered, washed twice with CH_2Cl_2, and then dried in vacuo to give a yellow powder, $[Mn(CO)_3(SC_4H_4)]BF_4$, yield 0.080 g (66%). The amount of deuterium in the thiophene ligand was determined by mass spectrometry using a solid probe. In this experiment the complex decomposed, and the relative intensities of the thiophene(1+) and monodeuteriated thiophene(1+) peaks were measured; 22.8% of the product was monodeuteriated; the remainder was undeuteriated.

$[Mn(CO)_3$(2-methylthiophene)$]SO_3CF_3$ (4). A mixture of $Mn(CO)_5OSO_2CF_3$ (2.10 g, 6.11 mmol) and 2-methylthiophene (17 mL) was placed in a 100-mL round-bottom flask equipped with a reflux condenser. The mixture was heated in an oil bath at 85 °C for 35 min and then cooled in an ice bath. The solution was decanted off leaving an oily solid. The oil was washed with hexanes (2 × 10 mL portions) and dried in vacuo: yield 0.91 g (39%); IR (CH_2Cl_2) 2059 (s), 2020 (s) cm^{-1}; ^{1}H NMR (CD_3NO_2) δ 6.68 (s, H_3), 6.66 (s, H_4), 6.51 (s, H_5), 2.59 (s, Me); FAB (dithioerythritol/dithiothreitol), *m/e* 237 (M^+).

$Mn(CO)_3$(2-methylthiophene·H) (5). To a solution of **4** (0.83 g, 2.1 mmol) in water (90 mL) was added first CH_2Cl_2 (60 mL) and then, in small portions, $NaBH_4$ (0.15 g, 4.0 mmol). The mixture was stirred for 15 min, and the two phases were separated. The aqueous layer was washed with CH_2Cl_2 (2 × 50 mL). These washings were combined with the CH_2Cl_2 layer and dried over Na_2SO_4. The solution was evaporated off, and the resulting red-orange solid was sublimed under vacuum at 40 °C to give orange crystals of **5**: yield 0.16 g (32%); IR (hexanes) 2021 (s), 1942 (vs), 1929 (vs) cm^{-1}; EIMS (70 eV), *m/e* 237.8 (M^+), 209.8 (M^+ – CO), 181.9 (M^+ – 2 CO), 153.9 (M^+ – 3 CO), 99.0 (base peak, 2 methylthiophene·H). Anal. Calcd for $C_8H_7MnO_3S$: C, 40.14; H 2.95. Found: C, 39.91; H, 3.22.

Reaction of 4 with $[PPN]BH_4$. To **4** (0.350 g, 0.906 mmol) in CH_2Cl_2 (50 mL) was added $[PPN]BH_4$ (0.520 g, 0.940 mmol). The solution was stirred for 15 min under N_2 and the solvent

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[24] Darensbourg, M. Y.; Darensbourg, D. J.; Barros, H. C. C. *Inorg. Chem.* **1978**, *17*, 297.

[25] Walker, H. W.; Ford, P. C. *Inorg. Chem.* **1982**, *21*, 2509.

[26] Thomas, A. F. *Deuterium Labeling in Organic Chemistry*; Appleton-Century-Crofts: New York, 1971; p 3.

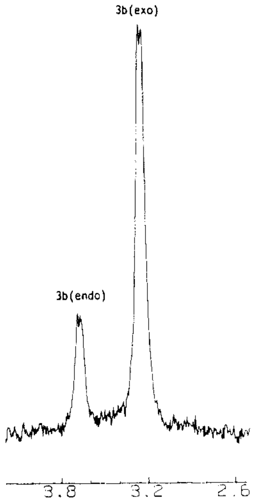


Figure 1. The ^2H NMR spectrum of **3b(exo)** and **3b(endo)** in $CHCl_3$.

removed under vacuum. The resulting orange solid was sublimed under vacuum at 40 °C to give orange crystals of **5**, yield 0.082 g (37%).

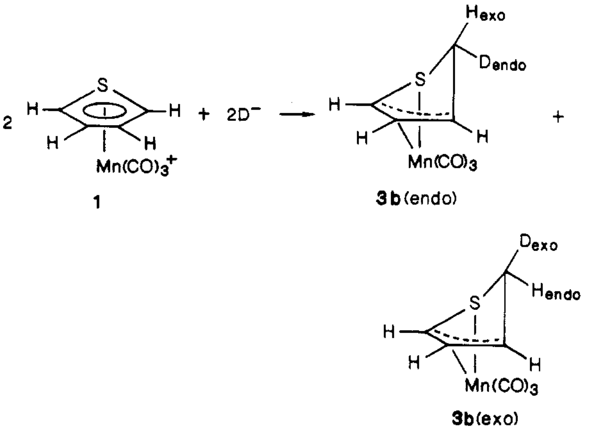
Reaction of 4 with PPN[HFe(CO)$_4$]. To **4** (0.30 g, 0.78 mmol) in CH_2Cl_2 (10 mL) was added PPN[HFe(CO)$_4$] (0.59 g, 0.81 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred for 30 min under N_2, evaporated to dryness, and extracted with hexanes. This extract was evaporated to a dark oil that was chromatographed on a silica gel column with hexanes. A gold band was eluted, and the solution was evaporated to dryness to give **5**, yield 0.0370 g (18.3%).

Reaction of 5 with [Ph$_3$C]BF$_4$. [Ph$_3$C]BF$_4$ (0.070 g, 0.21 mmol) in a minimum amount CH_2Cl_2 was added by syringe to **5** (0.060 g, 0.25 mmol) in CH_2Cl_2 (5 mL). The solution was stirred for 20 min after which time the yellow solid that formed was filtered off, washed with hexanes, and dried in vacuo overnight; yield 0.070 g (86%). IR and ^1H NMR spectra of the product [Mn(CO)$_3$(2-methylthiophene)]BF$_4$ were identical with those for **4**.

[Mn(CO)$_3$(2,5-dimethylthiophene)]SO$_3$CF$_3$ (6). A mixture Mn(CO)$_5$OSO$_2$CF$_3$ (1.45 g, 4.20 mmol) and 2,5-dimethylthiophene (15 mL) was placed in a 100-mL round-bottom flask equipped with a reflux condenser. The mixture was heated in an oil bath at 85 °C for 35 min and then cooled in an ice bath. The solution was decanted off, leaving an oily solid. The oil was washed with hexanes (2 × 50 mL) and dried in vacuo: yield 0.343 g (20.3%) of **6**; IR (CH_2Cl_2) 2040 (s), 2015 (s) cm^{-1}; ^1H NMR (CD_3NO_2) δ 6.40 (s, CH), 2.59 (s, CH_3).

Results and Discussion

Deuteride Addition to [Mn(CO)$_3$(SC$_4$H$_4$)]SO$_3$CF$_3$ (1). Addition of deuteride (D^-) to **1** is accomplished by using either NaBD$_4$ or PPN[DFe(CO)$_4$] (**2**) (eq 3). The data in Table II show that both reagents produce a mixture of endo, **3b(endo)**, and exo, **3b(exo)**, deuterium addition products as well as the hydride addition product [Mn(CO)$_3$(SC$_4$H$_4$·H)] (**3a**). Reaction of **1** with NaBD$_4$ in H_2O in the presence of CH_2Cl_2 results in the formation of **3a** and **3b** as an orange-brown oily solid. The product was identified by its IR spectrum (Table I) that had been reported previously.[17] The ^2H NMR spectrum (Figure 1, experiment 5 in Table II) in $CHCl_3$ displays only two resonances at 3.68 and 3.25 ppm that correspond to the endo and exo deuterium atoms, respectively. These signals are doublets with geminal hydrogen–deuterium coupling of 0.95 Hz. The assignments of these signals were made by comparison to the ^1H NMR spectrum of **3a** (Table I) since deuterium chemical shifts are known to be nearly identical with those of protons as long as primary or secondary isotope effects are not detectable.[27a] The assignment of the ^1H NMR spectrum of **3a** was made previously by analogy with that of Mn(CO)$_3$(benzene·H).[17] Integration of the ^2H peaks[27b] gives the relative amounts of deuterium at the endo and exo positions as 22:78, which is also the ratio of isomers **3b(endo)**:**3b(exo)**. Signals corresponding to deuterium at other positions in the thiophene ring are not observed. Quantitative mass spectral analysis shows that 34.8% of the product contains one deuterium atom and that multiply deuteriated products are not present. Since neither **3b** nor NaBD$_4$[28] exchanges with the solvents under these conditions, the hydride product **3a** is assumed to be formed from hydrogen impurities in the NaBD$_4$. When this reaction is performed with NaBD$_4$ known to have a higher deuterium content (experiment 6), 90.2% of the product is deuteriated. However, the **3b(endo)**:**3b(exo)** ratio remains the same within experimental error.



(3)

When **1** reacts with PPN[DFe(CO)$_4$] in CH_2Cl_2 for 30 min (experiments 1 and 4), a brown oil is produced that can be identified as a mixture of **3a** and **3b** by IR and ^1H NMR. This reaction was also performed by using dichloroethane (experiment 3) and CD_2Cl_2 (experiment 2) as the solvent. The use of alternate solvents does not significantly affect the yield, amount of deuteriated product, or relative amounts of **3b(exo)** and **3b(endo)** present (experiments 1–4). The low yield of **3**, 32%, can be attributed in part to side reactions of DFe(CO)$_4^-$ that form organometallic iron products.[17] The relative amounts of **3b(exo)** and **3b(endo)** were determined by integration of the corresponding peaks in the ^2H NMR spectrum. The mass spectrum showed that 18.2% of the product was monodeuteriated, and none contained more than one deuterium atom. The large amount (81.8%) of hydride addition product **3a** generated in this reaction is probably due to HFe(CO)$_4^-$ impurities in the DFe(CO)$_4^-$, which is known to exchange rapidly with the hydroxyl groups on glass.[29]

Nucleophilic addition to π-bound hydrocarbon ligands generally occurs exo to the metal;[30] however, endo hydride addition products have been observed in several reactions.[31] Two pathways have been proposed for endo addition. One involves initial attack at a carbonyl carbon

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(27) (a) Brevard, C.; Kintzinger, J. P. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic Press: New York, 1978; p 108. (b) To compare areas at a 90° pulse, an acquisition time of at least $5T_1$ must be used. The T_1 of the deuterium nuclei in this system is 0.3 s.

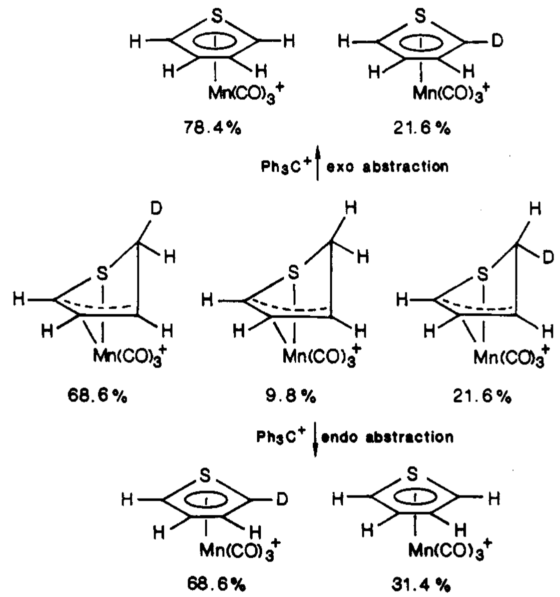
(28) (a) Girardot, P. R.; Parry, R. W. *J. Am. Chem. Soc.* **1951**, *73*, 2368. (b) Jolly, W. L.; Mesmer, R. E. *J. Am. Chem. Soc.* **1961**, *83*, 4470. (c) Cornforth, R. H. *Tetrahedron* **1970**, *26*, 4635.

(29) Darensbourg, M. Y., personal communication.

(30) Kane-Maguire, L. A. D.; Honig, E. D.; Sweigart, D. A. *Chem. Rev.* **1984**, *84*, 2665.

(31) (a) Weber, L.; Boes, R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 498. (b) Brookhart, M.; Lukacs, A. *Organometallics* **1983**, *2*, 649. (c) Davies, S. G.; Felkin, H.; Watts, O. J. *Chem. Soc., Chem. Commun.* **1980**, 159. (d) Brookhart, M.; Lamanna, W.; Humphrey, M. B. *J. Am. Chem. Soc.* **1982**, *104*, 2117. (e) Faller, J. W. *Inorg. Chem.* **1980**, *19*, 2857.

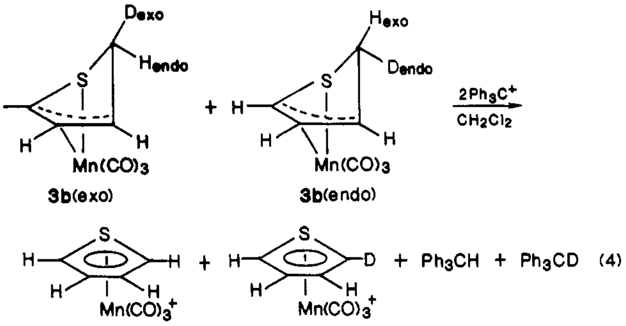
Scheme I



with subsequent migration to the coordinated hydrocarbon.[32] The other proceeds via attack at the metal followed by migration.[31e] In the present study, there is no evidence to exclude either of these mechanisms.

The PPN[DFe(CO)$_4$] reaction is especially interesting since $HFe(CO)_4^-$ could serve as a model for hydridic species present on the surface of the HDS catalyst. As seen in Table II, deuteride addition in this case results in an increased amount of **3b(endo)** relative to that produced when $NaBD_4$ is used (experiments 5 and 6).

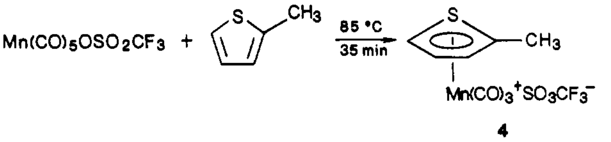
Hydride Abstraction from 3 by [Ph$_3$C]BF$_4$. Upon treatment of a mixture of **3a** (9.8%) and **3b** (90.2%) with [Ph$_3$C]BF$_4$ at room temperature in CH_2Cl_2, the manganese thiophene cation is regenerated and precipitates out of solution. The product was identified by its IR and ^{1}H NMR spectra (Table I), and the amount of deuteriated product was determined by quantitative EIMS analysis using the base peak thiophene(1+).



(4)

For determination of the specificity of hydride abstraction, Ph_3C^+ was added to a mixture of **3a** and **3b** having the composition shown in Scheme I. The mass spectrum of the product showed that it was 77.2% [Mn(CO)$_3$(SC$_4$H$_4$)]$^+$ and 22.8% [Mn(CO)$_3$(SC$_4$H$_3$D)]$^+$. Since endo abstraction would have resulted in a product composed of 31.4% [Mn(CO)$_3$(SC$_4$H$_4$)]$^+$ and 68.6% [Mn(CO)$_3$(SC$_4$H$_3$D)]$^+$ as opposed to a composition of 78.4% [Mn(CO)$_3$(SC$_4$H$_4$)]$^+$ and 21.6% [Mn(CO)$_3$(SC$_4$H$_3$D)]$^+$ for exo abstraction, as illustrated in Scheme I, the abstraction reaction clearly proceeds in an exo fashion. Exo hydride abstraction from π-coordinated ligands is the most common mode of action for Ph_3C^+; however, cases of endo hydride abstraction have been reported.[33]

Preparation of [Mn(CO)$_3$(2-methylthiophene)]SO$_3$CF$_3$ (4) and [Mn(CO)$_3$(2,5-dimethylthiophene)]SO$_3$CF$_3$ (6). Reaction of $Mn(CO)_5OSO_2CF_3$ with neat 2-methylthiophene at 85 °C for 35 min gives an air-stable gold oil, 4. Compound 6 was prepared analogously. Both 4 and 6 were previously prepared by Singer[16a] by the reaction of $Mn(CO)_5Cl$ with the thiophenes in the presence of $AlBr_3$ in 6.5% and 23.5% yields, respectively. These substituted thiophene complexes were identified by comparison of their IR and ^{1}H NMR spectra (Table I) with those reported by Singer as well as by a FAB mass spectrum.

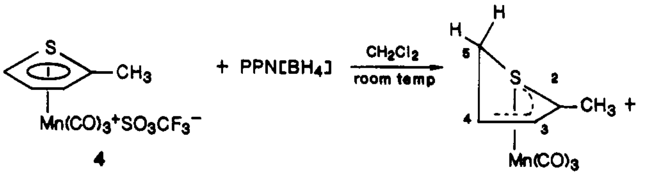


4

(5)

As with [Mn(CO)$_3$(thiophene)]SO$_3$CF$_3$, the 2-methyl- and 2,5-dimethylthiophene ligands in these complexes are quite readily displaced when dissolved in coordinating solvents such as acetone and acetonitrile to form Mn(CO)$_3$(solvent)$_3^+$.

Reaction of 4 and 6 with Hydride. The π-bound 2-methylthiophene in 4 is activated as was observed for the π-thiophene ring in 1 (see eq 2). Addition of PPN[BH$_4$] to a CH_2Cl_2 solution of 4 gives, after workup, a red-orange oil which is sublimed to give 5, in 37% yield, as orange crystals (eq 6). The ^{1}H and ^{13}C NMR and IR data for this complex are given in Table I. The ^{1}H NMR assignments listed in Table I follow those made for **3a**.[17] The observed geminal coupling indicates addition at the C_5 position rather than at the methyl-substituted carbon, C_2. The J value of 9.0 Hz is close to that seen for the geminal coupling in Mn(CO)$_3$(thiophene·H), 9.4 Hz.[17] No signals were observed in the NMR which might indicate that addition had occurred at the substituted C_2 position.



4
5
PPN[SO3CF3] (6)

The hydride complex 5 may also be formed by the reaction of 4 with $NaBH_4$ in a water/CH_2Cl_2 mixture, or by reaction with PPN[HFe(CO)$_4$] in CH_2Cl_2, in 32% and 18% yields, respectively.

Reaction of 6 with PPN[BH$_4$] was also attempted. No indication of hydride addition was seen either by IR or ^{1}H NMR when 6 was treated with up to 5 equiv of PPN[BH$_4$] at room temperature in CH_2Cl_2. No starting material remained by IR after 2 h of reaction. No products from the reaction other than $Mn_2(CO)_{10}$ were hexane soluble. The methyl groups at positions 2 and 5 in 6 apparently sterically hinder these carbons to nucleophilic attack. While nucleophilic addition to methyl-substituted carbons in π-bound arene rings does not occur as readily as for nonsterically hindered carbons, they have been observed in a few systems. Exo hydride addition was observed when

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[32] (a) Brown, D. A.; Glass, W. K.; Ubeid, T. M. *Inorg. Chim. Acta* **1984**, *89*, L47. (b) Rayoud, R. S.; Biehl, E. R. *J. Organomet. Chem.* **1979**, *179*, 297.

[33] (a) El Murr, N. *J. Organomet. Chem.* **1981**, *208*, 9. (b) Khand, I. V.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc. C* **1969**, 2024.

$[(C_6Me_6)Re(CO)_3]^+$ was treated with $LiAlH_4$.[34] A mixture of products was obtained upon reaction of $[M(CO)_3(\text{mesitylene})]^+$ (M = Re, Mn) with $PPN[BH_4]$, while only addition to nonsubstituted carbons was seen for the analogous *p*-xylene complexes.[35] For a series of manganese and iron complexes with methyl-substituted cycloheptatrienyl rings, studies suggest that while the electronic influence of methyl substituents is small, they have a marked steric retardation on nucleophilic addition.[30]

Reaction of 4 with Bases. An important reaction occurring over heterogeneous HDS catalysts at lower temperatures (ca. 200 °C) in the presence of D_2 is deuterium exchange into the 2- and 5-positions of thiophene. For 2-methyl- and 2,5-dimethylthiophenes exchange is not only observed for ring hydrogens, but small amounts of deuterium are exchanged into the α-methyl hydrogens as well.[19a] In an attempt to observe a similar exchange with 4, this complex was treated with KOH in D_2O/CD_3NO_2. The ^1H NMR spectrum of the CD_3NO_2 layer showed that rapid decomposition of 4 occurred. The sensitivity of the complex to base precludes any conclusion about whether exchange would occur into the methyl hydrogens. A similar reaction with $[CpRu(\eta\text{-thiophene})]BF_4$ showed that both the 2- and 5-positions are very rapidly exchanged.[18]

In other transition-metal-bound arene systems, CH_3 groups can be deprotonated, giving stable complexes with exocyclic double bonds.[36] Analogous reactions were attempted with 4 in an effort to determine whether or not an exocyclic methylene complex might be an intermediate in the exchange of the CH_3 hydrogens with deuterium. The 2-methylthiophene complex 4 was reacted with a series of bases (KO-*t*-Bu in *t*-BuOH and Et_3N, K_2CO_3, or NaF in CH_2Cl_2). Hexane extracts of reaction residues gave no isolable products other than $Mn_2(CO)_{10}$. No evidence for the desired deprotonated complexes was obtained by either IR or ^1H NMR.

Relevance to the Mechanism of Thiophene Hydrodesulfurization. On the basis of previous model studies (eq 2) from this group,[17,37] the initial step in the HDS of thiophene was proposed to involve a surface H^- (or possibly S^{2-}) addition to the 2-position of thiophene, which is π-bonded to a metal site on the catalyst surface. This step is likely to be important because it disrupts the aromaticity of the thiophene which is probably a major barrier in the HDS process. The results described herein show (eq 3) that addition of hydride to thiophene need not occur specifically at either the exo or endo face of the π-coordinated ring. This is significant since on the catalyst surface, both types of addition would seem possible. On a relatively flat surface, addition of hydride would be expected to occur from the same side (endo) as the coordinating metal. However, when surface irregularities, such as steps and kinks, are present exo hydride addition to the thiophene ring could become increasingly important. Steps and kinks are present on certain single-crystal surfaces, but supported catalyst surfaces are even more irregular.[38]

We observe (e.g., eq 6) that 2-methylthiophene is also susceptible to H^- addition at the non-methylated carbon, C_5, adjacent to the sulfur. Thus, it could react on an HDS catalyst surface much as thiophene does. If the initial step in HDS is surface H^- addition to the 2- or 5-position of a thiophene, one might expect thiophenes with the fewest methyl groups in the 2- and 5-positions to undergo HDS most rapidly, assuming they adsorb to the same extent to the catalyst. A comparison of the reactivities of 2- and 3-methylthiophenes illustrates this point. While these thiophenes have nearly equal tendencies to adsorb to $Co\text{–}Mo/Al_2O_3$ catalysts,[7a,11] 2-methylthiophene undergoes HDS only half as fast as 3-methylthiophene.[11] In terms of our proposed H^- addition mechanism, it is tempting to attribute the lower reactivity of the 2-methyl derivative to its having only one non-methylated carbon adjacent to the sulfur, as opposed to two such sites in 3-methylthiophene.

Our mechanism would predict that adsorbed 2,5-dimethylthiophene would be less reactive than either 2- or 3-methylthiophene. However, it is known that the 2,5-dimethyl derivative adsorbs more strongly to the catalyst[7a] than the monomethylthiophenes. The fact that 2,5-dimethyl- and 3-methylthiophene undergo HDS at very similar rates[7b] may be understood in terms of two counterbalancing factors. The greater extent of adsorption of 2,5-dimethylthiophene would be expected to increase its rate of HDS relative to 3-methylthiophene; however, this increase would be offset by the less favorable rate of H^- transfer to the methylated 2- and 5-positions. Thus, the HDS reactivities of methyl-substituted thiophenes may be rationalized in terms of a mechanism involving H^- (or possibly surface S^{2-})[37] addition to the 2- or 5-position of a surface π-bonded thiophene. Our results do not prove this mechanism; however, this is the first mechanism that is consistent with the reactivities of methylthiophenes on HDS catalysts and as ligands in model complexes.

Acknowledgment. We thank Dr. Glenn L. Schrader for helpful comments in the course of this work.

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(35) Calderazzo, F.; Poli, R.; Barbati, A. *J. Chem. Soc., Dalton Trans.* **1984**, 1059.

(36) Gladfelter, W. L.; Hull, J. W. *Organometallics* **1982**, *1*, 1716.

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(38) Somorjai, G. A. *Chemistry in Two Dimensions: Surfaces*; Cornell University Press: Ithaca, NY, 1981; pp 488–490.

(39) However, it is not known whether or not the adsorption occurs at the sites where HDS occurs.