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Polydentate Ligands Containing Phosphorus. 14. Synthesis and Molecular Structure of (1,5-Cyclooctadiene)[bis(diphenylphosphinoyl)(diphenylthiophosphinoyl)methanido]rhodium(I)–2-Propanol, $\mathrm{(COD)Rh\{[(O)PPh_2]_2[(S)PPh_2]C\}\cdot \mathit{i}\text{-}PrOH}$[1]

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$\mathrm{(COD)Rh\{[(O)PPh_2]_2[(S)PPh_2]C\}}$ (1) was synthesized by the reaction of $\mathrm{[(COD)RhCl]_2}$ with $\mathrm{Li\{[(O)PPh_2]_2[(S)PPh_2]C\}}$ in a 1:2 molar ratio in $\mathrm{CH_2Cl_2/MeOH}$. Recrystallization of 1 from benzene/2-propanol yielded crystals of 1·*i*-PrOH, which was the subject of a crystallographic structure determination. The crystallographic data are as follows: triclinic space group $P\bar{1}$, with a = 10.526 (8) Å, b = 10.846 (9) Å, c = 20.296 (11) Å, α = 77.09 (8)°, β = 77.83 (8)°, γ = 69.08 (3)°, and Z = 2. The coordination about the rhodium is essentially square planar with coordination to the two double bonds of COD and to the sulfur of the P(S) group and the oxygen of one of the P(O) groups of the anionic ligand. The second P(O) group is not coordinated to rhodium but is hydrogen-bonded to a molecule of *i*-PrOH. The arrangement of the three phosphorus atoms about the central carbon of the anionic ligand is trigonal planar. Variable-temperature phosphorus-31 NMR spectra indicate that in solution the ligand is anchored (on an NMR time scale) to the rhodium by the P(S) group while the P(O) groups are exchanging.

Introduction

The relatively new series[3-6] of uninegative ligands $\mathrm{\{[Ph_2P(X)][Ph_2P(Y)][Ph_2P(Z)]C\}^-}$, where X, Y, and Z are various combinations of electron pairs and the chalcogens O, S, and Se, is based on the original chemistry of Issleib and Abicht,[7] who in 1970 reported the synthesis of $\mathrm{(Ph_2P)_3CH}$ (HTris[8]) and $\mathrm{[Ph_2P(S)]_3CH}$ ($\mathrm{HTrisS_3}$). Deprotonation of these neutral tris(phosphine chalcogenide) precursors with methoxide anion[9] results in the mesomerically stabilized carbanions,[10] which are relatively unreactive to water and air. Although these ligands are potentially tridentate with bonding through the chalcogens, there are numerous cases where bidentate behavior is observed. For example, $\mathrm{TrisS_3^-}$ is tridentate in $\mathrm{(\mathit{n}\text{-}Bu_3P)Ag(TrisS_3)}$[1,11] and $\mathrm{HgCl(TrisS_3)}$,[12] whereas it is bidentate in $\mathrm{(Et_3P)PtCl(TrisS_3)}$.[13] In all examples to date $\mathrm{TrisO_3^-}$ appears always to have bidentate coordination.[14-16]

In the cases of $\mathrm{TrisO_2S^-}$ and $\mathrm{TrisOS_2^-}$ the possibility of ambidentate coordination arises if these ligands are bidentate, i.e., P(O),P(O)- or P(O),P(S)-bonding in the case of $\mathrm{TrisO_2S^-}$ and P(O),P(S)- or P(S),P(S)-coordination in the case of $\mathrm{TrisOS_2^-}$. This paper reports the first coordination complex of $\mathrm{TrisO_2S^-}$, viz. $\mathrm{(COD)Rh(TrisO_2S)}$, where COD is 1,5-cyclooctadiene. Previously, $\mathrm{TrisO_3^-}$ complexes of rhodium(I) and iridium(I) were reported.[17]

Experimental Section

General Considerations. $\mathrm{LiTrisO_2S}$[5] and $\mathrm{[(COD)RhCl]_2}$[18] were prepared as described earlier. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ and ^{1}H NMR spectra were recorded on an IBM WP200 spectrometer operating at 80.90 and 200 MHz, respectively. Samples for ^{31}P measurements were dissolved in $\mathrm{CDCl_3}$ or dimethyl-d_6 sulfoxide (DMSO). Chemical shifts are reported as positive values to the high-frequency side ("downfield") of 85% $\mathrm{H_3PO_4}$ as an external reference. Samples for ^{1}H measurements were dissolved in $\mathrm{CDCl_3}$ and are referenced to internal tetramethylsilane. FAB mass spectra were obtained on a VG Analytical VG 3070E instrument with *m*-nitrobenzyl alcohol as the supporting matrix. Infrared spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer using Nujol mulls.

$\mathrm{(COD)RhTrisO_2S}$. Into a 100-mL three-necked round-bottomed flask equipped with a magnetic stirbar, gas (argon) inlet tube, and addition funnel were added 20 mL of dry distilled $\mathrm{CH_2Cl_2}$, 3 mL of MeOH, and 0.638 g (1.0 mmol) of $\mathrm{LiTrisO_2S}$. To the stirred reaction mixture was added dropwise 0.247 g (0.50 mmol) of $\mathrm{[(COD)RhCl]_2}$ dissolved in 25 mL of dry $\mathrm{CH_2Cl_2}$. The original orange color of the solution became yellow-green after

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[8] $\mathrm{[Ph_2P(X)][Ph_2P(Y)][Ph_2P(Z)]CH}$ is abbreviated HTrisXYZ, $\mathrm{[Ph_2P(S)]_3CH}$ is $\mathrm{HTrisS_3}$, $\mathrm{[Ph_2P(O)][Ph_2P(S)]_2CH}$ is $\mathrm{HTrisOS_2}$, $\mathrm{\{[Ph_2P(O)]_2[Ph_2P(S)]C\}^-}$ is $\mathrm{TrisO_2S^-}$, $\mathrm{(Ph_2P)_3CH}$ is HTris, etc.

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several hours of stirring. The solvent was removed under reduced pressure, the yellow-green residue was redissolved in CH_2Cl_2, and this solution was filtered through Celite. Addition of hexane to the filtrate caused precipitation of 0.40 g (0.47 mmol; 47% yield) of the product, mp 145 °C dec. IR (in cm^{-1}): 3420 (s), 1166 (s), 1113 (s), 1056 (s), 1017 (m), 996 (s), 950 (s), 814 (w), 744 (s), 720 (s), 693 (s), 668 (w), 632 (w), 612 (w), 570 (s), 533 (s), 505 (s). Calculated molecular weight for $C_{45}H_{42}O_2P_3RhS$: 842.7. Mass spectrum (*m/e*): 843 (int 85), M + 1; 734 (int 100), M − COD. ^1H NMR (23 °C, $CDCl_3$, 200 MHz): δ 8.01, 7.97, 7.94, 7.90 (1:1:1:1 dd, ^3J(P–H) = 13.6, ^3J(H–H) = 7.0 Hz, 4 H, *o* arom P(S)), 7.62 (br s, 8 H, *o* arom P(O)), 7.37–7.09 (m, 18 H, *m,p* arom), 3.93 (br s, 4 H, COD, =CH), 2.34 (br s, 4 H, COD, CH_2), 1.72 (br d, 4 H, COD, CH_2). ^1H NMR (−60 °C, $CDCl_3$, 200 MHz): δ 7.94–7.79 (m, *o* arom), 7.47–6.94 (m, arom), 3.87 (br s, COD, =CH), 2.55–2.10 (v br m, COD, CH_2), 1.91–1.53 (v br m, COD, CH_2). ^{31}P NMR (23 °C, $CDCl_3$, 80.90 MHz): δ 40.3 (dt, ^2J[P(S)–P(O)] = 13.2, ^2J[P(S)–^{103}Rh] = 4.0 Hz, 1 P, P(S)), P(O) resonance not observed. ^{31}P NMR (−50 °C, $CDCl_3$, 80.90 MHz): δ 46.3 (dd, ^2J[P(O)$_{coord}$–P(S)] = 13.7, ^2J[P(O)$_{coord}$–P(O)$_{free}$] = 28.5 Hz, 1 P, P(O)$_{coord}$), 40.5 (t, ^2J[P(S)–P(O)]$_{av}$ = 13.5 Hz, 1 P, P(S)), 26.4 (br m, 1 P, P(O)$_{free}$). ^{31}P NMR (80 °C, DMSO-d_6, 80.90 MHz): δ 40.0 (dt, ^2J[P(S)–P(O)]$_{av}$ = 13.1, ^2J[P(S)–^{103}Rh] = 3.7 Hz, 1 P, P(S)), 36.2 (br s, 2 P, P(O)).

Crystallographic Structure Determination. Diffraction-quality crystals were grown from a benzene/2-propanol solution. A yellow, platelike crystal of dimensions 0.42 × 0.23 × 0.11 mm was mounted on a glass fiber in Paratone-N and frozen in place at −60 °C. Intensity data were collected on a Nicolet P3/F diffractometer with graphite-monochromated Mo Kα radiation at −60 °C. Lattice constants were determined with 25 well-centered reflections, and axial photographs were used to confirm the symmetry and the approximate axial lengths. The SHELXTL Plus[19] package was used for the structure solution and refinement. An empirical absorption correction based on 150 ψ scans was applied to the data. Initial heavy-atom positions were determined from a Patterson map, and the other non-hydrogen atoms were located from successive Fourier difference maps. The triclinic crystal structure was found to conform to centrosymmetric $P\bar{1}$ symmetry, with one molecule of 1 and one 2-propanol molecule comprising the crystallographically independent unit. Hydrogen atoms with assigned isotropic temperature factors were included as fixed-atom contributors with calculated idealized positions based upon and moving with the positions of the attached carbon atoms. Isotropic temperature factors for all hydrogen atoms were fixed at U = 0.08 Å^2. Least-squares refinement converged at $R_1(F)$ = 7.19% and $R_2(F)$ = 6.89%. A final electron-density difference map showed no abnormal features.

Results and Discussion

The first reported complex (1) of the new uninegative ligand $TrisO_2S^-$ has been synthesized in 47% yield by the reaction of $LiTrisO_2S$ with [(COD)RhCl]$_2$ in the molar ratio of 2:1. It is an air-stable yellow-green crystalline compound. $TrisO_2S^-$ is bidentate in the d^8 square-planar complex with coordination via the sulfur of the P(S) group and the oxygen of one of the P(O) groups. The second P(O) group is not coordinated to the rhodium, and thus, the potential tridentate behavior of the ligand resulting in a five-coordinate 18-electron rhodium(I) complex is not favored. The ^{31}P NMR spectrum at low temperature is consistent with bidentate ligand behavior, which is confirmed by the crystal structure determination. The ^{31}P NMR spectra show no evidence of the existence of the other possible isomer resulting from P(O),P(O)-coordination. On the basis of the hard/soft acid/base theory, it is reasonable to expect that the relatively soft sulfur rather than the hard oxygen would preferentially bond to the soft Rh(I).

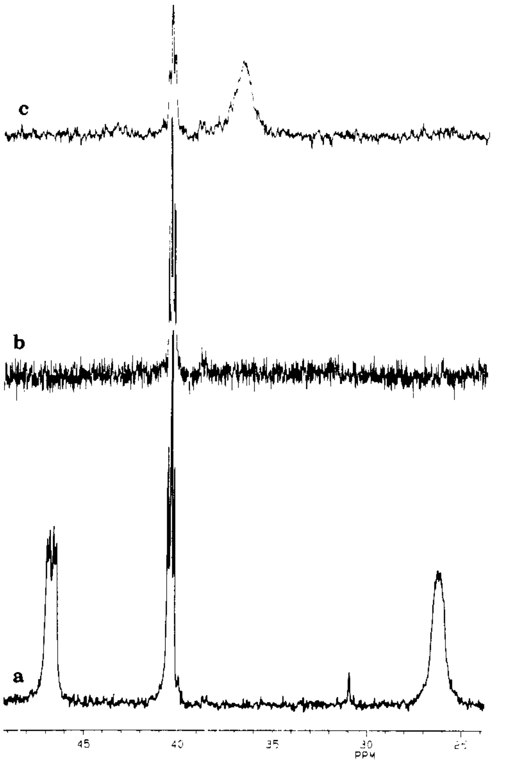

Figure 1. Variable-temperature ^{31}P NMR spectra of (COD)-$RhTrisO_2S$: (a) −50 °C; (b) 23 °C; (c) 80 °C. The center lines of the triplets in spectra a and b have been truncated for presentation purposes. Spectrum c has been moved about 0.5 ppm to the left for presentation purposes. The correct chemical shifts are given in the Experimental Section.

The variable-temperature ^{31}P NMR spectra (Figure 1) indicate that the P(O) groups of the $TrisO_2S^-$ ligand are exchanging at room temperature on the NMR time scale but that the P(S) group is not. At room temperature (Figure 1b) the P(S) signal is a sharp doublet of triplets (40.3 ppm) with ^2J[P(S)–P(O)] = 13.2 Hz and ^2J[P(S)–^{103}Rh] = 4.0 Hz. The observation of the two-bond rhodium–P(S) coupling is evidence of the kinetic nonlability of the Rh–S bond on the NMR time scale. No ^{31}P signal for the P(O) groups is observed at room temperature, due to exchange broadening. At −50 °C, the ^{31}P NMR spectrum is essentially an AMX type, which is the expected spectrum for the static structure of the complex. The coordinated P(O) resonance (46.3 ppm) is a doublet of doublets with ^2J[P(O)$_{coord}$–P(S)] = 13.7 Hz and ^2J[P(O)$_{coord}$–P(O)$_{free}$] = 28.5 Hz. The free P(O) group is a partially resolved doublet of doublets at 26.5 ppm. This peak is assigned to the noncoordinated P(O) group since it is within 2 ppm of all the other noncoordinated P(O) resonances that have been observed[14,15] in the $TrisXYZ^-$ ligand system and is also nearly the same as the chemical shift (24.4 ppm) of the P(O) groups in $HTrisO_3$.[5] The resonance of the P(S) group at −50 °C is a triplet with line separations of 13.5 Hz, which is roughly the average of ^2J[P(S)–P(O)$_{free}$] and ^2J[P(S)–P(O)$_{coord}$]. Since the two P(O) groups are unique at this temperature, the magnitude of their P–P coupling to the P(S) phosphorus is different, but only slightly, and the expected doublet of doublets in fact still appears as a triplet with some broadening. This broadening is sufficient to obscure the ^{103}Rh–P(S) coupling. No ^{103}Rh–P(O)$_{coord}$ coupling is observed at any of the experimental temperatures, which suggests that the P(O) groups may still be very slowly exchanging at −50 °C. At elevated temperatures (80 °C) the ^{31}P signals for the coordinated and noncoordinated P(O) groups reappear as a

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Table I. Crystallographic Data for (COD)RhTrisO$_2$S•*i*-PrOH

formula	$C_{48}H_{50}O_3P_3RhS$	T	−60 °C
space group	$P\bar{1}$	λ	0.71069 Å
fw	902.8	ρ_{calcd}	1.434 g cm^{-3}
a	10.526 (8) Å	scan mode	Wyckoff-ω
b	10.846 (9) Å	scan speed	4.0–29.3° min^{-1} (var)
c	20.296 (11) Å	2θ limits	3.4–45°
α	77.09 (8)°	total no. of rflns	5742
β	77.83 (8)°	no. of rflns, $\vert F\vert > 3.5\sigma(F)$	3981
γ	69.08 (3)°	$R_1(F)^a$	7.19%
V	2087 (3) Å^3	$R_2(F)^b$	6.89%
Z	2	GOF^c	1.27

[a] $R_1(F) = [[\sum(|F_o| - |F_c|)]/[\sum|F_o|]] \times 100$. [b] $R_2(F) = [[[\sum w_i(|F_o| - |F_c|)]/[\sum w_i(|F_o|)^2]]^{1/2}] \times 100$. [c] Goodness of fit $= [[\sum w_i(|F_o| - |F_c|)^2]/[m - n]]^{1/2}$, where m = number of independent data and n = number of variable parameters.

broad singlet at 36.2 ppm, which is nearly identical with the average (36.4 ppm) of the chemical shifts of the coordinated and noncoordinated P(O) groups at low temperature.

The fluxionality of the COD ligand and ligand exchange in COD–rhodium complexes were thoroughly investigated by numerous workers about two decades ago.[20–22] In a situation that is somewhat similar to this investigation, Heitner and Lippard[21] studied the diphenyl monothio-β-diketonate complex of (COD)Rh, which has one S- and one O-donor atom bonded to Rh(I). This results in each double bond of COD being chemically unique and their respective olefinic protons being magnetically nonequivalent. As a consequence, the olefinic protons are observed in the ^{1}H NMR spectrum at room temperature as two distinct singlets at about 4.8 and 4.2 ppm.[21] These singlets did not coalesce before decomposition of the complex at about 155 °C. However, the olefinic protons in the diphenyl monothio-β-diketonate (COD)Rh complex do equilibrate upon the addition of a fifth ligand, e.g., triphenylarsine, and the COD is fluxional under these conditions even at room temperature.[21] It was also shown in these earlier studies[21] that the equilibration of the olefinic protons is due to intramolecular processes rather than complete dissociation of the diene ligand. In the case of 1, we find that the olefinic protons of COD are fluxional and appear as a broad singlet (3.93 ppm) at room temperature and even as low as −60 °C. This is understandable, since TrisO$_2$S$^-$ has its own "excess" fifth ligand built in as the uncoordinated P(O) group and presumably this serves the same function as the triphenylarsine in the earlier work. The aliphatic COD protons in (COD)RhTrisO$_2$S appear as two broad singlets (2.34 and 1.72 ppm) at room temperature and become much broader (2.5–2.2 and 1.8–1.4 ppm) with undefined multiplet structure at −60 °C. Due to experimental difficulties spectra were not obtained at temperatures lower than −60 °C, but further studies of the fluxional behavior of both ligands in (COD)RhTrisO$_2$S may be worthwhile.

The X-ray crystallographic structural determination on 1·*i*-PrOH was carried out. Table I contains the general crystallographic data, Table II lists atomic coordinates, and Tables III and IV list selected bond lengths and angles, respectively. Figure 2 gives the structure and numbering scheme, and Figure 3 is the ORTEP view of the significant atoms of 1. The rhodium is coordinated to the two double bonds of COD and one sulfur and one oxygen of the P(S) and P(O) groups, respectively, of TrisO$_2$S$^-$ to give the usual square-planar coordination geometry of Rh(I) d^8 com-

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)^a

	x	y	z	U(eq)^b
Rh(1)	122 (2)	2231 (2)	2927 (1)	30 (1)
S(1)	−1473 (7)	1805 (9)	2466 (4)	34 (4)
O(1)	−107 (5)	4123 (1)	2355 (8)	43 (6)
O(2)	−4755 (4)	7443 (7)	2160 (8)	38 (6)
C(1)	−2968 (2)	4887 (6)	2497 (2)	45 (7)
P(1)	−3235 (7)	3353 (8)	2630 (4)	37 (3)
C(111)	−4276 (6)	1989 (9)	1982 (4)	45 (7)
C(112)	−5138 (3)	1843 (8)	1585 (3)	36 (6)
C(113)	−6076 (6)	2989 (9)	1302 (4)	45 (7)
C(114)	−6185 (5)	4219 (8)	1499 (9)	39 (6)
C(115)	−5317 (4)	4376 (8)	1838 (3)	38 (7)
C(116)	−4331 (6)	3219 (6)	2153 (6)	27 (6)
C(121)	−3087 (3)	2676 (3)	4026 (7)	69 (8)
C(122)	−3588 (4)	2324 (6)	4680 (3)	33 (6)
C(123)	−4770 (9)	1936 (7)	4852 (8)	66 (8)
C(124)	−5558 (8)	2197 (9)	4404 (5)	50 (7)
C(125)	−5131 (7)	2686 (9)	3722 (5)	51 (7)
C(126)	−3879 (5)	2904 (8)	3518 (4)	42 (7)
P(2)	−4186 (7)	6396 (8)	2724 (3)	28 (3)
C(211)	−3584 (5)	8407 (9)	3081 (4)	41 (7)
C(212)	−2926 (8)	8934 (5)	3453 (6)	62 (8)
C(213)	−2030 (4)	8055 (7)	3882 (3)	34 (6)
C(214)	−1784 (4)	6678 (7)	3966 (3)	37 (6)
C(215)	−2444 (7)	6153 (4)	3609 (7)	18 (5)
C(216)	−3379 (6)	7087 (6)	3156 (7)	29 (6)
C(221)	−6802 (5)	6393 (8)	3041 (5)	46 (7)
C(222)	−8006 (4)	6257 (6)	3517 (3)	33 (6)
C(223)	−7920 (5)	5823 (7)	4183 (4)	37 (6)
C(224)	−6721 (4)	5461 (7)	4458 (6)	43 (7)
C(225)	−5554 (3)	5637 (5)	4016 (6)	31 (6)
C(226)	−5669 (7)	6098 (6)	3317 (7)	17 (5)
P(3)	−1433 (7)	4938 (9)	1984 (3)	37 (3)
C(311)	−2461 (6)	4777 (5)	833 (3)	31 (6)
C(312)	−2266 (7)	4398 (6)	241 (5)	51 (7)
C(313)	−1026 (6)	3620 (9)	−90 (5)	51 (7)
C(314)	84 (5)	3244 (6)	287 (5)	58 (8)
C(315)	−86 (6)	3616 (8)	883 (4)	46 (7)
C(316)	−1263 (6)	4377 (6)	1192 (7)	30 (6)
C(321)	−2046 (4)	7582 (8)	1315 (3)	37 (6)
C(322)	−1958 (5)	8879 (8)	1149 (4)	40 (7)
C(323)	−954 (3)	9110 (7)	1473 (7)	72 (8)
C(324)	−232 (3)	8148 (7)	1953 (7)	75 (9)
C(325)	−354 (3)	6789 (7)	2048 (8)	78 (9)
C(326)	−1386 (6)	6560 (5)	1742 (6)	23 (6)
C(01)	543 (3)	2551 (6)	4283 (3)	59 (9)
C(02)	962 (6)	2953 (3)	3538 (6)	55 (8)
C(03)	2110 (2)	2236 (3)	3135 (5)	43 (8)
C(04)	2969 (9)	878 (3)	3442 (7)	56 (9)
C(05)	2493 (3)	−88 (3)	3183 (9)	64 (9)
C(06)	975 (3)	297 (6)	3289 (8)	64 (9)
C(07)	149 (6)	792 (5)	3861 (8)	59 (9)
C(08)	543 (8)	1109 (5)	4446 (6)	44 (8)
C(01A)	−6087 (7)	8064 (5)	495 (5)	58 (5)
C(02A)	−6431 (5)	9451 (8)	700 (4)	87 (6)
O(01A)	−5297 (9)	9304 (6)	1026 (5)	76 (5)
C(03A)	−7654 (7)	9972 (9)	1237 (5)	78 (4)

[a] Estimated standard deviations in parentheses. [b] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Selected Bond Lengths (Å)

Rh(1)–S(1)	2.307 (5)	Rh(1)–O(1)	2.074 (6)
Rh(1)–C(02)	2.078 (3)	Rh(1)–C(03)	2.226 (2)
Rh(1)–C(06)	1.992 (3)	Rh(1)–C(07)	2.167 (4)
S(1)–P(1)	2.036 (9)	O(1)–P(3)	1.603 (7)
O(2)–P(2)	1.478 (6)	C(1)–P(1)	1.733 (3)
C(1)–P(2)	1.767 (4)	C(1)–P(3)	1.746 (3)
P(1)–C(116)	1.716 (3)	P(1)–C(126)	1.814 (7)
P(2)–C(216)	1.762 (7)	P(2)–C(226)	1.843 (9)
P(3)–C(316)	1.797 (3)	P(3)–C(326)	1.727 (2)

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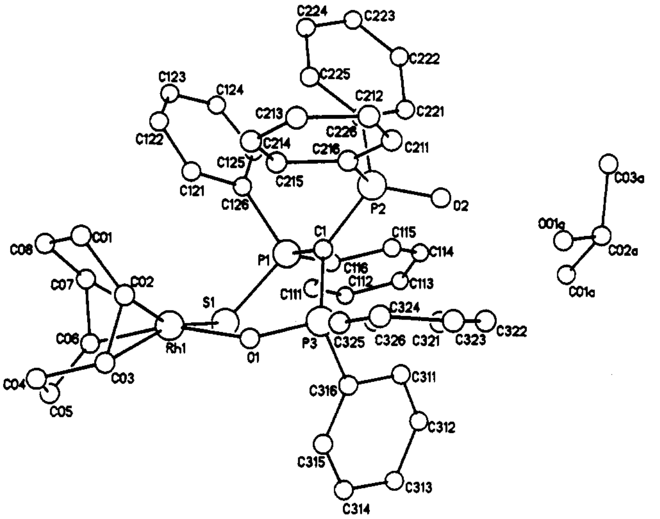

Figure 2. Structure and atom-numbering system for (COD)-RhTrisO$_2$S·*i*-PrOH with hydrogen atoms omitted for clarity.

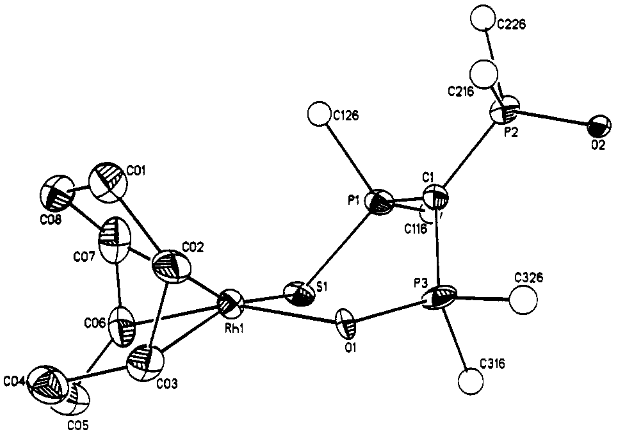

Figure 3. ORTEP diagram of the principal atoms of (COD)-RhTrisO$_2$S.

plexes. Since the rhodium lies only 0.02 Å out of the plane defined by S, O, and the centroids of the two double bonds, it is within experimental error of being planar. The ligand is thus bidentate with the noncoordinated P(O) group pointing away from the rhodium and hydrogen-bonded to a 2-propanol molecule of crystallization. The distance between the 2-propanol oxygen (O)(Ola)) and the P(O) oxygen (O(2)) is 2.72 Å, which is slightly shorter than the 2.74-Å interoxygen distance in the strongly hydrogen-bonded dimer of acetic acid[23] and shorter than the P(O)–O distance of 2.759 (24) Å in the hydrogen-bonded H_2O_2 in $[Ph_3P(O)]_2{\cdot}H_2O_2$.[24] The methine carbon of the TrisO$_2$S$^-$ ligand is essentially planar with an average P–C–P bond angle of 119.8° and with the carbon (C(1)) lying 0.08 Å out of the plane of the three phosphorus atoms. Similar planarity at carbon occurs for the analogous bidentate TrisS$_3^-$ and TrisO$_3^-$ ligands in Et$_3$PPt(Cl)TrisS$_3$[13] and Sn(TrisO$_3$)$_2$,[16] respectively, as well as for the TrisS$_3^-$ anion[10] itself. The six-membered chelate ring [Rh–O(1)–P(3)–C(1)–P(1)–S(1)] has a distorted boat configuration. It is folded along the S(1)–P(3) axis with the angle between the S(1)–Rh–O(1) and P(1)–C(1)–P(3) planes equal to 103.3°. Within the chelate ring, the angle at oxygen [Rh–O(1)–P(3)] of 121.4 (11)° is considerably smaller than is commonly observed (often about 150°,[25] but normally ranging from 133°[26] to 166°[27]) for coordinated monodentate tertiary phosphine oxides. This is primarily due to the constraints of the chelate ring. The angle at sulfur [Rh–S(1)–P(1)] of 104.9 (5)° is slightly smaller than the M–S–P angles commonly found in monodentate tertiary phosphine sulfide complexes such as $[(Me_3PS)_3Cu]ClO_4$[28] (mean 107.3°), *trans*-$(Et_2PhPS)_2PdCl_2$[29] (107.6°), and *trans*-$(i\text{-}Bu_3PS)_2PdCl_2$[30] (112.0°). However, in comparison to other chelate rings, the mean Cu–S–P angle in the six-membered ring of $Cu[Ph_2P(S)CH_2P(S)Ph_2]Cl$[31] is only 93.6°. The Rh–S bond length of 2.307 (5) Å is similar to the Rh–S bond length [2.303 (2) Å] of the two-coordinate S in $(COD)Rh[SS(CH_3)C_2(CN)_2]$.[22] The Rh–O bond [2.074 (6) Å] in 1 is marginally longer than the corresponding bonds [2.066 (5) and 2.054 (5) Å] in (COD)Rh(acac)[32] and those [2.050 (4) and 2.066 (5) Å] in $(COD)Rh[PhC(O)CHC(O)CF_3]$.[33]

Table IV. Selected Bond Angles (deg)

S(1)–Rh(1)–O(1)	95.7 (6)	S(1)–Rh(1)–C(02)	160.7 (7)
O(1)–Rh(1)–C(02)	82.0 (9)	S(1)–Rh(1)–C(03)	161.7 (8)
O(1)–Rh(1)–C(03)	87.5 (9)	C(02)–Rh(1)–C(03)	37.6 (10)
S(1)–Rh(1)–C(06)	92.7 (12)	O(1)–Rh(1)–C(06)	160.3 (10)
C(02)–Rh(1)–C(06)	95.7 (14)	C(03)–Rh(1)–C(06)	79.1 (14)
S(1)–Rh(1)–C(07)	98.4 (9)	O(1)–Rh(1)–C(07)	155.1 (8)
C(02)–Rh(1)–C(07)	77.9 (11)	C(03)–Rh(1)–C(07)	85.4 (12)
C(06)–Rh(1)–C(07)	38.7 (11)	Rh(1)–S(1)–P(1)	104.9 (5)
Rh(1)–O(1)–P(3)	121.4 (11)	P(1)–C(1)–P(2)	125.9 (14)
P(1)–C(1)–P(3)	114.4 (14)	P(2)–C(1)–P(3)	119.0 (17)
S(1)–P(1)–C(1)	113.0 (8)	S(1)–P(1)–C(116)	105.2 (9)
C(1)–P(1)–C(116)	116.7 (12)	S(1)–P(1)–C(126)	103.5 (8)
C(1)–P(1)–C(126)	110.4 (14)	C(116)–P(1)–C(126)	107.1 (13)
O(2)–P(2)–C(1)	116.6 (11)	O(2)–P(2)–C(216)	107.2 (12)
C(1)–P(2)–C(216)	107.3 (12)	O(2)–P(2)–C(226)	106.2 (9)
C(1)–P(2)–C(226)	111.9 (12)	C(216)–P(2)–C(226)	107.2 (12)
O(1)–P(3)–C(1)	113.4 (10)	O(1)–P(3)–C(316)	110.6 (10)
C(1)–P(3)–C(316)	111.1 (14)	O(1)–P(3)–C(326)	105.4 (12)
C(1)–P(3)–C(326)	111.6 (12)	C(316)–P(3)–C(326)	104.1 (12)
C(02)–C(01)–C(08)	111.6 (25)	C(01)–C(02)–C(03)	126.1 (23)
C(02)–C(03)–C(04)	118.8 (25)	C(03)–C(04)–C(05)	103.4 (28)
C(04)–C(05)–C(06)	111.4 (28)	C(05)–C(06)–C(07)	123.7 (16)
C(06)–C(07)–C(08)	129.0 (20)	C(01)–C(08)–C(07)	108.8 (20)

The planarity at the methine carbon of TrisO$_2$S$^-$ and the short P–C(1) bond lengths (mean 1.749 Å) indicate that the anionic ligand maintains the resonance stabilization of the type occurring in the anion TrisS$_3^-$, for which the mean phosphorus–methine carbon distance in 1.759 Å.[10] The P(2)–O(2) bond [1.478 (6) Å] of the noncoordinated P(O) group in 1 is significantly shorter than the P(3)–O(1) bond [1.603 (7) Å] of the coordinated P(O) group, as would be expected since P–O bonds generally lengthen upon coordination.[26] The same observation can be made for the noncoordinated P(O) [1.472 (7) Å] and coordinated P(O) groups (mean 1.534 Å) in Sn(TrisO$_3$)$_2$.[16] The methine C–P bonds within the chelate ring [1.733 (3) and 1.746 (3) Å]

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are slightly shorter than the P(2)–C(1) bond [1.767 (4) Å] to the coordinated P(O) group, indicating more delocalization within the chelate ring.

The Rh–COD bonding is normal. The four Rh–C distances average 2.116 Å in 1 compared to 2.103 Å in (COD)Rh(acac)[32] and 2.118 Å in (COD)Rh[PhC(O)CHC(O)CF3].[33] The olefinic bonds, 1.393 (5) and 1.387 (3) Å, are longer than the 1.341-Å distance in the free COD molecule[34] and only marginally shorter than in (COD)Rh(acac) (mean 1.405 Å)[32] and (COD)Rh[PhC(O)CHC(O)CF_3] (mean 1.402 Å).[33] The mean COD (C(sp^2)–C(sp^3) distance in 1 is 1.490 Å, and the mean C(sp^3)–C(sp^3) distance is 1.526 Å, which are well within the expected values.

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Supplementary Material Available: Tables S-I through S-V, listing bond lengths, bond angles, anisotropic displacement coefficients, hydrogen-atom coordinates, and equations for least-squares planes (5 pages); Table S-VI, listing structure factors (15 pages). Ordering information is given on any current masthead page.

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Class II Mixed-Valent Complexes from Oxidation of Doubly Linked (Arene)chromium Compounds

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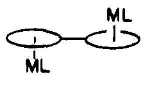
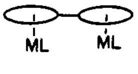
Oxidation of bridged d^6–d^6 dinuclear (arene)chromium complexes having a second linkage of P_2Me_4 has been studied by electrochemistry and by IR and ESR spectroscopies. Cyclic voltammetry shows that both (biphenyl)$[Cr(CO)_2]_2(\mu\text{-}P_2Me_4)$ (VII) and (diphenylmethane)$[Cr(CO)_2]_2(\mu\text{-}P_2Me_4)$ (VIII) undergo two separate reversible one-electron oxidations in CH_2Cl_2, with $E°$'s (vs SCE) of +0.32 and +0.69 V (for VII) and +0.23 and +0.52 V (for VIII). A third complex, (diphenylmethane)$[Cr(CO)_3]_2$, has a two-electron oxidation wave for which wave-shape analysis yields $E°$ values of +0.845 and +0.890 V. The monocations of VII and VIII were studied at 263 K by IR spectroscopy and shown to have separate Cr(I) and Cr(0) sites. A similar conclusion was drawn from the frozen-solution ESR spectrum of $VIII^+$. These ion are formulated as class II mixed-valent species in the Robin–Day classification scheme. The IR spectrum of $\{(biphenyl)[Cr(CO)_2PPh_3]_2\}^+$ was reinvestigated (see ref 16) at 203 K, and a spectrum similar to those of VII^+ and $VIII^+$ was obtained. All three class II mixed-valent cations showed carbonyl IR shifts for the Cr(0) site in the range 11–20 cm^{-1} as compared with the neutral starting materials. The structures of VII and VIII were crystallographically determined. For VII, crystal data are as follows: $C_{20}H_{22}Cr_2O_4P_2$, monoclinic, $P2_1/n$, $a = 13.489$ (4) Å, $b = 11.800$ (3) Å, $c = 13.726$ (3) Å, $\beta = 107.22$ (3)°, $V = 2086.79$ (11) Å^3, $Z = 4$, $R(F) = 4.09\%$. The biphenyl ligand is twisted 25.7° to accommodate the gauche conformation of the tetramethyldiphosphine group. A large Cr–Cr separation [4.773 (1) Å] appears to preclude a strong metal–metal interaction. For VIII, crystal data are as follows: $C_{21}H_{24}Cr_2O_4P_2$, monoclinic, $C2/c$, $a = 14.580$ (3) Å, $b = 10.359$ (3) Å, $c = 14.705$ (4) Å, $\beta = 108.56$ (2)°, $V = 2165$ (1) Å^3, $Z = 4$, $R(F) = 2.90\%$.

Introduction

The electronic delocalization properties of mixed-valent dinuclear complexes linked by two carbocyclic ligands continue to be of interest, in part because of the relevance of these models to studies of conducting organometallic polymers.[1-4] Relatively few such complexes have metals on the same face of a bridging hydrocarbon in a syn arrangement (structure IB). Owing to steric repulsions, syn complexes are generally disfavored with respect to the anti isomers (structure IA), and a second linkage is required (IC) to block rotation to the anti orientation. Ions resulting from oxidation of doubly linked systems (IC) form an important class of mixed-valent complexes in that they usually have a highly delocalized electronic structure when the linkages are cyclopentadienyl rings with intervening CY groups [Y = C[5,6] or H(Me)[7] (II, III)] or fulvalene itself[8]



IA



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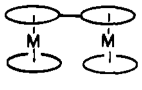

IC

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