observed in studies on $[Mo_3O_xS_{4-x}(H_2O)_9]^{4+}$,[3] when there are no complications from a third stage involving isomerization. This suggests that the effects are real and there are interactions between individual metal centers as the number of core sulfido ligand varies and/or structure deformations determined by the different number (and size) of oxo/sulfido core atoms prevent a better agreement.

There are clearly discernible trends to higher k_f rate constants as the number of μ_2-S core atoms increases. As in the case of the $[Mo_3O_xS_{4-x}(H_2O)_9]^{4+}$ clusters,[3] replacement of μ_3-O by μ_3-S in $[W_3O_4(H_2O)_9]^{4+}$ has an inhibitory effect. The total spread of rate constants for W is 4800, with $[W_3S_4(H_2O)_9]^{4+}$ reacting 350 times faster than $[W_3O_4(H_2O)_9]^{4+}$. For Mo, the spread of 570 is significantly less, with $[Mo_3S_4(H_2O)_9]^{4+}$ reacting $\sim 10^2$ times faster than $[Mo_3O_4(H_2O)_9]^{4+}$.[3] Overall, the trends observed are in excellent agreement and are consistent with a strong translabilization by the electron-rich μ_2-S ligands.

The third stages in the reactions of $[W_3O_2S_2(H_2O)_9]^{4+}$ and $[W_3OS_3(H_2O)_9]^{4+}$ are independent of $[NCS^-]$. The trinuclear complexes are themselves extremely stable, showing no signs of decomposition over the duration of experiments here described. Indeed, the complexes can be stored indefinitely, which is an indication of the stabilizing influence of core S atoms on W(IV). The most likely process would therefore seem to be isomerization although this is a surprisingly slow process. There are two possible mechanisms. The first is that S- and/or N-bonded thiocyanato products are obtained in the first stage, and isomerization then occurs. Crystal structures of thiocyanato complexes of W (and Mo) are all N-bonded, and it is reasonable therefore to assume that the N-bonded isomer is the more stable. A second explanation would involve a positional change of N-bonded NCS^- from a d-H_2O to the much less labile trans c-H_2O position. At present, we are unable to distinguish between these possibilities. Under similar conditions, only a single stage has been identified in the substitution of the $[Mo_3O_4(H_2O)_9]^{4+}$ and $[W_3O_4(H_2O)_9]^{4+}$ clusters.[18] Isomerization has recently been detected in the case of $[W_3S_4(H_2O)_9]^{4+}$ ($k_{isom} = 10.2 \times 10^{-5}$ s^{-1}), but not the Mo analogue,[19] and appears to be effective for μ_2-S-containing W but not Mo trimers. Since W is expected to be softer than Mo, linkage isomerization can be explained in terms of hard-soft (or class a and b) acid-base theory.[20,21] There are more core S atoms attached to the W's implicated in the first stage, and it is these W's which are likely to generate more of the S-bonded isomer and contribute most significantly to isomerization. Isomerization involving S- to N-bonded thiocyanate has been studied previously for Co(III) complexes.[22,23]

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(18) In a recent check on the reaction of NCS^- ($<3.5 \times 10^{-3}$ M) with $Mo_3O_4^{4+}$ (4×10^{-5} M), we find plots linear to >90% with no evidence for a second stage.
(19) Routledge, C. A.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.*, in press.
(20) Pearson, R. G. *Inorg. Chem.* **1988**, *27*, 734 and references therein.
(21) Ahrland, S.; Chatt, J.; Davies, N. R. *Q. Rev., Chem. Soc.* **1958**, *12*, 265.
(22) Buckingham, D. A.; Creaser, I. I.; Sargeson, A. M. *Inorg. Chem.* **1970**, *9*, 655.
(23) Jackson, W. G.; Jurisson, S. S.; McGregor, B. C. *Inorg. Chem.* **1985**, *24*, 1788.

Notes

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

η^1(S)- and η^6-Coordination of Dibenzothiophene (DBT) in $Cp^*MCl_2[\eta^1(S)\text{-DBT}]$ and $Cp^*M(\eta^6\text{-DBT})^{2+}$ (M = Ir, Rh)

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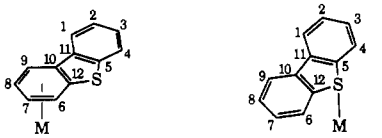
As part of our studies of the mechanism of thiophene hydrodesulfurization (HDS) on heterogeneous transition-metal catalysts, we have recently explored[2] the coordination and reactivity of η^6-coordinated (Chart I) dibenzothiophene (DBT) in $[CpRu(\eta^6\text{-DBT})]PF_6$ and $[(CpRu)_2(\mu\text{-}\eta^6,\eta^6\text{-DBT})](PF_6)_2$. While other η^6-DBT complexes are known, e.g., $Cr(CO)_3(\eta^6\text{-DBT})$,[3] $CpFe(\eta^6\text{-DBT})^+$,[4] and $[(CpFe)_2(\mu\text{-}\eta^6,\eta^6\text{-DBT})]^{2+}$,[4] there are no reactions of these η^6-derivatives that suggest[2] η^6-coordination activates DBT to desulfurization on HDS catalysts.

A recent report[5] describes a $Cp^*Rh(PMe_3)$-promoted DBT C-S cleavage which is proposed to occur through an η^1(S)-coordinated (Chart I) DBT intermediate. Only three isolated complexes containing η^1(S)-DBT have been reported: $Cp(CO)_2Re(\eta^1(S)\text{-DBT})$,[6] $Cl_2Ru[4\text{-}R_2P(DBT)]_2$,[7] in which the DBT is part of a phosphine chelating ligand, and $Cp(CO)_2Fe(\eta^1(S)\text{-DBT})^+$.[8] The last two complexes have been characterized by crystallography and show pyramidal sulfur coordination such that the metal does not lie in the plane of the DBT.

Chart I



η^6-DBT η^1(S)-DBT

In a recent kinetic study[6a] of the rate of dissociation of η^1-(S)-thiophenes (Th) from $Cp(CO)_2Re(\eta^1(S)\text{-Th})$, it was observed that DBT dissociates more slowly than benzo[*b*]thiophene (BT) or thiophene; this result suggested that DBT coordinates through the sulfur more strongly than the other thiophenes to transition metals. In the present note, we describe further evidence for the stronger coordinating ability of DBT and report the synthesis of η^1(S)-DBT complexes of Ir and Rh and their interconversion to η^6-DBT derivatives.

Experimental Section

The ^{1}H and ^{13}C NMR and mass spectra were recorded on Varian VXR-300 and Kratos MS-50 spectrometers, respectively. The ^{1}H and ^{13}C chemical shifts are given in δ units relative to the internal standard

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(2) Wang, C.-M. J.; Angelici, R. J. *Organometallics* **1990**, *9*, 1770.
(3) Fischer, E. O.; Goodwin, H. A.; Kreiter, C. G.; Simmons, H. D., Jr.; Sonogashira, K.; Wild, S. B. *J. Organomet. Chem.* **1968**, *14*, 359.
(4) Lee, C. L.; Steele, B. R.; Sutherland, R. G. *J. Organomet. Chem.* **1980**, *186*, 265.
(5) Jones, W. D.; Dong, L. *J. Am. Chem. Soc.* **1991**, *113*, 559.
(6) (a) Choi, M.-G.; Angelici, R. J. *Inorg. Chem.* **1991**, *30*, 1417. (b) Choi, M.-G.; Angelici, R. J. *Organometallics* **1991**, *10*, 2438. (c) Choi, M.-G.; Robertson, M. J.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 4005.
(7) Bucknor, S. M.; Draganjac, M.; Rauchfuss, T. B.; Ruffing, C. J. *J. Am. Chem. Soc.* **1984**, *106*, 5379.
(8) Goodrich, J. D.; Nickias, P. N.; Selegue, J. P. *Inorg. Chem.* **1987**, *26*, 3424.

0020-1669/91/1330-5046$02.50/0

Me_4Si. The DBT ^1H and ^{13}C atoms are numbered for the NMR assignments as in Chart I. Elemental analyses was carried out by Galbraith Laboratories. The $[Cp^*IrCl_2]_2$[9] and $[Cp^*RhCl_2]_2$[10] ($Cp^* = \eta$-C_5Me_5) complexes were prepared by literature methods. The solvents $CHCl_3$ and hexane were purified by distillation from CaH_2 under N_2; acetone was distilled under N_2 and stored over molecular sieves.

Cp^*IrCl_2(DBT) (1). To a solution of $[Cp^*IrCl_2]_2$ (0.100 g, 0.125 mmol) in chloroform (2 mL) was added solid DBT (0.050 g, 0.27 mmol) under N_2 or in air; immediately an orange precipitate formed. The complex was filtered out, washed with hexane, and dried. Addition of hexane to the filtrate precipitated more of the product to give an overall quantitative yield of **1**. Anal. Calcd for $C_{22}H_{23}Cl_2SIr$: C, 45.33; H, 3.98. Found: C, 45.09; H, 4.04. ^1H NMR ($CDCl_3$):[12] 8.14–8.11 (m, 2 H, H_1), 7.85–7.8 (m, 2 H, H_4), 7.44–7.40 (m, 4 H, H_2, H_3) for DBT, 1.55 (s, 15 H) for Cp^*. ^{13}C NMR ($CDCl_3$): 9.29 (CH_3), 86.32 (C of Cp^* ring); 121.53, 122.92, 124.51, 126.74, 135.62, 139.34 for DBT.

Cp^*RhCl_2(DBT) (2). This complex was prepared in the same manner as that for **1**. A solution of $[Cp^*RhCl_2]_2$ (0.100 g, 0.162 mmol) in 1 mL of chloroform was treated with DBT (0.070 g, 0.38 mmol) under N_2 or in air; immediately an orange-red precipitate formed. The precipitate was filtered off and hexane was added to the filtrate to complete the precipitation of **2** (yield 0.120 g, 75%). Anal. Calcd for $C_{22}H_{23}Cl_2SRh$: C, 53.54; H, 4.70. Found: C, 53.43; H, 4.47. ^1H NMR ($CDCl_3$):[12] 1.57 (s, 15 H, Me), 8.15–8.09 (m, 2 H, H_1, H_9), 7.83–7.79 (m, 2 H, H_4, H_6), 7.45–7.39 (m, 4 H) for DBT. ^{13}C NMR ($CDCl_3$): 9.34 (CH_3), 94.06 (d, C of Cp^* ring, J_{Rh-C} = 9.13 Hz); 121.49, 122.75, 124.32, 126.66, 135.46, 139.31 for DBT.

$[Cp^*Ir(\eta^6$-DBT)$](BF_4)_2$ (3). Method A. To a suspension of $[Cp^*IrCl_2]_2$ (0.100 g, 0.125 mmol) in 5 mL of acetone was added $AgBF_4$ (0.050 g, 0.26 mmol) under N_2; the resulting mixture was stirred for 2 min and filtered through Celite. The filtrate was refluxed with DBT (0.075 g, 0.41 mmol) for 5 min, upon which the white product **3** precipitated. It was filtered out, washed with CH_2Cl_2 and hexane, and dried under vacuum (yield 0.160 g, 90%). Anal. Calcd for $C_{22}H_{23}B_2F_8SIr$: C, 38.54; H, 3.38. Found: C, 38.39; H, 3.48. ^1H NMR (CD_3NO_2):[12] 1.99 (s, 15 H, Cp^*), 8.55 (dd, 1 H, H_1), 8.32 (pst, 1 H, H_2), 8.19 (pst, 1 H, H_3), 8.28 (dt, 1 H, H_4), 7.49–7.47 (m, 2 H, H_6, H_9), 7.91 (td, 1 H, H_7), 8.02 (td, 1 H, H_8); $J_{H_1-H_2}$ = 8.05 Hz, $J_{H_1-H_3}$ = 0.9 Hz, $J_{H_2-H_4}$ = 0.8 Hz, $J_{H_3-H_4}$ = 8.05 Hz, $J_{H_6-H_7} = J_{H_8-H_9}$ = 3.8 Hz, $J_{H_7-H_8}$ = 8.05 Hz, $J_{H_7-H_9}$ = 1.22 Hz, $J_{H_8-H_6}$ = 1.22 Hz. ^{13}C NMR (CD_3NO_2): 9.04 (CH_3), 105.98 (C of Cp^* ring), 90.64 (C_7), 93.54 (C_8), 95.66 (C_6), 95.93 (C_9), 111.74 (C_{10}), 127.96 (C_{12}), 123.24 (C_{11}), 126.25 (C_2), 127.48 (C_3), 129.70 (C_4), 135.65 (C_1), 143.89 (C_5). MS (FAB; 3-nitrobenzyl alcohol matrix), m/z: 598.9, $Cp^*Ir(DBT)(BF_4)^+$; 530.9, $Cp^*Ir(DBT)(F)^+$; 511.9 $[Cp^*Ir(DBT)]^+$.

Method B. To a suspension of Cp^*IrCl_2(DBT) (**1**) (0.050 g, 0.086 mmol) in acetone (3 mL) was added $AgBF_4$ (0.040 g, 0.20 mmol); after being stirred for 5 min, the solution was filtered through Celite. The filtrate was refluxed for 5 min; the white product that precipitated was washed with CH_2Cl_2 and hexane and then dried (yield 0.030 g, 50%).

$[Cp^*Rh(\eta^6$-DBT$)](BF_4)_2$ (4). This complex was synthesized in the same manner as that for **3** by using $(Cp^*RhCl_2)_2$ (0.115 g, 0.186 mmol), $AgBF_4$ (0.150 g, 0.77 mmol), and DBT (0.100 g, 0.54 mmol). The reaction with DBT was stirred at 25 °C (not refluxed as for Ir) for 10–15 min. The yellow complex **4** precipitated upon addition of CH_2Cl_2 (yield 0.140 g, 91%). Anal. Calcd for $C_{22}H_{23}B_2F_8SRh$: C, 44.31; H, 3.89. Found: C, 43.87; H, 3.95. ^1H NMR (CD_3NO_2):[12] 1.89 (s, 15 H, Cp^*), 8.6 (dq, 1 H, H_1), 8.31 (dt, 2 H, H_2, H_3), 8.28–8.26 (m, 1 H, H_4), 7.49–7.46 (m, 1 H, H_6), 7.93 (td, 1 H, H_7), 8.04 (td, 1 H, H_8), 8.13–8.09 (m, 1 H, H_9); $J_{H_1-H_2} = J_{H_2-H_3} = J_{H_3-H_4}$ = 7.91 Hz, $J_{H_1-H_3} = J_{H_2-H_4}$ = 0.74 Hz, $J_{H_7-H_8} = J_{H_7-H_6} = J_{H_8-H_9}$ = 7.47 Hz, $J_{H_7-H_9}$ = 0.98 Hz, $J_{H_8-H_6}$ = 1.22 Hz. ^{13}C NMR (CD_3NO_2): 9.60 (CH_3), 112.57 (d, C of Cp^* ring, J_{C-Rh} = 8.59 Hz), 99.74 (d, C_7, J_{C-Rh} = 4.84 Hz), 102.82 (d, C_8, J_{C-Rh} = 4.30 Hz), 103.60 (d, C_6, J_{C-Rh} = 4.84 Hz), 104.15 (d, C_9, J_{C-Rh} = 4.84 Hz), 117.68 (d, C_{10}, J_{C-Rh} = 3.76 Hz), 128.41 (d, C_{12}, J_{C-Rh} = 3.22 Hz), 126.33 (s, C_3), 127.24 (s, C_2), 128.55 (s, C_{11}), 129.72 (s, C_4), 135.26 (s, C_1), 144.12 (s, C_5). MS (FAB; 3-nitrobenzyl alcohol matrix), m/z: 509.0, $Cp^*Rh(DBT)(BF_4)^+$; 441, $Cp^*Rh(DBT)(F)^+$; 422.0, $[Cp^*Rh(DBT)]^+$.

$[Cp^*IrCl(bpy)]Cl$ (5). To a suspension of Cp^*IrCl_2(DBT) (**1**) (0.075 g, 0.128 mmol) in 3 mL of $CHCl_3$ was added bpy (0.025 g, 0.16 mmol).

Table I. Crystal and Data Collection Parameters for $[Cp^*IrCl_2(DBT)]$ (**1**)

formula	$IrCl_2SC_{22}H_{23}$
fw	582.61
cryst syst	monoclinic
a, Å	16.009 (5)
b, Å	7.515 (5)
c, Å	17.125 (4)
β, deg	92.70 (2)
V, Å^3	2058 (2)
space group	$P2_1/c$
Z	4
D_{calc}, g cm^{-3}	1.880
μ(Mo Kα), cm^{-1}	68.29
transm coeff	0.79–1.00
radiation (λ, Å)	Mo Kα (0.71069)
temp, °C	23
R, R_w[a]	0.0298, 0.0428

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

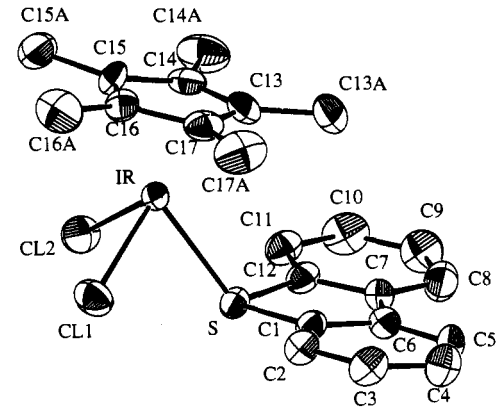

Figure 1. ORTEP drawing of $[Cp^*IrCl_2(DBT)]$ (**1**).

After being stirred for 2–3 min, the orange suspension changed to a lemon yellow solution. Addition of 5 mL of hexane precipitated the greenish yellow **5**. The compound was centrifuged out, washed a few times with hexane, and vacuum-dried; the yield was quantitative. ^1H NMR ($CDCl_3$): 1.67 (s, 15 H, Cp^*), 9.32 (d, 2 H, H_2, $J_{H_2-H_3}$ = 8.05 Hz), 8.0 (td, 2 H, H_3, $J_{H_3-H_2}$ = 8.0 Hz, $J_{H_3-H_5}$ = 1.1 Hz), 7.73 (td, 2 H, H_4, $J_{H_4-H_5} = J_{H_3-H_4}$ = 5.75 Hz, $J_{H_4-H_2}$ = 1.22 Hz), 8.77 (dd, 2 H, H_5, $J_{H_5-H_4}$ = 5.62 Hz, $J_{H_5-H_3}$ = 1.1 Hz). ^{13}C NMR ($CDCl_3$): 8.80 (CH_3), 89.23 (C of Cp^* ring), 125.87 (C_3), 128.91 (C_5), 140.73 (C_4), 150.90 (C_2), 155.28 (C_6). This compound was prepared previously from $(Cp^*IrCl_2)_2$.[13]

$Cp^*IrCl_2(L)$ (L = PPh_3, PMe_3). To a suspension of complex **1** (0.020 g, 0.034 mmol) in 2 mL of $CHCl_3$ was added at least 0.068 mmol of the phosphine. While being stirred for 2 min, the suspension became a clear solution. Addition of hexane precipitated the orange product, which was washed with hexane and dried under vacuum. These compounds, which were obtained in essentially quantitative yields, were identified by comparison of their ^{31}P NMR spectra with those reported in the literature.[14]

$[Cp^*IrCl(dppe)]Cl$. This complex was prepared as for the $Cp^*IrCl_2(L)$ complexes above by reaction with dppe ($Ph_2PCH_2CH_2PPh_2$) instead of a monodentate phosphine; the workup procedure was the same as above. The compound was identified by its ^{31}P NMR spectrum.[15]

X-ray Structural Characterization of Cp^*IrCl_2(DBT) (1). Orange crystals of **1** of approximate dimensions 0.40 × 0.30 × 0.40 mm were formed upon addition of solid DBT (10 mg) to a dilute solution of $(Cp^*IrCl_2)_2$ (15 mg in 1 mL of $CHCl_3$). The mixture was kept at 25 °C without disturbance for 1 day. Complex **1** crystallizes in the centrosymmetric, monoclinic space group $P2_1/c$ with a = 16.009 (5) Å, b = 7.515 (5) Å, c = 17.125 (4) Å, β = 92.70 (2)°, V = 2058 (2) Å^3, Z = 4, and D_{calc} = 1.880 g/cm^3. Data were collected (Table I) at 23 °C on a Rigaku AFC6R diffractometer with graphite-monochromated Mo Kα (λ = 0.71069 Å) radiation using an ω–2θ scan technique to a maximum 2θ of 50.1°. An empirical absorption correction was made where the

(9) Ball, R. G.; Graham, W. A. G.; Heinekey, D. M.; Hoyano, J. K.; McMaster, A. D.; Mattson, B. M.; Michel, S. T. *Inorg. Chem.* **1990**, *29*, 2023.
(10) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970.
(11) Bartle, K. D.; Jones, D. W.; Matthews, R. S. *Tetrahedron* **1971**, *27*, 5177.
(12) pst = pseudotriplet; dt = doublet of triplet; td = triplet of doublets.
(13) Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1988**, 16.
(14) Booth, B. L.; Haszeldine, R. N.; Hill, M. *J. Organomet. Chem.* **1969**, *16*, 491.
(15) Glueck, D. S.; Bergman, R. G. *Organometallics* **1990**, *9*, 2862.

Table II. Positional and Thermal Parameters for [Cp*IrCl$_2$(DBT)] (**1**)

atom	x	y	z	B_{eq},[a] Å^2
Ir	0.23662 (2)	0.16184 (3)	0.01006 (1)	2.01 (1)
Cl1	0.1183 (1)	0.0416 (3)	−0.0627 (1)	3.56 (9)
Cl2	0.3263 (1)	0.0411 (3)	−0.0852 (1)	3.61 (9)
S	0.2430 (1)	−0.1356 (2)	0.0568 (1)	2.28 (7)
C1	0.1769 (4)	−0.1780 (8)	0.1343 (4)	2.4 (3)
C2	0.0904 (5)	−0.160 (1)	0.1304 (5)	2.8 (3)
C3	0.0477 (5)	−0.207 (1)	0.1958 (5)	3.2 (4)
C4	0.0916 (5)	−0.274 (1)	0.2626 (5)	3.3 (4)
C5	0.1775 (5)	−0.291 (1)	0.2651 (5)	2.9 (3)
C6	0.2208 (4)	0.241 (1)	0.2007 (4)	2.4 (3)
C7	0.3111 (5)	−0.240 (1)	0.1910 (4)	2.7 (3)
C8	0.3744 (6)	−0.287 (1)	0.2462 (5)	3.7 (4)
C9	0.4566 (5)	−0.268 (1)	0.2250 (6)	4.0 (4)
C10	0.4764 (5)	−0.204 (1)	0.1531 (6)	3.9 (4)
C11	0.4148 (5)	−0.159 (1)	0.0971 (5)	3.1 (3)
C12	0.3330 (5)	−0.1776 (8)	0.1183 (4)	2.6 (3)
C13	0.2595 (5)	0.309 (1)	0.1173 (4)	3.2 (3)
C13A	0.2800 (7)	0.237 (1)	0.1973 (5)	4.8 (5)
C14	0.3201 (5)	0.3561 (9)	0.0614 (5)	2.8 (3)
C14A	0.4142 (6)	0.343 (1)	0.0721 (6)	4.8 (5)
C15	0.2739 (5)	0.436 (1)	−0.0036 (4)	3.0 (4)
C15A	0.3139 (6)	0.510 (1)	−0.0752 (5)	4.0 (4)
C16	0.1892 (5)	0.4298 (9)	0.0086 (4)	2.7 (3)
C16A	0.1209 (6)	0.500 (1)	−0.0447 (5)	4.6 (4)
C17	0.1781 (5)	0.3487 (9)	0.0840 (5)	3.0 (3)
C17A	0.0981 (6)	0.327 (1)	0.1230 (6)	4.8 (5)
H2	0.063 (4)	−0.10 (1)	0.077 (4)	3 (2)
H3	−0.008 (5)	−0.21 (1)	0.193 (4)	2 (2)
H4	0.061 (6)	−0.30 (1)	0.295 (5)	4 (2)
H5	0.199 (7)	−0.33 (1)	0.299 (6)	6 (3)
H8	0.357 (5)	−0.345 (9)	0.290 (4)	2 (2)
H9	0.505 (5)	−0.29 (1)	0.267 (5)	4 (2)
H10	0.531 (6)	−0.19 (1)	0.142 (6)	5 (2)
H11	0.419 (5)	−0.14 (1)	0.040 (5)	4 (2)

[a] $B_{eq} = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3}U_{ij}a_i^*a_j^*\vec{a}_i\cdot\vec{a}_j$.

maximum and minimum transmission factors were 1.00 and 0.79, respectively. The data were corrected for Lorentz and polarization effects. The structure was solved using direct methods and least-squares refinement.[16] The non-hydrogen atoms were refined anisotropically. The DBT hydrogens were refined isotropically. The Cp* hydrogen positions were calculated. The final cycle of full-matrix least-squares refinement, based on 3085 observed reflections ($I > 3\sigma(I)$) and 268 variable parameters, converged with $R = 0.0298$ and $R_w = 0.0428$. Atomic positional parameters are given in Table II. An ORTEP drawing[17] of **1** is shown in Figure 1.

Results and Discussion

Cp*IrCl$_2$(DBT) (1) and Cp*RhCl$_2$(DBT) (2). The dimers [Cp*MCl$_2$]$_2$ (M = Ir, Rh) react immediately with DBT to form Cp*MCl$_2$(DBT) in quantitative (Ir) and 75% (Rh) yields (eq 1).

$$[Cp^*MCl_2]_2 + 2\,DBT \xrightarrow{CHCl_3} 2\,Cp^*MCl_2(DBT) \quad (1)$$
$$1:\ M = Ir$$
$$2:\ M = Rh$$

Complexes **1** and **2** are air-stable in the solid state and in $CHCl_3$ solution. The DBT ligand in **1** is not displaced by the coordinating solvents acetone, methanol, and water, at least in part because of the insolubility of the complex in these solvents. Unlike DBT, benzo[*b*]thiophene (BT), thiophene, and 2,5-dimethylthiophene do not react with [Cp*MCl$_2$]$_2$ (M = Ir, Rh) under the conditions of reaction 1. This is consistent with the known greater stability of Cp(CO)$_2$Re(DBT)[6] and Cp(CO)$_2$Fe(DBT)$^+$,[8] as compared with their BT and thiophene analogues. Previous attempts[18] to prepare η^1(S)-thiophene (Th) complexes Cp*MCl$_2$(Th) (M = Ir, Rh) were also unsuccessful.

Table III. Bond Distances and Selected Bond Angles for [Cp*IrCl$_2$(DBT)] (**1**)

Bond Distances (Å)[a]			
Ir–Cl1	2.395 (2)	C7–C8	1.40 (1)
Ir–Cl2	2.401 (2)	C7–C12	1.39 (1)
Ir–S	2.375 (2)	C8–C9	1.39 (1)
Ir–Cl3	2.159 (7)	C9–C10	1.37 (1)
Ir–Cl4	2.140 (7)	C10–C11	1.38 (1)
Ir–Cl5	2.159 (7)	C11–C12	1.38 (1)
Ir–Cl6	2.152 (7)	C13–C13A	1.50 (1)
Ir–C17	2.136 (7)	C13–C14	1.44 (1)
S–C1	1.767 (7)	C13–C17	1.43 (1)
S–C12	1.772 (7)	C14–C14A	1.51 (1)
C1–C2	1.38 (1)	C14–C15	1.44 (1)
C1–C6	1.390 (9)	C15–C15A	1.52 (1)
C2–C3	1.38 (1)	C15–C16	1.38 (1)
C3–C4	1.40 (1)	C16–C16A	1.49 (1)
C4–C5	1.39 (1)	C16–C17	1.45 (1)
C5–C6	1.38 (1)	C17–C17A	1.48 (1)
C6–C7	1.46 (1)		
Selected Bond Angles (deg)[a]			
Cl1–Ir–Cl2	89.30 (8)	Ir–S–C1	113.9 (2)
Cl1–Ir–S	80.83 (7)	Ir–S–C12	112.9 (2)
Cl2–Ir–S	81.71 (7)	C1–S–C12	91.1 (3)
S–C1–C2	125.5 (5)	S–C1–C6	112.1 (5)
S–C12–C7	111.1 (6)	S–C12–C11	125.4 (6)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

The structure of **1** (Figure 1) is similar to that of [CpFe(CO)$_2$(DBT)]BF$_4$,[8] except the DBT ligand in **1** is oriented syn to the Cp* group while it is anti to the Cp in the iron complex; this could be caused by the larger Cl$^-$ ligands as compared with CO. The Ir–S bond length (2.375 (2) Å) is comparable to those in a variety of other iridium complexes.[19]

The coordinated sulfur is pyramidal, as indicated by the 128.0° angle between the Ir–S bond and the vector from S to the midpoint of the C6–C7 bond; the corresponding angle in Cp(CO)$_2$Fe(DBT)$^+$[8] is 119.4°, and those in RuCl$_2$[P(4-MeC$_6$H$_4$)$_2$(DBT)]$_2$ are 132.0 and 130.1°.[7] Another measure of the pyramidal character of the S is the small sum of the angles (317.9°) around the sulfur, which is substantially less than that (360°) required for a planar sulfur. The DBT ligand is planar except for the sulfur atom which is 0.14 Å out of the least-squares plane defined by C1, C6, C7, and C12 in the direction which is opposite that of the Ir. The DBT ligand dimensions are essentially the same as those in free DBT[20] with the C–S bond lengths (1.77 Å) and the C1–S–C12 angle (91.1°) being similar to the same parameters (1.74 Å and 91.5°) in free DBT.

Complex **1** reacts rapidly with the neutral ligands PPh$_3$, PMe$_3$, dppe, and bpy forming neutral and cationic complexes as shown in eq 2. This is a fast and easy route to these complexes as

$$Cp^*IrCl_2(DBT) + L \text{ or } L\text{-}L \xrightarrow{CHCl_3} Cp^*IrCl_2(L) \text{ or } [Cp^*IrCl(L\text{-}L)]Cl + DBT$$
$$L = PPh_3,\ PMe_3;\ L\text{-}L = bipy,\ dppe \quad (2)$$

compared to previously reported literature methods;[13-15] preparations by this method require only 10 min starting from [Cp*IrCl$_2$]$_2$. The thiophenes (2,5-dimethylthiophene and 3-methylthiophene) do not react with **1** under the same conditions.

Preparation of [Cp*M(η^6-DBT)](BF$_4$)$_2$ (M = Ir, Rh). Complexes **3** and **4** were prepared from [Cp*MCl$_2$]$_2$, AgBF$_4$, and DBT via the Cp*Ir(acetone)$_3^{2+}$ intermediate[21] as shown in eq 3. Complexes **3** and **4** are air-stable solids. The DBT ligand in **4**

(16) Direct-methods calculations: Gilmore, C. J. MITHRIL—an integrated direct methods computer program. *J. Appl. Crystallogr.* **1984**, *17*, 42–46. Least-squares and difference Fourier calculations: TEXSAN-TEXRAY Structure Solution Package, Molecular Structure Corp., The Woodlands, TX, 1985.
(17) Johnson, C. K. ORTEPII. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.
(18) Russell, M. J. H.; White, C.; Yates, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1978**, 857.
(19) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989** (Supplement).
(20) (a) Schaffrin, R. M.; Trotter, J. *J. Chem. Soc. A* **1970**, 1561. (b) Bechtel, F.; Chasseau, D.; Gaultier, J.; Hauw, C. *Cryst. Struct. Commun.* **1977**, *6*, 699.
(21) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1977**, 1654.

$$[Cp^*MCl_2]_2 + 4\,AgBF_4 \xrightarrow[\text{acetone}]{\text{DBT}} 2[Cp^*M(\eta^6\text{-DBT})](BF_4)_2 + 4\,AgCl \quad (3)$$

3: M = Ir
4: M = Rh

is easily displaced by acetone, but **4** is stable in nitromethane. DBT in **3** is not displaced by acetone because of the insolubility of the complex in this solvent; **3** is stable in nitromethane.

Assignments of the ^1H and ^{13}C NMR data for **3** and **4** indicate that coordination occurs through the benzene ring (C_6–C_{10}, C_{12}; Chart I) of DBT. In the ^1H NMR spectra, the resonances of the coordinated DBT are slightly downfield with respect to the free ligand, as was also observed in $Cp^*Ir(\eta^6\text{-BT})^{2+}$.[22] This contrasts with $Cr(CO)_3(\eta^6\text{-DBT})$,[3] $[CpM(\eta^6\text{-DBT})]PF_6$,[2,4] and $[(CpM)_2(\mu\text{-}\eta^6,\eta^6\text{-DBT})]^{2+}$,[2,4] where upfield shifts are observed presumably because of the lower oxidation state of the metal. However, the ^{13}C signals of the arene carbons directly bonded to the metal in **3** and **4** are upfield with respect to the free ligand. In complex **4**, all of the coordinated arene ^{13}C signals split into doublets due to coupling with Rh.

Complex **3** reacts immediately with 2 equiv of $[Et_4N]Cl$ in CH_3NO_2 to give the η^1(S)-DBT complex **1** (eq 4) at 25 °C.

$$\underset{3,\,4}{[Cp^*M(\eta^6\text{-DBT})](BF_4)_2} \underset{\Delta,\ \text{Acetone/AgBF}_4}{\overset{2[Et_4N]Cl}{\rightleftharpoons}} \underset{1,\,2}{Cp^*MCl_2(DBT)} + 2[Et_4N]BF_4 \quad (4)$$

Likewise **4** reacts immediately with 2 equiv of $[Et_4N]Cl$ in $CHCl_3$ at room temperature to give complex **2**. These reactions illustrate an interesting linkage isomerization of DBT from η^6- to η^1(S)-coordination. These reactions are reversed by adding 2 equiv of $AgBF_4$ to **1** and **2** in acetone solvent and refluxing for 5 min. Treatment of **3** and **4** in CH_3NO_2 with dppe at room temperature overnight gave no reaction. Also, **3** did not react with bpy under the same conditions.

In summary, these studies demonstrate that the sulfur of DBT is sufficiently strongly coordinating that it is capable of cleaving the chloro bridging ligands in $[Cp^*MCl_2]_2$ to give Cp^*MCl_2(DBT), **1** and **2**; in contrast, benzo[*b*]thiophene, 2,5-dimethylthiophene, and thiophene do not react similarly. This suggests that DBT would be a stronger S-coordinating ligand at a metal site on HDS catalysts.

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Registry No. **1**, 137516-63-3; **2**, 137540-28-4; **3**, 137516-65-5; **4**, 137516-67-7; **5**, 115565-17-8; $Cp^*IrCl_2(PPh_3)$, 66517-28-0; $Cp^*IrCl_2(PMe_3)$, 80298-81-3; $[Cp^*IrCl(dppe)]Cl$, 130353-02-5; $[Cp^*IrCl_2]_2$, 12354-84-6; $[Cp^*RhCl_2]_2$, 12354-85-7.

Supplementary Material Available: Tables of crystal data, calculated hydrogen atom positions, bond angles, least-squares planes, and displacement parameters (8 pages); a table of calculated and observed structure factors (21 pages). Ordering information is given on any current masthead page.

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

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A Superior Method for the Metalation of Hydroporphyrins

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The metalation of hydroporphyrin compounds is a more formidable challenge than the metalation of porphyrins. Both reactions are metatheses in which bases, the tetrapyrrole dianion and the ligand(s) in the metal carrier complex, compete with each other for acids, the metal ion and protons (eq 1). The hydroporphyrin reaction is complicated by the tendency of free-base- and metallohydroporphyrins to undergo oxidative dehydrogenation in the presence of trace amounts of oxygen or other oxidants.[1] This reaction transforms the initial hydroporphyrin compound, whose dianion is designated PH_{2N} in eq 2, into the next most

$$H_2(P) + ML_2 \rightleftharpoons M(P) + 2HL \quad (1)$$

$$M(PH_{2N}) \xrightarrow{-e^-} M(PH_{2N}^{\bullet})^+ \xrightarrow{-e^-,\,-2H^+} M(PH_{2N-2}) \longrightarrow M(P) \quad (2)$$

unsaturated tetrapyrrole compound and eventually into a porphyrin compound. Thus, metalation of a hydroporphyrin can afford mixtures of complexes, which may not be easy to separate. In extreme cases, a metalloporphyrin complex may be the sole product of the reaction.

Typical reaction systems for the metalation of porphyrins[2,3] represent a compromise between several conflicting requirements. Ideally, the solvent should dissolve both the porphyrin and the metal carrier but should not coordinate the metal ion so strongly that it competes with the porphyrin. The ligand(s) in the metal carrier complex should provide good solubility for the metal, be labile to permit ready displacement by the porphyrin, and have a weak conjugate acid. Commercial availability, stability, and ease of handling of the metal carrier complex are also desirable. In some cases, an additional base is required to shift eq 1 in favor of products, either by deprotonation of the free-base porphyrin or by complexation of the metalloporphyrin product.

Two commonly used methods for metalation of porphyrins, the acetate method[2,3] and the dimethylformamide method,[2-4] are less than ideal when applied to hydroporphyrins. For porphyrins, the high boiling point of DMF (153 °C) is advantageous because the solubilities of the porphyrin and metal chlorides are relatively high, reactions are rapid, and the expulsion of the HCl byproduct from an open reaction system drives metalation to completion.[4] Hydroporphyrins typically do not survive metalation in DMF completely intact, even if the reaction is run anaerobically at temperatures much lower than the boiling point of the solvent. This behavior is mirrored by the irreversibility of the electrochemical oxidations of many hydroporphyrins in DMF, which contrasts with their reversibility in other solvents.[5,6] Although less severe, oxidative dehydrogenation is not negligible in the acetate method. In both methods significant losses can also occur during the multistep workups and the inevitable chromatographic purification of the product.

A third method for metalation of porphyrins employs metal acetylacetonate complexes as the metal carrier.[7] It has not achieved as wide popularity as the other methods, perhaps because most reports imply that molten phenol at 180–240 °C or refluxing 1,2,4-trichlorobenzene (214 °C) is the solvent of choice for the reaction.[2,3,7,8] The high reaction temperature and the difficulty of removing the solvent would appear to obviate the use of this method for hydroporphyrins. Nonetheless, the acac[9] method has

(1) Stolzenberg, A. M.; Spreer, L. O.; Holm, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 364.
(2) Buchler, J. W. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; pp 157–231.
(3) Buchler, J. W. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. 1, pp 389–483.
(4) Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443.
(5) Stolzenberg, A. M.; Stershic, M. T. *Inorg. Chem.* **1988**, *27*, 1614.
(6) Stolzenberg, A. M.; Schussel, L. J. *Inorg. Chem.* **1991**, *30*, 3205.
(7) (a) Buchler, J. W.; Eikelmann, G.; Puppe, L.; Rohbock, K.; Schneehage, H. H.; Weck, D. *Liebigs. Ann. Chem.* **1971**, *745*, 135. (b) Buchler, J. W.; Folz, M.; Habets, H.; van Kaam, J.; Rohbock, K. *Chem. Ber.* **1976**, *109*, 1477.
(8) (a) Wong, C.-P.; Venteicher, R. F.; Horrocks, W. DeW., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 7149. (b) Buchler, J. W.; De Cian, A.; Fischer, J.; Kihn-Botulinski, M.; Paulus, H.; Weiss, R. *J. Am. Chem. Soc.* **1986**, *108*, 3652. (c) Buchler, J. W.; Hüttermann, J.; Löffler, J. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 71.

0020-1669/91/1330-5049$02.50/0