by a metal hydride, $Mn_2(CO)_9(CH_3CN)$ cannot be used in place of $Mn_2(CO)_9(\eta^1$-tolualdehyde) in the synthesis of $HMn_2Re(CO)_{14}$. When a $C_6D_6$ solution of $Mn_2(CO)_9(CH_3CN)$ (0.045 M) was treated with excess $HRe(CO)_5$ (1.0 M) and heated to 60 °C for 22 h, about half of the $Mn_2(CO)_9(CH_3CN)$ was consumed. The main products observed by $^1H$ NMR were $HMn(CO)_5$ ($\delta$ −7.87) and a bridging hydride species at $\delta$ −15.4 assigned as $HRe_3(CO)_{14}$; however, no formation of $HMn_2Re(CO)_{14}$ was observed. Clearly, the high lability of the complexed aldehyde is a critical requirement for the success of the synthesis of $HMn_2Re(CO)_{14}$. Warner and Norton[4] have reported the formation of heterometallic complexes from the reaction of metal alkyls with metal hydrides. For example, they reported that $HMnRe_2(CO)_{14}$ and $CH_3CHO$ resulted from the reaction of $CH_3Mn(CO)_5$ and $HRe(CO)_5$ in benzene. In view of our results indicating that $HRe(CO)_5$ reacts quickly with the $Mn_2(CO)_9(\eta^1$-aldehyde) complex, it is possible that a related aldehyde complex was an unobserved intermediate in their reaction as well.

We believe that the displacement of the aldehyde ligand of $Mn_2(CO)_9(\eta^1$-tolualdehyde) by metal hydrides will provide convenient access to a series of hydride-bridged heterometallic complexes, and we are continuing synthetic and crystallographic work in this area.

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**Registry No.** $HMn_2Re(CO)_{14}$, 120307-19-9; $Mn_2(CO)_9(\eta^1$-tolualdehyde), 120307-17-7; $HRe(CO)_5$, 16457-30-0; Re, 7440-15-5; Mn, 7439-96-5.

**Supplementary Material Available:** Tables S1 (further experimental data) and S2 (anisotropic displacement parameters) (4 pages); Table S3 (structure factors) (30 pages). Ordering information is given on any current masthead page.

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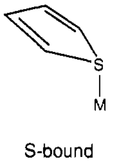
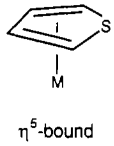
## Kinetic Studies of $PPh_3$ Substitution of Sulfur-Coordinated Thiophenes in $Cp'(CO)_2Re(Th)$: A Model for Thiophene Adsorption onto Hydrodesulfurization Catalysts

Moon-Gun Choi and Robert J. Angelici*

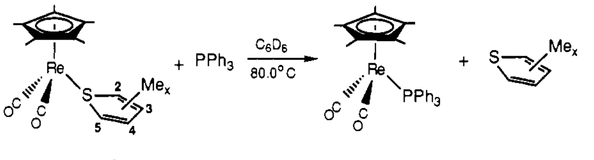
*Received August 21, 1990*

A point of central importance to the mechanism(s) of thiophene hydrodesulfurization (HDS) on heterogeneous catalysts is the mode of thiophene (T) adsorption and activation on a metal site.[2] Of the several known modes of thiophene coordination in transition-metal complexes,[3] the S- and $\eta^5$-bound forms are most often suggested for thiophene adsorption to catalyst surfaces. While there is much evidence to support $\eta^5$-coordination and activation of thiophene in organometallic complexes and on catalysts,[4–6] there is little such evidence for the S-bonded form. This arises from the weak donor ability of the thiophene sulfur atom. Thus, in the only known S-bound thiophene complexes, $Ru(NH_3)_5(T)^{2+}$,[7] $CpFe(CO)_2(T)^+$,[8] $CpFe(NCMe)_2(2,5\text{-}Me_2T)^+$,[9] $W(CO)_3(PCy_3)_2(T)$,[10] and $(C_5H_4CH_2C_4H_3S)Ru(PPh_3)_2^+$, in which thiophene is part of a chelate ligand,[11] the thiophene is very weakly coordinated and easily displaced. This suggests that it would also be weakly coordinated to a metal site on a catalyst. However, recently we reported[12] a stable S-bound thiophene complex $Cp^*(CO)_2Re(T)$ and showed that the diene portion of the thiophene is activated to bind to $Fe(CO)_3$, giving a dinuclear complex $Cp^*(CO)_2Re(\mu\text{-}T)Fe(CO)_3$, in which the thiophene is S-bound to the Re and $\eta^4$-bound through the four carbons to the $Fe(CO)_3$.


S-bound


$\eta^5$-bound

In addition to $Cp^*(CO)_2Re(T)$, we have prepared[13] a series of $Cp^*(CO)_2Re(Th)$ and $Cp(CO)_2Re(Th)$ complexes, where Th is thiophene, a methyl-substituted thiophene, or dibenzothiophene. These complexes allow us to compare the reactivity of these different S-bound thiophenes. In this paper, we report studies of the mechanism and compare the rates of substitution of a series of methyl-substituted thiophenes by $PPh_3$ according to eq 1. Of particular interest is the effect of methyl groups in the 2- and 5-positions on the rates of thiophene dissociation from these complexes. It has generally been stated[14,15] that such methyl groups would sterically inhibit thiophene adsorption to an HDS catalyst. This statement, however, was based on the assumption that S-bound thiophene is perpendicular to the surface, with the coordinated metal atom lying in the plane of the thiophene. In this configuration, methyl groups in the 2- and 5-positions would be expected to sterically weaken S-bonding to the metal. However, it is now known[3b,8b,11,13] that the metal does not lie in the thiophene plane (i.e., the sulfur is pyramidal), as shown for $Cp(CO)_2Re(Th)$ in eq 1. Thus, 2,5-methyl groups may pose less of a steric problem than previously suggested. Kinetic studies of the reaction in eq 1 offer one approach to assessing steric effects of 2,5-methyl groups on thiophene bonding to metals.



(1)

x = 0, 1, 2, 4 and the cyclopentadienyl ligand is $C_5H_5$ or $C_5Me_5$

### Experimental Section

**General Procedures.** The complexes, $Cp(CO)_2Re(Th)$ and $Cp^*(CO)_2Re(Th)$, where Cp = $\eta^5$-$C_5H_5$, Cp* = $\eta^5$-$C_5Me_5$, and Th = T, 2-MeT, 3-MeT, 2,5-$Me_2T$, $Me_4T$, and dibenzothiophene (DBT), were prepared as described elsewhere.[12,13] The $PPh_3$ was purified by recrystallization from warm hexanes and cooling to −20 °C. The $C_6D_6$ was distilled under Ar from Na/benzophenone. The products, $Cp(CO)_2Re(PPh_3)$ and $Cp^*(CO)_2Re(PPh_3)$, were identified[16] by their $^1H$ NMR and

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**Table I.** Rate Constants ($k_{obs}$) for the Reactions of $Cp'(CO)_2Re(Th)$ with $PPh_3$ in Benzene-$d_6$ at 80.0 °C According to Eq 1

| complex | $[PPh_3]$, M | $k_{obs}$, $s^{-1}$ |
|---|---|---|
| $Cp(CO)_2Re(T)$ | 0.10 | $2.9 \times 10^{-4}$ |
| | 0.20 | $3.1 \times 10^{-4}$ |
| | 0.30 | $3.0 \times 10^{-4}$ |
| $Cp(CO)_2Re(3\text{-}MeT)$ | 0.10 | $1.3 \times 10^{-4}$ |
| | 0.20 | $1.2 \times 10^{-4}$ |
| | 0.40 | $1.2 \times 10^{-4}$ |
| $Cp(CO)_2Re(2\text{-}MeT)$ | 0.10 | $9.0 \times 10^{-6}$ |
| | 0.20 | $8.9 \times 10^{-6}$ |
| | 0.40 | $9.5 \times 10^{-6}$ |
| $Cp(CO)_2Re(2,5\text{-}Me_2T)$ | 0.10 | $1.4 \times 10^{-6}$ |
| | 0.20 | $1.3 \times 10^{-6}$ |
| | 0.40 | $1.3 \times 10^{-6}$ |
| $Cp(CO)_2Re(Me_4T)$ | 0.10 | $2.8 \times 10^{-7}$ |
| | 0.20 | $2.6 \times 10^{-7}$ |
| | 0.40 | $2.6 \times 10^{-7}$ |
| $Cp(CO)_2Re(DBT)$ | 0.10 | $1.6 \times 10^{-7}$ |
| | 0.20 | $1.5 \times 10^{-7}$ |
| $Cp^*(CO)_2Re(3\text{-}MeT)$ | 0.10 | $4.1 \times 10^{-4}$ |
| | 0.20 | $4.3 \times 10^{-4}$ |
| $Cp^*(CO)_2Re(2,5\text{-}Me_2T)$ | 0.10 | $4.9 \times 10^{-6}$ |
| | 0.20 | $5.2 \times 10^{-6}$ |

IR spectra; they were the only products of the reactions studied.

**Kinetic Measurements.** The reaction solutions used in the kinetic studies were prepared as follows: the S-bound thiophene rhenium complex (0.005 mmol) and the desired amount (usually 0.05, 0.10, or 0.20 mmol) of $PPh_3$ were placed in an NMR tube; then 500 μL of benzene-$d_6$ was added by microsyringe. The solution was frozen immediately at liquid nitrogen temperature, and the NMR tube was sealed with a flame under vacuum. For the slow reactions ($t_{1/2} > 20$ h; $Cp(CO)_2Re(2\text{-}MeT)$, $Cp(CO)_2Re(2,5\text{-}Me_2T)$, $Cp^*(CO)_2Re(2,5\text{-}Me_2T)$, $Cp(CO)_2Re(Me_4T)$, and $Cp(CO)_2Re(DBT)$), the samples were thermostated in a constant-temperature bath (80.0 ± 0.2 °C), and the reactions were followed by removing the NMR tubes from the bath at appropriate times, taking their $^1H$ NMR spectra on a Nicolet NT-300 spectrometer, and returning the tubes to the bath. Since the reactions are negligibly slow at room temperature, the times of reaction were considered to be only those periods when the NMR tubes were in the 80.0 °C bath. For the fast reactions ($t_{1/2} < 1.5$ h; $Cp(CO)_2Re(T)$, $Cp(CO)_2Re(3\text{-}MeT)$, and $Cp^*(CO)_2Re(2\text{-}MeT)$), the NMR tubes were thermostated in the probe of a Bruker WM-200 NMR spectrometer at 80.0 ± 0.5 °C. After a few minutes of temperature equilibration, $^1H$ NMR spectra of the samples were recorded automatically at specific time intervals. Pseudo-first-order conditions were maintained in all runs by using at least a 10-fold excess of the $PPh_3$ ligand concentration over the Re complex concentration of 0.010 M.

The data were analyzed by using the NMR1 program.[17] Pseudo-first-order rate constants, $k_{obs}$, were obtained from least-squares slopes of linear plots of ln $(1 + F)$ vs time, where $F = P/R$, $P$ is the integrated area of the proton of interest in the product, and $R$ is the area of a reactant proton. Generally, the areas of the reactant and product Cp and Cp* signals were integrated; however, for the $2,5\text{-}Me_2T$ and $Me_4T$ complexes, the α-Me protons of the reactant and product were followed. Plots of ln $(1 + F)$ vs time were linear to 70–90% reaction completion with correlation coefficients greater than 0.984.

## Results and Discussion

The rates of $PPh_3$ substitution of various thiophenes in the $Cp'(CO)_2Re(Th)$ complexes according to eq 1 are independent of the $PPh_3$ concentration (Table I) and follow a first-order rate law (eq 2). This rate expression suggests that the reaction

$$-d[Cp'(CO)_2Re(Th)]/dt = k_1[Cp'(CO)_2Re(Th)] \quad (2)$$

proceeds by a dissociative mechanism (eq 3) in which the rate-determining step is dissociation of the thiophene from Re.

$$Cp'(CO)_2Re(Th) \xrightarrow[slow]{} \underset{\displaystyle Th}{\underset{+}{[Cp'(CO)_2Re]}} \xrightarrow[fast]{PPh_3} Cp'(CO)_2Re(PPh_3) \quad (3)$$

**Table II.** Rate Constants ($k_1$) for the Reactions of $Cp'(CO)_2Re(Th)$ with $PPh_3$ in Benzene-$d_6$ at 80.0 °C According to Eq 1

| complex | $10^7k_1$, $s^{-1}$ |
|---|---|
| $Cp(CO)_2Re(T)$ | 3000 |
| $Cp(CO)_2Re(3\text{-}MeT)$ | 1200 |
| $Cp(CO)_2Re(2\text{-}MeT)$ | 91 |
| $Cp(CO)_2Re(2,5\text{-}Me_2T)$ | 13 |
| $Cp(CO)_2Re(Me_4T)$ | 2.7 |
| $Cp(CO)_2Re(DBT)$ | 1.6 |
| $Cp^*(CO)_2Re(3\text{-}MeT)$ | 4200 |
| $Cp^*(CO)_2Re(2,5\text{-}Me_2T)$ | 51 |

For the cyclopentadienyl complexes $Cp(CO)_2Re(Th)$, the rate constants ($k_1$) decrease (Table II) with the thiophene in the following order: T > 3-MeT > 2-MeT > $2,5\text{-}Me_2T$ > $Me_4T$. From this order, it is clear that adding methyl groups to the thiophene ring *decreases* the rate of thiophene dissociation. Moreover, a methyl group on an α-carbon (2- or 5-position) decreases the rate much more than a methyl on a β-carbon (3- or 4-position). Thus, the rate of 2-MeT dissociation is 13 times slower than that of 3-MeT. This can be rationalized in terms of the electron-donating ability of methyl groups in α-positions making the sulfur a better σ-donor than methyl groups in the more distant β-positions; this is consistent with theoretical calculations[18] of S-bound thiophene complexes where the metal–sulfur interaction is primarily σ in character. In the $2,5\text{-}Me_2T$ complex, the rate of dissociation is 7 times even slower than 2-MeT and 230 times slower than thiophene (T) itself. These large electronic effects suggest that the donor ability of the thiophene is greatly enhanced by methyl groups. It is important to note that the trends in rates are opposite what would be expected if steric effects of the α-methyl groups governed the rates of thiophene dissociation. Molecular models indicate that the bent arrangement (eq 1) at the sulfur in these complexes greatly reduces steric interactions between α-methyl groups and the other ligands bound to the rhenium.

Consistent with sulfur being primarily a donor to the Re are the somewhat faster rates (~3.7 times faster) of 3-MeT and $2,5\text{-}Me_2T$ dissociation from the pentamethylcyclopentadienyl (Cp*) derivatives as compared with the analogous Cp compounds. In the Cp* complex the Re is more electron-rich and therefore a poorer Lewis acid for the sulfur donor ligand. It is interesting to note that $2,5\text{-}Me_2T$ dissociation is 87 ± 5 times slower than 3-MeT dissociation in both the $Cp(CO)_2Re(Th)$ and $Cp^*(CO)_2Re(Th)$ complexes; this indicates that there is little, if any, steric acceleration of $2,5\text{-}Me_2T$ dissociation in the pentamethylcyclopentadienyl (Cp*) complex.

The rate of dibenzothiophene (DBT) substitution is $1.9 \times 10^3$ times slower than that of thiophene. This greater kinetic stability of the DBT complex is also consistent with the generally higher stability[8b] of $Cp(CO)_2Fe(DBT)^+$ as compared with $Cp(CO)_2Fe(T)^+$.

The only related kinetic study reported[19] in the literature is that of the thioether complexes $CpMn(CO)_2(SR_2)$ with phosphines and phosphites (L) to give $CpMn(CO)_2(L)$ at 85.0 °C in methylcyclohexane solvent. As in the present study, the rates were independent of the L concentration. The rate of $(n\text{-}Pr)_2S$ dissociation was 2.4 times faster than that of $Me_2S$, presumably due to steric effects. A much larger increase in rate (203-fold) was observed for $Ph_2S$ dissociation as compared with that of $Me_2S$; this probably results from the weaker electron-donor ability of the Ph group as compared with Me. Thus, electronic rather than steric factors also appear to dominate rates of thioether dissociation from $CpMn(CO)_2(SR_2)$.

**Relevance to Thiophene Adsorption onto HDS Catalysts.** Relative adsorption coefficients ($K_{rel}$) for the adsorption of methyl-substituted thiophenes onto a $Co\text{–}Mo/Al_2O_3$ catalyst at 350 °C increase in the order[15] T (1.0) < 2-MeT (1.6) ~ 3-MeT (1.7) < $2,5\text{-}Me_2T$ (2.5). It should be noted that these adsorptions

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do not necessarily occur at HDS active sites. The relative HDS reactivities of methylthiophenes also increase with the number of methyl groups: T (1.0) < 2-MeT (1.5) < 3-MeT (1.9) < 2,5-$Me_2T$ (2.0).[20] Another HDS study[21] also over Co-Mo/$Al_2O_3$ shows a similar trend: T ~ 2-MeT < 3-MeT. Thus, methyl groups on the $\alpha$-carbons do not reduce the reactivity of thiophenes but actually enhance it. These results were interpreted to mean that S-coordination of thiophene was unlikely to be important in HDS since $\alpha$-methyl groups were thought to inhibit sterically the adsorption of thiophenes and should therefore reduce their HDS rates.

Steric inhibition would not be a problem for $\eta^5$-coordinated thiophenes. The $\eta^5$ binding mode accounts for the stronger adsorption of thiophenes with increasing methyl substitution;[5] it also explains relative rates of thiophene proton exchange with deuterium.[22] In addition, $\eta^5$ adsorption and reactivity provide a reasonable and useful mechanism for thiophene HDS.[4,23] Thus, $\eta^5$-coordination offers reasonable explanations for several types of thiophene behavior on HDS catalysts.

However, results of the studies presented in this paper indicate that S-coordination is not as unreasonable as previously assumed. Since 2,5-methyl groups do not sterically accelerate thiophene dissociation from $Cp'(CO)_2Re(Th)$ but inhibit it, this suggests that 2,5-methyl groups strengthen the Re-thiophene bond. A stronger metal-thiophene bond would presumably also increase equilibrium adsorption constants for methyl-substituted thiophenes on HDS catalysts, as observed.[15] Thus, one can account for the relative order of methylthiophene binding to HDS catalysts by assuming either $\eta^5$- or S-thiophene coordination. However, at this time, there is no evidence to suggest that S-binding promotes thiophene C-S bond cleavage as there is in $\eta^5$-thiophene complexes. So, the $\eta^5$ adsorption mode still offers the more complete explanation of thiophene reactivity on HDS catalysts.

**Registry No.** $Cp(CO)_2Re(T)$, 131758-95-7; $Cp(CO)_2Re(3\text{-MeT})$, 131758-96-8; $Cp(CO)_2Re(2\text{-MeT})$, 131758-97-9; $Cp(CO)_2Re(2,5\text{-}Me_2T)$, 131758-98-0; $Cp(CO)_2Re(Me_4T)$, 131758-99-1; $Cp(CO)_2Re(DBT)$, 131759-00-7; $Cp^*(CO)_2Re(3\text{-MeT})$, 131759-01-8; $Cp^*(CO)_2Re(2,5\text{-}Me_2T)$, 131759-02-9; $PPh_3$, 603-35-0.

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# Crystallographic Study of the Stretching of the Copper-Nitrogen Bond in the Complex of a Large-Cavity Reinforced Macrocycle

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*Received July 23, 1990*

In previous papers[1-3] the metal ion selectivity of the saturated tetraazamacrocycles has been investigated, and the results have suggested that these ligands are too flexible to exert genuine size-match selectivity. Metal ions that are too large for the macrocyclic cavity are simply accommodated in conformers where they lie outside the macrocyclic cavity and appear to suffer no significant drops in complex stability because of this. The factor that actually controls metal ion size selectivity is the size of the chelate ring, as has been extensively discussed.[4,5] In order to try to make the macrocyclic ring of saturated macrocycles more rigid, and so perhaps exert something more nearly corresponding to size-match selectivity, we have studied the *reinforced* macrocycles. These macrocycles, first synthesized by Wainwright et al.,[6,7] have double bridges between at least one pair of adjacent nitrogen donors, giving piperazine, homopiperazine, or DACO (1,5-diazacyclooctane) type bridges. We have previously reported structures and coordinating properties of complexes of B-12-$aneN_4$,[8,9] B-18-$aneN_4O_2$ and $B_2$-18-$aneN_4O_2$,[10] and HA-2,2-HP,

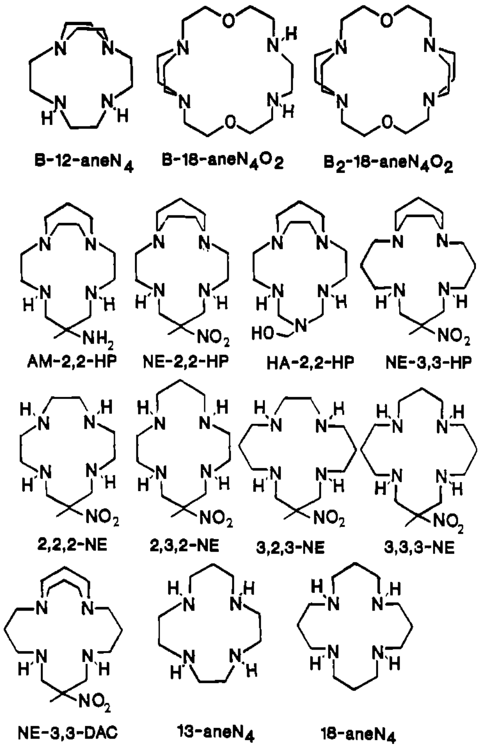
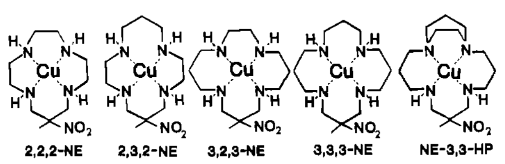


**Figure 1.** Ligands discussed in this paper.



| | 2,2,2-NE | 2,3,2-NE | 3,2,3-NE | 3,3,3-NE | NE-3,3-HP |
|---|---|---|---|---|---|
| Cu-N (Å): | (1.95) | 2.00 | 2.04 | 2.02 | 2.09 |
| best fit M-N for cavity (Å): | 1.92 | 2.07 | 2.15 | 2.22 | |
| $\nu$ d-d ($cm^{-1}$): | 18870 | 19570 | 17480 | 16560 | 16580 |
| d out of plane (Å): | 0.35 | 0.00 | 0.14 | 0.43 | 0.36 |

**Figure 2.** Mean Cu-N bond lengths and d-d band energies in complexes of macrocycles derived from template reaction of tetraamine complexes with nitroethane and formaldehyde. Also shown is the M-N bond length that fits the macrocycle with the least steric strain, as calculated by Busch et al.[13] for the unsubstituted analogues, i.e. 13-$aneN_4$ through 16-$aneN_4$ (Figure 1). Data are from ref 12 and this work. The very long Cu-N bond length in the complex of the reinforced macrocycle NE-3,3-HP (this work) should be noted.

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