(19) It could be argued that the absence of emission from $^*HD^+$ and $^*H_2D^{2+}$ arises from efficient bimolecular quenching of these species by D. This possibility is ruled out by the low concentrations employed. Either the quenching constants required to produce our observed results would have to exceed $10^{12}$ $M^{-1}$ $s^{-1}$, an impossibility, or the luminescence decay curves of $^*D$ would have to exhibit measurable rise times, which is not observed.

(20) $(\phi_0/\phi - 1) \sim 1.05$ and $\tau_0/\tau - 1 \sim 0.80$ for $Ru(phen)_2(CN)$ at 1.5 M $HClO_4$ while the corresponding values are 0.27 and 0.18 at 1.5 M $HClO_4$ for $Ru(bpy)_2(CN)_2$.

(21) Alternative explanations of the appearance of the $HD^+$ and $H_2D^{2+}$ emissions are (1) the media hinders equilibration of the excited state by decreasing $k_{-1}$ and $k_{-2}$ or (2) the media decreases the quenching component in $k_{H_2D}$ and $k_{HD}$. We consider these possibilities unlikely. Only emission from D is seen in glasses composed of aqueous 12 M HCl or methanol-water HCl glasses even though only protonated species are excited. With the far stronger acid, $H_2SO_4$, emissions of protonated species are seen, however, in methanol-water-sulfuric acid mixtures over a wide range in sulfuric acid and methanol concentrations. These possibilities would require either an enormous ability of the sulfuric acid media to suppress thermodynamically allowed excited-state deprotonation or a remarkable selectivity in the low-temperature media for deactivating one species in preference to another. To us the equilibrium maintenance of detectable amounts of $^*HD^+$ and $^*H_2D^{2+}$ at 77 K by the high acidity of these media is much more reasonable.

(22) This statement is based on the assumption that the relative energies of the CT states are changing continuously relative to the $^3(\pi-^*\pi)$ even for a given species. This, in turn, causes large changes in the $^3(\pi-^*\pi)$ component of the emitting state (eq 7). In view of the large solvatochromic shifts of the excited states of the complexes, this assumption seems quite reasonable.

(23) D. W. H. Carstens, Ph.D. Thesis, University of New Mexico, 1969.

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# Preparation and Reactivity of Some $\eta^2$-$S_2$ and $\eta^2$-$Se_2$ Complexes of Osmium and the X-ray Crystal Structure of $Os(\eta^2\text{-}Se_2)(CO)_2(PPh_3)_2$

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**Abstract:** The compounds $Os(\eta^2\text{-}Se_2)(CO)_2(PPh_3)_2$, $Os(\eta^2\text{-}Se_2)(CO)(CNR)(PPh_3)_2$ where R = *p*-tolyl, and $Os(\eta^2\text{-}S_2)(CO)_2(PPh_3)_2$ have been prepared. The reactivity of the $(\eta^2\text{-}S_2)$ and $(\eta^2\text{-}Se_2)$ ligands has been investigated and, in contrast to that of the $(\eta^2\text{-}O_2)$ analogues, which are oxidizing in character, has been found to be reducing in nature. Thus the ligands are readily attacked by alkylating agents to give cations of the type $[Os(\eta^2\text{-}Se_2Me)(CO)_2(PPh_3)_2]^+$ which react further with borohydride to yield complexes of the type $Os(H)(\eta^1\text{-}Se_2Me)(CO)_2(PPh_3)_2$. Reaction with iodine or dinitrogen tetroxide yields the known complexes $OsI_2(CO)_2(PPh_3)_2$ and $Os(NO_3)_2(CO)_2(PPh_3)_2$, respectively, with elemental selenium or sulfur being liberated. Reactions involving electrophiles such as $NO^+$ and $RN_2^+$ have been observed in which nitric oxide and nitrogen are evolved with elemental sulfur or selenium being deposited, followed by subsequent decomposition of the osmium residue in the absence of suitable ligands. The structure of dicarbonylbis(triphenylphosphine)diseleniumosmium(0) has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the triclinic space group $P\bar{1}$, with two molecules in a cell of dimensions $a$ = 10.479 (1) Å, $b$ = 17.933 (3) Å, $c$ = 10.416 (2) Å, $\alpha$ = 103.49 (3)°, $\beta$ = 115.10 (1)°, and $\gamma$ = 75.72 (2)°. Refinement by least-squares techniques, using 5319 observations above background, gave a final agreement factor on $F$ of 0.034. The coordination geometry at the Os atom is that of a distorted octahedron, with trans phosphine ligands and the $Se_2$ ligand "sideways" bonded. The Se-Se distance is lengthened to 2.321 (1) Å upon coordination. ESCA spectra show that the $S_2$ and $Se_2$ ligands are very effective at removing electron density from the Os atom.

## Experimental Section

Infrared data were recorded on a Beckman IR 12 spectrophotometer and $^1H$ NMR spectra were obtained on a Varian T-60 spectrometer. Microanalyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, West Germany. Melting points (uncorrected) were measured on a Reichert hot stage microscope. ESCA spectra were recorded using a McPherson ESCA 36 spectrometer and an Al anode. The carbon 1s peak of graphite was used as an internal reference (284.0 eV). Samples were smeared on graphite-coated Al plates.

**Preparation of Starting Materials. A. $Os(CO)_2(PPh_3)_3$.** $Os(H)ClCO(PPh_3)_3$[2a] (3.0 g) and $AgClO_4$ (0.596 g) were refluxed in $CH_3CN$ (80 mL) for 1 h. The solution was cooled to 60 °C and filtered quickly using warmed glassware. Solvent was removed under reduced pressure and the residue was recrystallized from a mixture of $CH_2Cl_2$ and ethanol to yield 2.62 g (99%) of $[Os(H)CO(CH_3CN)_2(PPh_2)_2]^+ClO_4^-$.[2b]

This product (2.0 g) was heated at 50 °C in $CH_2Cl_2$ (60 mL) under an atmosphere of CO (40 psi) for 90 min. It was then filtered and ethanol (60 mL) added followed by 70% $HClO_4$ (0.5 mL). Evaporation to a volume of 30 mL gave white crystals, 1.96 g (99%), of $[Os(H)(CO)_2(CH_3CN)(PPh_3)_2]^+$ $ClO_4^-$.

This product (1.6 g) and $PPh_3$ (3.0 g) were heated under reflux in 2-methoxyethanol (200 mL) for 24 h. The solution was evaporated to dryness and extracted twice with hot hexane (100 mL) to remove excess phosphine. The remaining oily solid was dissolved in $CH_3OH$ (100 mL) and filtered. Crushed NaOH (0.6 g) was added, and the system was flushed with nitrogen gas and then heated under reflux for 1 h.

The resulting yellow needles were filtered off and washed with ethanol and hexane, yield 1.27 g (70%), mp 164-166 °C. Anal. Calcd for $C_{56}H_{45}O_2OsP_3$: C, 65.73; H, 4.39; P, 9.00. Found: C, 65.16; H, 4.54; P, 8.39.

**B. $Os(CO)(CNC_7H_7)(PPh_3)_3$.**[3] $Os(H)ClCO(PPh_3)_3$[2a] (3.65 g) and $C_7H_7NC$ (0.45 g) were heated under reflux in benzene (180 mL) for 10 min. The solution was then cooled and evaporated with continuous addition of ethanol (100 mL) until the final volume was 50 mL. Hexane (50 mL) was then added to ensure complete crystallization and the product filtered off and recrystallized from $CH_2Cl_2$ and ethanol to yield 3.14 g (100%) of $Os(H)ClCO(CNC_7H_7)(PPh_3)_2$.

This product (2.10 g) and $AgClO_4$ (0.495 g) were heated under reflux in a mixture of benzene (50 mL) and ethanol (20 mL) for 3 h. The solvent was removed under reduced pressure and the residue was dissolved in the minimum of $CH_2Cl_2$ and filtered. Ethanol (30 mL) was added and the solvent removed until a final volume of 15 mL was achieved when hexane (50 mL) was added. The solid was filtered off and washed with ice-cold ethanol and hexane. A yield of 2.15 g (96%) of $Os(H)ClO_4(CO)(CNC_7H_7)(PPh_3)_2$ was obtained.

This product (1.47 g) and $PPh_3$ (0.50 g) were heated under reflux

0002-7863/79/1501-6577$01.00/0

in benzene (30 mL) for 30 min. The solution was cooled, hexane (100 mL) added, and the resulting white solid filtered off to yield 1.80 g (96%) of $[Os(H)(CO)(CNC_7H_7)(PPh_3)_3]^+ClO_4^-$.

This product (1.50 g) was dissolved in ethanol (20 mL) and filtered. The solution was flushed with nitrogen gas, NaOH (0.60 g) was added, and the solution was heated under reflux for 8 h. The orange crystals were then filtered off and washed with ethanol and hexane, yield 1.17 g (85%), mp 148-152 °C. Anal. Calcd for $C_{63}H_{52}NOOsP_3$: C, 67.41; H, 4.67; N, 1.25. Found: C, 67.09; H, 4.93; N, 1.24.

**Preparation of Complexes. A. $Os(\eta^2\text{-}Se_2)(CO)_2(PPh_3)_2$.** Sodium-dried benzene (50 mL) was freeze degassed three times, dry nitrogen being admitted after each of the thaw cycles. While still frozen and under nitrogen $Os(CO)_2(PPh_3)_3$ (2.0 g, 1.94 mmol) and red selenium (0.46 g, 5.8 mmol) were then added and the mixture was allowed to come to room temperature. The yellow zerovalent osmium complex rapidly dissolved and the color of the solution soon became reddish purple. After 30 min a clear solution was briefly obtained but soon afterward product began to separate as a silky suspension. The reaction was allowed to proceed for 3 h after which *n*-hexane was added (200 mL), causing the product to precipitate. The solid was filtered off quickly before the $Ph_3PSe$ began to crystallize out from the filtrate, washed with *n*-hexane, and recrystallized from chloroform/ethanol as small, reddish-purple crystals, yield 1.08 g (60%), mp 192-195 °C. Anal. Calcd for $C_{38}H_{30}O_2OsP_2Se_2$: C, 49.15; H, 3.23; Se, 17.01. Found: C, 48.85; H, 3.45; Se, 17.10.

**B. $Os(\eta^2\text{-}Se_2)(CO)(CNC_7H_7)(PPh_3)_2$.** $Os(CO)(CNC_7H_7)(PPh_3)_3$ (2.0 g, 1.78 mmol) and red selenium (0.42 g, 5.35 mmol) were treated as described above except that the reaction was faster and was complete in 1 h. The product was recrystallized from chloroform/ethanol as deep burgundy colored crystals, yield 1.12 g (62%), mp 142-144 °C. Anal. Calcd for $C_{45}H_{37}NOOsP_2Se_2$: C, 53.10; H, 3.66; N, 1.38; Se, 15.52. Found: C, 53.00; H, 3.67; N, 1.37; Se, 15.36.

**C. $[Os(\eta^2\text{-}Se_2Me)(CO)_2(PPh_3)_2]^+ClO_4^-$.** $Os(\eta^2\text{-}Se_2)(CO)_2(PPh_3)_2$ (1.0 g) was dissolved in dichloromethane (10 mL) and 1 equiv of methyl triflate added. The solution immediately became orange-yellow in color and ethyl alcohol (20 mL) was added together with sodium perchlorate (0.3 g) dissolved in ethyl alcohol (5 mL). Upon removal of the dichloromethane under vacuum the product crystallized out and was recrystallized from dichloromethane/ethanol/cyclohexane as yellow-orange crystals, yield 1.01 g (90%), mp 151-154 °C. Anal. Calcd for $C_{39}H_{33}ClO_6OsP_2Se_2$: C, 44.91; H, 3.16; Se, 15.14. Found: C, 44.77; H, 3.17; Se, 15.40.

**D. $[Os(\eta^2\text{-}Se_2Me)(CO)(CNC_7H_7)(PPh_3)_2]^+ClO_4^-$.** $Os(\eta^2\text{-}Se_2)(CO)(CNC_7H_7)(PPh_3)_2$ (1.0 g) was treated exactly as described in C above. Recrystallization from dichloromethane/ethanol/cyclohexane gave orange crystals of the product, yield 1.03 g (93%), mp 146-148 °C. Anal. Calcd for $C_{46}H_{40}ClNO_5OsP_2Se_2$: C, 48.79; H, 3.56; N, 1.24; Se, 13.95. Found: C, 48.71; H, 3.53; N, 1.19; Se, 14.10.

**E. $Os(\eta^1\text{-}Se_2Me)H(CO)_2(PPh_3)_2$.** $[Os(\eta^2\text{-}Se_2Me)(CO)_2(PPh_3)_2]^+ClO_4^-$ (0.50 g) was suspended in ethyl alcohol (5 mL) and a filtered solution of sodium borohydride (0.10 g) in ethyl alcohol (5 mL) was added dropwise with stirring. Gas was immediately evolved and the crystalline form of the solid changed and also became lighter yellow in color. When no more gas was evolved the product was filtered and washed with ethanol and *n*-hexane. It was recrystallized from dichloromethane/ethanol as light yellow crystals, yield 0.45 g (99%), mp 165-167 °C. Anal. Calcd for $C_{39}H_{34}O_2OsP_2Se_2$: C, 49.59; H, 3.60; Se, 16.72. Found: C, 49.74; H, 3.60; Se, 16.49.

**F. $Os(\eta^1\text{-}Se_2Me)H(CO)(CNC_7H_7)(PPh_3)_2$.** $[Os(\eta^2\text{-}Se_2Me)(CO)(CNC_7H_7)(PPh_3)_2]^+ClO_4^-$ (0.50 g) was treated exactly as described in E above. Recrystallization from dichloromethane/ethanol gave yellow crystals, yield 0.45 g (98%). Anal. Calcd for $C_{46}H_{41}NOOsP_2Se_2$: C, 53.44; H, 4.00; N, 1.35; Se, 15.30. Found: C, 53.37; H, 4.10; N, 1.30; Se, 15.15.

**Reaction with Iodine.** The reaction proceeded in an identical fashion for both the sulfur and selenium complexes. Only the latter is described.

$Os(\eta^2\text{-}Se_2)(CO)_2(PPh_3)_2$ (0.20 g, 0.22 mmol) was dissolved in dichloromethane (20 mL) under an atmosphere of nitrogen. Iodine (0.055 g, 0.44 mmol) dissolved in dichloromethane (5 mL) was added dropwise. The solution turned dark red and elemental selenium was precipitated, after which the color faded to an orange. Following filtration *n*-hexane was added and the dichloromethane was removed under vacuum. A yellow solid was then filtered off and upon treatment with activated charcoal in hot dichloromethane, followed by filtration and solvent removal in the presence of ethanol, white crystals were obtained. These were identified by their infrared spectrum (see text), positive iodide test, and negative selenium test, as the known complex $OsI_2(CO)_2(PPh_3)_2$.

**Table I.** Summary of Crystal Data and Experimental Conditions

| | | |
|---|---|---|
| compd | $C_{38}H_{30}O_2OsP_2Se_2$ | mol wt 928.73 |
| unit cell dimensions | $a = 10.479\ (1)$ Å | $\alpha = 103.48\ (3)°$ |
| | $b = 17.933\ (3)$ Å | $\beta = 115.10\ (1)°$ |
| | $c = 10.416\ (2)$ Å | $\gamma = 75.72\ (2)°$ |
| cell volume | 1699.5 Å$^3$ | |
| $Z$ | 2 | |
| density obsd | 1.81 (1) g cm$^{-3}$ | |
| calcd | 1.815 g cm$^{-3}$ | |
| space group | $P\bar{1}$ ($C_i^1$ no. 2) | |
| absorption coeff | $\mu = 99.95$ cm$^{-1}$ (Cu K$\alpha$) | |
| transmission coeff | 0.158-0.480 | |
| radiation | Cu, prefiltered with 0.018 mm Ni foil, $\lambda(K\alpha_1) = 1.540\ 56$ Å | |
| temp | 19 °C | |
| receiving aperture | 5.0 by 5.0 mm, 32 cm from crystal | |
| takeoff angle | 3.0°, 90% of available Bragg intensity | |
| scan | $\theta$-$2\theta$, at 2° min$^{-1}$ | |
| background counts | stationary crystal, stationary counter counts of 10 s at the scan limits | |
| scan range | 1.4-1.7°, corrected for dispersion | |
| $2\theta$ limits | $2 \leq 2\theta \leq 130°$ | |
| data collected | $\pm h, \pm k, l$ | |
| standard reflections | five, recorded every 200 observations: 001, 200, 020, $\bar{1}\bar{1}0$, and $0\bar{2}0$ | |

**Reaction with Dinitrogen Tetroxide.** $Os(\eta^2\text{-}Se_2)(CO)_2(PPh_3)_2$ (0.20 g) was dissolved in degassed dichloromethane. Dinitrogen tetroxide was then bubbled through the solution and an immediate green color developed characteristic of dinitrogen trioxide. Elemental selenium was deposited and was filtered off. Addition of hexane to the solution resulted in the precipitation of a pale yellow solid which was recrystallized from dichloromethane/ethanol as pale yellow crystals. They were identified as the known complex $Os(NO_3)_2(CO)_2(PPh_3)_2$ by their infrared spectrum (see text), melting point (211-213 °C), and negative selenium test.

The sulfur analogue reacted in an identical fashion.

**Collection and Reduction of X-ray Data.** Well-developed deep purple crystals of $Os(\eta^2\text{-}Se_2)(CO)_2(P(C_6H_5)_3)_2$ were recrystallized from chloroform and hexane. A photographic examination employing Weissenberg and precession techniques indicated that the crystals are triclinic. Cell constants obtained from the films were subjected to a cell reduction.[4] The density of the material, measured by flotation in a mixture of 1,2-dibromoethane and cyclohexane, was consistent with two molecules per cell. $P\bar{1}$ was chosen as the space group,[5] and was later confirmed by a successful analysis. Crystal data are summarized in Table I.

A crystal of approximate dimensions 0.24 × 0.08 × 0.27 mm was chosen from which to record intensity data. It was mounted in random orientation[6] and eight faces were identified by optical goniometry as (100), $(\bar{1}\bar{1}0)$ and the forms {010}, {001}, and $\{1\,1\,\bar{1}\}$. After data collection was complete, the crystal was measured on a microscope fitted with a filar eyepiece; the crystal volume was $5.12 \times 10^{-3}$ mm$^3$.[7]

Intensity data were recorded on a Picker FACS-1 diffractometer, running under the Vanderbilt disk operating system.[8] Cell constants and an orientation matrix were refined using 29 carefully centered reflections with $35° < 2\theta < 53°$ covering the regions of reciprocal space from which data were to be collected. $\omega$ scans of several intense, low-angle reflections, recorded with a takeoff angle of 0.6° and a wide-open counter,[9] had an average width at half-height of 0.09°; this was unchanged after data collection was completed. Details of the instrumental parameters are given in Table I. Five standard reflections were regularly monitored during the 10 days required to collect 6301 observations. Only random fluctuations were seen. Coincidence losses in counting were minimized for strong reflections by using Cu foil attenuators.

The recorded intensities were corrected for background, Lorentz, and polarization effects, and a standard deviation $\sigma(I)$ assigned to each intensity ($I$), such that $(\sigma(I))^2 = C + \frac{1}{4}(t_c/t_b)^2(b_l + b_h) + (pI)^2$, where $C$ = total count measured in time $t_c$, and $b_l$ and $b_h$ are background counts each measured in time $t_b$. $p$ was chosen as 0.03.[10] Of

**Table II.** Atomic Positional and Thermal Parameters ($\times 10^4$)

| atom | $x$ | $y$ | $z$ | $U_{11}$[b] | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Os | 2581.5(2)[a] | 2488.4(1) | 341.6(2) | 301(1) | 340(1) | 269(1) | −82(1) | 98(1) | 63(1) |
| Se(1) | 3778(1) | 2797.5(4) | −1112(1) | 506(4) | 588(4) | 383(3) | −227(3) | 191(3) | 65(3) |
| Se(2) | 1354(1) | 3271.1(4) | −1732(1) | 502(4) | 567(4) | 408(3) | −140(3) | 61(3) | 210(3) |
| P(1) | 1602(1) | 1454(1) | −1489(1) | 381(7) | 371(7) | 331(7) | −113(5) | 128(6) | 51(5) |
| P(2) | 3604(1) | 3557(1) | 2064(1) | 344(7) | 341(6) | 323(7) | −75(5) | 118(5) | 56(5) |
| C(1) | 3955(6) | 1792(3) | 1563(6) | 468(32) | 491(32) | 372(30) | −138(27) | 189(26) | −3(26) |
| O(1) | 4755(5) | 1358(3) | 2293(5) | 572(27) | 580(27) | 599(29) | 34(22) | 87(23) | 288(23) |
| C(2) | 1208(6) | 2567(3) | 1082(6) | 451(32) | 492(32) | 367(30) | −149(26) | 120(26) | 35(24) |
| O(2) | 352(5) | 2627(3) | 1535(5) | 557(28) | 1007(39) | 626(30) | −236(26) | 359(25) | 81(27) |

| atom | $x$ | $y$ | $z$ | $U$ | atom | $x$ | $y$ | $z$ | $U$ |
|---|---|---|---|---|---|---|---|---|---|
| C(11) | 1979(6) | 533(3) | −824(6) | 440(13) | C(41) | 3362(6) | 4485(3) | 1472(6) | 379(11) |
| C(12) | 2418(8) | −181(5) | −1508(9) | 709(20) | C(42) | 4512(7) | 4828(4) | 1747(7) | 535(15) |
| C(13) | 2603(10) | −866(6) | −949(11) | 899(26) | C(43) | 4271(8) | 5514(4) | 1218(8) | 667(19) |
| C(14) | 2340(9) | −833(5) | 217(10) | 810(23) | C(44) | 2956(8) | 5861(4) | 475(8) | 681(19) |
| C(15) | 1893(9) | −144(5) | 894(9) | 746(21) | C(45) | 1796(8) | 5543(4) | 215(8) | 681(19) |
| C(16) | 1715(7) | 537(4) | 368(8) | 596(17) | C(46) | 2012(7) | 4851(4) | 714(7) | 558(16) |
| C(21) | −353(6) | 1560(3) | −2402(6) | 399(12) | C(51) | 2939(6) | 3810(3) | 3499(6) | 413(12) |
| C(22) | −1241(6) | 2218(3) | −2124(7) | 487(14) | C(52) | 2348(8) | 4556(4) | 3903(8) | 638(18) |
| C(23) | −2722(7) | 2283(4) | −2842(8) | 603(17) | C(53) | 1901(9) | 4695(5) | 5021(9) | 756(21) |
| C(24) | −3259(8) | 1675(4) | −3895(8) | 681(19) | C(54) | 2007(9) | 4125(5) | 5729(9) | 737(21) |
| C(25) | −2407(8) | 1025(4) | −4198(8) | 643(18) | C(55) | 2605(7) | 3375(4) | 5343(8) | 607(17) |
| C(26) | −938(7) | 955(4) | −3426(7) | 553(15) | C(56) | 3041(6) | 3230(3) | 4233(7) | 488(14) |
| C(31) | 2228(6) | 1217(3) | −2951(6) | 406(12) | C(61) | 5539(6) | 3342(3) | 3063(6) | 403(12) |
| C(32) | 3645(7) | 902(4) | −2682(7) | 521(15) | C(62) | 6148(7) | 3585(4) | 4530(7) | 535(15) |
| C(33) | 4163(7) | 770(4) | −3745(8) | 611(17) | C(63) | 7614(7) | 3454(4) | 5246(8) | 611(17) |
| C(34) | 3271(8) | 956(4) | −5067(8) | 639(18) | C(64) | 8492(8) | 3103(4) | 4532(8) | 643(18) |
| C(35) | 1891(7) | 1269(4) | −5352(8) | 616(17) | C(65) | 7911(8) | 2866(5) | 3096(9) | 708(20) |
| C(36) | 1355(7) | 1404(4) | −4296(7) | 496(14) | C(66) | 6427(7) | 2970(4) | 2369(8) | 606(17) |

[a] Estimated standard deviations in this and other tables are given in parentheses, and correspond to the least significant digit(s). [b] $U_{ij} = \beta_{ij}/(2\pi^2 a_i^* a_j^*)$ Å$^2$. The thermal ellipsoid is given by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

the 6301 reflections recorded, 295 were standards. There were 5319 unique data with $I > 3\sigma(I)$ which were used in the solution and refinement of the structure.

**Solution and Refinement of the Structure.** The structure was solved by the heavy-atom method, and refined by full-matrix least-squares techniques on $F$. Scattering factors for neutral nonhydrogen atoms were taken from ref 5b, while those for H were from Stewart et al.[11] The real and imaginary corrections for anomalous dispersion of Cromer and Liberman[12] were included for Os, Se, and P.

In the early stages of refinement the phenyl rings were constrained as rigid groups ($D_{6h}$, C–C 1.392 Å)[13] and isotropic thermal parameters were assigned to nongroup atoms. Two cycles of refinement with all 45 nonhydrogen atoms included gave agreement factors $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.11$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2)^{1/2} = 0.14$. The function minimized was $\sum w(|F_o| - |F_c|)^2$ and the weight $w$ is given by $4F_o{}^2/\sigma^2(F_o{}^2)$. The data were then corrected for absorption effects, using the analytical method.[7] Further refinement proceeded smoothly, until, with anisotropic thermal parameters assigned to nongroup atoms and individual isotropic parameters refined for group atoms, the 30 H atoms were readily located. These were included in idealized positions (sp$^2$ hybridization at C, C–H 0.95 Å). Refinement of 154 variables converged at $R_1 = 0.035$ and $R_2 = 0.048$.

For the final cycles of refinement, the group constraints were removed, and the phenyl ring atoms refined with isotropic thermal parameters. H atom contributions were recalculated after each cycle, and the model converged (5319 unique data, 226 variables) with agreement factors $R_1 = 0.034$ and $R_2 = 0.046$. In the final cycle the largest shift, 0.09 esd, was associated with the $x$ coordinate of C(44). Of the data for which $0 < I < 3\sigma(I)$ no structure factor was in error by greater than $5\sigma$. A statistical analysis of $R_2$ over various ranges of $|F_o|$, $\lambda^{-1}\sin\theta$, and diffractometer setting angles $\chi$ and $\phi$ showed no abnormal trends. Secondary extinction effects could be ignored. The error in an observation of unit weight is 2.13 electrons. The highest peak in a difference Fourier synthesis is of electron density 1.1 (1) e Å$^{-3}$ at fractional corrdinates (0.334, −0.188, 0.340) and is of no chemical significance. Final positional and thermal parameters are listed in Table II. H atom parameters are given in Table III, which has been deposited, along with the structure amplitudes listed as $10|F_o|$ and $10|F_c|$ in electrons, Table IV.

## Results and Discussion

We have already reported[14] the preparation of the complexes $Ru(\eta^2\text{-}S_2)(CO)_2(PPh_3)_2$ and $Os(\eta^2\text{-}S_2)(CO)_2(PPh_3)_2$ together with the crystal structure of the alkylated derivative $[Os(\eta^2\text{-}S_2Me)(CO)_2(PPh_3)_2]ClO_4\cdot{}^1\!/_2C_6H_6$.

We now report that red selenium reacts with the zerovalent complexes $Os(CO)_2(PPh_3)_3$ and $Os(CO)(CNR)(PPh_3)_3$ (where R = $p$-tolyl) in rigorously degassed benzene solutions to yield the crystalline purple complexes $Os(\eta^2\text{-}Se_2)(CO)_2(PPh_3)_2$ and $Os(\eta^2\text{-}Se_2)(CO)(CNR)(PPh_3)_2$ respectively, together with 1 mol of $Ph_3PSe$. The reaction is quicker for the zerovalent isonitrile since the metal is more electron rich, and, by comparison, no reaction occurs with the $[Os(NO)(CO)(PPh_3)_3]^+$ cation. These complexes are air stable in the solid state and can be recrystallized from chloroform/alcohol mixtures with about 80% recovery. The dicarbonyl complexes exhibit two strong carbonyl stretching frequencies in the infrared, typical of cis carbonyls and very similar to those observed for the analogous dioxygen complexes.[2b] A weak frequency is also observed in the 310-cm$^{-1}$ region which is assigned to the (Se–Se) group, and a similar frequency has been reported[15] for the complex $[Ir(Se_2)(dppe)_2]Cl$ (where dppe = $Ph_2PCH_2CH_2PPh_2$). The analogous (S–S) vibration is obscured by phosphine absorption. Infrared data for these complexes are listed in Table V.

**Reactivity of the Disulfur and Diselenium Ligands.** In direct contrast to the established oxidizing nature of the coordinated dioxygen ligand[16] we have found these ligands to be electron rich and to be subject to electrophilic attack. Where the electrophile in its reduced state is a good ligand, the product is a stable complex containing the new ligand. This parallels the results for the oxidized substrate in the dioxygen system.[16] However, where the reduced electrophile is a poor ligand it leaves the complex, and the disulfur or diselenium ligand is

**Table V.** Infrared and $^1H$ NMR Data for the Complexes Reported[a]

| complex | $\nu_{CO}$, $cm^{-1}$ | $\nu_{CNR}$, $cm^{-1}$ | $\nu_{Se-Se}$, $cm^{-1}$ | $^1H$ NMR, $\tau$ |
|---|---|---|---|---|
| $Os(\eta^2\text{-}S_2)(CO)_2(PPh_3)_2$ | 1998 vs<br>1944 vs | | | |
| $Os(\eta^2\text{-}Se_2)(CO)_2(PPh_3)_2$ | 2000 vs<br>1937 vs | | 312 w | |
| $Os(\eta^2\text{-}Se_2)(CO)(CNC_7H_7)(PPh_3)_2$ | 1932 vs | 2108 vs | 309 w | |
| $[Os(\eta^2\text{-}S_2Me)(CO)_2(PPh_3)_2]^+SO_3CF_3^-$ | 2045 vs<br>1980 vs | | | 8.0 (s) (S-Me) |
| $[Os(\eta^2\text{-}Se_2Me)(CO)_2(PPh_3)_2]^+ClO_4^-$ | 2037 vs<br>1976 vs | | | 8.15 (s) (Se-Me) |
| $[Os(\eta^2\text{-}Se_2Me)(CO)(CNC_7H_7)(PPh_3)_2]^+ ClO_4^-$ | 1956 vs | 2157 vs | | 8.20 (s), 8.27 (s) (Se-Me)<br>7.7 (s) (*p*-tolyl) |
| $Os(\eta^1\text{-}Se_2Me)H(CO)_2(PPh_3)_2$ | 2024 vs<br>1951 vs | | | 9.13 (s) (Se-Me)<br>14.43 (t) (Os-H)<br>$J_{^{31}P-^{1}H}$ = 10 Hz |
| $Os(\eta^1\text{-}Se_2Me)H(CO)(CNC_7H_7)(PPh_3)_2$ | 1954 vs | 2100 vs | | 9.03 (s) (Se-Me)<br>7.7 (s) (*p*-tolyl)<br>14.42 (t), 14.65 (t) (Os-H)<br>$J_{^{31}P-^{1}H}$ = 10 Hz |

[a] vs = very strong, w = weak, s = singlet, t = triplet.

oxidized to elemental sulfur or selenium, which is deposited. The remaining osmium fragment $Os(CO)_2(PPh_3)_2$ then either coordinates two anionic ligands if they are available to yield stable $OsX_2(CO)_2(PPh_3)_2$ complexes or decomposes if they are not.

Thus, reaction with methyl triflate is rapid and results in yellow, cationic complexes of the type $[Os(\eta^2\text{-}Se_2Me)(CO)_2(PPh_3)_2]^+$ and $[Os(\eta^2\text{-}Se_2Me)(CO)(CNR)(PPh_3)_2]^+$ (where R = *p*-tolyl), the anion of which can readily be exchanged for perchlorate. Their infrared spectra show that the perchlorate ion is not coordinated to the metal, suggesting that the ($Se_2Me$) ligand is bidentate. We have previously reported the X-ray structure of the sulfur analogue.[14] These complexes also possess cis carbonyls, their infrared spectra showing the two strong carbonyl vibrations shifted to higher energy (~40 $cm^{-1}$) as a result of the charge on the central metal atom. For the isonitrile complex the (C≡N) frequency is raised by ~50 $cm^{-1}$ and the carbonyl by 24 $cm^{-1}$.

The $^1H$ NMR spectra of these complexes show the presence of the (S–Me) group as a singlet in the region of $\tau$ 8.0–8.2. In the case of $[Os(\eta^2\text{-}Se_2Me)(CO)(CNR)(PPh_3)_2]^+$ (where R = *p*-tolyl) the presence of geometric isomers is indicated by the methyl resonance appearing as two singlets at $\tau$ 8.20 and 8.27.

The alkylated complexes react further with sodium borohydride to yield neutral hydride complexes containing a unidentate (-Se-Se-Me) group. In the case of the sulfur analogue this complex is unstable and rapidly evolves an evil-smelling gas. For the selenium system, however, stable, yellow, crystalline compounds are obtained. The carbonyl frequencies are lowered somewhat in these neutral complexes and the (Se–Me) resonances in the $^1H$ NMR spectra are shifted upfield to ~$\tau$ 9.1. The hydride frequencies are seen as triplets through coupling with the two cis phosphines with a coupling constant of 10 Hz, and appear at ~$\tau$ 14.5. In the isonitrile case geometric isomers are again indicated since the hydride appears as two triplets at $\tau$ 14.52 and 14.65. Infrared and $^1H$ NMR data for these alkylated complexes are given in Table V.

Reaction of the $Os(\eta^2\text{-}R_2)(CO)_2(PPh_3)_2$ complexes (R = S or Se) with elemental iodine in degassed dichloromethane results in the formation of elemental sulfur or red selenium which is deposited, and the formation of the known[17] complex $OsI_2(CO)_2(PPh_3)_2$, which was identified by its infrared spectrum ($\nu_{CO}$ 2035, 1970 $cm^{-1}$), positive iodide, and negative sulfur or selenium tests.

It has been observed that $d^8$ dioxygen complexes readily oxidize nitric oxide to coordinated nitrite, but a similar reaction does not occur for $d^6$ dioxygen complexes.[16] We have found that the disulfur or diselenium ligands show no reaction whatsoever with nitric oxide gas even under the influence of heat or UV irradiation.

However, reaction occurs quickly with $NOPF_6$, the nitrosyl cation being reduced to nitric oxide, which is evolved. The osmium residue could not be characterized but some red selenium is deposited and the residue contains the hexafluorophosphate anion but no evidence of coordinated nitric oxide.

The reaction with dinitrogen tetroxide is similar. The nitrosyl cation formed by self-ionization of the solvent is again reduced. The formation of nitric oxide is readily seen by its reaction with the excess nitrogen dioxide to form the characteristic green solution of dinitrogen trioxide. Elemental sulfur and selenium are deposited and the nitrate ion from the self-ionization coordinates to the osmium yielding the known[3] complex $Os(NO_3)_2(CO)_2(PPh_3)_2$ which was identified by its infrared spectrum ($\nu_{CO}$ 2030, 1975 $cm^{-1}$; $\nu_{NO_3^-}$ 1505, 1270, 985, 790 $cm^{-1}$), melting point (211–213 °C), and a negative test for sulfur or selenium.

Reactions were also studied with *p*-tolyldiazonium tetrafluoroborate in degassed dichloromethane. Immediate rapid evolution of nitrogen was observed. In the sulfur case a deep red-orange color developed which with time faded to orange. In the selenium case a deep purple color was formed which on standing also went orange. If hexane was added to the purple solution a purple solid was precipitated, but it could not be characterized. This material contained selenium but less than 2 mol per mol of osmium, and in alcohol the material rapidly deposited selenium and an orange solution resulted. Both the initial purple solid and the final orange solids isolated contained the tetrafluoroborate anion and may well be hydroxy cations but satisfactory analysis could not be obtained. No evidence was found for the presence of the *p*-tolyl group in the osmium residues. It is clear that initially an electron is transferred to the diazonium cation liberating nitrogen gas, and that the oxidized osmium complex then slowly reacts with the solvent, elemental selenium being deposited.

The parent complexes form reversible Lewis base adducts in solution with both sulfur dioxide and tetracyanoethylene, but on pumping under vacuum only starting materials could be recovered. Solutions of the yellow disulfur complex in dichloromethane turned red when sulfur dioxide was admitted, and with tetracyanoethylene a green solution was obtained. By comparison the dioxygen complexes oxidize sulfur dioxide to coordinated sulfate.[16]

**Description of the Structure.** A stereoview of the molecule

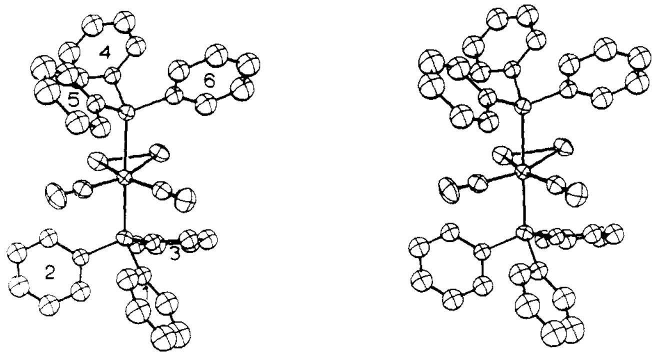

**Figure 1.** A stereoview of the molecule, showing the numbering scheme for the phenyl rings; 50% probability thermal ellipsoids are shown.

**Table VI.** Selected Intramolecular Dimensions

| | | | |
|---|---|---|---|
| | Distances (Å) | | |
| Se(1)-Se(2) | 2.321(1) | Os-C(1) | 1.884(6) |
| Os-Se(2) | 2.5403(8) | Os-C(2) | 1.865(6) |
| Os-Se(1) | 2.5526(7) | C(1)-O(1) | 1.141(7) |
| Os-P(1) | 2.400(1) | C(2)-O(2) | 1.152(7) |
| Os-P(2) | 2.412(1) | | |
| | Angles (deg) | | |
| P(1)-Os-Se(1) | 91.82(4) | P(1)-Os-P(2) | 176.09(5) |
| P(1)-Os-Se(2) | 82.68(4) | Se(1)-Os-Se(2) | 54.23(2) |
| P(2)-Os-Se(1) | 84.37(4) | Os-C(1)-O(1) | 177.9(5) |
| P(2)-Os-Se(2) | 94.34(4) | Os-C(2)-O(2) | 179.0(6) |
| P(1)-Os-C(1) | 92.7(2) | P(2)-Os-C(1) | 89.2(2) |
| P(1)-Os-C(2) | 90.8(2) | P(2)-Os-C(2) | 92.4(2) |
| | Phenyl Rings, Mean Dimensions | | |
| | Distances (Å) | | |
| P-C(1) | | | 1.830(4) |
| C(1)-C(2), C(1)-C(6) | | | 1.380(7) |
| C(2)-C(3), C(5)-C(6) | | | 1.39(1) |
| C(3)-C(4), C(4)-C(5) | | | 1.36(2) |
| | Angles (deg) | | |
| C(2)-C(1)-C(6) | | | 118.3(5) |
| C(3)-C(4)-C(5) | | | 121(1) |
| C(1)-C(2)-C(3), C(1)-C(6)-C(5) | | | 121(1) |
| C(2)-C(3)-C(4), C(4)-C(5)-C(6) | | | 120(1) |

is given in Figure 1, while details of the inner coordination sphere are shown in Figure 2. Selected bond distances and bond angles are listed in Table VI.

The crystal structure consists of discrete molecules, for the closest intermolecular distance of approach is 2.45 Å between H1C(12) and H1C(32). The shortest Os-Os distance is 9.146 (2) Å.

The coordination geometry around the Os atom may be considered that of a distorted octahedron, for, although the Se-Os-Se angle is only 54.23 (2)°, the C-Os-C angle is 94.6 (3)°. The Os atom and the CO ligands form the equatorial plane, Table VII, while the phosphine ligands occupy the apices. The Se-Se ligand is at an angle of 8.8 (2)° to this plane, for Se(1) is displaced 0.16 Å to one side and Se(2) 0.21 Å to the other. The Se-Se distance of 2.321 (1) Å is longer (4.4$\sigma$) than that of 2.19 (3) Å found in gaseous $Se_2$ by electron diffraction at 750 °C.[18] The gray allotrope of Se, the trigonal modification containing spiral chains of atoms, has a Se-Se distance of 2.373 (5) Å,[19] whereas values of 2.34 (2) and 2.34 (1) Å were found in the red, monoclinic forms, $\alpha$- and $\beta$-selenium, each of which contains $Se_8$ rings.[20,21] These and other structural aspects of Se chemistry have been reviewed by Cooper and Westbury[22] and Cordes.[22] Upon coordination there is a significant lengthening of the Se-Se bond to a value close to those found in the various allotropes. By comparison the S-S distance in the cation $[Ir(S_2)(Ph_2PCH_2CH_2PPh_2)_2]^+$ has been found[23] to be 2.066 (6) Å compared to 2.060 (3) Å[24] in $S_8$ and 1.887 Å for gaseous $S_2$.[25] We have also found[14] the S-S distance to be 2.04 Å in the complex $[Os(\eta^2\text{-}S_2Me)(CO)_2(PPh_3)_2]ClO_4{\cdot}{}^1\!/_2C_6H_6$.

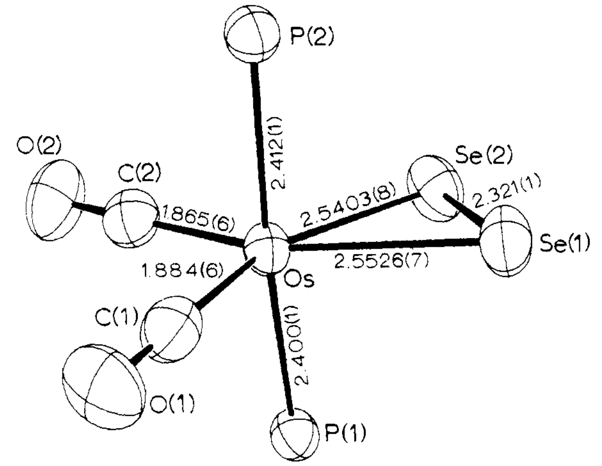

**Figure 2.** A perspective view of the molecule showing the atom numbering scheme and some selected bond distances. The phenyl rings of the triphenylphosphine ligands have been omitted.

**Table VIII.** $Os(4f_{7/2})$ Binding Energies (eV)

| | |
|---|---|
| $Os(CO)_2(PPh_3)_3$ | 49.4 |
| $Os(CO)_3(PPh_3)_2$ | 50.3 |
| $Os(\eta^2\text{-}S_2)(CO)_2(PPh_3)_2$ | 50.6 |
| $Os(\eta^2\text{-}Se_2)(CO)_2(PPh_3)_2$ | 50.8 |
| $OsCl_2(CO)_2(PPh_3)_2$ | 51.2 |

The Os-P distances differ by 6$\sigma$, and the Os-Se distances by 12$\sigma$. Though the standard deviations are probably underestimated on the Os, Se, and P atoms, it appears that these differences are significant, presumably due to nonbonded contacts. There is no such variation between dimensions in the Os-CO groupings; the weighted mean dimensions are Os-C 1.875 (4) Å, C-O 1.147 (5) Å, and Os-C-O 178.4 (4)°. These are normal.[26-31]

In the early stages of the refinement, $D_{6h}$ symmetry was imposed upon the phenyl rings, C-C 1.392 Å. Only small distortions from this ideal geometry were found when the group constraints were lifted, Table VI, though the P-C-C angles ranged from 118.5 (5) to 123.8 (5)°. All six rings are planar within experimental error, with the P atom significantly displaced from the plane, Table VII.

In an attempt to assign an oxidation state to the Os atom in the complex $Os(\eta^2\text{-}Se_2)(CO)_2(PPh_3)_2$, the ESCA spectra of some pertinent complexes were recorded. The data are presented in Table VIII, and indicate that the $S_2$ and $Se_2$ ligands are effective at removing electron density from the metal. This, together with the distorted octahedral geometry, suggests that the complex $Os(\eta^2\text{-}Se_2)(CO)_2(PPh_3)_2$ is best described formally as a compound of Os(II).

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**Supplementary Material Available:** Table III, hydrogen atom parameters, Table IV, observed and calculated structure amplitudes, and Table VII, weighted least-squares planes (16 pages). Ordering information is given on any current masthead page.

## References and Notes

(1) (a) University of Western Ontario; (b) University of Toronto.
(2) (a) N. Ahmad, J. J. Levison, S. D. Robinson, and M. F. Uttley, *Inorg. Synth.*,

15, 53 (1974); (b) B. E. Cavit, K. R. Grundy, and W. R. Roper, *J. Chem. Soc., Chem. Commun.*, 60 (1972).
(3) K. R. Grundy, Ph.D. Thesis, University of Auckland, New Zealand, 1975.
(4) The computer programs used include local modifications of the following for the CDC Cyber 73/14: cell reduction, TRACER, by S. L. Lawton; cell refinement and orientation matrix, PICKTT, from W. E. Hamilton's MODE1; full-matrix least-squares refinement, WOCLS, from J. A. Ibers' NUCLS; Patterson and Fourier syntheses, FORDAP, by A. Zalkin; function and errors, ORFFE, by W. R. Busing, K. O. Martin, and H. A. Levy; crystal structure illustrations, ORTEP, by C. K. Johnson.
(5) "International Tables for X-ray Crystallography", Kynoch Press, Birmingham, England: (a) Vol. I; (b) Vol. IV.
(6) W. H. Zachariasen, *Acta Crystallogr.*, **18**, 705 (1965).
(7) D. Cahen and J. A. Ibers, *J. Appl. Crystallogr.*, **5**, 298 (1972).
(8) P. G. Lenhert, *J. Appl. Crystallogr.*, **8**, 568 (1975).
(9) T. C. Furnas, "Single Crystal Orienter Instruction Manual", General Electric Co., Milwaukee, Wis., 1957.
(10) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).
(11) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(12) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(13) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).
(14) G. R. Clark, D. R. Russell, W. R. Roper, and A. Walker, *J. Organomet. Chem.*, **136**, C1 (1977).
(15) A. P. Ginsberg and W. E. Lindsell, *Chem. Commun.*, 232 (1971).
(16) J. S. Valentine, *Chem. Rev.*, **73**, 235 (1973).
(17) J. P. Collman and W. R. Roper, *J. Am. Chem. Soc.*, **88**, 3504 (1966).
(18) L. R. Maxwell and V. M. Mosley, *Phys. Rev.*, **57**, 21 (1940).
(19) P. Cherin and P. Unger, *Inorg. Chem.*, **6**, 1589 (1967).
(20) R. D. Burbank, *Acta Crystallogr.*, **4**, 140 (1951).
(21) R. E. Marsh and J. D. McCullough, *J. Am. Chem. Soc.*, **73**, 1106 (1951).
(22) W. C. Cooper and R. A. Westbury, "Selenium", Van Nostrand-Reinhold, Princeton, N.J., 1974, p 87; A. W. Cordes, *ibid.*, p 298.
(23) W. D. Bonds and J. A. Ibers, *J. Am. Chem. Soc.*, **94**, 3413 (1972).
(24) A. Caron and J. Donohue, *Acta Crystallogr.*, **18**, 562 (1965).
(25) "Tables of Interatomic Distances and Configuration in Molecules and Ions", The Chemical Society, London, 1958.
(26) J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, **8**, 419 (1969).
(27) D. Bright and J. A. Ibers, *Inorg. Chem.*, **8**, 1078 (1969).
(28) G. R. Clark, J. M. Waters, and K. R. Whittle, *J. Chem. Soc., Dalton Trans.*, 463 (1975).
(29) G. R. Clark, J. M. Waters, and K. R. Whittle, *J. Chem. Soc., Dalton Trans.*, 2233 (1975).
(30) M. Cowie, B. L. Haymore, and J. A. Ibers, *Inorg. Chem.*, **14**, 2617 (1975).
(31) J. M. Waters and J. A. Ibers, *Inorg. Chem.*, **16**, 3273 (1977).

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# A Novel Class of Thioketone Complexes. Crystal Structure of Bis($\eta^5$-cyclopentadienyl)(thiocamphor)tetracarbonyldimolybdenum[1]

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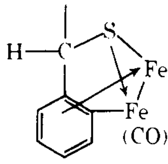
**Abstract:** Diaryl, aralkyl, and cycloalkyl thioketones react with dicyclopentadienylhexacarbonyldimolybdenum or -ditungsten to give a new class of thione complexes. These complexes, of formula $(R_2CS)M_2(CO)_4(C_5H_4R')_2$ (M = Mo, W), can also be synthesized by a very facile reaction of thioketones with the metal–metal triple-bonded complexes $[(C_5H_4R')M(CO)_2]_2$. The structures of these organosulfur compounds were elucidated on the basis of elemental analyses and infrared and magnetic resonance ($^1H$, $^{13}C$) data, as well as an X-ray analysis of the thiocamphor molybdenum complex. The X-ray analysis reveals novel bonding of the thioketone function, as well as the existence of one semibridging [Mo(1)–C(2)–O(2) angle of 161.9°] and three terminal carbonyl groups. The molybdenum–molybdenum bond distance is 3.145 Å. Several of the complexes undergo equilibration in solution.

## Introduction

There has been considerable interest, in recent years, in thioketone complexes of transition metals. Two classes of thione complexes have been reported in the literature: (1) sulfur-donor ligand ortho-metalated complexes with a transformed (e.g., **1**)[3,4] or retained (e.g., **2**)[5,6] thiocarbonyl function; (2) n-donor ligand complexes utilizing a lone pair of sulfur in bonding to a metal (e.g., **3**).[7-12]



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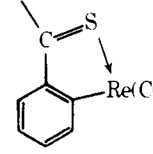

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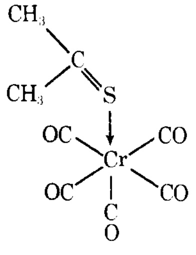

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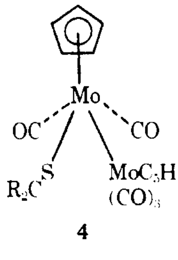
We decided to extend our investigations of thione–metal carbonyl chemistry to the reaction of the organosulfur compounds with the binuclear metal carbonyls, dicyclopentadienylhexacarbonyldimolybdenum and -ditungsten. It was anticipated that ligand substitution would take place, giving complexes capable of undergoing cis–trans isomerism (**4** ⇄ **5**).[13,14] Such complexes were not formed, but rather this study has led to the isolation and characterization by X-ray crystal-structure analysis of a third, and novel, class of thioketone complexes.



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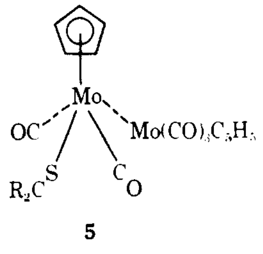

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## Results and Discussion

**Synthesis of the Complexes.** Treatment of a series of diaryl, aralkyl, and cycloalkyl thioketones (**6**) with the dimer of cyclopentadienylmolybdenum or -tungsten tricarbonyl (**7**, M = Mo, W; R′ = H) affords $(R_2CS)M_2(CO)_4(C_5H_4R')_2$ (**8**), with the disubstituted complex **9** being formed in several instances.

0002-7863/79/1501-6582$01.00/0