analogue with $PEtPh_2$ has longer average Tc–N bond distances (2.115 (8) Å) than the analogue with PMe_2Ph (2.058 (12) Å) because of the greater steric bulk associated with the $PEtPh_2$ moiety. This steric crowding is also apparent when the P–Tc–P bond angles are considered: 172.3 (1)° for the $PEtPh_2$ complex and 179.3 (2)° for the PMe_2Ph complex, both with the phosphine groups being canted away from the bpy ligand. The Tc–N distances in the complex containing phen are on the average ca. 0.05 Å longer than those in the bpy complex (same phosphine included) and are due to the rigidity of the phen ligand and the larger bite angle required by this rigidity.

The Tc–Cl distances vary by only 0.035 Å among the three complexes reported here and are approximately equal to the Tc–Cl(trans-to-Cl) distances reported for the *mer*-$TcCl_3(PMe_2Ph)_3$ starting material.[19] However, they are much smaller than the Tc–Cl distance reported where the Cl is trans to a phosphine in the starting material. This suggests that the Cl atoms in the complexes reported herein are not subjected to as significant a structural trans effect (STE) from the imine nitrogen atoms as are the Cl atoms that are trans to phosphine moieties.[21] They are approximately 0.08 Å shorter than the Tc–Cl(trans-to-N) distance reported for $TcCl(phsal)_2(PMe_2Ph)$.[23] The Tc–Cl distances are, however, somewhat larger than the Tc–Cl(trans-to-Cl) distances reported for *trans*-$[Tc(DPPE)_2Cl_2]^+$[16] and *trans*-$[Tc(DMPE)_2Cl_2]^+$[15] where no STE is expected. They are also larger than the Ru–Cl(trans-to-bpy) distances reported for *cis*-$[Ru(bpy)_2Cl_2]^+$[25] owing to the higher effective nuclear charge on Ru(III). However, they are somewhat shorter than the Re–Cl(trans-to-MeCN) distance observed for *trans*(*P*)-$ReCl_3(MeCN)(PPh_3)_2$.[27]

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Registry No. A, 119818-89-2; B, 119818-91-6; C, 119818-93-8; $[TcCl_2(PMe_2Ph)_2(bpy)]PF_6$, 119818-94-9; *mer*-$TcCl_3(PMe_2Ph)_3$, 53749-02-3; *cis*(*Cl*),*trans*(*P*)-$[TcCl_2(PMe_2Ph)_2(Me_2bpy)]^+$, 119818-95-0; *cis*(*Br*),*trans*(*P*)-$[TcBr_2(PMe_2Ph)_2(bpy)]^+$, 119818-96-1; $[TcCl_2(PMe_2Ph)_2(bpy)]$, 119818-97-2; *mer*-$TcBr_3(PMe_2Ph)_3$, 53749-03-4; *mer*-$TcCl_3(PEtPh_2)_3$, 65013-98-1.

Supplementary Material Available: Tables of anisotropic temperature parameters (Table A), hydrogen atom coordinates (Table B), and complete bond lengths (Table C) and bond angles (Table D) and structure plots for the counterions (Figure A) for *cis*(*Cl*),*trans*(*P*)-$[TcCl_2(PMe_2Ph)_2(bpy)]BPh_4$, *cis*(*Cl*),*trans*(*P*)-$[TcCl_2(PMe_2Ph)_2(phen)]BPh_4$, and *cis*(*Cl*),*trans*(*P*)-$[TcCl_2(PEtPh_2)_2(bpy)]SO_3CF_3$ (14 pages); a listing of observed and calculated structure factors (Table E) (40 pages). Ordering information is given on any current masthead page.

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Notes

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2,3-Dihydrothiophene (2,3-DHT) Complexes of Tungsten. Structure of $W(CO)_3(dppe)(2,3\text{-}DHT)$

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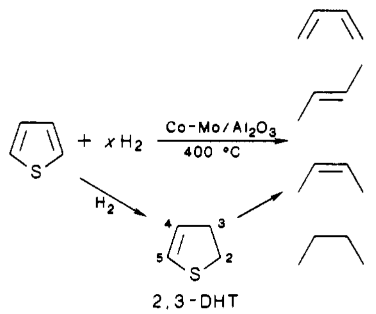
Catalytic hydrodesulfurization (HDS) is the process that removes sulfur from thiophene and other sulfur-containing organic compounds in crude oil. Model organometallic complexes of thiophene and thiophene derivatives have been studied in our research group in an effort to elucidate the mechanism of the HDS process.[1] The formation of 2,3-dihydrothiophene (2,3-DHT) has been proposed as the first step in the HDS of thiophene.[2] In an effort to examine the coordination modes of this partly hydrogenated thiophene, which potentially could coordinate through the olefin or the sulfur on the catalyst surface, a number of its transition-metal complexes have been prepared in recent years: $Mn(CO)_3Cl(2,3\text{-DHT})$,[1a] $W(CO)_5(2,3\text{-DHT})$,[3] $[Re(CO)_5(2,3\text{-DHT})]SO_3CF_3$,[3] $Ru(CO)_3Cl_2(2,3\text{-DHT})$,[3] and $PdCl_2(2,3\text{-DHT})_2$.[3] We report in this paper the syntheses of a variety of phosphine-substituted tungsten complexes and the first X-ray-determined structure of a 2,3-DHT compound.



Experimental Section

General Procedures. All reactions were carried out under an atmosphere of prepurified N_2 at room temperature by using standard inert-atmosphere and Schlenk[4] techniques unless otherwise stated. Tetrahydrofuran (THF) and Et_2O were distilled under N_2 from Na/benzophenone. Pentane, hexane, MeCN, and CH_2Cl_2 were distilled from CaH_2 under N_2. Trimethylphosphine was prepared by the reaction of methyl Grignard reagent and triphenyl phosphite.[5]

Infrared spectra were obtained by using a Perkin-Elmer 681 spectrophotometer, and spectra were referenced to the 1944.0-cm^{-1} band of polystyrene. The ^1H data were recorded on a Nicolet NT-300 300-MHz spectrometer using Me_4Si as the internal reference. Low-temperature ^1H NMR spectra were obtained on a Bruker WM 300 300-MHz instrument. Electron impact mass spectra (EIMS) were obtained on a Finnigan 4000 instrument. Fast atom bombardment (FAB, glycerol matrix) mass spectra were obtained by using a Kratos MS-50 spectrometer. Photochemical reactions were carried out in a quartz Schlenk tube equipped with a cooling probe by using a reactor obtained from Bradford Scientific, Inc., Marblehead, MA.

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Table I. Infrared Data for the Complexes in THF Solvent

compd	ν(CO), cm^{-1}
$W(CO)_3$(dppe)(2,3-DHT) (I)	1932 (s), 1844 (s), 1829 (ms, sh)
$Mo(CO)_3$(dppe)(2,3-DHT) (II)	1936 (s), 1851 (s), 1835 (s, sh)
$W(CO)_3$(dmpe)(2,3-DHT) (III)	1928 (s), 1838 (s), 1817 (s)
$W(CO)_4(PPh_3)$(2,3-DHT) (IV)	2020 (m), 1845 (vs), 1811 (s)
$W(CO)_4(PMe_3)$(2,3-DHT) (V)	2017 (m), 1840 (s, broad), 1790 (ms)
$W(CO)_4(PMePh_2)$(2,3-DHT) (VI)	2022 (ms), 1845 (vs), 1818 (s)
$W(CO)_4(PMe_2Ph)$(2,3-DHT) (VII)[a]	2022 (m), 1842 (s), 1815 (ms)
$W(CO)_5$(2,3-DHT) (VIII)	2080 (w), 1937 (vs), 1915 (s, sh)

[a] In hexane.

The following compounds were prepared by using methods published in the literature: 2,3-DHT,[3,6] $W(CO)_4$(dppe),[7] $Mo(CO)_4$(dppe),[7] $W(CO)_4$(dmpe),[8] $W(CO)_5(PPh_3)$,[9] and $W(CO)_5(PMe_3)$,[10] where dppe = $Ph_2PCH_2CH_2PPh_2$ and dmpe = $Me_2PCH_2CH_2PMe_2$.

Synthesis of $W(CO)_3$(dppe)(2,3-DHT) (I). A THF (35 mL) solution of $W(CO)_4$(dppe) (0.29 g, 0.42 mmol) was placed in a quartz tube equipped with a water-cooled probe and purged with N_2. The solution was irradiated with 254-nm light for 7.5 h, with the progress of the reaction to give $W(CO)_3$(dppe)(THF) being monitored by IR spectra. A pentane solution of 2,3-DHT[3] (0.36 M, 4.5 mL, 1.6 mmol) was added to the reaction mixture, which was then stirred for 30 min. The volume of solvent was then reduced in vacuo to ~5 mL. Addition of pentane (~10 mL) led to the precipitation of a yellow solid. The mixture was stored at −20 °C for 15 h. The solvent was decanted off and the yellow-green residue dried in vacuo. Compound I was obtained as a yellow-green powder (0.30 g, 95%). FAB MS: *m/e* 752 (M^+), 724 ($M^+ - CO$), 666 (M^+ − DHT), 610 [M^+ − (2 CO + DHT)], 582 [M^+ − (3 CO + DHT)], 398 (dppe$^+$). ^1H NMR (C_6D_6): δ 4.92 (m, 1 H, H(5)), 4.73 (td, 1 H, H(4), $J_{4-5} = 6.0$ Hz, $J_{3-4} = 2.1$ Hz), 2.32 (t, 2 H, H(2), $J_{2-3} = 7.9$ Hz), 1.97 (tt, 2 H, H(3)), 2.0–2.18 and 2.36–2.58 (m, 4 H, CH_2), 7.98–6.96 (m, 20 H, Ph). Anal. Calcd for $C_{33}H_{30}O_3P_2SW$: C, 52.68; H, 4.02; S, 4.25. Found: C, 52.52; H, 4.16; S, 3.70. Yellow-green cubelike crystals of I, which readily lost their luster when removed from the mother liquor, were obtained on storing a concentrated THF solution of I at −20 °C for 20 h.

X-ray Data Collection and Refinement of the Structure of $W(CO)_3$(dppe)(2,3-DHT)·2THF. Because crystals of the title compound rapidly deteriorated when removed from the parent solution, a crystal of approximate dimensions 0.3 × 0.4 × 0.5 mm was quickly mounted on the end of a glass fiber and then immediately moved to an Enraf-Nonius CAD4 diffractometer, where it was cooled to −110 °C. Unit-cell dimensions and crystal orientation matrix were determined from the least-squares refinement of the positions of 25 carefully centered reflections ($24° < 2\theta < 32°$) using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The complex crystallizes in the space group $P2_1/n$, with $a = 13.648$ (8) Å, $b = 16.263$ (7) Å, $c = 17.20$ (2) Å, $\beta = 93.62$ (8)°, $V = 3809$ (8) Å^3, $Z = 4$, and $d_{calc} = 1.563$ g/cm^3. Data were collected in the 2θ range of 4–45° by using a θ–2θ scan technique. A total of 4954 unique, non systematically absent reflections were collected; only the 4143 having $I \geq 3\sigma(I)$ were used in the refinement calculations. The intensities of three standard reflections monitored periodically during the data collection varied less than 3%. In the reduction of the data, Lorentz and polarization factors were applied.

The position of the W atom was determined by interpretation of the Patterson map. The remainder of the non-hydrogen atoms were located in subsequent difference Fourier maps. Since no absorption correction had been made initially, a numerical correction was made after isotropic refinement of the model.[11]

Although the data provided a large number of observed reflections, it was not possible to refine the structure with anisotropic thermal parameters for any but the heavy atoms. Expected carbon–oxygen bond lengths for the CO groups were added as observations in the least-squares calculations, and the phenyl rings were refined as rigid groups. The final discrepancy indices were $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.0896$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.1590$, with $w = 1/\sigma^2(|F_o|)$. The final atomic positional parameters are given in Table II. Refinement was carried out with the SHELX-76 program package.

Synthesis of $Mo(CO)_3$(dppe)(2,3-DHT) (II). This synthesis was carried out as described for the W analogue by starting with $Mo(CO)_4$(dppe) (0.15 g, 0.25 mmol) in THF (35 mL). A yellow powder of II, obtained in ~60% yield, was only characterized by its IR and ^1H NMR spectra. ^1H NMR (C_6D_6): δ 4.96 (m, 1 H, H(5)), 4.79 (td, 1 H, H(4), $J_{4-5} = 5.8$ Hz, $J_{3-4} = 2.1$ Hz), 2.19 (t, 2 H, H(2), $J_{2-3} = 8.1$ Hz), 1.98 (tt, 2 H, H(3)), 2.3–2.5 and 2.05–2.18 (m, 4 H, CH_2), 7.34–7.98 (m, 20 H, Ph). The solution NMR spectrum of II, taken 15 min after dissolution, showed the presence of a large amount of free 2,3-DHT. The formation of $Mo(CO)_4$(dppe) is also apparent in the NMR spectrum.

Synthesis of $W(CO)_3$(dmpe)(2,3-DHT) (III). A THF (35 mL) solution of $W(CO)_4$(dmpe) (0.21 g, 0.47 mmol) was placed in a quartz tube and irradiated with 254-nm light as described for $W(CO)_4$(dppe). Photolysis was discontinued after 6 h, a pentane solution of 2,3-DHT (0.20 M, 5 mL, 1.0 mmol) was added, and the mixture was stirred for 30 min. The volume of the solvent was reduced in vacuo and excess hexane (40 mL) added. The mixture was stored at −20 °C for 7 days. Yellow crystalline solid III (0.15 g, 63%) was obtained after filtering and drying. MS: *m/e* 504 (M^+), 476 ($M^+ - CO$), 446 [M^+ − (2 CO + 2 H)], 418 [M^+ − DHT or M^+ − (3 CO + 2 H)], 390 [M^+ − (CO + DHT)], 362 [M^+ − (2 CO + DHT)], 334 [M^+ − (3 CO + DHT)], 86 (DHT$^+$, base peak). ^1H NMR (C_6D_6): δ 5.75 (td, 1 H, H(5), $J_{4-5} = 5.7$ Hz, $J_{3-5} = 2.2$ Hz), 5.20 (m, 1 H, H(4)), 3.00 (t, 2 H, H(2), $J_{2-3} = 7.9$ Hz), 2.32 (tt, 2 H, H(3)), 0.7–1.5 (m, 4 H, CH_2), 1.37 (d) and 0.91 (d) (12 H, Me, $J = 7.5$ Hz, $J = 6.2$ Hz). Anal. Calcd for $C_{13}H_{22}O_3P_2SW$: C, 30.97; H, 4.40; S, 6.35. Found: C, 31.29; H, 4.40; S, 5.81.

Synthesis of $W(CO)_4(PR_3)$(2,3-DHT) ($PR_3 = PPh_3$). A THF (30 mL) solution of $W(CO)_5(PPh_3)$ (0.10 g, 0.17 mmol) was placed in a quartz tube and purged with N_2. The solution was then irradiated with 254-nm light for 2 h while N_2 was still bubbling through it. A pentane solution of 2,3-DHT (0.22 M, 1.8 mL, 0.40 mmol) was added, and the mixture was stirred for 30 min under N_2. The volume of the solvent was reduced to ~2 mL, pentane (20 mL) was added, and the solution was cooled at −20 °C for 3 days. The compound $W(CO)_4(PPh_3)$(2,3-DHT) (IV) (40 mg, 36%) was obtained as a yellow-green powder. MS: *m/e* 586 [M^+ − (2 H + 2 CO)], 558 [M^+ − (2 H + 3 CO) or M^+ − DHT], 530 [M^+ − (2 H + 4 CO) or M^+ − (DHT + CO)], 502 [M^+ − (DHT + 2 CO)], 474 [M^+ − (DHT + 3 CO)], 446 [M^+ − (DHT + 4 CO)], 262 (PPh_3^+), 84 (thiophene, base peak). ^1H NMR (C_6D_6): δ 4.99 (td, 1 H, H(5), $J_{4-5} = 5.8$ Hz, $J_{3-5} = 2.2$ Hz), 4.76 (m, 1 H, H(4)), 2.41 (t, 2 H, H(2), $J_{2-3} = 7.9$ Hz), 1.83 (tt, 2 H, H(3)), 7.37–7.31 and 6.90–6.65 (m, Ph).

The other $W(CO)_4(PR_3)$(2,3-DHT) complexes were obtained by analogous procedures as dark green oils.

***cis*-$W(CO)_4(PMe_3)$(2,3-DHT) (V).** Yield ~40%. MS: *m/e* 458 (M^+), 400 [M^+ − (2 CO + 2 H)], 86 (DHT$^+$, base peak), 76 (PMe_3^+). ^1H NMR (C_6D_6): δ 5.57 (td, 1 H, H(5), $J_{4-5} = 5.7$ Hz, $J_{3-5} = 2.2$ Hz), 5.07 (m, 1 H, H(4)), 2.81 (t, 2 H, H(2), $J_{2-3} = 8.0$ Hz), 2.17 (tt, 2 H, H(3)), 1.09 (d, 9 H, PMe_3, $J = 7.2$ Hz). The compound *cis*-$W(CO)_4(PMe_3)_2$ was also formed in this reaction and was not separated from V.

***cis*-$W(CO)_4(PMePh_2)$(2,3-DHT) (VI).** Yield ~50%. Some $W(CO)_4(PMePh_2)_2$ was also formed and was not separated. MS: *m/e* 582 (M^+), 554 ($M^+ - CO$), 524 [M^+ − (2 CO + 2 H)], 496 [M^+ − DHT or M^+ − (3 CO + 2 H)], 468 [M^+ − (DHT + CO) or M^+ − (4 CO + 2 H)], 440 [M^+ − (DHT + 2 CO)], 86 (DHT$^+$, base peak). ^1H NMR (C_6D_6): δ 5.24 (td, 1 H, H(5), $J_{4-5} = 5.7$ Hz, $J_{3-5} = 2.2$ Hz), 5.00 (m, 1 H, H(4)), 2.63 (t, 2 H, H(2), $J_{2-3} = 7.9$ Hz), 2.08 (tt, 2 H, H(3)), 1.90 (d, 3 H, PMe, $J = 7.3$ Hz), 8.0–7.0 (m, Ph).

***cis*-$W(CO)_4(PMe_2Ph)$(2,3-DHT) (VII).** Yield ~45%. *cis*-$W(CO)_4(PMe_2Ph)_2$ was also formed and was not separated from VII. MS: *m/e* 462 [M^+ − (2 CO + 2 H)], 434 [M^+ − DHT or M^+ − (3 CO + 2 H)], 378 [M^+ − (DHT + 2 CO)], 350 [M^+ − (DHT + 3 CO)], 86 (DHT$^+$, base peak). ^1H NMR (C_6D_6): δ 5.22 (td, 1 H, H(5), $J_{4-5} = 5.8$ Hz, $J_{3-5} = 2.2$ Hz), 4.93 (m, 1 H, H(4)), 2.58 (t, 2 H, H(2), $J_{2-3} = 7.9$ Hz), 2.02 (tt, 2 H, H(3)), 1.48 (d, $P\mathit{Me}_2Ph$, $J = 7.1$ Hz), 7.06–6.95 (m, $PMe_2\mathit{Ph}$).

Results and Discussion

Synthesis of *fac*-$W(CO)_3(\overset{\frown}{L\;L})$(2,3-DHT) and *cis*-$W(CO)_4$(L)(2,3-DHT). Reaction of $W(CO)_3(\overset{\frown}{L\;L})$(THF), obtained by photolytic decarbonylation of $W(CO)_4(\overset{\frown}{L\;L})$, with a pentane solution of 2,3-DHT in THF results in the formation of the facial sulfur-coordinated 2,3-DHT complexes I and III, which are characterized by their IR and MS spectra and elemental analyses. The three IR bands of approximately equal intensity observed for I and III (Table I) are characteristic of facial geometry.[12] While

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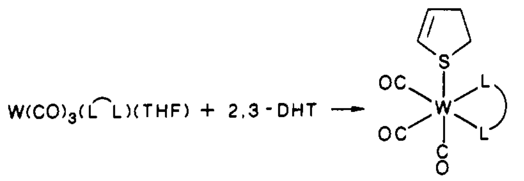

(1)

I, L⌒L = dppe
III, L⌒L = dmpe

compound I is stable as a solid, it slowly loses 2,3-DHT in solution to give $W(CO)_4(dppe)$ and an insoluble tungsten compound. The 2,3-DHT in I is also displaced by CO (1 atm) at room temperature over a period of 18 h to give $W(CO)_4(dppe)$ in 76% yield. The Mo analogue of I, II, was also prepared and found to be very unstable even as a solid at ambient temperature.

Similarly, the reaction of $W(CO)_4(L)(THF)$ with 2,3-DHT

$$W(CO)_4(L)(THF) + 2,3\text{-DHT} \rightarrow cis\text{-}W(CO)_4(L)(2,3\text{-DHT}) \quad (2)$$

$$L = PPh_3, PMe_3, PPh_2Me, PPhMe_2$$

in THF results in the formation of 2,3-DHT complexes with IR spectra characteristic of bis-substituted tetracarbonyltungsten compounds in which the two substituents are cis to each other.[7,8,10b] These unstable oils slowly decomposed even at −20 °C to give $W(CO)_4(L)_2$, $W(CO)_5(L)$, and an insoluble tungsten precipitate. The mass spectra of all the mono(phosphine)-substituted complexes of 2,3-DHT show a fragment with an m/e value attributable to $W(CO)_2(L)(\eta^6\text{-thiophene})$, suggesting that the formation of these thiophene compounds from the 2,3-DHT precursors occurs readily in the MS experiments.

NMR and Structural Studies. The ^1H NMR spectrum of I [δ 4.92 (H5), 4.73 (H4), 1.97 (H3), 2.32 (H2)] in benzene-d_6 solvent shows an upfield shift for the coordinated 2,3-DHT signals in comparison to the signals observed for free 2,3-DHT [δ 5.92 (H(5)), 5.23 (H(4)), 2.23 (H(3)), 2.77 (H(2))]. Similar shifts to higher fields were observed in the solvents $CDCl_3$, $(CD_3)_2CO$, and CD_3NO_2 for compound I. Such upfield shifts in olefin complexes are generally attributed to the formation of π-olefin complexes.[13] Also, in all the previously reported sulfur-coordinated 2,3-DHT compounds,[3,6] the olefin signals are shifted downfield with respect to those of the free ligand. An X-ray diffraction study of I was therefore undertaken in an effort to determine the bonding mode of the 2,3-DHT in I. An ORTEP plot of I showing the numbering scheme is given in Figure 1. Selected bond distances and angles are given in Table III. The X-ray crystal studies show that the 2,3-DHT is coordinated through the sulfur with a W–S bond distance of 2.573 (5) Å. Similar W–S bond distances have been reported in the literature: $W(CO)_5[(CH_3S)_2C{=}PPh_2Me]$ [2.555 (2) Å],[14a] $(CO)_4W[S(t\text{-Bu})CH_2CH_2S(t\text{-Bu})]$ [2.565 (4) and 2.559 (5) Å].[14b] The W–C(6) and W–C(7) distances of 3.61 and 4.64 Å indicate there is no interaction between the W and the olefin bond. The C(6)–C(7) bond distance of 1.30 (3) Å is comparable to reported C=C distances.[15] The C(8) atom of the 2,3-DHT ligand is in the plane defined by S, C(6), and C(7).

Table II. Table of Positional Parameters and Their Estimated Standard Deviations for $W(CO)_3(dppe)(2,3\text{-DHT})$ (I)

atom	x	y	z	B,[a,b] Å^2
W	0.24027 (6)	0.23531 (5)	0.21988 (4)	1.14 (2)
S	0.2589 (4)	0.2950 (3)	0.3586 (3)	1.3 (1)
P(1)	0.1226 (4)	0.1363 (3)	0.2773 (3)	1.2 (1)
P(2)	0.3582 (4)	0.1270 (3)	0.2669 (3)	1.3 (1)
C(1)	0.137 (1)	0.314 (1)	0.194 (1)	1.5 (2)*
C(2)	0.226 (2)	0.184 (1)	0.1173 (9)	2.1 (2)*
C(3)	0.346 (1)	0.307 (1)	0.186 (1)	2.2 (2)*
O(1)	0.077 (1)	0.3614 (8)	0.1703 (8)	1.9 (2)*
O(2)	0.223 (1)	0.1552 (9)	0.0541 (8)	2.7 (3)*
O(3)	0.407 (1)	0.3480 (9)	0.1599 (9)	2.8 (3)*
C(4)	0.195 (1)	0.056 (1)	0.333 (1)	1.0 (2)*
C(5)	0.287 (1)	0.034 (1)	0.291 (1)	1.0 (2)*
C(10)	0.0431 (9)	0.1774 (8)	0.3488 (6)	1.5 (4)*
C(16)	0.038 (1)	0.0792 (8)	0.2105 (7)	1.9 (4)*
C(22)	0.4519 (9)	0.0845 (8)	0.2069 (7)	1.5 (4)*
C(28)	0.4333 (9)	0.1508 (8)	0.3569 (6)	1.4 (4)*
C(6)	0.337 (2)	0.380 (1)	0.364 (1)	1.7 (4)*
C(7)	0.304 (2)	0.443 (1)	0.401 (1)	2.0 (4)*
C(8)	0.204 (2)	0.432 (1)	0.432 (1)	2.2 (4)*
C(9)	0.159 (2)	0.361 (1)	0.383 (1)	1.5 (4)*
C(11)	0.0529 (9)	0.1614 (8)	0.4286 (6)	2.3 (4)*
C(12)	−0.0118 (9)	0.1971 (8)	0.4783 (6)	2.4 (4)*
C(13)	−0.0864 (9)	0.2490 (8)	0.4483 (6)	2.6 (5)*
C(14)	−0.0962 (9)	0.2650 (8)	0.3685 (6)	2.5 (4)*
C(15)	−0.0315 (9)	0.2292 (8)	0.3187 (6)	1.5 (4)*
C(17)	−0.007 (1)	0.0072 (8)	0.2352 (7)	3.2 (5)*
C(18)	−0.074 (1)	−0.0341 (8)	0.1852 (7)	2.4 (4)*
C(19)	−0.098 (1)	−0.0036 (8)	0.1105 (7)	2.1 (4)*
C(20)	−0.054 (1)	0.0684 (8)	0.0859 (7)	2.9 (5)*
C(21)	0.014 (1)	0.1097 (8)	0.1359 (7)	1.7 (4)*
C(23)	0.5109 (9)	0.0204 (8)	0.2367 (7)	1.9 (4)*
C(24)	0.5774 (9)	−0.0175 (8)	0.1898 (7)	1.8 (4)*
C(25)	0.5849 (9)	0.0086 (8)	0.1132 (7)	1.7 (4)*
C(26)	0.5259 (9)	0.0727 (8)	0.0834 (7)	1.8 (4)*
C(27)	0.4594 (9)	0.1106 (8)	0.1302 (7)	1.8 (4)*
C(29)	0.4938 (9)	0.2197 (8)	0.3537 (6)	1.1 (3)*
C(30)	0.5501 (9)	0.2448 (8)	0.4200 (6)	2.8 (5)*
C(31)	0.5459 (9)	0.2009 (8)	0.4895 (6)	2.4 (4)*
C(32)	0.4854 (9)	0.1320 (8)	0.4926 (6)	2.7 (5)*
C(33)	0.4291 (9)	0.1070 (8)	0.4263 (6)	1.8 (4)*
O(100)	0.198 (2)	0.016 (1)	0.520 (1)	4.5 (4)*
C(101)	0.243 (2)	−0.060 (2)	0.514 (1)	3.4 (5)*
C(102)	0.275 (2)	−0.082 (2)	0.597 (2)	4.3 (6)*
C(103)	0.198 (2)	−0.040 (2)	0.642 (1)	3.0 (5)*
C(104)	0.139 (2)	0.012 (2)	0.587 (2)	3.9 (6)*
O(200)	0.757 (1)	0.332 (1)	0.2110 (9)	3.2 (3)*
C(201)	0.808 (2)	0.329 (2)	0.141 (2)	4.6 (6)*
C(202)	0.778 (3)	0.254 (2)	0.097 (2)	6.8 (9)*
C(203)	0.738 (3)	0.195 (3)	0.162 (2)	6.8 (9)*
C(204)	0.702 (3)	0.255 (2)	0.213 (2)	4.6 (7)*

[a] Starred values indicate atoms refined isotropically. [b] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Table III. Selected Bond Distances (Å) and Angles (deg) for $W(CO)_3(dppe)(2,3\text{-DHT})$ (I)[a]

Bond Distances			
W–S	2.573 (5)	W–P(1)	2.519 (5)
W–C(O)	1.93–1.97	W–P(2)	2.486 (6)
S–C(6)	1.75 (2)	C(6)–C(7)	1.30 (3)
S–C(9)	1.82 (2)	C(8)–C(7)	1.52 (3)
C(4)–C(5)	1.53 (3)	C(8)–C(9)	1.53 (3)
Bond Angles			
S–W–P(1)	84.6 (2)	W–S–C(9)	114.2 (7)
S–W–P(2)	86.6 (2)	C(6)–S–C(9)	89 (1)
S–W–C(1)	89.7 (6)	S–C(6)–C(7)	115 (2)
S–W–C(2)	176.7 (6)	S–C(9)–C(8)	107 (1)
S–W–C(3)	91.1 (6)	C(6)–C(7)–C(8)	116 (2)
W–S–C(6)	111.8 (7)	C(7)–C(8)–C(9)	103 (2)

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

While it is apparent that 2,3-DHT is coordinated through the sulfur in the solid state, it is possible that in solution there is an equilibrium between sulfur- and olefin-coordinated forms. A temperature-dependent ^1H NMR study of I in toluene-d_8 was, therefore, carried out over the temperature range of +22 to −90 °C. With the exception of H(2), which remained a triplet, the

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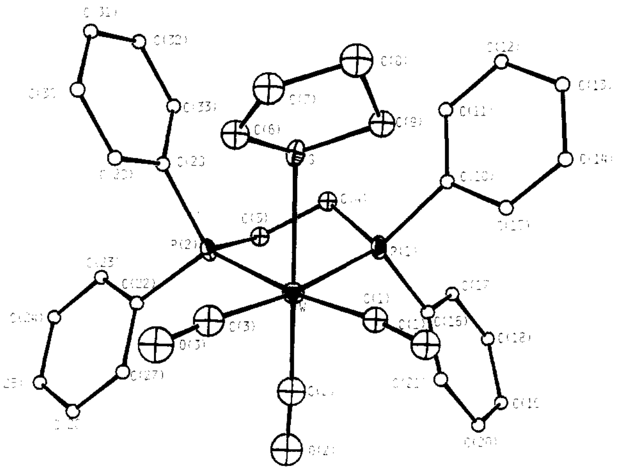

Figure 1. ORTEP drawing of $W(CO)_3(dppe)(2,3\text{-DHT})$ (I).

signals corresponding to 2,3-DHT in I are broadened with no distinct splitting at low temperature (−80 °C). Also, in comparison to the ambient-temperature spectrum, the low-temperature spectra of I show a further upfield shift (~0.2 ppm). However, there are no new signals that may be attributed to a distinctly different coordination mode for 2,3-DHT. Due to the instabilities of I and III over long acquisition times, efforts to obtain evidence for an olefin-coordinated form of 2,3-DHT by the use of W–^{13}C coupling were unsuccessful. Compound I does not react with $[Me_3O]BF_4$; methylation of the sulfur might be expected if 2,3-DHT were coordinated through the olefin.

Other phosphine-substituted 2,3-DHT complexes were prepared in an attempt to understand the observed high-field chemical shifts of the olefinic protons in I. Although trends in their ^{1}H NMR spectra are not completely understood, it appears that shielding of 2,3-DHT by the phenyl rings of the phosphines in these compounds is primarily responsible for the upfield shifts observed. The solvent also probably plays a role since the 2,3-DHT protons in $W(CO)_5(2,3\text{-DHT})$ are downfield in $CDCl_3$ [δ 6.19 (H(5)), 5.87 (H(4)), 2.96 (H(3)), 3.53 (H(2))] as compared with those in C_6D_6 [δ 5.23 (H(5)), 4.83 (H(4)), 1.87 (H(3)), 2.44 (H(2))].

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Registry No. I, 119638-26-5; II, 119638-27-6; III, 119638-28-7; IV, 119638-29-8; V, 119638-30-1; VI, 119638-31-2; VII, 119638-32-3; VIII, 108617-81-8; $W(CO)_4(dppe)$, 29890-05-9; $Mo(CO)_4(dppe)$, 15444-66-3; $W(CO)_4(dmpe)$, 40544-99-8; $W(CO)_5(PPh_3)$, 15444-65-2; $W(CO)_5(PMe_3)$, 26555-11-3; $W(CO)_5(PMePh_2)$, 18534-36-6; $W(CO)_5(PMe_2Ph)$, 42565-94-6.

Supplementary Material Available: Listings of calculated atomic coordinates for hydrogen atoms and all bond angles and distances for $W(CO)_3(dppe)(2,3\text{-DHT})$ (5 pages); a table of calculated and observed structure factors (21 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry
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Edge-Sharing Bioctahedral Molecules without Metal–Metal Bonds: The d^6–d^6 Complexes $Rh_2X_4(\mu\text{-}X)_2(\mu\text{-dppm})_2$ (X = Cl, Br)

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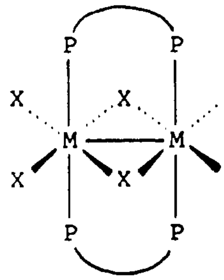
There is now a body of structural data for compounds with the edge-sharing bioctahedral structure sufficient to show how bond length and bond order are influenced by various factors, but especially by the d-electron count on each metal atom.[1-3] The influence of electron count alone, other factors being held as constant as possible, has been addressed most effectively by a study of compounds of type I, for which we have examples[2,3] with M = Nb, Ta, Mo, W, Re, and Ru. A less extensive series comprises compounds of type II.[4]



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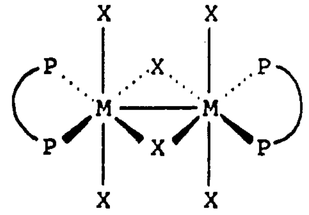

II

For neither of these series, however, has there been data for a compound with either a d^0 or a d^6 pair of metal atoms, wherein a M–M bond order of 0 would be expected. Our purpose in undertaking the work reported here was to supply such data. We chose the rhodium compounds of type I for three reasons. (1) We felt that without a M–M bond, a type I molecule with its bridging diphosphine ligands would probably be more accessible and stable than one of type II. (2) It seemed that a d^6–d^6 system would be more tractable than a d^0–d^0 system, since Sc^{III}, Y^{III}, and the La^{III} ions are not prone to form bonds to phosphines, whereas rhodium and iridium are. (3) Rhodium seemed a more likely candidate than iridium for many, fairly obvious, reasons.

We first obtained $Rh_2Br_6(dppm)_2$ by chance, but subsequently devised a rational preparation. We include it here for comparison with $Rh_2Cl_6(dppm)_2$ (which was prepared deliberately in the first instance) and with other $M_2Br_6(dppm)_2$ species that we shall report in the future. The preparation and chemical properties of $Rh_2Cl_6(dppm)_2$ have been presented earlier.[5] The preparation of $Rh_2Br_6(dppm)_2$ is described here, and the crystal structures of both compounds are reported.

Experimental Section

The following materials were used as supplied from the indicated sources: $RhBr_3 \cdot 3H_2O$, AESAR, dppm, Aldrich; Br_2, MCB; CO, Matheson. Solvents were freshly distilled from drying agents under dinitrogen prior to use: CH_2Cl_2 from P_2O_5; Et_2O from CaH_2. EtOH (95%) was degassed prior to use. All manipulations, unless otherwise stated, were done under an argon atmosphere by using standard vacuum-line techniques. Infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer by using Nujol mulls between CsI plates. $^{31}P\{^1H\}$ NMR spectra were recorded on a XL-200 Varian spectrometer at 81 MHz. Chemical shifts were referenced to external 85% H_3PO_4; more positive values represent deshielding.

Preparation of $Rh_2Br_6(dppm)_2$. Method A. This is the method of choice. $[Rh_2(\mu\text{-}Br)(\mu\text{-}CO)(CO)_2(dppm)_2]Br$, 0.152 g, dissolved in 100 mL of CH_2Cl_2 was treated with 10 mL of a Br_2 solution (0.2 g Br_2 in 100 mL of CH_2Cl_2) in a dimly lighted fume hood, or otherwise protected from strong light. The pale yellow-orange solution became cherry red as the Br_2 solution was added gradually over 5 min. After 8 h an additional 10 mL of the stock solution of Br_2 was added. This produced no immediate or marked color change, but after 18 h a solid had precipitated. The solvent was removed under vacuum, leaving 0.180 g (99%) of nearly pure $Rh_2Br_6(dppm)_2$. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): $\delta = -2.78$ ppm, $J_{Rh-P} = 85.0$ Hz. IR (Nujol, CsI plates): 2720 (w), 1730 (w), 1710 (w),

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