or dioxane. For runs in water, alcohols, and aqueous-organic mixtures, 5-mL portions were removed at suitable time intervals into 25 mL of acetone, containing Lacmoid (resorcinol blue) indicator, and cooled in a solid CO_2–acetone slush bath. The acid produced was titrated against a standardized solution of sodium methoxide in methanol. The procedure for runs in acetic acid and the calculation of first-order solvolytic rate coefficients were as previously described.[36] All runs were performed, at least, in duplicate.

Product Studies. A stock solution of 2-adamantyl perchlorate in dioxane was used to prepare reaction mixtures in 100–50% ethanol (by volume). These reaction mixtures were allowed to stand at the appropriate temperature for in excess of 10 half-lives. The products were directly analyzed by response-calibrated GLC using a Packard instrument (Model GC-430) with flame ionization detector and microprocessor integrator. The stationary phase consisted of 15% Carbowax-20M on Chromosorb WNAW, within a 6 ft × 1/4 in. column. All determinations were made at least in duplicate and an error of ±5% is estimated for the product ratio.

Acknowledgments. This research was supported, in part, by the award of a Doctoral Research Fellowship to S.W.A. by the NIU Graduate School. One of us (D.N.K.) wishes to thank Professor M. Hanack, Lehrstuhl Für Organische Chemie 2, Universität Tübingen, for hospitality during the time that this manuscript was prepared.

Registry No. 2-Adamantyl perchlorate, 83187-55-7; 2-adamantyl bromide, 7314-85-4; silver perchlorate, 7783-93-9.

Reactions of the π-Thiophene Ligand in (η-C_4H_4S)$Mn(CO)_3^+$. Mechanistic Possibilities for Catalytic Hydrodesulfurization

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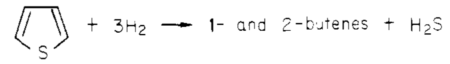
Contribution from the Department of Chemistry and Ames Laboratory,[1] Iowa State University, Ames, Iowa 50011. Received September 26, 1983

Abstract: Reaction of $Mn(CO)_5OSO_2CF_3$ with refluxing thiophene gives a high yield of $[Mn(CO)_3(\text{thiophene})]SO_3CF_3$ (**1**). This complex reacts with CN^- to give $Mn(CO)_3(\text{thiophene·CN})$ (**2a**) and with BH_4^-, $HFe(CO)_4^-$, and $HW(CO)_5^-$ to give $Mn(CO)_3(\text{thiophene·H})$ (**2c**). A single-crystal X-ray diffraction study of **2a** shows that it crystallizes in the monoclinic cell $P2_1/c$ with $a = 12.008$ (2) Å, $b = 6.6935$ (8) Å, $c = 12.172$ (2) Å, $\beta = 95.63$ (2)°, and four molecules per unit cell. The structure demonstrates that cyanide addition occurs at a carbon atom adjacent to sulfur causing this now-saturated carbon to be 0.59 Å out of the plane of the thiophene ring. Compound **1** reversibly adds $P(n\text{-Bu})_3$ to form $Mn(CO)_3(\text{thiophene·PBu}_3)^+$. Protonation of **2c** by HCl, HSO_3CF_3, HI, and CF_3CO_2H yields an unstable complex of 2,3-dihydrothiophene. The dihydrothiophene is readily displaced by MeCN or CO. Hydride addition to the π-bonded thiophene in **2c**, followed by protonation, is suggested as a possible model for the first steps in hydrodesulfurization of thiophene.

The mechanism of catalytic hydrodesulfurization (HDS) of thiophene has been the subject of numerous investigations.[2] In general, these studies have involved commercial Co–Mo/Al_2O_3 catalysts. Two key features of the mechanism which are not well



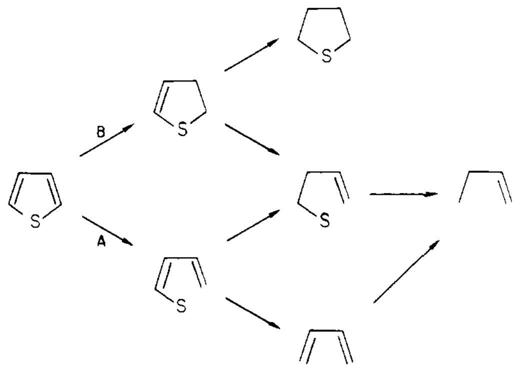
(1)

defined are (1) the initial mode of bonding of thiophene to the catalyst surface and (2) the nature of the first step in the HDS process; does it involve C–S bond cleavage or hydrogenation of an unsaturated carbon–carbon bond?

The most commonly invoked mode of thiophene adsorption is via the sulfur lone-electron pair to a metal cation. Kwart and co-workers recently reviewed this "one point" model and also discussed its shortcomings.[3a] Kwart proposed instead a model whereby thiophene adsorbed by coordination through a C=C double bond. Earlier Cowley[3b] and Zdrazil[3c] suggested that the entire aromatic π system of thiophene is coordinated to metal sites on the surface.

The detection of small amounts of butadiene among the HDS products has been the basis for suggesting that C–S bond cleavage occurs prior to carbon–carbon bond hydrogenation (path A).[4] The presence of tetrahydrothiophene, on the other hand, suggests a mechanism involving initial hydrogenation of unsaturated carbon–carbon bonds (path B).[5,6]

Scheme I. Possible Pathways for Thiophene HDS



arrows indicate H_2 addition

As is true in all catalytic systems, determining the nature of shortlived intermediates is very difficult. The use of discrete metal complexes has proven useful in modeling types of substrate reactivity which might occur on heterogeneous catalysts.[7] A number

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(1) Ames Laboratory is operated for the U. S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the office of Basic Energy Sciences, Chemical Sciences Division.

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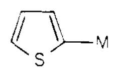
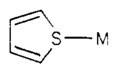
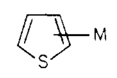
of thiophene complexes have been reported; they can be categorized into three types based on the mode of bonding to the metal:



C bonded



S bonded



π bonded

C-bonded thiophene is the most common form; however, it has not been suggested as a structure in the catalytic HDS of thiophene. The S-bonded thiophene has been suggested as a possible intermediate, but the S atom is very weakly coordinating. Only two complexes of this type, $Ru(NH_3)_5(thiophene)^{2+}$,[8] and $CpFe(MeCN)_2(2,5\text{-dimethylthiophene})^+$,[9] are known, and neither has been fully characterized due to instability with respect to thiophene dissociation. There is also only marginal evidence for thiophene S coordination even in complexes where the thiophene is part of a multidentate ligand.[10,11]

Two examples of thiophene π bonded to discrete metal centers have been reported: $[Mn(CO)_3(thiophene)][Cr(NH_3)_2(SCN)_4]$[12] and $Cr(CO)_3(thiophene)$.[13] In addition, several π-bonded transition-metal complexes of tetramethylthiophene have been described: $CpFe(Me_4thiophene)^+$,[14] $Fe(Me_4thiophene)_2^{2+}$,[15] $(Me_5C_5)Rh(Me_4thiophene)^{2+}$, $(Me_5C_5)Ir(Me_4thiophene)^{2+}$, $(COD)Rh(Me_4thiophene)^+$, and $(p\text{-cymene})Ru(Me_4thiophene)^{2+}$.[16]

The objective of this study was to investigate the reactivity of a π-thiophene complex from the viewpoint of evaluating such species as intermediates in HDS reactions of thiophene. To our knowledge the only previous reports on the reactivity of π-thiophene complexes are an investigation of their activity in the catalytic hydrogenation of olefins,[16] the observation that in $Cr(CO)_3(thiophene)$ the thiophene is easily displaced by better donor ligands,[17a] and the lithiation of thiophene in $Cr(CO)_3(thiophene)$ with n-BuLi.[17b]

Experimental Section

^1H NMR spectra were obtained on Varian EM 360, Bruker WM-300, and Nicolet NT-300 spectrometers with use of deuterated solvents as internal locks. ^{13}C NMR spectra were obtained on a Jeol FX-90Q spectrometer with proton decoupling and an internal deuterium lock. All NMR spectra are referenced to internal Me_4Si. IR spectra were recorded on a Perkin-Elmer 681 spectrophotometer and were calibrated by using the 2138.5-cm^{-1} peak of cyclohexane and the 1944-cm^{-1} peak of polystyrene. Electron ionization mass spectra (EIMS) were run on a Finnigan 4000 spectrometer. Elemental analyses were performed by the Ames Laboratory analytical group.

Reactions were performed under nitrogen in reagent grade solvents, but the workups, unless indicated otherwise, were done in air. Prepared as previously described were $PPN[HFe(CO)_4]$[18a], $PPN[HW(CO)_5]$,[18b] and $Mn(CO)_5Br$.[19] All other reagents were obtained from commercial sources and, except where indicated, were used without purification.

Purification of Thiophene. Commercially available thiophene (Aldrich 99+%) was found to contain impurities which gave ^1H NMR signals in the region δ 0.7–2.4 (in neat thiophene). Distillation proved to be an ineffective method of removing these impurities. Purification was accomplished by passing the neat thiophene through a column of $AgNO_3$-impregnated silica gel. The $AgNO_3$–silica gel was prepared by slurrying 100 g of 230–400-mesh silica gel in a solution containing 1.6 g of $AgNO_3$ in 300 mL of H_2O for 1.5 h. After being filtered and washed with MeOH, the silica gel was dried under vacuum at 40 °C in the dark. The dried material had a light brown color. To purify 1 mL of thiophene, 1 g of the impregnated silica gel was required. After removal of impurities, thiophene has an odor very much like benzene.

$Mn(CO)_5OSO_2CF_3$. To a solution of 3.0 g (11 mmol) of $Mn(CO)_5Br$ in 100 mL of CH_2Cl_2 was added 2.8 g (11 mmol) of $AgSO_3CF_3$. After being stirred for 2.5 h at room temperature in the dark, the gray-white precipitate was filtered and washed with CH_2Cl_2. The filtrate was evaporated to dryness, and the yellow residue was recrystallized by dissolving in 1 L of Et_2O and then evaporating the solution to a small volume. The resulting yellow crystals were identified by IR,[20] yield 2.5 g (68%). The compound sublimed under vacuum at 40 °C.

$[Mn(CO)_3(thiophene)]SO_3CF_3$ (1). A mixture of 2.0 g (5.8 mmol) of $Mn(CO)_5OSO_2CF_3$ and 15 mL of purified thiophene was refluxed for 20 min. After the solution was cooled to room temperature, the yellow precipitate was filtered, washed with 2 × 15-mL portions of CH_2Cl_2, and then dried in vacuo, yield 1.6 g (74%). Anal. Calcd for $C_8H_4F_3MnO_6S_2$: C, 25.82; H, 1.08; S, 17.23. Found: C, 26.92; H, 1.05; S, 16.76. If the recrystallization of $Mn(CO)_5OSO_2CF_3$ is omitted the overall conversion of $Mn(CO)_5Br$ to **1** is greater than 70%. **1** can be recrystallized from $MeCN/Et_2O$ to achieve a more crystalline product.

$Mn(CO)_3(thiophene{\cdot}CN)$ (2a). To a solution of 1.1 g (2.8 mmol) of **1** in 80 mL of H_2O was added 100 mL of hexane. Then a solution of 1.0 g (15 mmol) of KCN in 10 mL of H_2O was added. The mixture was shaken for 10 min, the layers were separated, and the aqueous layer was further extracted with 50 mL of hexane. The combined extracts were dried over Na_2SO_4 and then evaporated to a small volume. The resulting yellow crystals were filtered and washed with cold hexane: yield 84 mg (12%), mp 68–69 °C. Anal. Calcd for $C_8H_4MnNO_3S$: C, 38.57; H, 1.62; N, 5.62; S, 12.87. Found: C, 38.59; H, 1.52; N, 5.20; S, 12.85. EIMS: m/e 249 (M^+), 221 ($M^+ - CO$), 193 ($M^+ - 2CO$), 165 ($M^+ - 3CO$).

$Mn(CO)_3(thiophene{\cdot}H)$ (2c). To a solution of 2.0 g (5.4 mmol) of **1** in 100 mL of H_2O was added first 50 mL of CH_2Cl_2 and then, in portions, 0.50 g (13 mmol) of $NaBH_4$. The mixture was vigorously stirred for 15 min. After the phases were separated, the aqueous layer was washed with another 50 mL of CH_2Cl_2. The combined CH_2Cl_2 extracts were dried over Na_2SO_4 and then evaporated to dryness. The resulting orange oil was sublimed at room temperature in vacuo onto a water-cooled probe to give orange crystals: yield 1.0 g (86%); mp 32–33 °C. Anal. Calcd for $C_7H_5MnO_3S$: C, 37.52; H, 2.25. Found: C, 37.61; H, 2.32. EIMS: m/e 224 (M^+), 196 ($M^+ - CO$), 168 ($M^+ - 2CO$), 140 ($M^+ - 3CO$), 85 ($thiophene{\cdot}H^+$).

1 + $PPN[HFe(CO)_4]$. To a solution of 1.6 g (2.3 mmol) of $PPN[HFe(CO)_4]$ in 50 mL of N_2-saturated CH_2Cl_2 was added 0.86 g (2.3 mmol) of **1**. After the mixture was stirred for 30 min at room temperature it was evaporated to dryness, and the residue was extracted with 3 × 50-mL portions of hexane. The combined extracts were evaporated to dryness in vacuo (thereby also removing the $Fe(CO)_5$ which formed). The remaining dark brown oil was dissolved in a small amount of hexane and chromatographed on a (1.5 × 20)-cm silica gel (Merck) column. Eluting with hexane gave the following bands: red, $Fe_2(CO)_6SC_4H_4$ (0.6 mg, 0.2%); yellow, $Fe_2(CO)_6C_4H_4$ (7.0 mg, 1.8%); green, $Fe_3(CO)_{12}$ (trace); red-brown, undetermined; yellow, **2c** (0.15 g, 29%). The products were identified by IR, TLC, and in the case of $Fe_2(CO)_6SC_4H_4$, EIMS: m/e 336 ($M^+ - CO$), 308 ($M^+ - 2CO$), 280 ($M^+ - 3CO$), 252 ($M^+ - 4CO$), 224 ($M^+ - 5CO$), 196 ($M^+ - 6CO$), 144 (Fe_2S). Reversing the order of addition, namely adding $PPN[HFe(CO)_4]$ to a solution of **1**, resulted in a 50% yield of **2c** and smaller amounts of the iron products.

1 + $PPN[HW(CO)_5]$. A solution containing 1.1 mmol of $PPN[HW(CO_5]$ in 8 mL of THF was added to 0.20 g (0.54 mmol) of **1**. After the mixture was stirred for 10 min at room temperature it was evaporated to dryness. The orange oily residue was extracted with 3 × 10-mL portions of hexane. The combined hexane extracts were concentrated, filtered through a silica gel plug, and evaporated to dryness, yield 55 mg (45%) of **2c** (identified by IR).

2c + $(Ph_3C)BF_4$. To a solution of 0.11 g (0.47 mmol) of **2c** in 5 mL of CH_2Cl_2 was added 0.16 g (0.47 mmol) of $(Ph_3C)BF_4$. After the mixture was stirred for 20 min at room temperature the yellow precipitate was filtered and washed with CH_2Cl_2. The product was identified by IR

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as $[Mn(CO)_3(thiophene)]BF_4$, yield 0.13 g (90%).

2c + HCl. Dry HCl gas was bubbled through a solution of 0.20 g (0.89 mmol) of **2c** in 25 mL of N_2-saturated hexane for 5 min. The resulting yellow precipitate, $Mn(CO)_3(thiophene{\cdot}H_2)Cl$ (**3**), was filtered under N_2, washed with hexane, and dried in vacuo, yield 0.15 g (63%). Anal. Calcd for $C_7H_6ClMnO_3S$: C, 32.27; H, 2.32. Found: C, 32.17; H, 2.47.

Crystal Data. $Mn(CO)_3(thiophene{\cdot}CN)$: mol wt 249.13, monoclinic $P2_1/c$, $a = 12.008$ (2) Å, $b = 6.6935$ (8) Å, $c = 12.172$ (2) Å, $\beta = 95.63$ (2)°, $V = 973.7$ (2) Å^3, ρ(calcd) = 1.70 g/cm^3, ρ(found) = 1.65 ± 0.09 g/cm^3, $Z = 4$, $\mu_{abs} = 16.02$ cm^{-1} for Mo K_α radiation, λ 0.71034 Å.

A single crystal of $Mn(CO)_3(thiophene{\cdot}CN)$ of approximate dimensions 0.18 × 0.20 × 0.32 mm was mounted on a glass fiber and positioned on a standard goniometer head. Four preliminary ω-oscillation photographs at various χ and ϕ positions were taken on an automated four-circle X-ray diffractometer, and the coordinates of 12 independent reflections were input to the automatic indexing procedure ALICE.[21] The resulting reduced-cell scalars indicated primitive monoclinic symmetry. Inspection of the axial ω-oscillation photographs confirmed this symmetry. The lattice constants were obtained from least-squares refinement with use of precise $\pm 2\theta$ measurements of 15 independent high-angle reflections.

Collection and Reduction of X-ray Data. The data were collected at 25 °C with graphite-monochromated Mo Kα radiation on an automated four-circle diffractometer designed and built at the Ames Laboratory and previously described by Rohrbaugh and Jacobson.[22] All data (2071 reflections) within the range $0° < 2\theta < = 50°$ from the hkl and $-h$, $-k$, l octants were measured by using an ω stepscan technique (step size 0.01°, 0.5-s counting time/step).

As a check for crystal stability and alignment, the intensities of 3 standard reflections were measured every 75 reflections. These intensities were found to decrease considerably (by approximately 50% during the course of data collection), and a correction for this decay was made. Examination of the data revealed the systematic absence for $0k0$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$, thus uniquely defining the space group as $P2_1/c$. At the conclusion of data collection a reflection scan near $\chi = 90°$ indicated that absorption effects were minimal and hence no correction was applied.

These data were corrected for Lorentz and polarization effects, and of the 2071 measured reflections, 1598 were considered observed I(obsd) $\geq 3\sigma(I)$. The estimated error in each intensity was calculated by $\sigma(I)^2 = C_T + K_tC_B + (0.03C_T)^2 + (0.03C_B)^2$, where C_T, K_t, and C_B represent the total count, a counting time factor, and background count, respectively, and the factor 0.03 represents an estimate of the nonstatistical errors. The estimated standard deviations in the structure factors (F) were calculated by the finite difference method.[23] Equivalent reflections were averaged yielding 1450 unique observed reflections. The internal agreement factor from averaging $R_{av} = \sum||F_o| - |F_o^{av}||/\sum|F_o^{av}|$ was 0.032.

Solution and Refinement of the Structure. The position of the manganese atom was determined by Harker vector analysis of a sharpened three-dimensional Patterson map. All remaining atoms were found by successive structure factor[24] and electron density map[25] calculations. The atomic positional parameters and all anisotropic thermal parameters for each non-hydrogen atom were refined by using a block-matrix least-squares procedure with a final refinement using full-matrix least-squares. All hydrogen atomic positions were calculated but not refined. The minimized function for both least-squares-refinement procedures is $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$. The final conventional residual index was $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.059$, and the associated weighted residual index was $R_w = 0.077$. The scattering factors were those of Hanson et al.;[26] those for manganese and sulfur were modified for the real and imaginary parts of anomalous dispersion.[27]

Results and Discussion

Preparation of $[Mn(CO)_3(Thiophene)]SO_3CF_3$ (1). Reaction of $Mn(CO)_5Br$ with an equimolar amount of $AgSO_3CF_3$ in CH_2Cl_2 gives a yellow solution from which crystalline $Mn(CO)_5OSO_2CF_3$ can be obtained. This compound had previously been prepared by the reaction of $HMn(CO)_5$ with HSO_3CF_3.[20] Refluxing $Mn(CO)_5OSO_2CF_3$ in neat thiophene for 20 min gave a yellow, air-stable precipitate which was determined by IR, ^1H NMR, and elemental analysis to be $[Mn(CO)_3(thiophene)]SO_3CF_3$ (**1**).

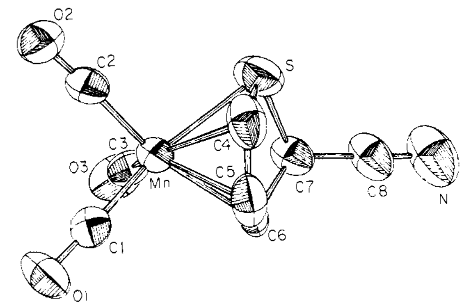
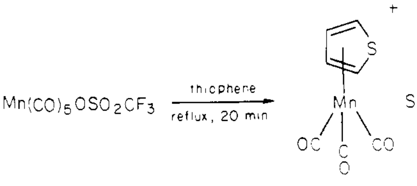


Figure 1. ORTEP drawing of $Mn(CO)_3(thiophene{\cdot}CN)$ (**2a**).



(2)

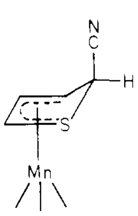
1

In 1967 Singer reported the preparation of $[Mn(CO)_3(thiophene)][Cr(NH_3)_2(SCN)_4]$ from the reaction of $Mn(CO)_5Cl$ and thiophene in the presence of $AlBr_3$.[12] The reported yield for this reaction was, however, very poor (3.5%). We have found that the analogous compound **1** can be prepared in 74% yield by using the method in eq 2. Although I can be recrystallized from $MeCN/Et_2O$ or acetone/Et_2O to obtain a more crystalline product, the purity is not generally improved and substantial losses in yield occur. This is due to the easy displacement of the thiophene by coordinating solvents (MeCN and acetone) to form $Mn(CO)_3(solvent)_3^+$. The converison of **1** to $Mn(CO)_3(MeCN)_3^+$ is complete after the mixture is left at room temperature in MeCN for 16 h.

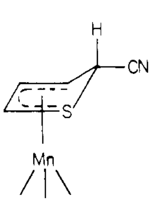
Synthesis and Structure of $Mn(CO)_3(thiophene{\cdot}CN)$ (2). Addition of excess KCN to an aqueous solution of **1** in the presence of hexane resulted in the formation of yellow crystals of $Mn(CO)_3(thiophene{\cdot}CN)$ (**2a**). After standing several days in air this compound decomposes to a brown insoluble material.

$$\mathbf{1} + KCN \rightarrow \underset{\mathbf{2a}}{Mn(CO)_3(thiophene{\cdot}CN)} + KSO_3CF_3 \quad (3)$$

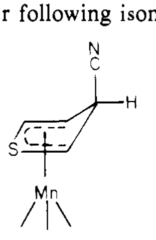
Assuming cyanide addition to one of the thiophene carbons of **1**, **2a** could have one of the four following isomeric structures:



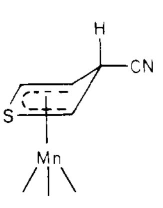
I



II



III



IV

An X-ray crystal structure determination of **2a** revealed that I is the observed isomer. This structure is shown in Figure 1; corresponding angles, distances, and atomic coordinates are given in Tables I, II, and III. The sulfur and three carbon atoms of the organic ring are planar to within 0.037 Å while the remaining carbon atom is 0.597 Å out of this plane. This plane forms a dihedral angle of 147° with a plane passing through C6, S, and C7. The carbonyl groups in **2a** are positioned so that one CO is eclipsed with the out-of-plane ring carbon atom. The Mn–C distance for the carbonyl which is approximately trans (161°) to the sulfur atom appears to be slightly shorter (0.021 Å) than the remaining two Mn–CO distances.

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Table I. Bond Angles with Esd's for Mn(CO)$_3$(thiophene·CN) (2a)

type	angle, deg	type	angle, deg
S-Mn-C4	46.4 (2)	C6-Mn-C1	99.1 (2)
S-Mn-C2	98.1 (2)	Mn-S-C4	58.6 (2)
S-Mn-C3	104.2 (2)	Mn-S-C7	83.0 (2)
S-Mn-C5	70.1 (2)	C4-S-C7	92.5 (3)
S-Mn-C6	70.0 (1)	Mn-C4-S	75.0 (3)
S-Mn-C1	160.6 (2)	Mn-C4-C5	71.4 (4)
C4-Mn-C2	98.0 (2)	S-C4-C5	108.6 (4)
C4-Mn-C3	147.7 (2)	Mn-C2-O2	176.6 (5)
C4-Mn-C5	38.6 (3)	Mn-C3-O3	177.1 (6)
C4-Mn-C6	65.5 (2)	Mn-C1-O1	178.1 (5)
C4-Mn-C1	114.8 (2)	Mn-C5-C4	70.1 (4)
C2-Mn-C3	99.7 (3)	Mn-C5-C6	76.4 (4)
C2-Mn-C5	130.2 (3)	C4-C5-C6	117.9 (6)
C2-Mn-C6	163.5 (2)	Mn-C6-C5	67.7 (4)
C2-Mn-C1	88.8 (2)	Mn-C6-C7	94.0 (3)
C3-Mn-C5	130.0 (3)	C5-C6-C7	109.6 (5)
C3-Mn-C6	94.5 (2)	S-C7-C6	99.2 (3)
C3-Mn-C1	92.4 (2)	S-C7-C8	111.5 (4)
C5-Mn-C6	35.8 (2)	C6-C7-C8	113.5 (6)
C5-Mn-C1	91.6 (2)	C7-C8-N	178.1 (7)

Table II. Bond Distances with Esd's for Mn(CO)$_3$(thiophene·CN) (2a)

type	length, Å	type	length, Å
Mn-C1	1.783 (6)	C4-C5	1.375 (9)
Mn-C2	1.805 (6)	C5-C6	1.322 (8)
Mn-C3	1.803 (6)	C6-C7	1.584 (8)
Mn-C4	2.073 (7)	C7-S	1.831 (6)
Mn-C5	2.090 (6)	C7-C8	1.469 (10)
Mn-C6	2.195 (6)	C8-N	1.136 (12)
Mn-S	2.346 (2)	C1-O1	1,153 (7)
Mn···C7	2.796 (6)	C2-O2	1.143 (7)
S-C4	1.759 (7)	C3-O3	1.145 (8)

Table III. Atomic Coordinates (×10^4) with Esd's for Mn(CO)$_3$(thiophene·CN) (2a)

atom	x	y	z
Mn	7076.4 (6)	4348.3 (12)	9549.7 (6)
S	7401 (2)	5359 (3)	7763 (1)
C1	6645 (4)	4416 (8)	10910 (5)
C2	5978 (5)	2563 (9)	9176 (4)
C3	8213 (5)	2660 (9)	9956 (5)
C4	6470 (4)	6666 (11)	8531 (6)
C5	7064 (5)	7465 (9)	9450 (5)
C6	8140 (4)	7021 (9)	9630 (4)
C7	8625 (4)	6577 (10)	8491 (5)
C8	8939 (5)	8385 (13)	7912 (6)
O1	6343 (4)	4423 (7)	11780 (3)
O2	5257 (3)	1463 (7)	8985 (3)
O3	8963 (4)	1655 (8)	10223 (5)
N	9152 (5)	9799 (14)	7461 (6)
H4	5611	6809	8338
H5	6673	8396	9985
H6	8590	6960	10397
H7	9335	5685	8650

In **2a** the C–C bond distances for C4–C5 and C5–C6 are 1.375 (9) and 1.322 (9) Å, respectively. These distances indicate considerable double bond character as they differ only slightly from the "normal" C═C double bond distance of 1.335 Å,[28] but they are much shorter than a C–C single bond distance (1.526 Å).[28] The average C–C bond length in thiophene is 1.386(5) Å,[29a] The three-carbon unit C4–C5–C6 can be described as an allyl system which has delocalized π-electron density. This notion is supported by the fact that the angle C4–C5–C6 is 118° while the angles about the remaining carbons, C4, C6, and C7, are only 109°, 110°, and 99°, respectively. Allyl complexes which have been previously characterized display C–C–C angles of 112–123° and C–C bond distances of 1.346–1,485 Å.[29b] The thiophene ligand distances and angles are shown in Figure 2.

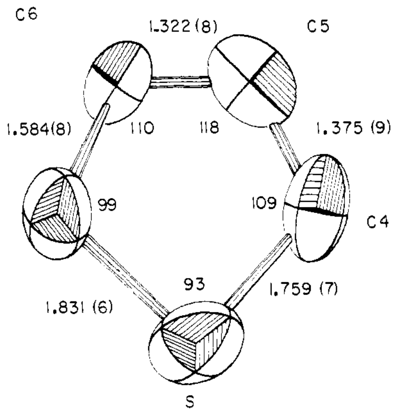
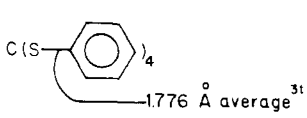
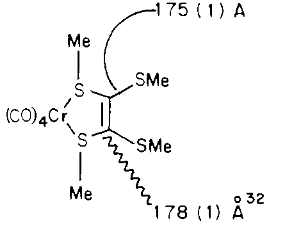


Figure 2. Bond distances and angles for the thiophene·CN ligand in Mn(CO)$_3$(thiophene·CN) (**2a**).

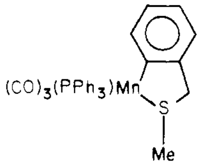
Although the S–C4 bond distance in **2a** (1.759 (7) Å) is less than those of the C–S single bonds in ethylene sulfide (1.819 (1) Å)[30] and tetrahydrothiophene (1.839 (1) Å),[30] it is approximately the same as found in compounds with S–C(sp^2) bonds:



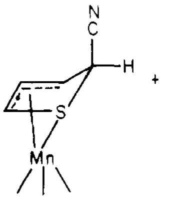


This comparison suggests there is probably little π bonding in the S–C4 bond. The S–C4 distance is much longer, however, than the C–S bonds in thiophene (1.718 (5) Å), where there is substantial delocalization.[29a] The S–C7 distance (1.831 (6) Å) is that expected for a C–S single bond.

The Mn–S bond distance in **2a** (2.346 (2) Å) is similar to that (2.310 (4) Å) reported for the sulfide complex:[33]



In view of the above observations, the ligand in **2a** is perhaps best represented by the following structure, which shows bonding of the organic ligand through allyl and sulfide donor groups.



Reaction of 1 with Nucleophiles. In addition to cyanide, other anionic nucleophiles such as NaOMe, LiPh, and Li(SC$_4$H$_3$) react with **1** to give small amounts of yellow, hexane-soluble products

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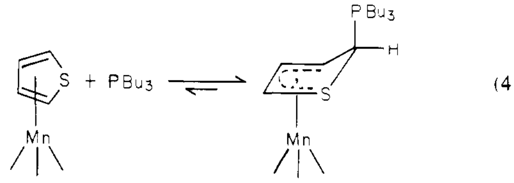
Table IV. IR and ^1H NMR Spectral Data

compound	IR	^1H NMR^a
$[Mn(CO)_3(thiophene)]SO_3CF_3$ (1)	2078 s, 2021 s (CH_3NO_2)	6.90, 6.77 (CD_3NO_2)
$Mn(CO)_3(thiophene\cdot CN)$ (2a)	2029 s, 1957 vs, 1945 vs, (C_6H_{12})	6.56^5, 6.13^4, 4.88^2, 3.56^3 ($CDCl_3$)^b
$[Mn(CO)_3(thiophene\cdot PBu_3)]SO_3CF_3$ (**2b**)	2025 s, 1946 s (br), 1930 s (br), (CH_3NO_2)	6.67^5, 6.30^4, 5.41^2, 3.64^3, ($CDCl_3$)
$Mn(CO)_3(thiophene\cdot H)$ (**2c**)	2020 s, 1944 vs, 1929 vs (C_6H_{12})	6.42^5, 5.89^4, $3.79d^2$,^{c} 3.30^3, $3.29d^1$ ^{c} ($CDCl_3$)^d
$Mn(CO)_3(thiophene\cdot H_2)Cl$ (3)	2041 s, 1973 s, 1947 s (CH_2Cl_2)	6.48^5, 6.28^4, 3.73^6, 3.11^7 (CD_2Cl_2)
$Mn(CO)_3(thiophene\cdot HCN)Cl$	2040 s, 1962 s, 1946 s (CH_2Cl_2)	6.25^5, 5.68^4, 4.73^2, 3.32^3, 3.23^3 ($CDCl_3$)
$Fe_2(CO)_6C_4H_4$	2074 w, 2036 vs, 2003 s, 2000 s (C_6H_{12})	
$Fe_2(CO)_6SC_4H_4$	2078 w, 2044 s, 2013 s, 2005 s (C_6H_{12})	
$Mn(CO)_5OSO_2CF_3$	2073 s, 2021 m (CH_2Cl_2)	
2,3-dihydrothiophene		6.14^5, 5.59^4, 3.19^6, 2.71^7 ($CDCl_3$)^e
2,3-dihydro-2-cyanothiophene		6.18^5, 5.59^4, 4.36^2, 3.02^3 ($CDCl_3$)

[a] Numerical superscripts indicate the following assignments: 1, H_2(exo); 2, H_2(endo), 3, H_3, 4, H_4, 5, H_5, 6, H_2(2 protons), 7, H_3(2 protons). [b] $\delta(^{13}C)$ 93.08, 69.89, 50.77, 53.10 (acetone-d_6). [c] $^2J_{HH} = 9.8$ Hz. [d] $\delta(^{13}C)$ 92.75, 70.05, 52.82, 56.83 (acetone-d_6). [e] Reference 46.

which have IR spectra in the ν(CO) region similar to **2a**. None of these, however, was further characterized.

In 1976 Sweigart and Kane-Maguire reported that $P(n\text{-}Bu)_3$ reacts with $Mn(CO)_3(arene)^+$ to give the phosphonium ring adduct $Mn(CO)_3(arene\cdot PBu_3)^+$.[34] This process was readily reversible, and equilibrium constants were found to be dependent on the degree of methyl substitution in the arene. Reaction of **1** with equimolar $P(n\text{-}Bu)_3$ in acetone gives a solution in which no **1** is detectable by IR, thereby suggesting that $P(n\text{-}Bu)_3$ addition to **1** is more favorable than to $Mn(CO)_3(benzene)^+$. The product, $[Mn(CO)_3(thiophene\cdot PBu_3)]SO_3CF_3$ (**2b**), has an IR spectrum with ν(CO) bands at 2025, 1946, and 1930 cm^{-1} compared to 2028 and 1950 cm^{-1} for $[Mn(CO)_3(benzene\cdot PBu_3)]BF_4$.[35] Evaporating the solvent from the above reaction mixture left an orange oil. Attempts to crystallize this compound by dissolving it in CH_2Cl_2 then adding hexane gave an orange oil (**2b**) plus a yellow crystalline solid. This solid was identified by IR as **1**, thus demonstrating the reversibility of the addition of $P(n\text{-}Bu)_3$.



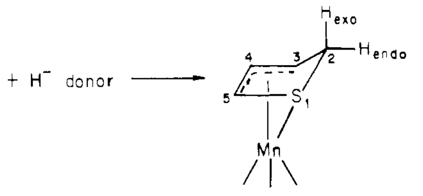
(4)

2b

The ^1H NMR spectrum (Table IV) of **2b** shows four singlets for the ring protons. Comparison of this spectrum with that of **2a** shows a close correlation except for δ H_2(endo) (5.41) which is directly influenced by the geminal substituent. There is no observed coupling between the phosphorus and H_2.

Less basic phosphines such as PPh_2Me also react with **1** (as determined by IR) to give adducts of the type **2b**. The equilibrium in this case, however, is shifted considerably to the left. The reactivity of **1** toward nucleophiles parallels in some respects that of $[Mn(CO)_3(benzene)]^+$.[34-41] This similar reactivity furthers the analogy between thiophene and benzene, which are both 6-π-electron, aromatic-ring compounds.

Reactions of 1 with Hydrides. Addition of excess $NaBH_4$ to an aqueous solution of **1** in the presence of CH_2Cl_2 results in the formation in 86% yield of an orange crystalline, volatile solid, $Mn(CO)_3(thiophene\cdot H)$ (**2c**), which melts just above room temperature. As in the case of **2a**, **2c** decomposes slowly (days) in air.



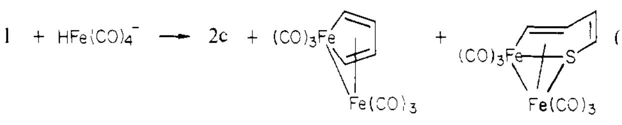
(5)

2c

H^- donor = BH_4^-, $HFe(CO)_4^-$, or $HW(CO)_5^-$

The ^1H NMR spectrum of **2c** (Table IV) displays five resonances of equal intensity. The signals at δ 3.79 and 3.29 are doublets with coupling constants of 9.8 Hz. By analogy with $Mn(CO)_3(benzene\cdot H)$,[36] which shows a geminal coupling of 11 Hz, these signals can be assigned to the methylene protons, with H_2(exo) being further upfield. The remaining assignments given in Table IV are made by analogy with the benzene system and by assuming a deshielding effect from the sulfur atom; they also closely parallel those for **2a**.

Addition of 1 equiv of $PPN[HFe(CO)_4]$ to **1** in CH_2Cl_2 gives a 50% yield of **2c**. This reaction is significant in that $HFe(CO)_4^-$ may serve as a model for metal hydride species one might expect to find on an HDS catalyst surface. The relatively low yield of this reaction compared with that from the reaction of BH_4^- with **1** may be attributed, in part, to side reactions of $HFe(CO)_4^-$:



(6)

V VI

V was previously isolated in 5% yield from the reaction of $Fe_3(CO)_{12}$ with neat refluxing thiophene.[42] VI was isolated in trace amounts from this same reaction although it has not been completely characterized. The mechanisms leading to the formation of V and VI are not clear; however, their formation under mild conditions in the present reaction, albeit in low yields, is a further indication of the enhanced reactivity of coordinated thiophene.

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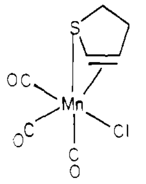
The reaction of excess PPN[HW(CO)$_5$] with **1** also results in hydride transfer to the thiophene ligand. In this case, the yield of **2c** is 45%, and no other hexane-soluble products are formed.

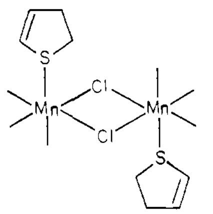
Addition of (Ph$_3$C)BF$_4$ to a CH$_2$Cl$_2$ solution of **2c** results in the rapid and quantitative formation of [Mn(CO)$_3$(thiophene)]BF$_4$. On the basis of previous studies of analogous systems,[43] the hydride which is removed by Ph$_3$C$^+$ is assumed to be the same one (H$_2$(exo)) which was added by BH$_4^-$.

Protonation of Mn(CO)$_3$(thiophene·H)). Bubbling HCl gas through a hexane solution of **2c** gives a yellow, air-stable precipitate, **3**. The IR spectrum of **3** in CH$_2$Cl$_2$ shows three strong ν(CO) bands at 2041, 1973, and 1947 cm^{-1}, which is similar to spectra observed for Mn(CO)$_3$L$_2$X complexes (cf.: Mn(CO)$_3$(tetrahydrothiophene)$_2$Br, 2038 s, 1956 s, 1939 s (CH$_2$Cl$_2$);[44] Mn(CO)$_3$(MeCN)$_2$Cl, 2035 s, 1953 s, 1927 s (Nujol)).[45] A structure which is consistent with this formula is the following:



VII

The ^{1}H NMR spectrum of **3** displays four resonances at δ 6.48, 6.28, 3.73, and 3.11 which are quite broad, probably due to quadrupolar broadening by ^{55}Mn or formation of trace amounts of paramagnetic Mn^{2+} species. While the first two signals are further downfield than is generally found for a coordinated C=C double bond, their position is approximately the same as that in **2c**, which is a coordinated allyl system. Another possible structure for **3** is a dimer, VIII.

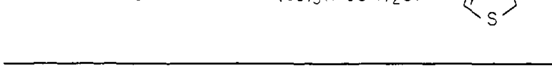


VIII

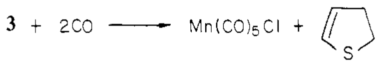
The solution IR spectrum (in CHCl$_3$) of the analogous compound Mn$_2$(CO)$_6$(MeCN)$_2$Cl$_2$ also gives three ν(CO) bands (2043 s, 1957 (sh), 1946 s).[45] One can readily envision the displacement in VII of the C=C double bond, which is typically quite labile, to form the dimer.

Attempts to resolve the question of whether Mn(CO)$_3$(thiophene·H$_2$)Cl has structure VII or VIII by obtaining a molecular weight or crystals suitable for an X-ray analysis failed because of the decomposition which occurs upon standing in solution. This decomposition is evidenced by the formation of several new bands in the IR spectrum of **3** upon standing at room temperature for 1 h.

Dissolving **3** in MeCN immediately yields Mn(CO)$_3$(MeCN)$_2$Cl (identified by IR)[45] and free 2,3-dihydrothiophene, which can be distilled from the manganese complex and was identified by ^{1}H NMR.[46] It is interesting that only the thermodynamically less stable[46] 2,3 isomer is formed instead of the 2,5 isomer. Bubbling CO through a CH$_2$Cl$_2$ solution of **3** for 15 min results in quantitative conversion to Mn(CO)$_5$Cl, as determined by IR.



(7)



(8)

In qualitative experiments, it was found that HSO$_3$CF$_3$, HI, and CF$_3$CO$_2$H also protonate **2c**. These reactions were followed by IR and ^{1}H NMR, and in each case the odor of 2,3-dihydrothiophene was detected, but no pure 2,3-dihydrothiophene metal complexes could be isolated. Acetic acid did not react with **2c** after 30 min at room temperature.

2a also reacts with HCl gas to give the protonated complex Mn(CO)$_3$(thiophene·HCN)Cl, which was characterized by its IR and ^{1}H NMR spectra (Table IV). Addition of MeCN also results in ligand displacement to give free 2,3-dihydro-2-cyanothiophene, as determined by ^{1}HNMR spectroscopy (Table IV). This compound has not been previously reported.

Comments on the Mechanism of Thiophene HDS. We initially asked if thiophene π bonded to a surface metal atom might be considered as a possible intermediate in the heterogeneously catalyzed HDS of thiophene. Of special importance was whether or not π-bonded thiophene is activated to react in a way that would lead to HDS products. In the present study, we have found that thiophene in Mn(CO)$_3$(thiophene)$^+$ is highly activated to react with nucleophiles under mild conditions. These nucleophilic additions are particularly important because they break the aromatic stabilization of the thiophene ring, which is probably a major barrier in the HDS process. A nucleophile which is likely to be available on an HDS catalyst surface is a metal hydride. The transfer (eq 5) of a hydride ligand from the metal hydrides HFe(CO)$_4^-$ and HW(CO)$_5^-$ to Mn(CO)$_3$(thiophene)$^+$ may serve as a model for an analogous surface reaction. Moreover, the observed addition of the hydride to the α (i.e., 2) position of the coordinated thiophene suggests an explanation for the facile exchange of the α hydrogens of thiophene with deuterium over supported Mo-containing catalysts.[47]

The reaction of Mn(CO)$_3$(thiophene·H) with proton sources such as HCl to give 2,3-dihydrothiophene (DHT) suggests that DHT could be an intermediate in the HDS process. Certainly the proton sources, such as metal–SH groups, available on the catalyst are much less acidic than those used in our studies; however, the more extreme conditions (300–500 °C) of the HDS reaction may allow for proton transfer from an SH surface group. In fact, acidic hydrogen sites have been identified on single-crystal MoS$_2$ HDS catalysts.[48]

Since our studies do not involve an HDS-active metal nor conditions that approach those of the heterogeneous HDS reaction, we have certainly not established π-bonded thiophene as an intermediate in HDS catalysis. Our results do, however, suggest that it is a possible intermediate, and other investigations can be designed to explore this possibility further.

Acknowledgment. We thank Dr. Glenn L. Schrader for many useful discussions.

Supplementary Material Available: Tables of the final thermal parameters and observed and calculated structure factors for Mn(CO)$_3$(thiophene·CN) (**2a**) (5 pages). Ordering information is given on any current masthead page.

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