Insertion of 2,3-Dihydrothiophene into Platinum and Osmium Hydrides: A Model for Reactions Occurring during Thiophene Hydrodesulfurization

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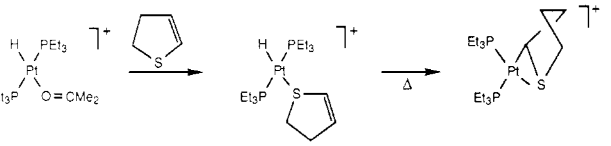
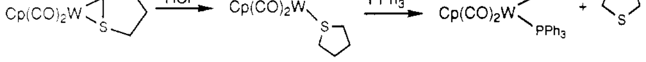
Reaction of HPt(acetone)$(PEt_3)_2^+$ with 2,3-DHT results in the formation of the sulfur-coordinated 2,3-DHT compound I. Subsequent rearrangement by slow insertion of the 2,3-DHT olefin into the Pt–H bond gives II, which was characterized by an X-ray diffraction study. Compound II reacts with H_2 at 150 °C to yield butane. A tungsten analogue (VIIIa) of II is prepared from the reaction of $CpW(CO)_3^-$ with 2-chlorotetrahydrothiophene followed by photolytic decarbonylation. The reaction of VIIIa with HCl yields an unstable tetrahydrothiophene (THT) complex IX. These reactions serve as models for the conversion of thiophene to THT and C_4 products. Insertion of 2,3-DHT into a metal cluster hydride is achieved in the reaction of 2,3-DHT with $H_2Os_3(CO)_9PPh_3$ to form X whose structure was established by X-ray diffraction.



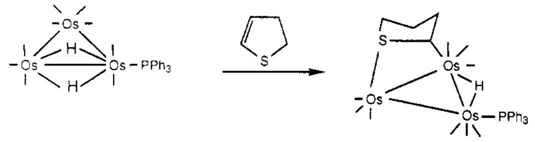
I

II



VIIIa

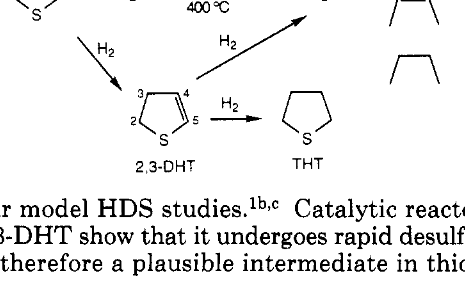
IX



X

Introduction

Catalytic hydrodesulfurization (HDS), a process which is used to remove sulfur from thiophene and other sulfur-containing organics in crude oil and coal liquids, is carried out over a sulfided Co–Mo/Al_2O_3 catalyst. Of the many organosulfur compounds present in petroleum feedstocks, thiophene has been studied most intensively as a representative component which is difficult to desulfurize. Numerous investigations have been directed at understanding how thiophene undergoes HDS on heterogeneous catalysts.[1] Dihydrothiophene (2,3-DHT) has been proposed as an intermediate in the HDS of thiophene (eq 1) by Amberg and others;[2] this proposal is supported by our model HDS studies.[1b,c] Catalytic reactor studies[3] of 2,3-DHT show that it undergoes rapid desulfurization and is therefore a plausible intermediate in thiophene HDS.



(1)

However, considerable hydrogenation to tetrahydrothiophene (THT) also occurs (eq 1). This latter reaction may occur by olefin insertion, a reaction that may be particularly favorable because of the coordinating ability of the sulfur in 2,3-DHT,[4] which brings the olefinic group near the catalyst surface.

It was therefore of interest to explore the reactivity of 2,3-DHT with metal hydride complexes to see if hydrogen migration to the partly hydrogenated thiophene occurs. The results in this paper demonstrate that insertion of 2,3-DHT into metal hydride bonds occurs readily to give metallathiacyclopropane complexes which upon protonation yield tetrahydrothiophene.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of prepurified N_2 at room temperature using

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Table I. Infrared Spectra of the Complexes in Hexanes

complex	ν(CO), cm^{-1}
$[HPt(PEt_3)_2(2,3\text{-DHT})]PF_6$ (I)	
$[Pt(PEt_3)_2(DHT{\cdot}H)]PF_6$ (II)	
$[Pt(PPh_3)_2(DHT{\cdot}H)]PF_6$ (III)	
$[Pt(PPh_2Me)_2(DHT{\cdot}H)]PF_6$ (IV)	
$Cp(CO)_3W(DHT{\cdot}H)$ (Va)	2030 (ms), 1940 (s), 1927 (s)
$Cp(CO)_3Mo(DHT{\cdot}H)$ (Vb)	2033 (ms), 1951 (s), 1935 (s)
$Cp(CO)_2Fe(DHT{\cdot}H)$ (VI)	2020 (s), 1959 (s)
$[Cp(CO)_2Fe(DHT{\cdot}H{\cdot}Me]PF_6$ (VII)[a]	2040 (s), 1978 (s)
$Cp(CO)_2W(\eta^2\text{-DHT}{\cdot}H)$ (VIIIa)	1936 (s), 1849 (s)
$Cp(CO)_2Mo(\eta^2\text{-DHT}{\cdot}H)$ (VIIIb)	1944 (s), 1858 (s)
$Cp(CO)_2W(THT)Cl$ (IX)[a]	1954 (s), 1851 (s)
$HOs_3(CO)_9(PPh_3)(DHT{\cdot}H)$ (X)	2090 (mw), 2052 (s), 2030 (vs), 2009 (s), 1991 (ms), 1969 (s), 1965 (m, sh), 1955 (m), 1944 (w)
$HOs_3(CO)_{10}(DHT{\cdot}H)$ (XI)	2090 (w), 2082 (m), 2070 (s), 2060 (ms), 2047 (w), 2034 (s), 2014 (m), 1991 (mw)

[a] In CH_2Cl_2 solvent.

standard inert atmosphere and Schlenk[5] techniques unless otherwise stated. Tetrahydrofuran (THF) and Et_2O were distilled under N_2 from Na/benzophenone. Hexanes, MeCN and CH_2Cl_2 were distilled from CaH_2 under N_2. Acetone was purged with N_2 and dried over molecular sieves for several weeks. Benzene was distilled from $LiAlH_4$ under N_2 and stored over Na metal.

Infrared spectra were obtained by using a Perkin Elmer 681 spectrophotometer; the spectra were referenced to the 1944.0 cm^{-1} band of polystyrene. The ^1H and $^{13}C\{H\}$ NMR data were obtained on a Nicolet NT 300-MHz spectrometer using Me_4Si as the internal reference. The ^{31}P and temperature-dependent NMR spectra were recorded on a Bruker WM 300 MHz instrument. The ^{31}P signals which are upfield of the H_3PO_4 external reference are given as negative values. The ^{195}Pt NMR spectra were obtained on a Bruker WM 200-MHz instrument. Chemical shifts were measured relative to 0.2 M K_2PtCl_4 (in 0.4 M KCl/D_2O), which was used as an external reference (−1627.0 ppm vs 0.2 M K_2PtCl_6 in H_2O).[6] Electron-impact mass spectra (EIMS) and GC–MS spectra were obtained on a Finnigan 4000. Fast atom bombardment (FAB, glycerol matrix) mass spectra were obtained by using a Kratos MS-50 spectrometer.

Diphenylmethylphosphine and PEt_3 were obtained from Strem Chemicals and used without further purification. Triphenylphosphine was used as received from SCM Chemicals. Adsorption (80–200 mesh) alumina was used as received from Fisher Scientific.

Photochemical reactions were carried out with a 254-nm light in a quartz Schlenk tube equipped with a cooling probe using a reactor obtained from Bradford Scientific, Inc., Marblehead, MA.

The compounds *trans*-$HPt(PEt_3)_2Cl$,[7] *trans*-$HPt(PMePh_2)_2Cl$,[8] *trans*-$HPt(PPh_3)_2Cl$,[9] $H_2Os_3(CO)_{10}$,[10] and $H_2Os_3(CO)_9(PPh_3)$[11] were prepared by using reported routes. The compounds $[HPt(acetone)(PR_3)_2]^+$ (PR_3 = PEt_3, $PMePh_2$, PPh_3) were generated as described by Clark and Jablonski.[12] The X-ray crystal structure analysis data are summarized in Table IV. In addition to the data given below, the compounds were characterized by their IR, NMR and mass spectra (Tables I–III).

Reaction of $[HPt(acetone)(PR_3)_2]^+$ with 2,3-DHT. An acetone (15 mL) solution of $HPt(PEt_3)_2Cl$ (0.21 g, 0.48 mmol) was added to an acetone (15 mL) solution of $AgPF_6$ (0.12 g, 0.48 mmol). This mixture was stirred for 15 min, and the AgCl formed was removed by filtration through a medium glass frit. The filtrate was then treated with 2,3-DHT[4] (0.20 M solution in pentane, 2.5 mL, 0.50 mmol), and the mixture was stirred for 2 h. The volume of the solution was reduced to ~5 mL, layered with Et_2O (25 mL), and stored at −20 °C for 3 days. The white needlelike solid $[HPt(PEt_3)_2(2,3\text{-DHT})]PF_6$ (I) (0.19 g, 83%) was filtered off and dried. Anal. Calcd for $C_{16}H_{37}F_6P_3PtS$: C, 28.96; H, 5.62; S, 4.83. Found: C, 29.01; H, 6.02; S, 5.08. ^{13}C NMR ($CDCl_3$): δ 133.82 (m, C5), 121.35 (m, C4), 38.04 and 34.95 (C2, C3), 18.70 [m, $P(CH_2CH_3)_3$], 8.60 [m, $P(CH_2CH_3)$]. ^{31}P NMR ($CDCl_3$): δ 20.11 (J_{PtP} = 2565 Hz). ^{195}Pt NMR ($CDCl_3$): δ −3381.3 (pseudo dt, J_{PPt} ~ 2547 Hz, J_{HPt} = 1237 Hz). Compound I is stable in air and can be handled at ambient temperature for short periods of time. No changes were observed in I when stored at −20 °C for 9 months. However, when I was stored at room temperature, it slowly became pale yellow. The yellow solid was found to be $[Pt(PEt_3)_2DHT{\cdot}H)]PF_6$ (II). The complete conversion of I to II occurred over a period of 3 months in the solid state at room temperature. In solution at ambient temperature I is converted to II in a month, and at 60 °C, I goes to II in 1 week. The conversion of I to II was monitored by ^1H and ^{195}Pt NMR at 60 °C and ^{31}P NMR at ambient temperature. Spectral data for II: ^{13}C NMR ($CDCl_3$) δ 64.07 (d, J_{PtC} = 339 Hz, $J_{transPC}$ = 61.3 Hz, C2), [41.17 (pseudo triplet), 37.61 (s), 31.58 (J_{PtC} = 29.1 Hz) C3, C4, C5]; ^{31}P NMR ($CDCl_3$) δ 15.75 (J_{PtP} = 2796 Hz), 17.01 (J_{PtP} = 4339 Hz); ^{195}Pt NMR ($CDCl_3$) δ −3387.4 (pseudo dd, J_{PPt} = 4330 Hz, J_{PPt} = 2796 Hz).

As described for $HPt(PEt_3)_2Cl$, an acetone (20 mL) solution of $HPt(PPh_3)_2Cl$ (0.15 g, 0.20 mmol) was treated with an acetone (10 mL) solution of $AgPF_6$ (0.053 g, 0.21 mmol). After the solution was stirred for 15 min, the AgCl formed was filtered off through a medium frit. The filtrate was treated with 1.5 equiv (0.30 mmol) of a 0.28 M pentane solution of 2,3-DHT. The mixture was stirred for 2 h. The resulting pale yellow solution was reduced in volume in vacuo to ~5 mL, layered with Et_2O (~25 mL), and stored at −20 °C for 3 days. Compound $[Pt(PPh_3)_2(DHT{\cdot}H)]PF_6$ (III) (0.12 g, 65%) was filtered off and dried. Anal. Calcd for $C_{40}H_{37}F_6P_3PtS$: C, 50.48; H, 3.92. Found: C, 50.73; H, 4.51.

Similarly an acetone (20 mL) solution of $HPt(PMePh_2)_2Cl$ (0.16 g, 0.25 mmol) was treated with $AgPF_6$ (0.058 g, 0.23 mmol) for 15 min. After filtration through a medium frit, a pentane solution of 2,3-DHT (3.8 mL, 0.15 M, 0.57 mmol) was added, and the solution was stirred for 2 h. Upon workup, as described for the PPh_3 analogue, $[Pt(PMePh_2)_2(DHT{\cdot}H)]PF_6$ (IV) (0.097 g, 47%) was obtained.

X-ray Structure Determination of $[Pt(PEt_3)_2(DHT{\cdot}H)]PF_6$ (II). A colorless crystal of $[Pt(PEt_3)_2(DHT{\cdot}H)]PF_6$, formed by diffusion of Et_2O into a $CDCl_3$ solution at −20 °C, was mounted on a glass fiber in a random orientation. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement by using the setting angles of 17 reflections in the range 25° < 2θ < 32°. Important crystallographic data are summarized in Table IV.

A total of 6089 reflections were collected in the $+h,+k,\pm l$ quadrant, of which 5421 were unique and not systematically absent. Three representative reflections measured every 60 min indicated a total loss in intensity of 18.1%. A decay correction was therefore applied to the data.

Lorentz and polarization corrections were applied to the data. Intensities of equivalent reflections were averaged. The agreement factors for the averaging of 847 observed reflections were 1.7% based on intensity and 1.4% based on F_0.

The positions of the two independent Pt cations in a unit cell were given by direct methods.[13a] Following isotropic refinement of the Pt atoms, the P and S atoms in the coordination sphere were placed based on a difference Fourier map. The two Pt complexes are very similar in internal structure, but an analysis of the molecular packing indicated that they are in different environments with respect to the PF_6^- groups, and so indeed are crystallographically distinct. While one of the PF_6^- ions behaved normally, the second could not be successfully refined as the expected seven-atom model. Peaks in the difference Fourier

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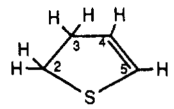
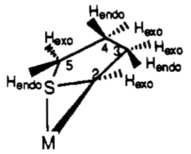
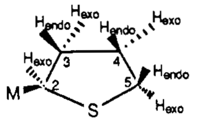
Table II. ^{1}H NMR Data for the Complexes in $CDCl_3$

	hydrothiophene ligand resonances	other resonances
2,3-DHT[a]	3.22 (t, 2 H, H2), 2.74 (tt, 2 H, H3), 5.63 (dt, 1 H, H4), 6.16 (dt, 1 H, H5)	
I	3.66 (m, 2 H, H2[a]), 3.08 (m, 2 H, H3), 6.14 (m, 1 H, H4), 6.27 (m, 1 H, H5)	1.93 [m, 12 H, $P(CH_2CH_3)_3$], 1.14 [m, 18 H, $P(CH_2CH_3)_3$], −13.32 (9 lines, 1 H, Pt−*H*)[b]
II	3.70 (m, 1 H, H2[c]), 3.32 (m, 1 H, $H5_{exo}$), 3.18 (m, 1 H, $H5_{endo}$), 2.82 (m, 1 H, $H3_{endo}$), 2.79 (m, 1 H, $H3_{exo}$), 2.00 (m, 1 H, $H4_{exo}$), 1.74 (m, 1 H, $H4_{endo}$)	1.96 [m, 12 H, $P(CH_2CH_3)_3$], 1.10 [m, 18 H, $P(CH_2CH_3)_3$]
III[d]	3.74 (m, 1 H, H2[c]), 2.83 (m, 1 H, $H5_{exo}$), 2.56 (m, 1 H, $H3_{endo}$), 2.19 (m, 1 H, $H3_{exo}$), 1.83 (m, 2 H, $H5_{endo}$ and $H4_{exo}$), 1.53 (m, 1 H, $H4_{endo}$)	7.32 (m, 15 H, PPh_3)
Va[e]	3.35 (dd,[f] 1 H, H2[g]), 2.66 (m, 2 H, $H5_{exoandendo}$), 2.54 (m, 1 H, $H3_{exo}$), 1.86 (m, 1 H, $H4_{exo}$), 1.70 (m, 1 H, $H3_{endo}$), 1.38 (m, 1 H, $H4_{endo}$)	4.76 (s, 5 H, Cp)
Vb[e]	3.47 (dd,[h] 1H, H2[g]), 2.68 (m, 2 H, $H5_{exoandendo}$), 2.59 (m, 1 H, $H3_{exo}$), 1.90 (m, 1 H, $H4_{exo}$), 1.74 (m, 1 H, $H3_{endo}$), 1.35 (m, 1 H, $H4_{endo}$)	4.76 (s, 5 H, Cp)
VI[e]	3.47 (dd[i], 1 H, H2[g]), 2.71 (m, 2 H, $H5_{exoandendo}$), 2.41 (m, 1 H, $H3_{exo}$), 1.97 (m, 1 H, $H4_{exo}$), 1.60 (m, 1 H, $H3_{endo}$), 1.41 (m, 1 H, $H4_{endo}$)	4.72 (s, 5 H, Cp)
VII	1.7–3.6[j]	5.17, 5.09 (10:6, Cp), 2.54, 2.79 (10:6, Me)
VIIIa[e]	3.56 (d[k], 1 H, H2[c]), 2.49 (dd[l], 1 H, $H5_{endo}$), 1.95 (m, 2 H, $H3_{endo}$ and $H5_{exo}$), 1.56 (m, 1 H, $H3_{exo}$), 1.32 (m, 1 H, $H4_{exo}$), 0.97 (m, 1 H, $H4_{endo}$)	4.73 (s, 5 H, Cp)
VIIIb[e]	3.67 (d[m], 1 H, H2[c]), 2.46 (dd[n], 1 H, $H5_{endo}$), 1.87 (m, 2 H, $H3_{endo}$ and $H5_{exo}$), 1.64 (m, 1 H, $H3_{exo}$), 1.24 (m, br, 1 H, $H4_{exo}$), 0.87 (m, 1 H, $H4_{endo}$)	4.73 (s, 5 H, Cp)
IX[o]	3.16 (m, 4 H), 3.08 (m, 4 H)	5.32 (s, 5 H, Cp)
X	3.18 (m, 1 H, H2[p]), 2.98 (m, 1 H, $H5_{exo}$), 2.82 (m, 1 H, $H5_{endo}$), 2.51 (m, 2 H, $H3_{endo}$ and $H4_{endo}$), 2.34 (m, 1 H, $H3_{exo}$), 1.89 (m, 1 H, $H4_{exo}$)	7.49 (m, 15 H, PPh_3), −16.50[q] (s, br, 1 H, Os−*H*)
XI[e,r]	3.00 (m, 1 H, H2[p]), 2.68 (m, 1 H, $H5_{exo}$), 2.46 (m, 1 H, $H5_{endo}$), 2.33 (m, 2 H, $H3_{endo}$ and $H4_{endo}$), 1.92 (m, 1 H, $H3_{exo}$), 1.77 (m, 1 H, $H4_{exo}$)	−16.56 (s, 1 H, Os−*H*)

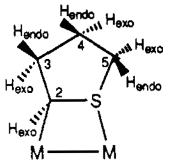
[a] 

[b] J_{PH} = 14.4 Hz, J_{PtH} = 1242 Hz. [c] 

[d] Assignment made by comparison with II. [e] In C_6D_6.

[f] J = 4.5 Hz, J = 11.8 Hz. [g] 

[h] J = 4.8 Hz, J = 11.6 Hz. [i] J = 4.6 Hz, J = 10.9 Hz. [j] Two isomers of VII are apparent from the Cp and Me signals. The signals corresponding to the methylene protons, however, are indistinguishable. [k] J = 5.6 Hz.

[l] J = 12.9 Hz, J = 6.3 Hz. [m] J = 5.9 Hz. [n] J = 13.5 Hz, J = 6.3 Hz. [o] In CD_2Cl_2. [p] 

[q] Observed as two doublets at −54 °C; δ −16.48 (J_{PH} = 2.6 Hz), −16.52 (J_{PH} = 2.6 Hz). [r] By comparison to X.

Table III. Mass Spectra of the Complexes

I[a]	518 (M^+), 489 (M^+ − Et), 431 [M^+ − (DHT + H), base peak], 399 [M^+ − (PEt_3 + H)], 313 ($PtPEt_3^+$)
II[a]	518 (M^+, base peak), 489 (M^+ − Et), 431 [M^+ − (DHT + H)], 399 [M^+ − (PEt_3 + H)], 313 ($PtPEt_3^+$)
III[a]	806 (M^+, base peak), 719 [M^+ − (DHT + H)], 457 [M^+ − (DHT + H + PPh_3)]
IV[a]	682 (M^+, base peak), 595 [M − (DHT + H)], 481 [M^+ − ($PMePh_2$ + H)], 395 ($PtPMePh_2^+$)
Vb	306 (M^+ − CO), 278 (M^+ − 2CO), 248 [M^+ − (2CO + 2H)], 220 [M^+ − (3CO + 2H)], 87 (DHT·H^+, base peak)
VI	236 (M^+ − CO), 208 (M^+ − 2CO), 121 ($CpFe^+$), 87 (DHT·H^+, base peak)
VII[a]	279 (M^+, base peak), 223 (M^+ − 2CO), 177 ($CpFe(CO)_2^+$), 102 (DHT·H·Me)
VIIIa	392 (M^+, base peak), 364 (M^+ − CO), 336 (M^+ − 2CO), 87 (DHT·H^+)
VIIIb	306 (M^+), 278 (M^+ − CO), 248 [M^+ − (2CO + 2H), base peak], 220 ($CpMo(CO)_2H^+$), 87 (DHT·H^+)
X[a]	1174 (M^+, base peak), 1146 (M^+ − CO), 1118 (M^+ − 2CO), 1090 (M^+ − 3CO)
XI	940 (M^+), 912 (M^+ − CO), 882 (M^+ − 2CO), 856 (M^+ − 3CO), 828 (M^+ − 4CO), 800 (M^+ − 5CO), 86 (DHT, base peak)

[a] By FAB.

syntheses persisted which seemed to define a second significant orientation of the PF_6 unit. A model was therefore developed in which two F_6 octahedrons were refined about the single phosphorus labeled P(6). For the two sets of F atoms [labeled F(7)–F(12) and F(7′)–F(12′)] the expected P–F and F–F distances were added to the refinement as observations. Refinement was then carried out with the further requirement that the sum of the occupancies of the two F_6 groups equal 1. These groups so constrained refined to 58.0% occupancy in the major orientation and 42.0% occupancy in the minor orientation. Hydrogen atoms were not included in the model. The atomic positional parameters are given in Table VI. The atoms Pt, S, P(1), P(2), etc. correspond to one independent cation in the unit cell, while Pt′, S′, P(1′), P(2′), etc. correspond to the other cation of II in the unit cell.

Refinement of the structure was carried out by using the SHELX76 package.[13b] Scattering factors were taken from Cromer and Waber.[14] Anomalous dispersion effects were included in F_c;[15] the values for f' and f'' were those of Cromer.[16]

Reaction of $[Pt(PEt_3)_2(DHT{\cdot}H)]PF_6$ (II) and H_2. A THF (3.0 mL) solution of II (0.050 g, 0.075 mmol) was placed in an autoclave in a glass liner under H_2. The H_2 pressure was increased to 500 psi and the autoclave heated to 150 °C. The mixture was allowed to cool to ambient temperature after 3 h. An evacuated

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Table IV. Summary of Crystal Data for $[Pt(PEt_3)_2(DHT\bullet H)]PF_6$ (II) and $HOs_3(CO)_9(PPh_3)(DHT\bullet H)$ (X)

	II	X
formula	$C_{16}H_{37}F_6P_3PtS$	$C_{31}H_{23}O_9Os_3PS$
fw	663.59	1173.16
space group	$P2_1/n$	$P2_1/c$
a, Å	8.0162 (9)	9.474 (2)
b, Å	35.246 (8)	12.752 (1)
c, Å	17.811 (4)	27.020 (3)
β, deg	90.82 (1)	91.98 (1)
V, Å^3	5032 (3)	3262 (1)
Z	8	4
d_{calcd}, g/cm^3	1.752	2.388
cryst size, mm	0.25 × 0.27 × 0.15	0.3 × 0.3 × 0.2
μ(Mo K*α*), cm^{-1}	59.46	118.4
diffractometer	Enraf-Nonius CAD4 graphite monochromator Mo K*α* (λ = 0.71073 Å)	Enraf-Nonius CAD4 graphite monochromator Mo K*α* (λ = 0.71073 Å)
orientatn reflectns, no., range (2*θ*)	17, 25–32°	25, 20–33°
temp, °C	22 ● 1	22 ± 1
scan method	*θ*–2*θ*	*θ*–2*θ*
data collectn range, 2*θ*, deg	4–45	4–50
no. of unique data, total	5421	5728
with $F_o^2 > 3\sigma(F_o^2)$	3932	4422
no. of parameters refined	482	406
trans. factors, max, min (*ψ* scans)	0.999, 0.752	0.999, 0.428
R^a	0.0480	0.0277
R_w^b	0.0685	0.0394
quality-of-fit indicator^c	2.44	1.12
largest shift/esd, final cycle	0.02	<0.01
largest peak, e/Å^3	1.03	0.97

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c}Quality-of-fit $= [(\sum w|F_o| - |F_c|)^2/(N_{obsd} - N_{parameters})]^{1/2}$.

Schlenk flask was filled with a portion of the gas phase of the reaction mixture and the GC–MS obtained. Analysis of the GC showed butane (0.023 mmol, 30%) was produced. It is also evident from the GC–MS of the solution that some butane was present in the liquid phase. A black-brown residue was generated in this reaction. The ^{1}H NMR ($CDCl_3$) and MS spectra of this residue showed that it contained Pt, PEt_3, and S. However, we were unable to determine its exact nature.

Synthesis of $Cp(CO)_3M(DHT{\cdot}H)$ (Va, M = W; Vb, M = Mo). To a stirred THF (25 mL) solution of $CpW(CO)_3^-$ prepared as described by Gladysz and co-workers[17] from $[CpW(CO)_3]_2$ (0.97 g, 1.5 mmol) and $Na(BEt_3H)$ (1.0 M in THF, 2.5 mL, 2.5 mmol), a benzene (20 mL) solution of chlorotetrahydrothiophene was added. The chlorotetrahydrothiophene was prepared by slowly adding *N*-chlorosuccinimide (NCS) (1.5 g, 11.2 mmol) (over a period of 15–30 min) to a benzene (20 mL) solution of tetrahydrothiophene (1.0 mL, 11.4 mmol) under N_2.[18] After stirring for 1 h, the succinimide generated was filtered off. The $CpW(CO)_3^-$ and chlorotetrahydrothiophene mixture was stirred for 1 h and the solvent removed in vacuo. The residue was dissolved in a minimum amount of Et_2O and transferred onto a column of alumina (1 × 10 cm). Elution with hexanes led to the isolation of Va from the first yellow band. Removal of solvent from the yellow solution yielded Va (0.69 g, 55%) as a yellow oil. The elemental analysis of Va was not obtained because it was air and thermally unstable.

The Mo analogue of Va, Vb, was prepared in a similar fashion starting with $[CpMo(CO)_3]_2$ (0.50 g, 1.0 mmol) in THF (30 mL), $Na(BEt_3H)$ (1.0 M in THF, 2.5 mL, 2.5 mmol), and a benzene (10 mL) solution of chlorotetrahydrothiophene prepared from THT (0.12 mL, 1.4 mmol) and NCS (0.15 g, 1.12 mmol). Compound Vb (0.20 g, 30%) was isolated as a yellow oil upon workup as described in the synthesis of the W analogue. Because of the instability of Vb, its elemental analysis was not obtained.

Synthesis of $CpFe(CO)_2(DHT{\cdot}H)$ (VI). To a stirred THF (40 mL) solution of $CpFe(CO)_2^-$ prepared from $[CpFe(CO)_2]_2$[19] (1.4 g, 3.8 mmol) using sodium amalgam generated from sodium metal (0.32 g, 14 mmol) and 8 mL of Hg was added a benzene (10 mL) solution of chlorotetrahydrothiophene synthesized as described in the preceding procedure from THT (1.0 mL, 11 mmol) and NCS (1.6 g, 11 mmol). The mixture was stirred for 1 h and the volume of the solvent reduced to 2 mL in vacuo. Diethyl ether (5 mL) was added to the mixture and the slurry transferred on to a column of alumina (2.5 × 12 cm). Elution with hexanes led to the isolation of VI (0.60 g, 29%) as a yellow-brown oil. Because of the instability of VI, its elemental analysis was not obtained. Some $[CpFe(CO)_2]_2$ (0.50 g, 37%) was recovered on elution with Et_2O. ^{13}C NMR (C_6D_6) of VI: δ 217.26 and 216.68 (CO); 85.78 (Cp); 45.88, 33.78, 31.71, and 29.98 (DHT·H).

Reaction of $CpFe(CO)_2(DHT{\cdot}H)$ (VI) with $[Me_3O]BF_4$. A CH_2Cl_2 (20 mL) solution of VI (0.093 g, 0.35 mmol) was treated with $[Me_3O]BF_4$ (0.072 g, 0.49 mmol). The mixture was stirred for 1 h, KPF_6 (~1.0 g) added, and stirring continued for 30 min. Addition of excess Et_2O (~80 mL) led to the precipitation of a yellow solid. After filtration, the residue was washed with several portions of Et_2O and then extracted with CH_2Cl_2 (20 mL). The CH_2Cl_2 extract was layered with hexanes (100 mL) and stored at −20 °C for 3 days. The air-stable yellow solid $[CpFe(CO)_2(DHT{\cdot}H{\cdot}Me)]PF_6$ (VII) (0.097 g, 65%) was filtered off and dried in vacuo. Anal. Calcd for $C_{12}H_{15}F_6FeO_2PS$: C, 33.99; H, 3.57; S, 7.55. Found: C, 33.99; H, 3.93; S, 7.97.

Synthesis of $Cp(CO)_2M(\eta^2\text{-}DHT{\cdot}H)$ (VIIIa, M = W; VIIIb, M = Mo). A hexanes (30 mL) solution of Va (0.16 g, 0.38 mmol) was placed in a quartz tube equipped with a water-cooled probe and purged with N_2. The solution was irradiated with a 254-nm light for 90 min. The mixture was then transferred onto a column of alumina (1 × 10 cm). A yellow band containing unreacted Va was first eluted with hexanes. Elution with hexanes/Et_2O (8:2) gave pure VIIIa, as the second yellow band. Slow removal of the solvent in vacuo yielded an air-stable yellow crystalline solid, VIIIa (0.11 g, 75%). ^{13}C NMR (C_6D_6): δ 237.78 and 233.70 (CO); 90.44 (Cp); 35.94, 35.30, 34.59, and 32.52 (DHT·H). Anal. Calcd for $C_{11}H_{12}O_2SW$: C, 33.70; H, 3.08; S, 8.16. Found: C, 33.62; H, 2.95; S, 8.33.

The Mo analogue VIIIb was prepared similarly starting with Vb (0.10 g, 0.30 mmol). Chromatographic purification on a column of alumina (1 × 15 cm) eluting with hexanes/Et_2O (5:1) led to the isolation of VIIIb as the first yellow band which yielded 0.020 g (22%) of VIIIb as a yellow solid when the solvent was removed in vacuo.

Attempts to prepare $Cp(CO)Fe(\eta^2\text{-}DHT{\cdot}H)$ by photolysis of VI were unsuccessful.

Reaction of $CpW(CO)_2(\eta^2\text{-}DHT{\cdot}H)$ (VIIIa) with HCl. Hydrogen chloride gas (3.5 mL, 0.18 mmol) was syringed into a stirred CH_2Cl_2 (20 mL) solution of VIIIa (0.048 g, 0.12 mmol). An instant color change from yellow to red was observed which signified the formation of the unstable compound $CpW(CO)_2(THT)Cl$ (IX) (IR and ^{1}H NMR are given in Tables I and II, respectively). The reaction mixture was immediately treated with PPh_3 (0.033 g, 0.13 mmol), and stirring was continued for 15 min. After removal of solvent, the residue was extracted with $CHCl_3$. Removal of the solvent from $CHCl_3$ extract under vacuum led to the isolation of $CpW(CO)_2(PPh_3)Cl$[20] (0.060 g, 81%), which was identified by comparing its IR and ^{1}H NMR with those reported in the literature. Free tetrahydrothiophene [^{1}H NMR (CD_2Cl_2): δ 2.78 (m, 4 H), 1.91 (m, 4 H)] was also generated in this reaction.

Reaction of $H_2Os_3(CO)_9L$ (L = CO, PPh_3) with 2,3-DHT. To a stirred hexane (50 mL) slurry of $H_2Os_3(CO)_9(PPh_3)$ (0.25 g, 0.23 mmol) was added a 0.22 M solution of 2,3-DHT[4] in pentane (7.5 mL, 1.6 mmol). The mixture was stirred continuously for

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7 days after which it was transferred onto a column of silica gel (1.0 × 12 cm). The long reaction time was presumably due in part to the fact that $H_2Os_3(CO)_9(PPh_3)$ is only sparingly soluble in hexanes. Elution with hexanes resulted in the removal of a small amount of unreacted $H_2Os_3(CO)_9(PPh_3)$. Addition of hexane/Et_2O (1:1) to the column resulted in the elution of a yellow band. The solvent was removed in vacuo and the residue redissolved in a minimum amount of hexanes and stored at −20 °C for 3 days. Extremely stable gold cubelike crystals of $HOs_3(CO)_9(PPh_3)(DHT{\cdot}H)$ (X) (0.21 g, 78%) were obtained. Anal. Calcd for $C_{31}H_{23}O_9Os_3PS$: C, 31.76; H, 1.98. Found: C, 31.85; H, 1.92.

The analogous reaction of $H_2Os_3(CO)_{10}$ (0.071 g, 0.083 mmol) with 0.36 M 2,3-DHT[4] (4.4 mL, 1.6 mmol in pentane) in hexane (20 mL) for 40 h resulted in the formation of $HOs_3(CO)_{10}(DHT{\cdot}H)$ (XI) (0.051 g, 72%) as an air-stable yellow powder which was only sparingly soluble in common organic solvents such as hexanes, THF, toluene, CH_2Cl_2, DMSO, $(CH_3)_2C{=}O$, and CH_3CN. Anal. Calcd for $C_{14}H_8O_{10}Os_3S$: C, 17.91; H, 0.86. Found: C, 17.85; H, 1.09.

X-ray Structure Determination of $HOs_3(CO)_9(PPh_3)(DHT{\cdot}H)$ (X). A yellow crystal of $HOs_3(CO)_9(PPh_3)(DHT{\cdot}H)$ was mounted on a glass fiber in a random orientation. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement using setting angles of 25 reflections in the range $20° < 2\theta < 33°$. A total of 6298 reflections were collected in the $+h,+k,\pm l$ quadrant of which 5728 were unique and not systematically absent. No decay correction was applied.

Lorentz and polarization corrections were applied to the data. An empirical absorption correction based on a series of ψ-scans of five reflections and their Friedel mates was applied to the data. Additional crystallographic data appear in Table IV.

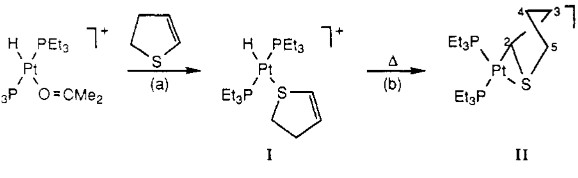
The positions of the three Os atoms were given by the direct method. Following isotropic refinement of the Os atoms, the P and S atoms in the coordination sphere were placed on the basis of a difference Fourier map. The remainder of the non-hydrogen atoms were then located via subsequent cycles of least-squares refinement followed by difference Fourier maps. The positions of the hydrogen atoms were calculated for the PPh_3 and hydrothiophene (DHT·H) and were used to calculate structure factors only.

The largest peak in the final difference Fourier had a height of 0.97 e/Å^3. This peak was 2.0530 from Os(2) and 1.9120 from Os(3) (Figure 2). The Os(2)–Os(3) distance of 3.0178 (5) Å was the longest Os–Os distance in the molecule. While attempts to refine this peak as a hydride led to lower R and R_w values, the isotropic thermal parameter associated with this peak was negative. This peak was therefore excluded from the final model for X.

Procedures for structure solution were the same as described for II.[13-16]

Results and Discussion

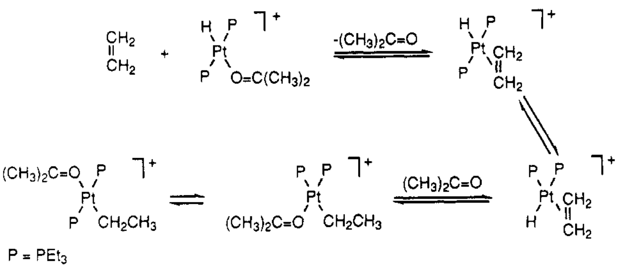
Reaction of $HPt(acetone)(PEt_3)_2^+$ and 2,3-DHT. The reaction of *trans*-$HPt(acetone)(PEt_3)_2^+$ and 2,3-DHT leads to the formation of the sulfur-coordinated *trans*-$HPt(2,3\text{-}DHT)(PEt_3)_2^+$ (I) which is isolated as a colorless crystalline solid (eq 2, step a). Compound I is characterized by its mass and ^1H NMR spectra as well as elemental analysis. The FAB mass spectrum of I shows an m/e value of 518 (M^+) which represents $HPt(2,3\text{-}DHT)(PEt_3)_2^+$. The hydride of I is observed at −13.32 ppm as a triplet with coupling constants of $J_{PtH} = 1242$ Hz and $J_{PH} = 14.4$ Hz. The olefin signals of the 2,3-DHT in compound I (Table II) are shifted downfield with respect to that of the free ligand [δ 6.16 (H5), 5.63 (H4), 2.74 (H3), 3.22 (H2)]. In coordinated olefin complexes, there is an upfield shift of the olefin signals with respect to the free ligand as illustrated in compound B;[21] in free styrene (A), protons H_A, H_B, and H_C occur at δ 6.71, 5.27, and 5.82, respectively, as compared with (δ 4.77, 4.50), (δ 4.84, 5.70), and δ 4.48 for the same protons in B. Such upfield shifts upon coordination of olefins have been well documented in the literature.[22] The downfield shift observed for the olefin signals in I therefore suggests that the 2,3-DHT is coordinated through the sulfur. Similar downfield shifts have been observed in previously reported sulfur-coordinated 2,3-DHT complexes: *trans*-$PdCl_2(2,3\text{-}DHT)_2$,[4a] $Ru(CO)_3Cl_2(2,3\text{-}DHT)$,[4a] $[Re(CO)_5(2,3\text{-}DHT)]^+$,[4a] $W(CO)_5(2,3\text{-}DHT)$,[4a] and $Cr(CO)_5(2,3\text{-}DHT)$.[23]

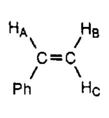


(2)

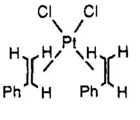
I II

Scheme I





A



B

Compound I slowly rearranges to II (eq 2, step b) by migration of the terminal hydride ligand to the β-olefin carbon with the formation of a Pt–C σ-bond. Compound II was isolated as a pale yellow crystalline solid and characterized by its FAB mass spectrum, ^1H and ^{13}C NMR, and an X-ray structural study (see below). This rearrangement occurs both in solution and in the solid state at ambient temperature over a period of 30 and 90 days, respectively. A relatively fast (7 days) rearrangement is observed at 60 °C in $CDCl_3$ solution.

Similar reactions of $HPt(acetone)(PMePh_2)_2^+$ and $HPt(acetone)(PPh_3)_2^+$ result in the direct formation of the DHT·H inserted products analogous to II with no ^1H NMR evidence for S-coordinated 2,3-DHT intermediates. A similar effect of phosphine ligands is observed for ethylene insertion into the Pt–H bond in $HPt(C_2H_4)(PMePh_2)_2^+$, which is much faster than the analogous reaction of $HPt(C_2H_4)(PEt_3)_2^+$.[12,24]

The mechanism of reaction 2 is probably related to that of other olefin insertions into Pt–H bonds. Clark and co-workers[24] reported that $HPt(acetone)(PMePh_2)_2^+$ rapidly coordinates ethylene at −50 °C to give a square-planar hydrido olefin complex (eq 3). The same reaction carried out at room temperature results in facile insertion of ethylene into the Pt–H bond to give, after halide

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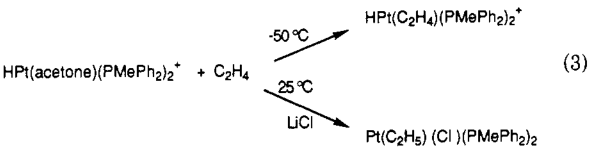


$$\mathrm{HPt(acetone)(PMePh_2)_2^+ + C_2H_4 \xrightarrow{-50\,°C} HPt(C_2H_4)(PMePh_2)_2^+}$$
$$\mathrm{HPt(acetone)(PMePh_2)_2^+ + C_2H_4 \xrightarrow[LiCl]{25\,°C} Pt(C_2H_5)(Cl)(PMePh_2)_2} \qquad (3)$$

quenching, the alkyl product *trans*-Pt(C_2H_5)X($PMePh_2$)$_2$. A mechanistic scheme (Scheme I) involving reversible ethylene substitution and a slower rate-determining insertion step was suggested on the basis of kinetic studies carried out with *trans*-HPt(acetone)(PEt_3)$_2^+$.[12] It was noted by these authors that the kinetic studies could not distinguish between insertion from a rearranged four-coordinate intermediate and an insertion which is essentially associative in nature proceeding from a five-coordinate solvent-containing complex.

In light of the above results, it is reasonable to envisage the insertion of 2,3-DHT into *trans*-HPt(acetone)(PR_3)$_2^+$ as occurring via a similar mechanism (Scheme II). The initial coordination of 2,3-DHT via the S is supported by the isolation of *trans*-HPt(2,3-DHT)(PEt_3)$_2^+$ (I) in good yield (83%). Subsequent rearrangement of I to give the olefin-inserted product Pt(PEt_3)$_2$(DHT·H)$^+$ (II) has been monitored by ^{1}H NMR spectrometry in the hydride region at 60 °C. The spectrum obtained 30 min after a $CDCl_3$ solution of I was warmed to 60 °C shows the growth of a new hydride peak at −4.73 ppm. A steady-state concentration of this hydride is observed in the spectrum recorded 5 h later. This signal, which is assigned to the hydride in C, is a 9-line pattern ($J_{\mathrm{Pt-H}}$ = 954 Hz, $J_{\mathrm{P_{cis}-H}}$ = 13.4 Hz). There is no coupling between the hydride and the olefin protons presumably because their dihedral angle approaches 90°. A new set of hydride signals becomes apparent in the spectrum obtained within 90 min after heating the $CDCl_3$ solution to 60 °C. This 18-line pattern ($J_{\mathrm{Pt-H}}$ = 792 Hz, $J_{\mathrm{P_{trans}-H}}$ = 158 Hz, J_{HH} = 16.3 Hz due to coupling with the olefinic protons) at −6.29 ppm corresponds to D (Scheme II), and like the hydride signal observed at −4.73 ppm, reaches a steady-state concentration in the spectrum recorded 5 h later. A cis phosphorus hydride coupling is not observed, presumably because it is small. It is also worth noting that examples of Pt$^{\mathrm{II}}$ (e.g., {HPt($AsEt_3$)$_2$[P(OMe)$_3$]}ClO_4, $J_{\mathrm{P_{cis}-H}}$ = <2 Hz) have been reported where the cis phosphorus–hydride coupling constants are extremely small.[25,26] The stationary state of C and D persists for 2–3 days as the starting hydride signals slowly disappear and II forms by slow transfer of the H ligand to the β-olefin carbon with concomitant Pt–C and Pt–S bond formation. At the end of the reaction, C and D disappear. Thus, the NMR spectra are consistent with the mechanism in Scheme II but do not prove it.

Structure of [Pt(PEt_3)$_2$(DHT·H)]PF_6 (II). A perspective view of one of the cations from II showing the numbering scheme and thermal ellipsoids is given in Figure 1. Selected angles and distances are listed in Table V.

Scheme II

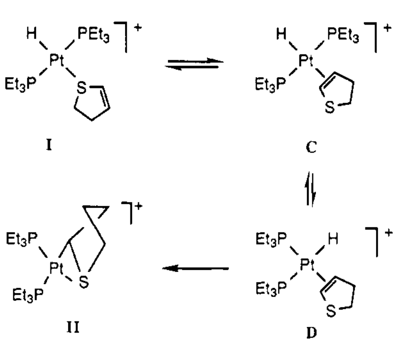


Table V. Selected Bond Distances (Å) and Angles (deg) for [Pt(PEt_3)$_2$(DHT • H)]PF_6 (II)

	Bond Distances (Å)		
Pt–S	2.328 (6)[a]	S–C(2)	1.78 (2)
Pt–P(1)	2.242 (5)	C(5)–C(4)	1.52 (3)
Pt–P(2)	2.306 (4)	C(4)–C(3)	1.59 (3)
Pt–C(2)	2.12 (1)	C(3)–C(2)	1.53 (3)
S–C(5)	1.83 (2)		
Pt′–S′	2.319 (6)	S′–C(2′)	1.78 (2)
Pt′–P(1′)	2.242 (5)	C(5′)–C(4′)	1.55 (3)
Pt′–P(2′)	2.304 (4)	C(4′)–C(3′)	1.55 (3)
Pt′–C(2′)	2.16 (2)	C(3′)–C(2′)	1.55 (3)
S′–C(5′)	1.83 (2)		
	Bond Angles (deg)		
S–Pt–P(2)	107.9 (1)	Pt–S–C(2)	60.6 (6)
S–Pt–C(2)	46.7 (4)	Pt–C(2)–S	72.7 (5)
P(1)–Pt–P(2)	101.8 (2)	Pt–C(2)–C(3)	117.0 (1)
P(1)–Pt–C(2)	103.5 (5)	Pt–S–C(5)	104.8 (7)
C(2)–S–C(5)	95.7 (8)	S–C(2)–C(3)	109 (1)
S–C(5)–C(4)	105 (1)	C(2)–C(3)–C(4)	105 (1)
C(5)–C(4)–C(3)	106 (2)		
S′–Pt′–P(2′)	108.9 (2)	Pt′–S′–C(2′)	62.1 (6)
S′–Pt′–C(2′)	46.7 (5)	Pt′–C(2′)–S′	71.2 (6)
P(1′)–Pt′–P(2′)	102.6 (1)	Pt′–C(2′)–C(3′)	114 (1)
P(1′)–Pt′–C(2′)	101.7 (5)	Pt′–S′–C(5′)	106.3 (8)
C(2′)–S′–C(5′)	97 (1)	S′–C(2′)–C(3′)	108 (1)
S′–C(5′)–C(4′)	104 (1)	C(2′)–C(3′)–C(4′)	107 (2)
C(5′)–C(4′)–C(3′)	109 (2)		

[a] The numbers in parentheses are estimated standard deviations.

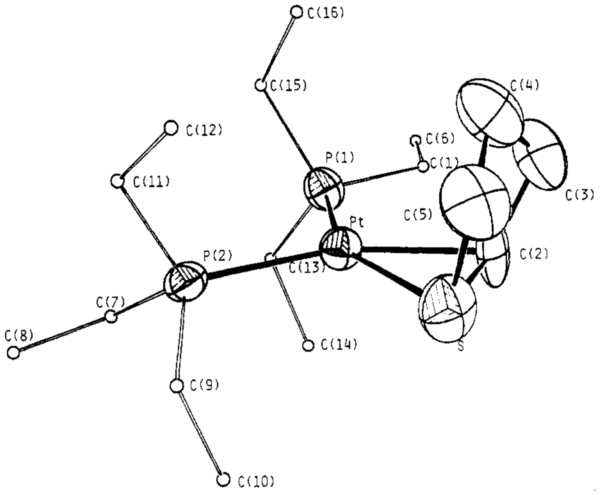
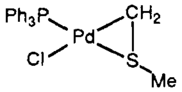


Figure 1. An ORTEP drawing of the [Pt(PEt_3)$_2$(DHT-H)]$^+$ cation in II showing the numbering scheme.

There are two independent cationic Pt complexes and two PF_6^- anions in a unit cell. The bond angles and distances for both cations are, however, the same within experimental error; the discussion is therefore limited to one of the cations. The core atoms of the cation in II, Pt, S, C(2), P(1), and P(2) lie in a plane. The angle between this plane and that defined by S, C(2), C(3), and C(5) is 107.3 (6)°. The Pt–S distance of 2.328 (6) Å is similar to Pt–S distances found in the following compounds: the α and β isomers of [(Pr_3P)ClPt(μ-SCN)$_2$PtCl(PPr_3)][27] (2.327 and 2.408 Å, respectively) as well as the Pd–S distance of 2.371 (1) Å in E.[28] The Pt–C bond distance of 2.12 (1) Å is



E

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Table VI. Positional Parameters and Their Estimated Standard Deviations for $[Pt(PEt_3)_2(DHT{\bullet}H)]PF_6$ (II)[a]

atom	*x*	*y*	*z*	*B*,[b] Å^2
Pt	0.67560 (9)	0.20692 (2)	0.23616 (3)	3.36 (2)
S	0.5140 (7)	0.2575 (2)	0.2772 (3)	6.1 (2)
P(1)	0.7976 (7)	0.1507 (1)	0.2578 (3)	4.5 (1)
P(2)	0.7265 (6)	0.2159 (1)	0.1103 (2)	3.7 (1)
C(1)	0.793 (3)	0.1363 (5)	0.357 (1)	6.0 (6)
C(2)	0.572 (2)	0.2212 (5)	0.3416 (7)	3.8 (5)
C(3)	0.691 (3)	0.2381 (7)	0.401 (1)	7.2 (7)
C(4)	0.793 (3)	0.2697 (6)	0.357 (1)	7.3 (7)
C(5)	0.665 (3)	0.2925 (5)	0.312 (1)	6.5 (6)
C(6)	0.855 (3)	0.0960 (6)	0.375 (2)	9.5 (9)
C(7)	0.710 (2)	0.1738 (5)	0.0477 (9)	5.2 (5)
C(8)	0.734 (3)	0.1845 (7)	−0.038 (1)	7.6 (7)
C(9)	0.576 (3)	0.2489 (5)	0.070 (1)	4.6 (5)
C(10)	0.398 (3)	0.2336 (6)	0.079 (1)	6.4 (7)
C(11)	0.925 (2)	0.2372 (6)	0.088 (1)	6.7 (7)
C(12)	0.969 (3)	0.2710 (6)	0.144 (1)	7.4 (7)
C(13)	0.685 (3)	0.1098 (5)	0.208 (1)	6.4 (7)
C(14)	0.505 (3)	0.1115 (6)	0.223 (1)	8.2 (8)
C(15)	1.016 (2)	0.1473 (6)	0.229 (1)	5.6 (6)
C(16)	1.122 (3)	0.1791 (7)	0.265 (1)	8.4 (8)
Pt′	−0.29645 (9)	0.04237 (2)	0.71497 (4)	3.66 (2)
S′	−0.4570 (8)	−0.0046 (2)	0.6582 (3)	7.0 (2)
P(2′)	−0.2650 (6)	0.0284 (1)	0.8407 (2)	3.7 (1)
P(1′)	−0.1688 (7)	0.0988 (1)	0.7056 (2)	4.1 (1)
C(7′)	−0.272 (3)	0.0662 (6)	0.910 (1)	6.5 (6)
C(8′)	−0.278 (3)	0.0541 (6)	0.992 (1)	7.3 (7)
C(11′)	−0.073 (3)	0.0036 (6)	0.864 (1)	6.7 (7)
C(12′)	−0.036 (3)	−0.0287 (6)	0.813 (2)	9.2 (9)
C(9′)	−0.430 (3)	−0.0048 (6)	0.870 (1)	6.5 (7)
C(10′)	−0.605 (3)	0.0130 (7)	0.860 (1)	7.8 (8)
C(15′)	0.059 (2)	0.0978 (6)	0.730 (1)	5.5 (6)
C(16′)	0.147 (3)	0.0668 (7)	0.685 (1)	7.4 (8)
C(13′)	−0.254 (3)	0.1362 (5)	0.767 (1)	6.2 (7)
C(14′)	−0.442 (3)	0.1387 (6)	0.760 (1)	7.9 (8)
C(1′)	−0.183 (2)	0.1192 (5)	0.6132 (9)	5.3 (5)
C(6′)	−0.116 (3)	0.1588 (6)	0.603 (1)	7.6 (7)
C(5′)	−0.311 (3)	−0.0398 (6)	0.623 (1)	8.0 (8)
C(4′)	−0.175 (3)	−0.0157 (6)	0.584 (1)	7.7 (8)
C(3′)	−0.259 (3)	0.0192 (6)	0.546 (1)	7.3 (7)
C(2′)	−0.390 (3)	0.0341 (5)	0.6016 (9)	6.1 (6)
P(5)	0.3314 (8)	0.1387 (2)	0.4920 (3)	5.5 (2)
P(6)	0.2073 (8)	0.1161 (2)	−0.0100 (3)	6.2 (2)
F(1)	0.323 (2)	0.1437 (4)	0.5789 (6)	11.5 (5)
F(2)	0.347 (2)	0.1330 (3)	0.4055 (5)	8.5 (4)
F(3)	0.487 (2)	0.1662 (4)	0.4927 (8)	12.5 (6)
F(4)	0.217 (2)	0.1733 (4)	0.4816 (8)	12.5 (6)
F(5)	0.457 (2)	0.1042 (4)	0.5013 (8)	11.5 (5)
F(6)	0.182 (2)	0.1110 (4)	0.4947 (7)	10.2 (5)
F(7)	0.052 (2)	0.1132 (7)	0.044 (1)	8.4 (8)*
F(8)	0.329 (4)	0.115 (1)	0.060 (2)	18.0 (1)*
F(9)	0.357 (3)	0.1156 (9)	−0.063 (2)	14.0 (1)*
F(10)	0.086 (3)	0.1205 (8)	−0.082 (1)	10.7 (9)*
F(11)	0.201 (3)	0.0713 (6)	−0.014 (2)	11.5 (9)*
F(12)	0.198 (3)	0.1613 (6)	−0.002 (2)	11.0 (1)*
F(7′)	0.353 (4)	0.0889 (9)	0.017 (2)	12.0 (1)*
F(8′)	0.178 (4)	0.087 (1)	−0.076 (2)	12.0 (1)*
F(9′)	0.067 (4)	0.142 (1)	−0.050 (2)	14.0 (2)*
F(10′)	0.235 (4)	0.143 (1)	0.059 (2)	12.0 (1)*
F(11′)	0.078 (5)	0.094 (1)	0.040 (2)	21.0 (3)*
F(12′)	0.347 (4)	0.1405 (9)	−0.050 (2)	10.0 (1)*

[a] Parameters with an asterisk were refined isotropically. [b] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

comparable to the bond distances found in the following compounds: Pd–C in E [2.042 (6) Å] and *cis*-$\{(Ph_3P)_2Pt[(NC)_2C{=}C(CN)_2]\}$ (2.11 Å),[29] which has a metallacyclopropane geometry. Of the Pt–P bond distances in II, the longer (2.306 (4) Å) is trans to the carbon; it is similar to the Pt–P distance in *cis*-$\{(Ph_3P)_2Pt[(NC)_2C{=}C(CN)_2]\}$ (2.29 Å).[29] The short Pt–P distance (2.242 (5) Å) is comparable to the Pd–P bond distance (2.267 (1) Å) in E.[28] The longer Pt–P(2) is a result of the stronger trans influence of C(2) than S.[30,31] The S–C(2) bond (1.78 (2) Å) is a relatively short S–C(alkyl) distance (range 1.80–1.84 Å)[32] but is not nearly as short as the C=S double bond (1.618 (8) Å) in the thioacetone ligand of $W(CO)_5(S{=}CMe_2)$.[33] The S–C bond length in E [1.756 (6) Å][28] is also slightly shorter than a S–C(alkyl) distance. Kasai and co-workers[28] argue that the S–C bond in E is a single bond which may have partial double-bond character. In light of the similarity between the interaction of the η^2-CH_2SMe ligand with the Pd metal center in E and the η^2-DHT·H ligand with Pt in II, it is reasonable to suggest there may be some double-bond character in the S–C bond in II, albeit small. The Pt–S–C(2) bond angle [60.6 (6)°] in II is comparable to the 57.0 (2)° observed for Pd–S–C in E. Other angles in the DHT·H ligand are given in Table V. The C–C distances in the DHT·H ligand which range between 1.50 and 1.59 Å are comparable to reported[34] $C(sp^3)$–$C(sp^3)$ distances. Even though C(4) is puckered in such a way as to place one of its hydrogens above the Pt, the calculated Pt–H distance (2.85 Å) is much longer than Mo–H distances (2.27 (8) and 1.88 (8) Å) observed in molybdenum complexes in which agostic interactions have been established.[35] The metallic radius of Pt is similar to that of Mo (1.39 and 1.36 Å, respectively).[36]

Reaction of $[Pt(PEt_3)_2(DHT{\cdot}H)]PF_6$ (II) with H_2. HDS studies of 2,3-DHT show[3] that both desulfurization and THT formation occur (eq 1). These reactions may proceed via initial olefin insertion as in eq 2, followed by subsequent desulfurization or hydrogenation. That desulfurization is possible is demonstrated by the reaction of II with H_2 at 150 °C in THF over a period of 3 h to yield butane in greater than 30% yield. Although this reaction did not yield H_2S in the gaseous phase, the mass spectrum of the black oily residue generated in this reaction showed fragments which were made up of S, Pt, and PEt_3. Hardly any reaction occurred between II and H_2 at 90 °C in 5 h.

Synthesis and Reactions of $Cp(CO)_{n-1}M(DHT{\cdot}H)$. In order to explore the chemistry of complexes, other than II, containing the DHT·H ligand, we prepared compounds Va, Vb, and VI by the reaction of $Na[CpM(CO)_n]$ and C_4H_7ClS (eq 4). The yellow oils Va,b were characterized

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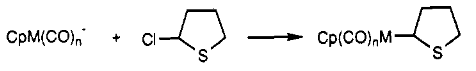
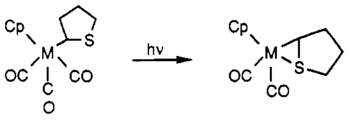


(4)

M = W; n = 3, Va
M = Mo; n = 3, Vb
M = Fe; n = 2, VI

by their mass, IR, and ^1H NMR spectra. The yellow-brown iron analogue VI was also characterized by its MS, IR, ^1H, and ^{13}C NMR spectra. Because the hydrogens on the DHT·H are all inequivalent, a complicated ^1H NMR pattern was obtained. A combination of two-dimensional NMR (COSY) and selective decoupling were employed in making proton assignments to VI (Table II). The ^1H assignments to Va and Vb were done by analogy.

Compounds VIIIa and VIIIb were obtained by photolysis of Va and Vb, respectively. Compound VIIIa was isolated as a yellow crystalline solid in 75% yield whereas the less stable Mo analogue VIIIb was obtained in 22% yield. These complexes presumably have a structure similar to that of the oxygen analogue (η^5-C_5H_4Me)-$(CO)_2Mo[CH(CH_2)_3O]$, which was characterized by X-ray diffraction.[37] The metallathiacyclopropane (VIIIa) was characterized by its MS, IR, ^1H, and ^{13}C NMR spectra as well as by elemental analysis. A combination of two-dimensional NMR (COSY) and selective decoupling experiments were employed in making the ^1H assignments (Table II) to the complicated spectrum of the DHT·H ligand. Proton assignments in VIIIb were done by analogy. Attempts to form CpFe(CO)(η^2-DHT·H) by photolysis of $CpFe(CO)_2$(DHT·H) were unsuccessful.

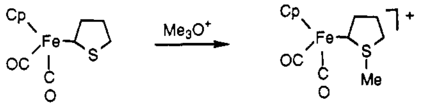


(5)

V

M = W, VIIIa
M = Mo, VIIIb

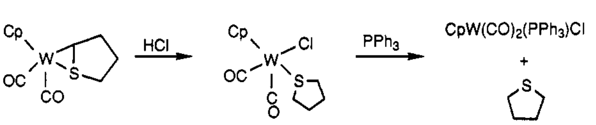
However, VI reacts with Me_3O^+ to give the corresponding alkylated product (eq 6), which was characterized by IR, MS, and ^1H NMR spectra and by elemental analysis. The ^1H NMR shows there are two isomers of VII (eq 6) which presumably result from slow inversion at the pyramidal sulfur at room temperature.



(6)

VI VII

Reaction of VIIIa with HCl leads to the formation of an unstable tetrahydrothiophene (THT) complex IX (eq 7), which was only characterized by its IR and ^1H NMR spectra. The THT is readily displaced by PPh_3 to give



(7)

VIIIa IX

$CpW(CO)_2(PPh_3)Cl$[20] and free THT which was observed by ^1H NMR. Compound VIIIa does not react with PMe_3 at ambient temperature. The Pt analogue II does not react with PPh_3 or [PPN]Cl at 25 °C.

Reaction of $H_2Os_3(CO)_9L$ (L = CO, PPh_3) with 2,3-DHT. Reaction of $H_2Os_3(CO)_9(PPh_3)$ with 2,3-DHT at ambient temperature over a period of 7 days results in the formation of $HOs_3(CO)_9(PPh_3)$(DHT·H) (X) (eq 8).

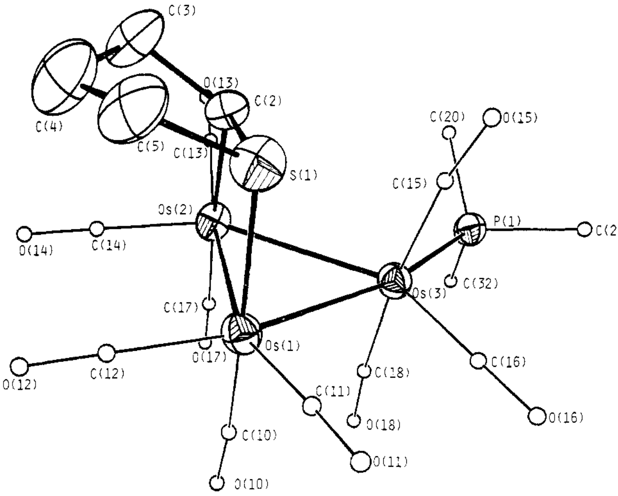
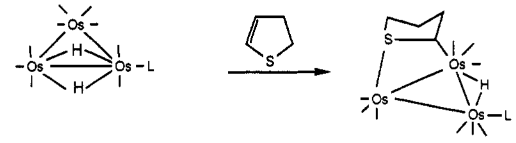


Figure 2. Molecular structure of $HOs_3(CO)_9(PPh_3)$(DHT·H) (X).



(8)

X

Compound X was obtained as a yellow crystalline solid and characterized by its IR, MS, and ^1H NMR spectra as well as by elemental analysis and X-ray structure determination. In the analogous reaction of $H_2Os_3(CO)_{10}$, the DHT·H complex is formed in only 40 h and precipitates out of hexanes as a yellow powder which is only sparingly soluble in most organic solvents. Compound $HOs_3(CO)_{10}$(DHT·H) (XI) was characterized by its IR and MS spectra and elemental analysis.

The hydride in complex X is observed as a broad signal at −16.50 ppm at ambient temperature in the ^1H NMR ($CDCl_3$) spectrum. On cooling to −53 °C it becomes two doublets which integrate to $^1/_2$ proton each which indicates equal occupancy of the bridging hydride positions on the two Os–Os bonds containing the $Os(PPh_3)$ group. Owing to the inequivalency of all the hydrogens in the DHT·H ligand, a complicated pattern is observed in the ^1H NMR spectrum; the assignments in Table II were made by a 2-D COSY experiment.

It has been reported that the reaction of $H_2Os_3(CO)_{10}$ with neat methyl vinyl ether, $MeOCH{=}CH_2$, at ambient temperature over a period of 1 week gives the 1-methoxyethyl compound $HOs_3(MeOCHMe)(CO)_{10}$, coordinated through a carbon and oxygen.[38a] The methoxyethyl cluster compound reverts to $H_2Os_3(CO)_{10}$ and methyl vinyl ether over several weeks in the absence of the ether. A similar reaction of $H_2Os_3(CO)_{10}$ and $PhSCH{=}CH_2$ over a period of 2 h gives the thioether compound $HOs_3(PhSCHMe)$-$(CO)_{10}$ in 90% yield.[38b] The reaction of 2,3-DHT and $H_2Os_3(CO)_{10}$ is considerably slower than the analogous reaction described for $PhSCH{=}CH_2$.

Structure of $HOs_3(CO)_9PPh_3$(DHT·H) (X). A perspective view of the molecule showing the thermal ellipsoids and numbering scheme is given in Figure 2. The carbons in the phenyl ring of the PPh_3 are not shown.

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Table VII. Selected Bond Distances (Å) and Angles (deg) for $HOs_3(CO)_9(PPh_3)(DHT \bullet H)$ (X)

	Bond Distances (Å)		
Os(1)–Os(2)	2.7907 (4)[a]	Os(2)–C(2)	2.215 (8)
Os(1)–Os(3)	2.8977 (4)	Os(3)–P(1)	2.373 (2)
Os(2)–Os(3)	3.0718 (5)	S(1)–C(2)	1.815 (8)
Os(1)–S(1)	2.407 (2)	S(1)–C(5)	1.82 (1)
C–C	1.52 (av)	Os–C(O)	1.88–1.94
	Bond Angles (deg)		
Os(1)–Os(2)–Os(3)	59.01 (1)[a]	Os(1)–S(1)–C(5)	112.7 (3)
Os(2)–Os(3)–Os(1)	55.65 (1)	Os(2)–C(2)–C(3)	118.8 (5)
Os(3)–Os(1)–Os(2)	65.34 (1)	S(1)–C(5)–C(4)	106.8 (7)
S(1)–Os(1)–Os(2)	76.64 (6)	C(4)–C(3)–C(2)	109.3 (8)
Os(1)–Os(2)–C(2)	78.8 (2)	Os(2)–C(2)–S(1)	106.5 (3)
Os(1)–S(1)–C(2)	97.9 (4)	Os(3)–Os(2)–C(2)	86.4 (2)

[a] See Table V for footnote.

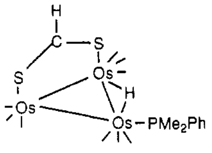
Table VIII. Positional Parameters for $HOs_3(CO)_9(PPh_3)(DHT \bullet H)$ (X)[a]

atom	*x*	*y*	*z*	*B*, Å^2
Os(1)	0.33432 (3)	0.43523 (2)	0.17478 (1)	2.582 (6)
Os(2)	0.12751 (3)	0.58784 (3)	0.15715 (1)	2.615 (6)
Os(3)	0.42534 (3)	0.61317 (2)	0.11730 (1)	2.383 (6)
S(1)	0.3661 (3)	0.5522 (2)	0.24417 (9)	3.74 (5)
P(1)	0.4423 (2)	0.7725 (2)	0.07251 (8)	2.46 (4)
O(10)	0.2464 (8)	0.3158 (5)	0.0822 (3)	5.5 (2)
O(11)	0.6222 (7)	0.3324 (6)	0.1969 (3)	6.3 (2)
O(12)	0.1633 (8)	0.2782 (6)	0.2317 (3)	7.0 (2)
O(13)	−0.053 (1)	0.7851 (6)	0.1587 (3)	8.1 (2)
O(14)	−0.0909 (8)	0.4508 (8)	0.2041 (4)	8.4 (2)
O(15)	0.5791 (9)	0.7220 (6)	0.2037 (3)	6.7 (2)
O(16)	0.7101 (7)	0.5071 (6)	0.1053 (3)	6.0 (2)
O(17)	0.0154 (8)	0.5114 (6)	0.0560 (3)	5.7 (2)
O(18)	0.3317 (8)	0.4989 (5)	0.0212 (2)	4.9 (2)
C(2)	0.2199 (8)	0.6400 (6)	0.2294 (3)	2.4 (1)
C(3)	0.127 (1)	0.6333 (8)	0.2767 (4)	4.7 (2)
C(4)	0.144 (1)	0.5266 (9)	0.3000 (4)	5.7 (3)
C(5)	0.295 (1)	0.4994 (8)	0.3008 (4)	4.7 (2)
C(10)	0.2833 (9)	0.3626 (6)	0.1156 (4)	3.6 (2)
C(11)	0.516 (1)	0.3728 (7)	0.1881 (3)	3.6 (2)
C(12)	0.229 (1)	0.3369 (7)	0.2109 (4)	4.3 (2)
C(13)	0.015 (1)	0.7142 (8)	0.1571 (3)	4.4 (2)
C(14)	−0.006 (1)	0.5023 (9)	0.1872 (4)	5.2 (3)
C(15)	0.514 (1)	0.6811 (7)	0.1743 (4)	3.9 (2)
C(16)	0.602 (1)	0.5472 (7)	0.1096 (4)	3.9 (2)
C(17)	0.0602 (9)	0.5384 (7)	0.0928 (4)	3.8 (2)
C(18)	0.3598 (9)	0.5411 (7)	0.0580 (4)	3.6 (2)
C(20)	0.3517 (9)	0.8871 (6)	0.0986 (3)	3.2 (2)
C(21)	0.328 (1)	0.8955 (7)	0.1474 (4)	5.4 (3)
C(22)	0.261 (1)	0.9815 (9)	0.1677 (4)	6.4 (3)
C(23)	0.218 (1)	1.0623 (7)	0.1352 (4)	5.1 (3)
C(24)	0.238 (1)	1.0560 (7)	0.0853 (4)	4.8 (2)
C(25)	0.305 (1)	0.9687 (7)	0.0670 (4)	3.9 (2)
C(26)	0.6239 (8)	0.8188 (6)	0.0638 (3)	2.6 (2)
C(27)	0.6651 (9)	0.9217 (6)	0.0714 (3)	3.2 (2)
C(28)	0.802 (1)	0.9516 (7)	0.0618 (4)	4.3 (2)
C(29)	0.894 (1)	0.8803 (9)	0.0450 (4)	4.8 (2)
C(30)	0.8553 (9)	0.7775 (7)	0.0367 (4)	3.9 (2)
C(31)	0.7178 (9)	0.7460 (7)	0.0467 (3)	3.5 (2)
C(32)	0.3664 (8)	0.7670 (6)	0.0096 (3)	2.7 (2)
C(33)	0.4440 (9)	0.7882 (7)	−0.0327 (4)	3.8 (2)
C(34)	0.380 (1)	0.7800 (8)	−0.0788 (4)	4.6 (2)
C(35)	0.241 (1)	0.7484 (8)	−0.0852 (4)	4.6 (2)
C(36)	0.163 (1)	0.7285 (8)	−0.0440 (4)	4.1 (2)
C(37)	0.225 (1)	0.7386 (7)	0.0026 (4)	3.9 (2)

[a] See Table VI for footnotes.

Selected bond distances and angles are given in Table VII.

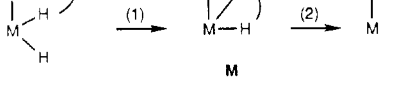
The plane described by the three osmium atoms is at an angle of 89.82° with respect to the plane defined by Os(1), Os(2), S, and C(2). The latter plane is 117.7 (2)° from the plane in which S, C(2), C(3), and C(5) are found. Carbon 4 lies 0.53 (1) Å beneath the S, C(2), C(3), C(5) plane. The distances in the core of the complex are similar in many respects to those of the dithioformate-bridged complex (μ-H)(μ-S_2CH)$Os_3(CO)_9(PMe_2Ph)$ (F).[39] The



F

DHT·H-bridged Os(1)–Os(2) distance (2.7907 (4) Å) is the shortest Os–Os bond length in X; likewise, the dithioformate-bridged Os–Os distance (2.854 (1) Å) is the shortest in F. The longest Os–Os distance (3.043 (1) Å) in F was assigned to the hydride-bridged Os–Os bond, as it is known[40–42] that metal–metal bonds are lengthened by a hydride bridge. In X, the longest distance (3.0718 (5) Å) is Os(2)–Os(3), which is presumably also the site of the bridging hydride; this is supported by a peak of electron density in this region found in the structure solution (see the Experimental Section). The Os(1)–C(2) bond in X is 2.215 (8) Å. This distance is similar to the sum (2.21 Å) of the metallic and covalent radii[36] of Os and C(sp^3). The distance (2.407 (2) Å) between Os(1) and S(1) in X is comparable to the Os–S distances in F (2.424 (2) and 2.442 (2) Å) and Os_3(μ-SPh)(μ-CH=CH_2)$(CO)_{10}$ (2.459 (4) and 2.446 (4) Å).[38b] The average C–C distance (1.52 Å) in the DHT·H ligand and the C–S distances of 1.815 and 1.82 Å are in the range of normal C–C[34] and C–S[32] distances, respectively.

Relevance to Thiophene HDS. As noted in the Introduction, 2,3-DHT undergoes ready hydrogenation to tetrahydrothiophene (eq 2) under HDS conditions. A possible mechanism (eq 9) for this hydrogenation involves



M (9)

initial coordination of the S to a metal hydride site followed by hydrogen transfer to the β-carbon of the olefin to give an η^2-DHT·H intermediate (step 1). This may occur by linkage isomerization from S-coordinated to olefin-coordinated 2,3-DHT as proposed (Scheme II) for the insertion reaction with $HPt(acetone)(PR_3)_2^+$. It is also possible that hydrogen transfer occurs to an η^3-coordinated (through both the S and olefin) 2,3-DHT.

One could also imagine the H transfer to 2,3-DHT as occurring at two metal centers on a catalyst surface (eq 10). An analogous transfer was observed in the reaction

N (10)

of $H_2Os_3(CO)_{10}$ with 2,3-DHT (eq 8). The final conversion of the η^2-DHT·H intermediates, M in eq 9 and N in eq 10, to THT could occur by transfer of another hydrogen to the ligand. Perhaps related to this later step is the reaction (eq 7) of $CpW(CO)_2(\eta^2\text{-DHT}\cdot H)$ with HCl to give $CpW(CO)_2(THT)Cl$. These studies demonstrate that there are model reactions of 2,3-DHT complexes which reasonably account for the hydrogenation of 2,3-DHT to THT on HDS catalysts.

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Registry No. I, 121268-41-5; II, 121268-43-7; III, 121268-55-1; IV, 121288-51-5; Va, 121268-44-8; Vb, 121268-45-9; VI, 121268-46-0; VII, 121268-48-2; VIIIa, 121268-49-3; VIIIb, 121268-50-6; IX, 121268-51-7; X, 121268-52-8; XI, 121268-53-9; 2,3-DHT, 1120-59-8; $HPt(PEt_3)_2Cl$, 16842-17-4; $HPt(PPh_3)_2Cl$, 16841-99-9; $HPt(PMePh_2)Cl$, 36464-72-9; $CpW(CO)_3^-$, 12126-17-9; $CpMo(CO)_3Na$, 12107-35-6; $CpFe(CO)_2^-$, 12107-09-4; $CpW(CO)_2(PPh_3)Cl$, 12115-03-6; $H_2OS_3(CO)_9(PPh_3)$, 88510-52-5; $H_2OS_3(CO)_{10}$, 41766-80-7; butane, 106-97-8; 2-chlorotetrahydrothiophene, 22342-03-6; thiophene, 110-02-1.

Supplementary Material Available: Listings of bond distances, bond angles, planes, calculated hydrogen positions, and thermal parameters for $[Pt(PEt_3)_2(DHT{\cdot}H)]PF_6$ and $HOs_3(CO)_9(PPh_3)(DHT{\cdot}H)$ (18 pages); listings of calculated and observed structure factors (43 pages). Ordering information is given on any current masthead page.

Electron-Transfer Reactions of Divalent Ytterbium Metallocenes. Synthesis of the Series $[(Me_5C_5)_2Yb]_2[\mu\text{-}E]$ (E = O, S, Se, or Te) and Crystal Structure of $[(Me_5C_5)_2Yb]_2[\mu\text{-}Se]$

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The preparation of the divalent, base-free compounds $(Me_5C_5)_2M$ (M = Eu or Sm) from their respective diethyl ether complexes is described. Reaction of $(Me_5C_5)_2M$ (M = Yb or Sm) with N_2O gives $[(Me_5C_5)_2M]_2[\mu\text{-}O]$ in high yield. Additionally, $(Me_5C_5)_2Yb$ reacts with Ph_3PS or As_2S_3 or COS, Ph_3PSe or elemental Se, or $n\text{-}Bu_3PTe$ or elemental Te, to give the bridging chalcogenides $[(Me_5C_5)_2Yb]_2[\mu\text{-}E]$ where E is S, Se, or Te, respectively. Magnetic susceptibility studies show that there is no magnetic exchange between the paramagnetic f metals across the bridging group 16 dianions. The variable-temperature magnetic studies also show that $(Me_5C_5)_2Sm$ and $[(Me_5C_5)_2Sm]_2[\mu\text{-}O]$ display temperature-independent paramagnetism as predicted by Van Vleck. The crystal structure of $[(Me_5C_5)_2Yb]_2[\mu\text{-}Se]$ is tetragonal, $P\bar{4}2_1c$, with a = 14.984 (5) Å and c = 19.165 (9) Å. For Z = 4 the calculated density is 1.491 g/cm^3. The structure was refined by full-matrix least squares to a conventional R factor of 0.031 [3797 data, $F^2 > 2\sigma(F^2)$]. The selenium atom is on a twofold axis and bonds to two Yb atoms in a nearly linear structure (Yb–Se–Yb angle = 171.09 (6)°). The Yb atom is η^5-bonded to two cyclopentadienyl rings and is on a plane defined by the centers of the two rings and the selenium atom. Distances are Yb–Se = 2.621 (1) Å, Yb–C(av) = 2.609 (7) Å, and ⟨Yb–Cp(ring)⟩ = 2.319 (2) Å, and Yb–Se–Yb is 171.09 (6)°.

The divalent lanthanide metallocene $(Me_5C_5)_2Yb(OEt_2)$ has been shown to be an electron-transfer reagent toward a variety of organic and organo-transition-metal compounds.[1] In these reactions $(Me_5C_5)_2Yb(OEt_2)$ acts as a soluble source of an electron (the reduction potential of $(Me_5C_5)_2Yb(OEt_2)$ in acetonitrile is −1.35 V (SCE)[1d]) and the tight ion-pair complexes that result are often readily soluble in and crystallize from hydrocarbon solvents. The tight ion pairs are of considerable interest since deductions about the electronic structure of the anionic fragments can be made from the solid-state structure. In this way insight into the bonding in negative ions, radical anions, and dianions has been obtained. The electron-transfer chemistry of the trivalent uranium metallocene $(RC_5H_4)_3U$ has been explored pairwise with $(Me_5C_5)_2Yb$, and the results have been used in a similar way.[2] One of the most interesting structural features in the uranium studies is the reaction product of $(MeC_5H_4)_3U(thf)$ and Ph_3PS, $[(MeC_5H_4)_3U]_2[\mu\text{-}S]$, in which the U–S–U angle is 164.9 (5)° and the U–S distance of 2.60 (1) Å is the shortest U–S distance so far determined. There is no magnetic interaction in the chalcogenide-bridged complexes $[(MeC_5H_4)_3U]_2[\mu\text{-}E]$, where E is S, Se, or Te, since the magnetic susceptibility as a function of temperature (4–300 K) shows that the 5f^2 ions behave as isolated paramagnets.[2b] The related ytterbium(III) complexes $[(Me_5C_5)_2Yb]_2[\mu\text{-}E]$ were of interest

Table I. Some Physical Properties of $[(Me_5C_5)_2Yb]_2[\mu\text{-}E]$

E	mp, °C	color	ν(Yb–E–Yb),[a] cm^{-1}	^{1}H NMR ($\nu_{1/2}$)[b]
O	334–337	orange	673	24.4 (980)
S	278–282	red	379	13.4 (640)
Se	265–270	purple	247	12.1 (500)
Te	235–238	green		12.6 (290)

[a] The asymmetric stretching frequency, assuming a linear molecule, in the infrared spectrum. The assignment is made by comparison of the individual spectra. The band is of strong intensity. [b] The ^{1}H NMR spectrum in toluene-d_8 at 32 °C; the chemical shift is expressed in δ units and the width at half-height expressed in hz.

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