Sulfur-Coordinated Thiophene and Benzothiophene in $Cp(NO)(PPh_3)Re(thiophene)^+$: Conversion to Thienyl and Thienylcarbene Complexes

Mitchell J. Robertson, Carter J. White, and Robert J. Angelici*

Contribution from the Department of Chemistry and Ames Laboratory,[1] Gilman Hall, Iowa State University, Ames, Iowa 50011

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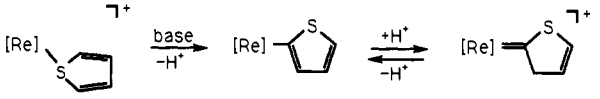
Abstract: A series of stable sulfur-coordinated thiophene complexes $Cp(NO)(PPh_3)Re(\eta^1(S)\text{-Th})^+$, Cp = η^5-C_5H_5, Th = thiophene (T), 2,5-Me_2T, benzo[*b*]thiophene (BT), and 2-MeBT, are prepared by the reaction of $Cp(NO)(PPh_3)Re(ClCH_2Cl)^+$ with thiophenes. The T and BT complexes react with bases to abstract a proton from the 2-carbon of the η^1(S)-coordinated thiophenes to give neutral 2-thienyl (2-Tyl) or 2-benzothienyl (2-BTyl) complexes.

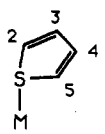


[Re] = $Cp(NO)(PPh_3)Re$

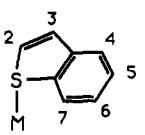
Reaction of the 2,5-Me_2T complex with base results in proton abstraction at the 3-carbon to give the 3-(2,5-Me_2Tyl) complex. The 2-Tyl and 2-BTyl complexes react with CF_3SO_3H to give cationic thienylcarbene and benzothienylcarbene complexes, respectively, which are isomers of the starting η^1(S)-coordinated thiophene complexes. This series of facile reactions demonstrates that η^1(S) coordination can activate thiophenes in a way that leads to the disruption of the aromaticity of the thiophene ligand upon formation of the thienylcarbene complexes. The base removal of the 2-proton from $\eta^1(S)$-thiophene ligands also suggests a mechanism for the exchange of these protons with deuterium during the hydrodesulfurization of thiophenes on heterogeneous catalysts.

Introduction

Of all the possible modes of thiophene adsorption[2,3] at metal sites on heterogeneous catalysts during the hydrodesulfurization (HDS) of thiophene (T), the η^1(S) mode was one of the first to be proposed. Several transition metal complexes containing an η^1(S)-coordinated thiophene or benzo[*b*]thiophene (BT) have been reported,[4] but there is no direct evidence that this mode of bonding



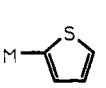
η^1(S)-T



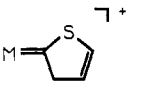
η^1(S)-BT

activates the thiophene to undergo C–S bond cleavage, which is required in the HDS process. However, $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(\eta^1(S)\text{-T})$ is a proposed intermediate in a reaction that leads to Rh insertion into a thiophene C–S bond.[5] There is also no direct evidence for cleavage of a C–H bond in η^1(S)-coordinated T or BT; such a cleavage would provide a model for the deuterium exchange of thiophene hydrogens, which is observed when thiophene is passed with D_2 over HDS catalysts.[6]

In the present study, we explore reactions of η^1(S)-coordinated thiophenes (Th represents thiophene and its substituted derivatives) in $Cp(NO)(PPh_3)Re(\eta^1(S)\text{-Th})^+$, which undergo C–H cleavage to give thienyl complexes. Upon reaction with acids, the thienyl complexes are converted to thienylcarbene derivatives. These model reactions open new ways of thinking about the reactivity of thiophenes on HDS catalysts.



thienyl



thienylcarbene

Experimental Section

General Procedures. All reactions and manipulations were carried out under a N_2 atmosphere using standard Schlenk techniques[7] unless stated otherwise. All solvents were reagent grade and dried under N_2 by the following standard methods.[8] Diethyl ether (Et_2O) was distilled from sodium/benzophenone. Hexanes and CH_2Cl_2 were distilled from CaH_2. Methanol was distilled from Mg/I_2. The neutral alumina (Brockman, activity I, ~150 mesh) used for chromatography was

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deoxygenated at room temperature under high vacuum overnight, then deactivated with 5% w/w deionized water, and stored under N_2.

The ^1H and ^{13}C NMR spectra were recorded on either a Nicolet NT-300 or a Varian VXR-300 spectrometer with CD_2Cl_2 as the internal lock and internal reference (δ 5.32 for ^1H and δ 53.8 for ^{13}C). Fast atom bombardment (FAB) spectra were obtained on a Kratos MS-50 mass spectrometer. Infrared spectra were recorded in CH_2Cl_2 on a Nicolet 710 FT-IR spectrophotometer. Elemental analyses were performed by either Desert Analytics or Galbraith Laboratories, Inc.

Thiophene (T) was purified by a published method.[9] Triflic acid, CF_3SO_3H, was distilled over P_2O_5 under dry argon. $Cp(NO)(PPh_3)Re(CH_3)$[10] and 2-methylbenzo[*b*]thiophene (2-MeBT)[11] were prepared by literature methods. All other reagents were used as received from commercial sources.

[Cp(NO)(PPh$_3$)Re(η^1(*S*)-T)]BF$_4$ (1). Compounds **1–4** containing an η^1(S)-bonded thiophene were prepared by a method similar to that previously reported by Gladysz and co-workers.[12a] A solution of $Cp(NO)(PPh_3)Re(CH_3)$ (0.210 g, 0.375 mmol) in 20 mL of CH_2Cl_2 was cooled to −78 °C. Then, $HBF_4{\cdot}OEt_2$ (80 μL, 0.40 mmol) was added to the solution with stirring; the color of the solution turned from bright orange to dark orange-brown. After stirring for 2 min, thiophene (60 μL, 0.75 mmol) was added to the solution, which was stirred and slowly warmed to room temperature over an 8-h period. Solvent was then removed under vacuum to leave an oily brown residue. The residue was taken up in ~20 mL of CH_2Cl_2 and filtered through a short plug of Celite. The brown solution was cooled to 0 °C, and 20 mL of Et_2O was added to precipitate $[Cp(NO)(PPh_3)Re(\eta^1(S)\text{-T})]BF_4$ (0.162 g, 61%) as a moderately air-stable tan solid: ν(NO) 1724 cm^{-1}. Anal. Calcd for $C_{27}H_{24}BF_4NOPReS$: C, 45.20; H, 3.38. Found: C, 44.62; H, 3.34.

[Cp(NO)(PPh$_3$)Re(η^1(*S*)-2,5-Me$_2$T)]BF$_4$ (2). This complex was prepared analogously to **1** from $Cp(NO)(PPh_3)Re(CH_3)$ (0.150 g, 0.269 mmol) and 2,5-Me_2T (61 μL, 0.54 mmol) to give **2** as a brown powder (0.068 g, 39%): ν(NO) 1720 cm^{-1}.

[Cp(NO)(PPh$_3$)Re(η^1(*S*)-BT)]BF$_4$ (3). Compound **3** was prepared in the same manner as **1** using $Cp(NO)(PPh_3)Re(CH_3)$ (0.200 g, 0.358 mmol) and BT (0.098 g, 0.72 mmol) to give **3** as a moderately air-stable pale mustard yellow powder (0.21 g, 78%): ν(NO) 1721 cm^{-1}; FAB *m/e* 677 (M^+), based on ^{187}Re.

[Cp(NO)(PPh$_3$)Re(η^1(*S*)-2-MeBT)]BF$_4$ (4). This complex was prepared in the same manner as **1** using $Cp(NO)(PPh_3)Re(CH_3)$ (0.175 g, 0.313 mmol) and 2-MeBT (0.11 g, 0.74 mmol). Excess 2-MeBT was sublimed from the residue under vacuum before the filtration step. Compound **4** was isolated as a moderately air-stable brown-orange powder (0.14 g, 57%): ν(NO) 1721 cm^{-1}.

Cp(NO)(PPh$_3$)Re(2-Tyl) (5). Method A. Compound **1** (0.108 g, 0.151 mmol) was suspended in 5 mL of methanol. Crushed KOH pellets (0.021 g, 0.38 mmol) were added with stirring. The suspension turned from brown to orange within 60 s. The methanol was removed under vacuum, and the orange residue was dissolved in a 2:1 mixture of hexanes/CH_2Cl_2. This solution was chromatographed on neutral alumina (1 × 15 cm), and an orange band was eluted using a 2:1 hexanes/CH_2Cl_2 solution. The volume of the orange solution was reduced to ~10 mL under vacuum, precipitating an orange solid. The clear colorless solvent was decanted, and the air-stable orange powder **5** was dried under vacuum (0.057 g, 60%): ν(NO) 1653 cm^{-1}. Anal. Calcd for $C_{27}H_{23}NOPReS$: C, 51.52; H, 3.69. Found: C, 51.83; H, 3.43.

Method B. The starting material $CpRe(NO)(PPh_3)(OTf)$[12b] was generated from the reaction of $CpRe(NO)(PPh_3)(CH_3)$ (0.160 g, 0.286 mmol) in 20.0 mL of CH_2Cl_2 at 0 °C with 100 μL of neat HO_3SCF_3 (HOTf). The deep red solution, which formed immediately, was filtered through silica gel, and the solvent was removed under vacuum to give the red solid $CpRe(NO)(PPh_3)(OTf)$. This solid was redissolved into 10 mL of THF; the resulting solution was cooled to 0 °C and treated with 0.60 mL of 1.0 M 2-thienyllithium (2 equiv) in tetrahydrofuran (THF). The solution was stirred for 1 h while slowly warming to room temperature. The volatiles were removed under vacuum to give an orange/red oily solid, which was extracted with 2:1 hexanes/CH_2Cl_2. Chromatography of the extracts on neutral alumina yielded an orange band, which was eluted with a 2:1 hexanes/CH_2Cl_2 solution. When the volume of the orange solution was reduced to ~10 mL under vacuum, an orange solid precipitated. The air-stable orange powder was dried under vacuum (0.032 g, 18%). Its ^1H NMR and IR spectra were identical to those of **5** prepared by method A.

Cp(NO)(PPh$_3$)Re[3-(2,5-Me$_2$Tyl)] (6). This compound was prepared in the same manner as **5**, using **2** (0.040 g, 0.054 mmol) and KOH (0.006 g, 0.1 mmol) in methanol to give **6** as an orange solid (0.011 g, 28%): ν(NO) 1655 cm^{-1}.

Cp(NO)(PPh$_3$)Re(2-BTyl) (7). Method A. In the same manner as **5**, using **3** (0.100 g, 0.144 mmol) and KOH (0.021 g, 0.38 mmol) in methanol, **7** was prepared as an orange powder (0.035 g, 36%): ν(NO) 1653 cm^{-1}. Anal. Calcd for $C_{31}H_{25}NOPReS$: C, 54.80; H, 3.72. Found: C, 54.14; H, 3.42.

Method B. Following a literature procedure[4b] for the synthesis of 2-benzo[b]thienyllithium, a solution of 0.1899 g (1.415 mmol) of BT in 30 mL of THF was cooled to 0 °C. To this solution was added 0.70 mL (1.5 mmol) of a 2.1 M *n*-BuLi solution in *n*-hexane. The solution was removed from the ice bath and stirred for 30 min at room temperature. It was then refluxed for 30 min, cooled to room temperature, and cooled again in the ice bath. To this solution was added a 10-mL THF solution of $CpRe(NO)(PPh_3)(OTf)$ (0.286 mmol) generated as described in the synthesis of **5** (method B). The solution, which immediately became light orange, was stirred for 1 h while slowly warming to room temperature. The volatiles were removed under vacuum, and the orange/red oily residue was extracted with 2:1 hexanes/CH_2Cl_2. The extracts were chromatographed on neutral alumina, and an orange band was eluted with a 2:1 hexanes/CH_2Cl_2 solution. The orange solution was reduced to ~10 mL under vacuum, which resulted in precipitation of the orange solid product **7**. The air-stable orange powder was dried under vacuum (0.051 g, 26%). Its ^1H NMR and IR spectra were identical to those of **7** prepared by method A.

Cp(NO)(PPh$_3$)Re[3-(2-MeBTyl)] (8). Compound **8** was prepared in the same manner as **5**, using **4** (0.050 g, 0.072 mmol) and KOH (0.011 g, 0.20 mmol) in methanol. Compound **8** was isolated as an orange powder (0.010 g, 20%): ν(NO) 1653 cm^{-1}. However, **8** is not stable, as indicated by the gradual color change of the CD_2Cl_2 solution from clear orange to a cloudy dark brown during a period of several minutes. In a ^1H NMR spectrum of the solution, free 2-MeBT appeared, based on the presence of the methyl resonance at 2.58 ppm.

[Cp(NO)(PPh$_3$)Re(2-Tylcarbene)]O$_3$SCF$_3$ (9). A 5-mm NMR tube was charged with **5** (0.018 g, 0.029 mmol) and 0.55 mL of CD_2Cl_2. Then, CF_3SO_3H (2.6 μL, 0.029 mmol) was added, and the tube was shaken. The solution immediately changed from clear orange to clear yellow. A ^1H NMR spectrum of the solution showed nearly quantitative conversion to **9**: ν(NO) 1716 cm^{-1}. Compound **9** was characterized spectroscopically as discussed in the Results and Discussion. Compound **9** is not stable, as indicated by the change in solution color from clear yellow to green-yellow after several minutes. Attempts to isolate the compound from solution were unsuccessful.

[Cp(NO)(PPh$_3$)Re(2-BTylcarbene)]O$_3$SCF$_3$ (10). Compound **10** was prepared in the same manner as **9** using **7** (0.015 g, 0.022 mmol) and CF_3SO_3H (2 μL, 0.022 mmol). The color of the solution immediately changed from clear orange to clear ruby red upon addition of the CF_3SO_3H. A ^1H NMR spectrum of the solution showed nearly quantitative conversion to **10**. ν(NO) 1720 cm^{-1}. Compound **10** behaved similarly to compound **9** and could not be isolated from solution. It was characterized spectroscopically, as discussed in detail later.

Results and Discussion

Synthesis of Cp(NO)(PPh$_3$)Re(η^1(*S*)-Th)$^+$ Complexes (1–4). The thiophene-containing complexes $Cp(NO)(PPh_3)Re(\eta^1(S)\text{-Th})^+$ (**1–4**) were synthesized in a manner similar to that used for the $Cp(NO)(PPh_3)Re(L)^+$ complexes,[12a] where L can be one of many two-electron donor ligands, including dialkyl sulfides CH_3SR, where R = CH_3, Et, *i*-Pr, and Bu^t.[13] Thus, $Cp(NO)(PPh_3)Re(CH_3)$ and $HBF_4{\cdot}OEt_2$ are reacted in CH_2Cl_2 at −78 °C to generate the reactive complex $Cp(NO)(PPh_3)Re(ClCH_2Cl)^+$. In this complex, the very weakly coordinated CH_2Cl_2 ligand[12a] is displaced by a thiophene to give the η^1(S)-bonded thiophene complex (eq 1).

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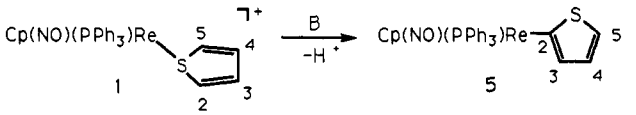
$$Cp(NO)(PPh_3)Re(ClCH_2Cl)^+ + Th \longrightarrow Cp(NO)(PPh_3)Re(\eta^1(S)\text{-}Th)^+ \quad (1)$$

1, Th = T 2, Th = 2,5-Me_2T
3, Th = BT 4, Th = 2-MeBT

Compounds **1–4** were characterized by FT-IR, ^1H and $^{13}C\{^1H\}$ NMR, FAB mass spectrometry, and elemental analyses (see Experimental Section and Tables 1 and 2). The ν(NO) absorption in the FT-IR spectra of these cationic compounds is ~90 cm^{-1} higher than the band in the neutral starting material, Cp(NO)(PPh_3)Re(CH_3) (ν(NO) = 1630 cm^{-1}). The Cp resonances in the ^1H NMR spectra are downfield (~0.3 ppm) compared to that of Cp(NO)(PPh_3)Re(CH_3) (δ 4.95). The thiophene ring protons in **1** are upfield (~0.2 ppm) of those in free T (δ 7.37 (m) and 7.14 (m)). These resonances are also slightly upfield of those in the two similar complexes $Cp^*(CO)_2Re(\eta^1(S)\text{-}T)$[14] and Cp(CO)($PPh_3$)Ru($\eta^1(S)$-T)$^+$.[15] If the thiophene ligands in complexes **1–4** were bound to the metal in an η^2 fashion through one of the C–C double bonds, the thiophene ring proton signals would be expected to shift significantly upfield, as reported for complexes of η^2-thiophene,[16] η^2-selenophenes,[17] η^2-benzo[*b*]-thiophene,[18] and olefins.[19] In the ^{13}C NMR spectra of complexes **1–4**, the thiophene carbon resonances are slightly downfield of those in free thiophene, as was also observed for $Cp(CO)_2Fe(\eta^1(S)\text{-}T)^+$,[20] Cp(CO)($PPh_3$)Ru($\eta^1(S)$-T)$^+$,[15] $Cp(CO)_2Ru(\eta^1(S)\text{-}T)^+$,[4] and $Cp(CO)_2Re(\eta^1(S)\text{-}T)$.[14] Again, an upfield shift in the ^{13}C resonances would have been expected[16-19] for the η^2-bonded carbons if the thiophenes were η^2-bonded. Thus, the NMR spectra establish that the thiophenes, including the benzo[*b*]thiophenes, in compounds **1–4** are η^1(S)-bonded. This type of coordination is confirmed by X-ray diffraction studies of $Cp^*(CO)_2Re(\eta^1\text{-}(S)\text{-}T)$[14], Cp(CO)($PPh_3$)Ru($\eta^1(S)$-2-MeT)$^+$,[15] and $Cp^*(CO)_2Re(\eta^1(S)\text{-}3\text{-}MeBT)$.[18b]

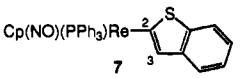
Synthesis of Cp(NO)(PPh_3)Re(Thienyl) Complexes (5–8). A proton can be abstracted from the η^1(S)-bonded thiophene ligands in complexes **1–4** with KOH in methanol to give the corresponding thienyl complexes **5–8** (eq 2). Conversion from the cationic



(2)

complex to the neutral thienyl compound is immediate, as evidenced by a change in color of the suspension from brown to orange. The ν(NO) band in the FT-IR spectrum of **5** at 1653 cm^{-1} is 70 cm^{-1} lower than that of the starting $\eta^1(S)$-thiophene complex **1** (ν(NO) = 1724 cm^{-1}). The ν(NO) bands of the other thienyl compounds **6–8** also shift ~70 cm^{-1} to lower wavenumbers compared to those of their starting cationic complexes. In the ^1H NMR spectrum of **5**, only three thiophenic proton resonances are observed: two doublets and a doublet of doublets. This pattern is consistent with the assignment of **5** as a 2-thienyl (2-Tyl) complex and is similar to those in $Cp_2Zr(2\text{-}Tyl)_2$, $Cp_2Ti(2\text{-}Tyl)_2$,[21] and $Cp^*(PMe_3)(Cl)Rh(2\text{-}Tyl)$,[5] whose structure has been established unequivocally by an X-ray diffraction investigation. In addition, the Cp resonance of **5** shifts upfield from 5.42 ppm in **1** to 5.18 ppm in **5**, again indicative of the change from a cationic compound to a neutral species. In the $^{13}C\{^1H\}$ NMR spectrum of **5**, all four thienyl carbons are observed. However, unlike the spectrum of the η^1(S)-bonded compound **1**, where the four thiophene carbons are all singlets, two of the carbons in **5**, presumably C2 and C3, are split into doublets by the phosphorus in the PPh_3 ligand (see Table 2). These two- and three-bond couplings (J_{PC} = 9.7 and 2.2 Hz, respectively) to the phosphorus again support the structure in which the C2 carbon is bonded to the metal to give the 2-thienyl complex. This structure is further confirmed by the synthesis of **5** from the reaction of Cp(NO)(PPh_3)Re(O_3SCF_3) with 2-thienyllithium.

The FT-IR, ^1H NMR, and $^{13}C\{^1H\}$ NMR spectra of Cp(NO)(PPh_3)Re(2-BTyl) (**7**) establish a structure with a 2-benzo[*b*]-thienyl (2-BTyl) ligand. In the ^1H NMR spectrum of **7**, the pattern of singlets, doublets, and triplets of the BTyl protons (Table 1) is well resolved and is similar to the resonances in the BTyl complexes Cp(CO)(PPh_3)Ru(2-BTyl) and $Cp(PMe_3)_2Ru$-(2-BTyl).[4b] In the $^{13}C\{^1H\}$ NMR spectrum of **7**, the C2, C3, and C7 signals are split into doublets by the phosphorus in the PPh_3 ligand, again similar to the previously cited 2-BTyl complexes. All of these spectral data are consistent with bonding of the C2 carbon of the BTyl ligand to the metal. The independent synthesis of **7** from the reaction of Cp(NO)(PPh_3)Re(O_3SCF_3) with 2-benzo[*b*]thienyl further supports this structure.



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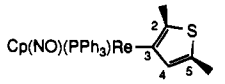
In compounds **2** and **4**, containing $\eta^1(S)$-2,5-Me_2T and η^1-(*S*)-2-MeBT ligands, respectively, no H2 proton is present, which eliminates the possibility of forming 2-Tyl and 2-BTyl complexes upon deprotonation by base. When compounds **2** and **4** are reacted with KOH in methanol, the H3 proton is abstracted to give Cp-(NO)(PPh_3)Re[3-(2,5-Me_2Tyl)] (**6**) and Cp(NO)(PPh_3)Re[3-(2-MeBTyl)] (**8**), respectively. In compound **2**, the two methyl



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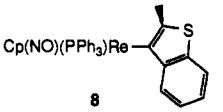

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groups of the 2,5-Me_2T ligand are diastereotopic and therefore could give separate NMR signals, but only one singlet is observed at ambient temperature in the ^1H NMR (δ 1.95 (s)) and ^{13}C NMR (δ 14.9) spectra, presumably as a result of rapid inversion at the sulfur atom.[4,15,20,22,23] When **2** is converted to the 3-(2,5-Me_2Tyl) complex **6**, the methyl groups are now inequivalent and are observed as two distinct singlets in the ^1H NMR (δ 2.40 (s) and 2.08 (s)) and ^{13}C NMR (δ 19.0 and 14.8) spectra of the compound. In the ^1H NMR spectra, the single H4 proton is shifted significantly upfield from δ 6.69 (s) in **2** to δ 5.51 (s) in **6**. The analogous 3-(2-MeBTyl) compound **8** is not sufficiently stable in solution to obtain a satisfactory ^{13}C NMR spectrum. Presumably, the bulkiness of the 2-MeBTyl and PPh_3 ligands makes the compound unstable. However, a ^1H NMR spectrum shows peaks ascribable to 3-(2-MeBTyl) (Table 1) as well as only one Cp (δ 5.25 (s)) and one methyl group (δ 3.95 (d)).

Two mechanisms may be considered for the base-promoted transformation (eq 2) from the η^1(S) complex to the thienyl complex (Scheme 1). One (path *a*, Scheme 1) involves initial deprotonation of the most acidic hydrogen at the C2 carbon to give a carbanionic center, which rapidly migrates to the Re to give the 2-thienyl product. Coordination of the thiophene to the

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Table 1. ^{1}H NMR Data for Complexes in CD_2Cl_2[a]

	PPh_3[b]	Th or BT[b]	Cp	Me
1	7.56 (m), 7.27 (m)	7.22 (m), 6.91 (m, 2H)	5.42 (s, 5H)	
2	7.49 (m), 7.28 (m)	6.69 (s, 2H)	5.29 (s, 5H)	1.95 (s, 6H)
3	7.60 (m)	7.80 (m, 2H), 7.36 (m, 3H), 6.27 (d, 1H)[c]	5.23 (s, 5H)	
4	7.54 (m), 7.26 (m)	7.69 (d, 1H),[d] 7.42 (t, 1H),[e] 7.10 (t, 1H),[d] 6.73 (d, 1H)[d,f]	5.32 (s, 5H)	2.37 (d, 3H)[g]
5	7.36 (s)	7.07 (d, 1H),[h] 6.69 (d of d, 1H),[i] 6.36 (d, 1H)[j]	5.18 (s, 5H)	
6	7.35 (s)	5.51 (s, 1H)	5.12 (s, 5H)	2.40 (s, 3H), 2.08 (s, 3H)
7	7.36 (s)	7.56 (d, 1H),[d] 7.22, (d, 1H),[d] 7.04 (t, of d, 1H),[k] 6.84 (t of d, 1H),[k] 6.44 (s, 1H)	5.26 (s, 5H)	
8	7.44 (m)	7.65 (m, 2H), 7.55 (d, 1H)[d]	5.25 (s, 5H)	3.95 (d, 3H)[g]
9	7.55 (m), 7.24 (m)	7.37 (d, 1H),[l] 6.80 (d, 1H),[l] 3.97 (d, 1H),[m] 4.11 (d, 1H)[m]	5.78 (s, 5H)	
10	7.57 (m), 7.36 (m)	7.20 (m, 1H), 4.84 (d, 1H),[n] 3.81 (d, 1H)[n,f]	5.90 (s, 5H)	

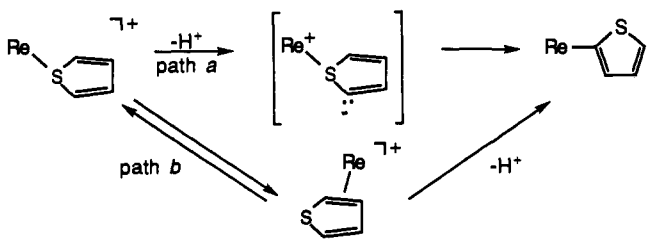
[a] All coupling constants are J_{HH} values. [b] Some overlap of PPh_3, thiophene, and benzothiophene resonances occurs. [c] J = 5.7 Hz. [d] J = 7.8 Hz. [e] J = 7.5 Hz. [f] One or more proton signals are apparently contained in the PPh_3 multiplet. [g] J = 1.2 Hz. [h] J = 4.8 Hz. [i] J = 4.8 and 3.0 Hz. [j] J = 3.0 Hz. [k] J = 7.8 and 1.2 Hz. [l] J = 5.4 Hz. [m] On C3, J = 24 Hz. [n] On C3, J = 26 Hz.

Table 2. ^{13}C NMR Data for Complexes in CD_2Cl_2

	PPh_3[a]	Th or BT	Cp	Me
1	133.9 (d), 133.6(d), 132.5 (d),129.9 (9)	138.3, 132.4	93.3	
2	133.8 (d), 133.6 (d), 132.2 (d), 130.1, 129.5 129.8 (d)	130.1, 129.5	93.2	14.9
3	133.6 (d), 132.6 (d), 132.4 (d), 129.9 (d)	148.3 (d),[b] 138.7, 131.8, 130.9, 129.5, 128.3, 126.8, 124.3	93.7	
4	133.2 (d), 132.6 (d), 131.8 (d), 129.4 (d)	148.1, 144.6, 139.8, 128.9, 127.3, 126.5, 125.3, 123.6	93.6	15.3
5	135.8 (d), 134.1 (d), 130.4 (d), 128.4 (d)	136.0, (d),[c] 128.4, 127.5 (d),[d] 127.3	91.4	
6	136.6 (d), 134.0 (d), 130.5 (d), 128.5 (d)	142.3, 133.2, 132.6, 126.0 (d)[e]	91.8	19.0, 14.8
7	136.3 (d), 134.1 (d), 130.2 (d), 128.3 (d)	146.7, 146.4, 136.6 (d),[f] 131.7 (d),[c] 122.5, 119.7 (d),[g] 119.1	90.6	
9	133.2 (d), 132.4, 130.2 (d), 129.5 (d)	268.7 (d),[h,i] 150.5, 146.2, 56.6[j]	97.3	
10	133.1 (m), 132.6 (d), 129.8 (d)	278.5 (d),[h,k] 144.5, 142.0, 128.4, 127.1, 124.0, 120.5, 67.3[j]		

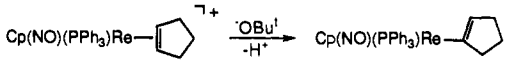
[a] Typical coupling constants for PPh_3 in **1–10**: $J_{PC\alpha}$ = 56.9 Hz; $J_{PC\beta}$ = 10.7 Hz; $J_{PC\gamma}$ = 2.7 Hz; $J_{PC\delta}$ = 11.3 Hz. [b] J_{PC} = 2.7 Hz. [c] J_{PC} = 2.2 Hz. [d] J_{PC} = 9.7 Hz. [e] J_{PC} = 8.4 Hz. [f] J_{PC} = 10.2 Hz. [g] J_{PC} = 6.5 Hz. [h] C2. [i] J_{PC} = 7.3 Hz. [j] C3. [k] J_{PC} = 7.8 Hz.

Scheme 1



electron-withdrawing metal may make the proton on C2 more acidic than it is in free thiophene or benzo[*b*]thiophene. Thus, the conversions of **1–4** to **5–8** are complete within 60 s while free T[24] and BT[25] undergo much slower base-catalyzed deuterium exchange at ambient temperature. In the cases where there is no C2 proton, as in the 2,5-Me_2T (**2**) and 2-MeBT (**4**) complexes, path *a* would require Re migration from the sulfur to the deprotonated C3 carbanion. While not impossible, a migration from the 1-position to the 3-position seems unlikely.

The other mechanism (path *b*, Scheme 1) involves initial migration of the Re atom from the sulfur to the 2,3-olefin bond of the thiophene. Since there is no spectroscopic evidence for 2,3-η^2 coordination in complexes **1–4**, they would have to be present at low concentrations. However, such a migration is supported by the existence of 2,3-η^2-olefin-coordinated thiophene in $Os(NH_3)_5(2,3\text{-}\eta^2\text{-T})^{2+}$.[16] Also, the BT ligand in $Cp(CO)_2Re(BT)$[18] exists as an equilibrium mixture of the η^1(S) and 2,3-η^2 isomers. In addition, the selenium analog of thiophene forms a complex $Cp^*(CO)_2Re(Sel)$[17] in which the selenophene (Sel) is 2,3-η^2-bonded to the Re. In other $Cp'(CO)_2Re$(selenophene) complexes,[17] the η^1(Se) and 2,3-η^2 isomers both are present in solution, the relative amounts depending on the number of methyl groups in the Cp′ ligand and the degree of methyl substitution in the selenophene. Furthermore, isomerization between η^1(Se) and 2,3-η^2 isomers is possible even though only one isomer is observed spectroscopically. This was established for $Cp^*(CO)_2Re(2,3\text{-}\eta^2\text{-Sel})$,[17] in which the Re rapidly migrates from the 2,3-olefin to the 4,5-olefin bond, presumably through an η^1(Se)-coordinated intermediate. Although there is no evidence for this fluxionality in complexes **1–4**, the protons on the 2,3-carbons of the postulated 2,3-η^2 isomer should be easily removed to give the product thienyl complexes, as has been demonstrated in the deprotonation of alkene[26] and cycloalkene[27] complexes of $Cp(NO)(PPh_3)Re^+$ with $KOBu^t$ to give the corresponding vinyl complexes (eq 3).



(3)

Deprotonation of either the 2- or 3-proton of the postulated 2,3-η^2 isomers of the $Cp(NO)(PPh_3)Re(Th)^+$ complexes provides a reasonable route to both the the 2- and 3-thienyl complexes found in the reactions of **1–4** with KOH in methanol. Thus, path *b* (Scheme 1) appears to be the most likely mechanism for the reaction in eq 2.

Bases besides KOH in methanol are also effective in deprotonating the η^1(S)-coordinated thiophene in **1**. Triethylamine (pK_a = 11.01 in H_2O)[28] effects the transformation (eq 2) almost immediately when an excess of the base is reacted with **1** in CD_2Cl_2 at room temperature in an NMR tube experiment; in contrast, pyridine (pK_a = 5.25 in H_2O)[28] does not give **5** under these conditions, even after several hours. Sources of H^-, such as $LiHBEt_3$ and $HFe(CO)_4^-$, do convert **1** to **5** immediately in CH_2Cl_2 solution. In all of these conversions of **1** to **5**, a competing reaction is displacement of the η^1(S)-bonded thiophene by the base. For example, the reaction of **1** with $LiHBEt_3$ produces both the thienyl complex **5** and the hydride complex $Cp(NO)(PPh_3)Re(H)$[29] in about equal proportions. A solution of compound **1** when stirred with neutral alumina or passed down a column of neutral alumina is also converted to the thienyl complex **5**. However, there is also decomposition of the starting

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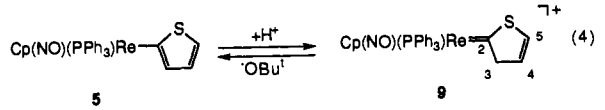
compound **1** on the alumina. The best reagent for promoting the conversion of the $\eta^1(S)$-thiophene complexes to their thienyl analogs (eq 2) is KOH in methanol.

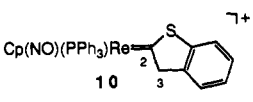
In an effort to explore the Diels–Alder reactivity of η^1(S)-coordinated thiophene, **1** was reacted in solution with dienophiles, such as maleic anhydride and 4-phenyl-1,2,4-triazoline-3,5-dione, up to temperatures of 190 °C and pressures of 800 psi. However, no Diels–Alder products were observed; either compound **1** did not react or the thiophene was simply displaced.

Reactions of Cp(NO)(PPh$_3$)Re(2-Tyl) and Cp(NO)(PPh$_3$)-Re(2-BTyl) with CF$_3$SO$_3$H. The thienyl compound **5** reacts with 1 equiv of triflic acid, CF_3SO_3H, in CD_2Cl_2 in a 5-mm NMR tube to give the cationic thienylcarbene complex **9** (eq 4) in nearly quantitative yield, as determined by a ^{1}H NMR spectrum. The



reaction is instantaneous, as observed by the immediate color change of the clear solution from orange to bright yellow. While **9** is not sufficiently stable to be isolated, it was characterized spectroscopically. The ν(NO) band in the FT-IR spectrum of **9** (1716 cm^{-1}) is 63 cm^{-1} higher than that in the neutral thienyl compound **5**. In the ^{1}H NMR spectrum of **9**, two of the thienylcarbene protons are shifted significantly upfield (δ 3.97 (d, J_{HH} = 24 Hz) and 4.11 (d, J_{HH} = 24 Hz)) and are assigned as the two diastereotopic hydrogens on the C3 atom on the basis of their large mutual coupling constant. Also, the Cp resonance shifts downfield from 5.18 ppm in **5** to 5.78 ppm in **9**. In addition, no metal hydride resonance is observed at high field (up to −30 ppm), even at −60 °C. In the $^{13}C\{^1H\}$ NMR spectrum of **9**, the C2 alkylidene resonance is observed at 268.7 ppm, which is similar to the alkylidene resonance (δ 275.5) of the related compound Cp(NO)(PPh$_3$)Re(=CHSCH$_3$)$^+$.[30] In the ^{1}H-coupled ^{13}C NMR spectrum of **9** (in CD_2Cl_2 at −75 °C), the C2 signal occurs as a doublet of triplets due to coupling with the phosphorus (J_{PC} = 7.3 Hz) and two equivalent or nearly equivalent hydrogens (J_{CH} = 12.4 Hz). The magnitude of J_{CH} strongly suggests that the CH_2 group is at the 3-position rather than the more distant 5-position. This finding supports the structure shown in eq 4 rather than that resulting from protonation at C5. The resonance of the C3 carbon, which is now sp^3 hybridized, is shifted upfield (δ 56.6) while the C4 and C5 olefin carbons (δ 150.5 (s) and 146.2 (s)) shift slightly downfield compared to those in the thienyl compound **5** (see Table 2).

The BTyl compound Cp(NO)(PPh$_3$)Re(2-BTyl) (**7**) also protonates at the C3 carbon when reacted with 1 equiv of CF_3SO_3H to give the benzothienylcarbene complex Cp(NO)(PPh$_3$)-Re(2-BTylcarbene)$^+$ (**10**). In this case, the solution of **7** turns



from orange to ruby red immediately upon addition of the acid. The infrared spectrum of **10** shows a shift of the ν(NO) band to higher wavenumbers (1653 cm^{-1} to 1720 cm^{-1}). The ^{1}H NMR spectrum of **10** has resonances for the two diastereotopic hydrogens (δ 4.84 (d, 26 Hz) and 3.81 (d, 26 Hz)) on the C3 carbon. The Cp resonance of **10** (δ 5.90) is downfield of the resonance in the neutral BTyl complex **7** (δ 5.26). In the $^{13}C\{^1H\}$ NMR spectrum of **10**, the resonance for the alkylidene carbon C2 is characteristically shifted downfield (δ 278.5) and, in this case, is split (J_{PC} = 7.8 Hz) by the phosphorus of the PPh$_3$ ligand. The resonance for the sp^3-hybridized C3 carbon is shifted upfield (δ 67.3), similar to shifts in the thienylcarbene complex **9**.

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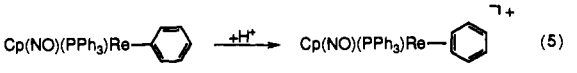
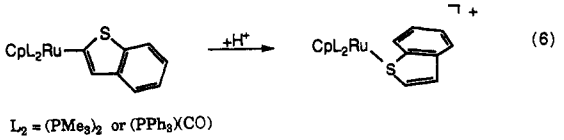
Both carbene complexes **9** and **10** were deprotonated with 1 equiv of KOBu^t in CD_2Cl_2 in an NMR tube experiment within several minutes to give back the 2-thienyl complexes **5** and **7**, respectively, as the major products (>70%) (eq 4). This same type of acid/base chemistry has been observed previously by Gladysz and co-workers with the alkylidene complexes Cp(NO)-(PPh$_3$)Re[=CH(CH$_2$R)]$^+$, where R = H, CH$_3$, or n-C$_3$H$_7$.[31] These complexes were deprotonated with KOBu^t at the β-carbon to give the corresponding vinyl complexes Cp(NO)(PPh$_3$)Re-(CH=CHR).

Due to the instability of **9** and **10**, attempts to work up solutions of the complexes resulted in darkening of the color of the compounds with decomposition. Attempts to grow crystals by slow vapor diffusion of hexanes or diethyl ether into a CH_2Cl_2 solution of the compound resulted only in an intense green solution and residue that contained many products, none of which were the carbene or thienyl compounds. Unstable alkylidene complexes can often be stabilized by addition of a suitable nucleophile to the carbene carbon.[32] In an attempt to isolate a stable adduct of **9**, a CD_2Cl_2 solution of **9** was reacted with equimolar PPh_2Me in a 5 mm NMR tube. A ^{31}P NMR spectrum of the solution taken immediately after reaction showed that **9** and the PPh_2Me were consumed, and a mixture of products had formed. Even though the alkylidene complexes **9** and **10** could not be isolated from solution, their spectral data support the assignment of **9** as the thienylcarbene complex and **10** as the benzothienylcarbene analog.

It is somewhat surprising that the thienylcarbene complexes even form (eq 4), because it involves disruption of the aromaticity of the thiophene ring. In the related phenyl complex Cp(NO)-(PPh$_3$)Re(C$_6$H$_5$),[33,34] reaction with acid yields the η^2-benzene complex (eq 5). Similarly, when the ruthenium BTyl complexes



CpL$_2$Ru(BTyl)[4b] are reacted (eq 6) with CF_3SO_3H, the Ru–C bond is cleaved, and the proton adds to the 2-position of the BTyl ligand to give the η^1(S)-coordinated benzothiophene complexes.



Thus, in the reactions of Cp(NO)(PPh$_3$)Re(C$_6$H$_5$) and CpL$_2$-Ru(BTyl)$^+$ complexes, the aromaticities of the phenyl group and the BTyl group, respectively, are maintained by cleaving the metal–carbon bond while forming the benzene and benzothiophene ligands. In contrast, protonation of complexes **5** and **7** does not result in cleavage of the Re–C bond but formation of the thienylcarbene complexes instead. It is not clear why these complexes behave differently. It is interesting that the $\eta^1(S)$-thiophene complexes **1** and **3** are isomers of the thienylcarbene complexes **9** and **10**. The isomerization of one form to the other has not been observed; so, it is not known which isomer is the most stable.

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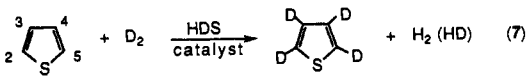
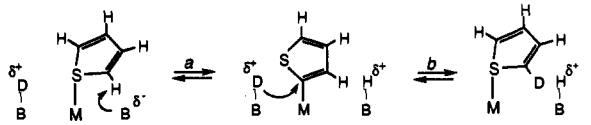
Comments on the Mechanism of D_2 Exchange of Thiophene over HDS Catalysts. Catalytic reactor studies[6,35] have shown that deuterium exchange (eq 7) with thiophene over HDS catalysts occurs most readily in the 2- and 5- positions with lesser amounts of exchange at the 3- and 4-positions. Thiophenes also undergo



exchange with deuterio acids, including those generated by reaction of D_2 with $(Cp'Mo)_2(S_2CH_2)(\mu\text{-}S)(SH)^+$.[36] Rates of deuterium exchange in the η^5-bound thiophene in the model complex $CpRu(\eta^5\text{-}T)^+$[35] are also faster in the 2,5- than in the 3,4-positions. Therefore, the η^5-coordination mode offers a reasonable explanation for the exchange on HDS catalysts. The base-promoted conversion of η^1(S) thiophene to a thienyl ligand (eq 2) reported in this paper provides the basis for another explanation for deuterium exchange of thiophenes over HDS catalysts (Scheme 2). This exchange could proceed by η^1(S) adsorption of the thiophene on the catalyst surface. Then, deprotonation at either the 2,5- or 3,4-positions of the thiophene by a basic oxide, sulfide, or hydride ion would give a surface

Scheme 2



thienyl species; this step is similar to the reaction in eq 2 and Scheme 1. Transfer of D^+ from an acidic surface site, e.g., $S\text{–}D^{\delta+}$, formed in the reaction of D_2 with surface sulfur atoms, to the σ-bonded carbon of the 2- or 3-thienyl group would give the 2- or 3-deuterated thiophene; this step is modeled by the reaction in eq 6. While Cowley previously proposed a mechanism[4b,37] very similar to this, the reactions in eqs 2 and 6 provide examples of these reactions which actually occur at metal centers.

We sought to observe deuterium exchange into the thiophene ligand of $Cp(NO)(PPh_3)Re(\eta^1(S)\text{-}T)^+$ when it was dissolved in MeOD with 1 equiv of pyridine base catalyst. Unfortunately, no exchange was observed when the solution was allowed to sit for 24 h at room temperature. Stronger bases such as NEt_3 under the same conditions simply converted **1** to **5** (eq 2). Thus, while both steps a and b in Scheme 2 have not been observed in a single metal complex, the separate reactions (eqs 2 and 6) suggest that the thienyl species are logical intermediates in the deuterium exchange of thiophene[6] and benzo[*b*]thiophene[38] on HDS catalysts.

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