2-*tert*-butylpropene 3-position, and the *tert*-butylcyclopropane 1-position. Integration of the ^{2}H NMR peaks against an internal standard (C_6D_6 or C_7D_8) allowed rough estimates of the levels of deuterium incorporation and showed the 2-*tert*-butylproene and *tert*-butylcyclopropane to contain, on average, one deuterium/molecule and the propene to contain 0.5 deuterium/molecules.

Reaction of 1a or 1c with [Rh(CO)$_2$(μ-Cl)]$_2$ or PdCl$_2$(PhCN)$_2$. The reaction of **1c** with excess [Rh(CO)$_2$(μ-Cl)]$_2$ or PdCl$_2$(PhCN)$_2$ according to the procedure given above for the corresponding [(η^3-allyl)Pd(μ-Cl)]$_2$ reaction gave a mixture of *tert*-butylcyclopropane, 2-*tert*-butylpropene, (η^5-C$_5$H$_5$)$_2$TiCl$_2$, and an intractable black precipitate of (presumably) Rh$_x$(CO)$_y$ or Pd metal. The ratio of *tert*-butylcyclopropane to 2-*tert*-butylpropene was roughly 82:18 for both reactions. The corresponding reactions of **1a** gave dimethylcyclopropane.

Acknowledgment. We wish to acknowledge the support of the Department of Energy (DE AM03-76SF00767).

Registry No. **1a**, 80122-07-2; **1b**, 90076-32-7; **1c**, 75687-68-2; **1c**-β, 117119-24-1; **2a**, 12092-47-6; **2b**, 12148-72-0; **2c**, 12112-67-3; **2d**, 12081-18-4; **2e**, 87145-39-9; **2f**, 15278-97-4; **2g**, 56954-39-3; **2h**, 117119-25-2; **3a**, 90076-34-9; **3b**, 90076-35-0; **3c**, 90076-36-1; **3d**, 117119-19-4; **3e**, 117119-20-7; **3f**, 117119-21-8; **3g**, 117119-22-9; **3h**, 117119-23-0; (η^5-C$_5$H$_5$)$_2$Ti(μ-CH$_2$)(μ-Cl)AlMe$_2$, 67719-69-1; [(η^3-allyl)(μ-Cl)Pd]$_2$, 12012-95-2; [Rh(CO)$_2$(μ-Cl)]$_2$, 14523-22-9; PdCl$_2$(PhCN), 14220-64-5; chloro(η^3-2-methylallyl)(pyridine)palladium(II), 50497-55-7; dimethylcyclopropane, 1630-94-0; propene, 115-07-1; 2-*tert*-butylpropene, 594-56-9; *tert*-butylcyclopropane, 4741-87-1; propene-*3d*$_1$, 1117-89-1; 2-tert-butylpropene-*3-d*$_1$, 117021-99-5; *tert*-butylcyclopropane-*1-d*$_1$, 117022-00-1; [Rh(C$_2$H$_4$)$_2$(μ-Cl)]$_2$, 12122-73-5.

Supplementary Material Available: Tables of Gaussian amplitudes and hydrogen atom coordination (1 page); a listing structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

Equilibrium Studies of Thiophene Exchange in (η-Thiophene)Ru(η-C$_5$H$_5$)$^+$: A Model for Thiophene Adsorption on Hydrodesulfurization Catalysts

Johannes W. Hachgenei and Robert J. Angelici*

Department of Chemistry and Ames Laboratory,[1] Iowa State University, Ames, Iowa 50011

Received January 29, 1988

Equilibrium constants (K') for the displacement of the π- (i.e., η^5-) thiophene (T) ligand in CpRu(T)$^+$ by methyl-substituted thiophenes (Th′), CpRu(T)$^+$ + Th′ $\rightleftharpoons$ CpRu(Th′)$^+$ + T, increase as the number of methyl groups in Th′ increases: T (1) < 2-MeT (6) < 3-MeT (7) < 2,5-Me$_2$T (35) < 2,3-Me$_2$T (50) < 2,3,4-Me$_3$T (200) < 2,3,5-Me$_3$T (300) < Me$_4$T (1300). The K' values increase by a factor of approximately 6 for each methyl in the thiophene (Th′). That thiophenes also adsorb to a Co–Mo/Al$_2$O$_3$ HDS catalyst more strongly as the number of methyl groups in the thiophene increases suggests that they are also π-bonded to the catalyst surface. The results suggest that trends in rates of deuterium exchange and hydrodesulfurization on HDS catalysts for a series of methyl-substituted thiophenes are determined by their relative strengths of adsorption to the catalyst surface.

Introduction

Catalytic hydrodesulfurization (HDS), the process by which sulfur is removed from crude oil by treatment with hydrogen over a Mo–Co/γ-Al$_2$O$_3$ catalyst, is practiced industrially on a very large scale.[2] Despite a large number of studies, little is understood about the basic steps of this process,[3] especially for thiophene compounds which are the most difficult to desulfurize. The first question concerns the binding mode of the thiophene to the catalyst. Three types of adsorption have been proposed: via the S-atom only,[4] as a π-complex involving the unsaturated carbon atoms,[5] or via the entire π-system in an η^5-fashion.[6,7]

One approach to understanding the HDS activity of thiophenes is to prepare thiophene transition-metal complexes and to compare their reactivities with that of thiophene on HDS catalysts. Only a few S-coordinated thiophene complexes (where T = thiophene) are known: Ru(NH$_3$)$_5$(T)$^{2+}$,[8] CpFe(CO)$_2$(T)$^+$,[9] W(CO)$_3$(PCy$_3$)$_2$(T),[10] and Ru(PPh$_3$)$_2$(CpCH$_2$C$_4$H$_3$S)$^+$, in which the thiophene is attached to the cyclopentadienyl ligand.[11] No reactions of these rather unstable S-coordinated complexes have been reported. More common are compounds with η^5-thiophene coordination: (CO)$_3$Cr(T),[12] (CO)$_3$Mn(T)$^+$,[13] CpM(T)$^+$ (M = Fe,[14] Ru[15-17]), Cp*M(T)$^{2+}$ (M = Rh, Ir),[18] (PPh$_3$)$_2$M(T)$^+$ (M = Rh, Ir).[19] The Ru complex is noteworthy because on the one hand, Ru is an excellent HDS

---

(1) Ames Laboratory is operated by the U.S. Department of Energy by Iowa State University under Contract W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Chemical Sciences Division.

(2) Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. *Chemistry of Catalytic Processes*; McGraw-Hill: New York, 1979.

(3) Zdrazil, M. *Appl. Catal.* **1982**, *4*, 107.

(4) Kolboe, S. *Can. J. Chem.* **1969**, *47*, 352.

(5) Kwart, H.; Schuit, G. C. A.; Gates, B. C. *J. Catal.* **1980**, *61*, 128.

(6) Schoofs, G. R.; Presont, R. E.; Benziger, J. B. *Langmuir* **1985**, *1*, 313.

(7) (a) Zdrazil, M. *Collect. Czech. Chem. Commun.* **1977**, *42*, 1484. (b) *Ibid.* **1975**, *40*, 3491.

(8) Kuehn, C. G.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 689.

(9) Guerchais, V.; Astruc, D. *J. Organomet. Chem.* **1986**, *316*, 335. Kuhn, N.; Schumann, H. *J. Organomet. Chem.* **1984**, *276*, 55.

(10) Wasserman, H. J.; Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2294.

(11) Draganjac, M.; Ruffing, C. J.; Rauchfuss, T. B. *Organometallics* **1985**, *4*, 1909.

(12) Fischer, E. O.; Oefele, K. *Chem. Ber.* **1958**, *91*, 2395. Bailey, M. F.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1306.

(13) (a) Singer, H. *J. Organomet. Chem.* **1967**, *9*, 135. (b) Lesch, D. A.; Richardson, J. W.; Jacobson, R. A.; Angelici, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 2901.

(14) Lee, C. C.; Iqbal, M.; Gill, U. S.; Sutherland, R. G. *J. Organomet. Chem.* **1985**, *288*, 89.

(15) Spies, G. H.; Angelici, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 5569.

(16) Sauer, N. N.; Angelici, R. J. *Organometallics* **1987**, *6*, 1146.

(17) Spies, G. H.; Angelici, R. J. *Organometallics* **1987**, *6*, 1897.

(18) Huckett, S. C.; Miller, L. L.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1988**, *7*, 686.

(19) Sanchez-Delgado, R. A.; Marquez-Silva, R. L.; Puga, J., Tiripicchio, A.; Tiripicchio Camellini, M. *J. Organomet. Chem.* **1986**, *316*, C35.

0276-7333/89/2308-0014$01.50/0 © 1989 American Chemical Society

Table I. ^1H NMR Data for the Methylthiophenes (in Acetone-d_6)

	δ
T	7.48 (m; H2,5), 7.14 (m; H3,4)[a,b,e]
2-MeT	7.18 (dd; H5), 6.88 (dd; H4), 6.78 (m; H3), 2.46 (s, 3 H; Me2)[b,f]
3-MeT	7.34 (dd; H5), 7.02 (m; H2), 6.95 (d; H4), 2.25 (s, 3 H; Me3)[c,g]
2,3-Me_2T	7.04 (d; H5), 6.75 (d; H4), 2.31 (s, 3 H; Me2), 2.12 (s, 3 H; Me3)[b,h]
2,5-Me_2T	6.54 (s; H3,4), 2.37 (s, 3 H; Me2,5)
2,3,4-Me_3T	6.75 (s; H5), 2.29 (s, 3 H; Me2), 2.07 (s, 3 H; Me4), 1.99 (s, 3 H; Me3)[d]
2,3,5-Me_3T	6.42 (s; H4), 2.31 (s, 3 H; Me2), 2.21 (s, 3 H; Me5), 2.01 (s, 3 H; Me3)[d]
Me_4T	2.23 (s; Me2,5), 1.92 (s; Me3,4)[d]

[a] Assignments according to ref 24. [b] Assignments according to ref 25. [c] Assignments according to coupling pattern. [d] Assignments are based on monomethylthiophene assignments where Me2 occurs at lower field but are not established unequivocably. [e] J(H2–H3) = 6.0 Hz. [f] J(H3–H4) = 3.4 Hz, J(H3–H5) = 1.1 Hz, J(H4–H5) = 5.2 Hz. [g] J(H2–H5) = 2.8 Hz, J(H4–H5) = 4.7 Hz. [h] J(H4–H5) = 5.2 Hz.

Table II. ^1H NMR Data for the $[CpRu(Th)]PF_6$ Complexes (in Acetone-d_6)

Th	δ[g]
T[a]	6.57 (d, 2 H; H3,4), 6.49 (d, 2 H; H2,5), 5.49 (s, 5 H; Cp)[d]
2-MeT[b]	6.47 (d; H3), 6.42 (t; H4), 6.32 (d; H5), 5.47 (s, 5 H; Cp), 2.47 (s, 3 H)[e]
3-MeT[b]	6.58 (d; H4), 6.39 (m, 2 H; H2,5), 5.45 (s, 5 H; Cp), 2.46 (s, 3 H)[d,f]
2,3-Me_2T	6.50 (d; H4), 6.22 (d; H5), 5.42 (s, 5 H; Cp), 2.44 (s, 6 H)[d]
2,5-Me_2T[b]	6.34 (s, 2 H; H3,4), 5.45 (s, 5 H; Cp), 2.40 (s, 6 H)
2,3,4-Me_3T	6.22 (s; H5), 5.38 (s, 5 H; Cp), 2.44 (s, 3 H), 2.43 (s, 6 H)
2,3,5-Me_3T	6.45 (s; H4), 5.40 (s, 5 H; Cp), 2.37 (s, 3 H), 2.36 (s, 3 H), 2.34 (s, 3 H)
Me_4T	5.32 (s, 5 H; Cp), 2.42 (s, 6 H), 2.38 (s, 6 H)
BT[c]	8.16 (d), 7.55 (d), 7.46 (d), 7.26 (d), 6.37 (t), 6.32 (t), 5.20 (s, 5 H; Cp)
DBT	8.43 (d), 8.05 (d), 7.7 (m, 3 H), 7.51 (d), 6.47 (m, 2 H), 5.25 (s, 5 H; Cp)

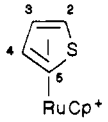
[a] References 15 and 17. [b] Reference 16. [c] Reference 18. [d] Assignments according to ref 25. [e] Assignments according to ref 25 except that positions 3 and 4 are interchanged. [f] Assignments corrected from that given in ref 16. [g] All coupling constants ^3J(HCCH) $\simeq$ 3 Hz.

Table III. Equilibrium Constants, K, for the Exchange Reactions (Eq 1) of $[CpRu(Th)]^+$ with Free Thiophene (Th′) in Acetone-d_6 at 50.0 °C

Th	Th′	K
T	2-MeT	5.6
T	3-MeT	6.7
2-MeT	3-MeT	1.2
2-MeT	2,5-Me_2T	6.8
3-MeT	2,5-Me_2T	4.7
3-MeT	2,3-Me_2T	6.0
2,5-Me_2T	2,3-Me_2T	1.5
2,5-Me_2T	2,3,5-Me_3T	8.3
2,3-Me_2T	2,3,5-Me_3T	6.2
2,3-Me_2T	2,3,4-Me_3T	3.7
2,3,4-Me_3T	Me_4T	6.1
2,3,5-Me_3T	Me_4T	4.7

catalyst,[20] and on the other, nucleophilic addition (H^-, RS^-, $(MeO_2C)_2CH^-$, MeO^-) to $CpRu(T)^+$ leads to cleavage of a thiophene C–S bond forming a butadienethiolate ligand.[17,21] Thus, the π-bonded thiophene is activated to react in a manner which may account for the reactivity of thiophene on HDS catalysts. The π-thiophene ligand in $(CO)_3Mn(T)^+$ also adds nucleophiles,[13b,22] to form an η^4-coordinated ligand which suggests another thiophene HDS mechanism.[22] Studies of deuterium exchange[16] in the π-thiophene ligand of $CpRu(T)^+$ also support the proposal that thiophene adsorbs to HDS catalysts as an η^5-ligand and is activated in this form to undergo deuterium exchange.

The purpose of the present study was to compare trends in the adsorption of methyl-substituted thiophenes on HDS catalysts with their coordinating abilities in $CpRu(Th)^+$ (where Th represents any thiophene). It is known[7a] that the adsorption coefficients for different thiophenes on Co–Mo/Al_2O_3 HDS catalysts at 350 °C decrease in the order 2,5-Me_2T > 3-MeT ~ 2-MeT > T. To support the suggestion that these thiophenes adsorb to the surface in the η^5-mode, we have measured equilibrium constants for reaction 1 in order to establish the preferred order of η^5-bonding of methyl-substituted thiophenes in this system. The results do indeed suggest that thiophenes adsorb to HDS catalysts via the π-system, i.e., the η^5-mode.



$$CpRu(Th)^+ + Th' \underset{50\ ^\circ C}{\overset{acetone}{\rightleftharpoons}} CpRu(Th')^+ + Th \qquad (1)$$

Experimental Section

Preparation of the Thiophenes. Thiophene (Alfa, 99%) was purified as previously described.[17] 2-MeT, 3-MeT, 2,5-Me_2T, and dibenzothiophene (DBT) (Aldrich Chemicals) were used without further purification. 2,3-Me_2T, 2,3,4-Me_3T, 2,3,5-Me_3T, and Me_4T were obtained from the corresponding bromothiophenes by metalation with BuLi and further reaction with Me_2SO_4.[23] The reaction of thiophene with bromine yielded a mixture of Br_4T and 2,3,5-Br_3T which was separated by distillation.[23] 2,3,4-Br_3T was obtained by reacting Br_4T with Mg and 1,2-dibromoethane.[23] 2,3-Br_2T was prepared from 3-BrT and Br_2.[23] Commercial benzo[*b*]thiophene (BT) was sublimed prior to use. All of the thiophenes were identified by their ^1H NMR spectra (Table I).

Preparation of the $[CpRu(Th)]PF_6$ Complexes. The complexes of T,[17] 2-MeT,[16] 3-MeT,[16] 2,5-Me_2T,[16] and BT[18] were prepared from $[CuRu(CH_3CN)_3]PF_6$ as described previously. The analogous complexes of 2,3-Me_2T, 2,3,4-Me_3T, 2,3,5-Me_3T, and dibenzothiophene (DBT) were prepared by the same method and characterized by their proton NMR spectra (Table II).

Exchange Reaction. About 0.02 mmol of a $[CpRu(Th)]PF_6$ complex was dissolved in 0.5 mL of acetone-d_6, mixed with an equimolar amount of a differently substituted thiophene (~3 μL), and placed in an NMR tube. The solution was frozen with liquid nitrogen and the tube sealed under vacuum. The NMR tube was kept in a constant temperature bath (T = 50.0 ± 0.2 °C). The exchange was monitored by ^1H NMR on a Nicolet NT-300 spectrometer using acetone-d_6 as the internal lock and reference (δ 2.04). Exchange reactions of the thiophene complex were complete within 3 days. Reactions of complexes containing the more highly substituted thiophenes took more time, up to 4 weeks for the reaction of $CpRu(Me_3T)^+$ with Me_4T. The NMR spectra of the equilibrated reaction mixtures were taken at room tem-

---

[20] Pecoraro, T. A.; Chianelli, R. R. *J. Catal.* **1981**, *67*, 430.

[21] Hachgenei, J. W.; Angelici, R. J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 909.

[22] Huckett, S. C.; Sauer, N. N.; Angelici, R. J. *Organometallics* **1987**, *6*, 591.

[23] Janda, M.; Srogl, J.; Stibor, I.; Nemec, M.; Vopatrná, P. *Synthesis* **1972**, 545.

[24] Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectroscopic Identification of Organic Compounds*; Wiley: New York, 1981.

[25] Segard, G.; Roques, B.-P.; Pommier, C.; Guichon, G. *J. Organomet. Chem.* **1974**, *77*, 59.

Table IV. Relative Equilibrium Constants, *K′*, for the Reactions (Eq 2) of $[CpRu(T)]^+$ with Th′ in Acetone-d_6 at 50.0 °C

Th′	*K′*	Th′	*K′*
T	1	2,3-Me_2T	50
2-MeT	6	2,3,4-Me_3T	200
3-MeT	7	2,3,5-Me_3T	300
2,5-Me_2T	35	Me_4T	1300

perature, but there was no change in the concentrations from those at 50 °C due to the slow reaction rates. The relative concentrations of all four components in each solution were obtained from integrations of the NMR spectra. All signals of the Ru complexes and free thiophenes were integrated at least twice, and the values were averaged.

Results

The equilibrium constants, $K = [CpRu(Th')^+][Th]/[CpRu(Th)^+][Th']$, for the exchange reactions (eq 1) are shown in Table III. In order to establish the reproducibility of the *K* values, the reaction of $CpRu(T)^+$ with 2-MeT was studied three times, giving values for *K* between 5.4 and 5.8. In general, we estimate that the *K* values are accurate within at least ±20%. The values are more accurate than this for the less substituted thiophenes where the signals are well separated. Up to 20% error occurs in the more highly methylated thiophenes because the signals occur in a smaller region and they overlap with each other. The equilibria for the reactions of $CpRu(T)^+$ with 2-MeT and $CpRu(2\text{-}MeT)^+$ with 2,5-Me_2T were also approached from the other side; i.e., the complex of the higher-methylated thiophene was reacted with the lesser methylated thiophene. The *K* constants were the same within experimental error regardless of the direction of approach to equilibrium.

Using the equilibrium constants in Table III, we have calculated *K′* values (Table IV) for the displacement of thiophene by the various methyl-substituted thiophenes (eq 2). Within the experimental errors of the studies, the *K′* values are internally consistent within ±25% regardless of the *K* values used to calculate them.

$$CpRu(T)^+ + Th' \overset{K'}{\rightleftharpoons} CpRu(Th')^+ + T \qquad (2)$$

The acetone-d_6 solvent clearly accelerates the rate of exchange (eq 1) as compared with CD_3NO_2 in which no exchange of $CpRu(T)^+$ with 2-MeT was observed at 50.0 °C over a period of 4 days. However, after a small amount of acetone was added to this solution, the exchange reaction slowly took place. In acetonitrile as the solvent, the thiophene ligand in $CpRu(T)^+$ is displaced to form $CpRu(NCMe)_3^+$.[17]

The reaction of $CpRu(T)^+$ with benzothiophene (BT) and dibenzothiophene (DBT) in acetone-d_6 at 50.0 °C results within 4 days in total displacement of the η^5-thiophene to give the η^6-coordinated complexes $CpRu(BT)^+$ and $CpRu(DBT)^+$, respectively. No exchange was observed after 5 days between the BT complex and free DBT and vice versa. Although no kinetic studies of the thiophene exchange reactions were performed, the solvent plays an important role as also indicated by studies[26] of the rates of arene displacement from $CpRu(arene)^+$ by acetonitrile to give $CpRu(NCMe)_3^+$.

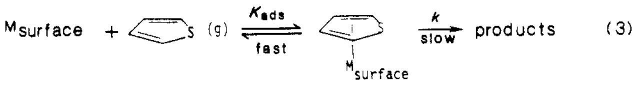
Discussion

Trends in *K′* Values for Reaction 2. As seen in Table IV, equilibrium constants, *K′*, for the coordination of thiophenes in $CpRu(Th')^+$ increase with an increasing number of methyl groups in the thiophene ligand. In general, *K′* increases by a factor of approximately 6, i.e., ~1.2 kcal/mol from $\Delta G = -RT \ln K$ at 50 °C, for each Me group in the thiophene. A similar trend is observed[27] in ΔH values for the displacement of methyl-substituted arenes from $(arene)Mo(CO)_3$ complexes, which also increase by roughly 1 kcal/mol for each methyl group added to the benzene ligand. Thus, both thiophenes and benzenes[28] coordinate more strongly as the donor ability of the ligand is increased by adding methyl groups. This result also accounts for the substantially greater stability of tetramethylthiophene (Me_4T) complexes as compared to those of thiophene.[29]

Relevance to Thiophene Adsorption on HDS Catalysts. Using a gas chromatographic technique, Zdrazil[7a] determined relative adsorption coefficients (K_{rel}) for methyl-substituted thiophenes on a sulfided Co–Mo/Al_2O_3 catalyst at 350 °C; the K_{rel} values increase in the following order: T (1.0) < 2-MeT (1.6) ~ 3-MeT (1.7) < 2,5-Me_2T (2.5). Thus, increasing numbers of Me groups in the thiophene favor adsorption, and there is no evidence for steric blocking by Me groups at the 2 and 5-positions as one might expect for S-coordinated thiophenes. Therefore, this order has been used[7a] to support the proposal that thiophenes are π-bonded (i.e., η^5) to the catalyst, although it has not been established that the adsorption sites involved in these studies are the same as those at which thiophenes HDS occurs.

We have previously argued in favor of η^5-thiophene adsorption to HDS catalysts based on model deuterium exchange[16] studies of $CpRu(Th)^+$ which show that η^5-thiophene is activated to deuterium exchange and the patterns of exchange are the same as observed over HDS catalysts. Also, we have demonstrated that η^5-thiophene in $CpRu(Th)^+$ [17,21] and $(CO)_3Mn(T)^+$ [13b,22] is reactive toward nucleophiles in ways which reasonably account for early steps in the HDS of thiophene. In the present equilibrium studies of reaction 1, we find that η^5-coordination of methyl-substituted thiophenes in $CpRu(Th')^+$ is strengthened in the same order (Table IV) as observed by Zdrazil[7a] on the HDS catalyst, further supporting the proposal for η^5-thiophene adsorption.

For an HDS mechanism (eq 3) involving rapid thiophene adsorption followed by slower reactions leading to products of deuterium exchange or desulfurization, the equilibrium constant (K_{ads}) for adsorption will affect the overall rates of further reactions and may determine overall trends in reactivity of a series of methyl-substituted thiophenes.



(3)

This may be the case for deuterium exchange of the 3- and 4-protons in methyl-substituted thiophenes on Mo/Al_2O_3. Here the amount of $H_{3,4}$ exchange increases with increasing numbers of methyl groups: T < 2-MeT < 2,5-Me_2T.[16,30] This trend is likely determined by the more favorable adsorption of methyl-substituted thiophenes; the rates of exchange of the adsorbed thiophenes probably follow the

---

[26] McNair, A. M.; Mann, K. R. *Inorg. Chem.* **1986**, *25*, 2519.

[27] Nolan, S. P.; de la Vega, R. L.; Hoff, C. D. *Organometallics* **1986**, *5*, 2529 and references therein.

[28] Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499.

[29] (a) Braitsch, D. M.; Kumarappan, R. *J. Organomet. Chem.* **1975**, *84*, C37. (b) Singer, H. *J. Organomet. Chem.* **1967**, *9*, 135. (c) Russell, M. J. H.; White, C.; Yates, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1978**, 857.

[30] Smith, G. V.; Hinckley, C. C.; Behbahany, F. *J. Catal.* **1973**, *30*, 218.

reverse trend, as discussed previously,[16] but the larger changes in K_{ads} determine the overall trend.

Also, the increasing order of HDS reactivities of methyl-substituted thiophenes, T (1.0) < 2-MeT (1.5) < 3-MeT (1.9) < 2,5-Me_2T (2.0),[7] on Co–Mo/Al_2O_3 follows the trend expected from the adsorption equilibrium constants (K_{ads}). It is likely[22] that the reactivity order of the adsorbed thiophenes follows the opposite trend with the more methyl-substituted thiophenes undergoing slower desulfurization. But here, as for deuterium exchange, larger differences in K_{ads} than in k would explain the overall trend in reactivity.

In conclusion, the K' values for reaction 2 support η^5-bonded thiophene as the form of adsorption on HDS catalysts and also reasonably account for trends in the deuterium exchange and HDS reactivity of methyl-substituted thiophenes on HDS catalysts.

Acknowledgment. We thank Johnson Matthey, Inc., for a generous loan of $RuCl_3$.

Registry No. T, 110-02-1; DBT, 132-65-0; 2-MeT, 554-14-3; 3-MeT, 616-44-4; 2,3-Me_2T, 632-16-6; 2,5-Me_2T, 638-02-8; 2,3,4-Me_3T, 1795-04-6; 2,3,5-Me_3T, 1795-05-7; Me_4T, 14503-51-6; [CpRu(T)]PF_6, 107799-36-0; [CpRu(2-MeT)]PF_6, 107799-43-9; [CpRu(3-MeT)]PF_6, 117094-83-4; [CpRu(2,3-Me_2T)]PF_6, 117094-84-5; [CpRu(2,5-Me_2T)]PF_6, 114571-22-1; [CpRu(2,3,4-Me_3T)]PF_6, 117094-86-7; [CpRu(2,3,5-Me_3T)]PF_6, 117094-87-8; [CpRu(Me_4T)]PF_6, 117094-89-0; [CpRu(BT)]PF_6, 112068-98-1; [CpRu(DBT)]PF_6, 117094-91-4; [CpRu($CH_3CN)_3$]PF_6, 80049-61-2.

Addition of Sc–H, Sc–C, and Sc–N Bonds to Coordinated Carbon Monoxide. Structure of a Methylscandoxycarbene Derivative of Cobalt[1]

Martin A. St. Clair, Bernard D. Santarsiero, and John E. Bercaw*

Division of Chemistry and Chemical Engineering,[†] *California Institute of Technology, Pasadena, California 91125*

Received February 9, 1988

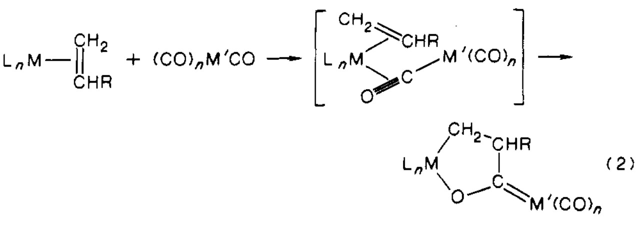
Cp^*_2ScR ($Cp^* = \eta^5$-C_5Me_5; R = H, CH_3) react with Cp_2MCO ($Cp = \eta^5$-C_5H_5, M = Mo, W) to give the corresponding R-substituted scandoxycarbenes $Cp_2M{=}C(R)OScCp^*_2$. Similarly, Cp^*_2ScR (R = H, CH_3, CH_2CH_2Ph, NMe_2) react with $CpM(CO)_2$ (M = Co, Rh) to afford the R-substituted scandoxycarbenes. The structure of $CpCo(\mu_2,\eta^1,\eta^1\text{-}CO)\{{=}C(CH_3)OScCp^*_2\}$ has been determined by a single-crystal X-ray diffraction methods, revealing a $\mu_2,\eta^1\eta^1$-carbonyl ligand in addition to the scandoxycarbene moiety bridging the Sc and Co atoms. $CpCo(\mu_2,\eta^1,\eta^1\text{-}Co)\{{=}C(CH_3)OScCp^*_2\}$ crystallizes in space group $P\bar{1}$ (a = 8.592 (4) Å, b = 10.923 (2) Å, c = 14.648 (2) Å; α = 91.074 (14)°, β = 100.84 (2)°, γ = 100.77 (3)°; Z = 2). Least-squares refinement led to a value for R of 0.046 ($I > 3\sigma$) and a goodness of fit of 3.51 for 4593 reflections.

Introduction

Despite the extensive chemistry which has been developed for "Fischer carbene" complexes, the original synthesis, with slight variations, has remained the principal route into this important class of compounds[2] (eq 1). While this method has been used to prepare a wide range of derivatives, relatively few carbene complexes of cobalt have been synthesized by this route.[3]

$$L_nMC{\equiv}O + LiR \rightarrow L_nM{=}C(OLi)R \xrightarrow[-LiX]{R'X} L_nM{=}C(OR')R \quad (1)$$

Several reports of novel routes into this class of compounds have recently appeared. Lappert and others have utilized electron-rich olefins to synthesize bis(amine)-substituted carbenes.[4] Erker[5] has utilized olefin complexes of the group 4 transition metals to effect the synthesis of metallacyclic carbenes from metal carbonyls, including those of cobalt, likely via a concerted electrocyclic ring closure (eq 2). Recently Mashima[6] has used this strategy to prepare exocyclic titanoxycarbenes of Cr, Mo, W, and Re. Reactions of metal carbonyls with titanium or aluminum amides to yield NMe_2-substituted "titanoxy" or "alumoxy" carbenes have been reported by Petz.[7] Earlier work from these laboratories demonstrated that $Cp^*_2ZrH_2$ and Cp^*_2ZrHX are effective reagents for converting metal carbonyls to hydrogen-substituted "zirconoxycarbenes",[8] $L_nM{=}C(H)OZrXCp^*_2$ (X = H, halide).



All of these methods lack generality and are apparently specific in affording exocyclic, NR_2 or H-substituted carbenes. We report herein that Cp^*_2ScR (R = H, alkyl, amide) is an effective and more general reagent for the synthesis of hydride-, alkyl-, or amide-substituted "scandoxycarbene" complexes from carbonyls of the type

---

[†] Contribution no. 7735.

[1] Part of this work was previously presented at the 192nd National Meeting of the American Chemical Society in Anaheim, CA, Sept 1986.

[2] Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1–32.

[3] Fischer, E. O.; Kreissl, F. R.; Winkler, E. *Chem. Ber.* **1972**, *105*, 588–598.

[4] (a) Macomber, D. W.; Rogers, R. D. *Organometallics* **1985**, *4*, 1485–1487. (b) Lappert, M. F.; Pyl, P. L. *J. Chem. Soc., Dalton Trans.* **1977**, 2172–2180.

[5] (a) Erker, G.; Dorf, U.; Benn, R.; Reinhardt, R. *J. Am. Chem. Soc.* **1984**, *106*, 7649–7650. (b) Erker, G.; Lecht, R.; Petersen, J. L.; Bonneman, H. *Organometallics* **1987**, *6*, 1962–1967. (c) Erker, G.; Lecht, R.; Kruger, C.; Tsay, Y.; Bönneman, H. *J. Organomet. Chem.* **1987**, *326*, C75–C78.

[6] Mashima, K.; Jyodoi, K.; Ohyoshi, A.; Takaya, H. *J. Chem. Soc., Chem. Commun.* **1986**, 1145–1146.

[7] (a) Petz, W. *J. Organomet. Chem.* **1974**, *72*, 369–375. (b) Petz, W.; Schmid, G. *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 934–935.

[8] (a) Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 218–220. (b) Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650.