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Insertion Reactions of $[\mathrm{M(SR)_3(PMe_2Ph)_2}]$ with $\mathrm{CS_2}$ (M = Ru, Os; R = $\mathrm{C_6F_4H}$-4, $\mathrm{C_6F_5}$). X-ray Structures of $[\mathrm{Ru(S_2CSC_6F_4H\text{-}4)_2(PMe_2Ph)_2}]$, *trans*-Thiolates $[\mathrm{M(SR)_2(S_2CSR)(PMe_2Ph)_2}]$ (M = Ru; R = $\mathrm{C_6F_5}$ and M = Os; R = $\mathrm{C_6F_4H}$-4), and *trans*-Thiolate–Phosphine $[\mathrm{Os(SC_6F_5)_2(S_2CSC_6F_5)(PMe_2Ph)_2}]$

Maribel Arroyo,*,[†] Sylvain Bernès,[†] Joaquín Cerón,[†] Jordi Rius,[‡] and Hugo Torrens[§]

Centro de Química del Instituto de Ciencias, Benemérita Universidad Autónoma de Puebla, Apdo. Postal J-42, San Manuel, C. P. 72571, Puebla, Pue., Mexico, Institut de Ciencia de Materials de Barcelona, Campus de la Universidad Autónoma de Barcelona, 08193 Bellaterra, Spain, and División de Estudios de Posgrado, Facultad de Química, Universidad Nacional Autónoma de México, Cd. Universitaria, 04510 México D.F., Mexico

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Reactions of $[\mathrm{M(SR)_3(PMe_2Ph)_2}]$ (M = Ru, Os; R = $\mathrm{C_6F_4H}$-4, $\mathrm{C_6F_5}$) with $\mathrm{CS_2}$ in acetone afford $[\mathrm{Ru(S_2CSR)_2(PMe_2Ph)_2}]$ (R = $\mathrm{C_6F_4H}$-4, **1**; $\mathrm{C_6F_5}$, **3**) and *trans*-thiolates $[\mathrm{Ru(SR)_2(S_2CSR)(PMe_2Ph)_2}]$ (R = $\mathrm{C_6F_4H}$-4, **2**; $\mathrm{C_6F_5}$, **4**) or the isomers *trans*-thiolates $[\mathrm{Os(SR)_2(S_2CSR)(PMe_2Ph)_2}]$ (R = $\mathrm{C_6F_4H}$-4, **5**; $\mathrm{C_6F_5}$, **7**) and *trans*-thiolate–phosphine $[\mathrm{Os(SR)_2(S_2CSR)(PMe_2Ph)_2}]$ (R = $\mathrm{C_6F_4H}$-4, **6**; $\mathrm{C_6F_5}$, **8**) through processes involving $\mathrm{CS_2}$ insertion into M–SR bonds. The ruthenium(III) complexes $[\mathrm{Ru(SR)_3(PMe_2Ph)_2}]$ react with $\mathrm{CS_2}$ to give the diamagnetic thiolate–thioxanthato ruthenium(II) and the paramagnetic ruthenium(III) complexes while osmium(III) complexes $[\mathrm{Os(SR)_3(PMe_2Ph)_2}]$ react to give the paramagnetic thiolate–thioxanthato osmium(III) isomers. The single-crystal X-ray diffraction studies of **1**, **4**, **5**, and **8** show distorted octahedral structures. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ and $^{19}\mathrm{F}$ NMR studies show that the solution structures of **1** and **3** are consistent with the solid-state structure of **1**.

Introduction

The interaction of small unsaturated molecules such as carbon disulfide and carbon dioxide, which are potential sources of $\mathrm{C_1}$ chemistry, with transition metal complexes has been reviewed[1−3] and has been shown to produce a variety of chemical transformations. The development of practical methods for the generation of organic compounds from carbon dioxide, an abundant and inexpensive source of carbon, is essential in the future management of this greenhouse gas. $\mathrm{CS_2}$ is highly reactive, and its coordination, addition, cleavage, and insertion reactions are currently being intensively investigated. The interest in the coordination chemistry of $\mathrm{CS_2}$ with transition metal complexes stems mainly from the fact that this molecule is structurally related to carbon dioxide[4−12] although it is clear that both molecules exhibit different reactivities.

There are several reports of $\mathrm{CS_2}$ insertion into M−SR bonds during the past decade;[13−17] $\mathrm{CS_2}$ insertion into Ru−

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* To whom correspondence should be addressed. E-mail: slarroyo@siu.buap.mx.

[†] Centro de Química del Instituto de Ciencias, BUAP.

[‡] Institut de Ciencia de Materials de Barcelona, Campus de la UAB.

[§] División de Estudios de Posgrado, Facultad de Química, UNAM.

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SR bonds has also been studied,[18−20] but to date, there have been few examples in the case of Os−SR bonds.[19] In addition, a study exploring the insertion reactions of CO$_2$ and CS$_2$ into M−SR bonds provides the first report of a complex isolated from the insertion of CO$_2$ into a metal−sulfur bond[15] which increases the interest in this class of processes.

The formally pentacoordinated M(III) d^5 complexes [M(SR)$_3$(PMe$_2$Ph)$_2$] (M = Ru, Os; R = C$_6$F$_4$H-4, C$_6$F$_5$) have been previously reported.[21−24] The X-ray molecular structure determinations of the ruthenium[21,22] and osmium[23,24] compounds (R = C$_6$F$_5$) showed that these complexes bear C−F−Ru or C−F−Os interactions in the solid state. The interaction of an *ortho*-fluorine of one of the SC$_6$F$_5$ ligands with the metal create an S−F chelate ligand, and the metal achieves six coordination in an approximately octahedral arrangement. The compounds [M(SR)$_3$(PMe$_2$Ph)$_2$] have shown to react with CO,[25] carboxylic[26,27] and monothiocarboxylic[28] acids, and *N*,*N*-diethyldithiocarbamate, *O*-ethyldithiocarbonate, and *O*,*O*-diethyldithiophosphate ligands.[29] We have also found that the thermolysis of [Os(SR)$_3$(PMe$_2$Ph)$_2$] in refluxing toluene causes a substantial rearrangement-oxidative reaction giving a mixture of isolated products that involves phosphine dissociation, cleavage of an *ortho*-carbon−fluorine bond at a thiolate ligand, transfer of a sulfur atom, and oxidation of the metal center.[23,24] On one hand it is known that CS$_2$ readily inserts into M−S bonds; on the other hand, the potential unsaturation on [M(SR)$_3$(PMe$_2$Ph)$_2$] can be exploited for further reactions including those of carbon disulfide. We have now found that the reactions of [M(SR)$_3$(PMe$_2$Ph)$_2$] (M = Ru, Os; R = C$_6$F$_4$H-4, C$_6$F$_5$) with CS$_2$ in acetone cause CS$_2$ insertion into M−SR bonds giving thioxanthato complexes. The ruthenium(III) complexes [Ru(SR)$_3$(PMe$_2$Ph)$_2$] react with CS$_2$ to give the diamagnetic thiolate−thioxanthato ruthenium(II) complexes [Ru(S$_2$CSR)$_2$(PMe$_2$Ph)$_2$] (R = C$_6$F$_4$H-4, **1**; C$_6$F$_5$, **3**) and the paramagnetic ruthenium(III) complexes *trans*-thiolates [Ru(SR)$_2$(S$_2$CSR)(PMe$_2$Ph)$_2$] (R = C$_6$F$_4$H-4, **2**; C$_6$F$_5$, **4**) while osmium(III) complexes [Os(SR)$_3$(PMe$_2$Ph)$_2$] react to give the paramagnetic thiolate−thioxanthato osmium(III) isomers *trans*-thiolates [Os(SR)$_2$(S$_2$CSR)(PMe$_2$Ph)$_2$] (R = C$_6$F$_4$H-4, **5**; C$_6$F$_5$, **7**) and *trans*-thiolate−phosphine [Os(SR)$_2$(S$_2$CSR)(PMe$_2$Ph)$_2$] (R = C$_6$F$_4$H-4, **6**; C$_6$F$_5$, **8**).

Experimental Section

Solvents were dried and degassed using standard techniques.[30] Thin-layer chromatography (TLC) (Merck, silica gel 60 F$_{254}$ and neutral aluminum oxide 60 F$_{254}$) was used to monitor the progress of the reactions under study. All reactions were performed under dry nitrogen or argon using Schlenk techniques. Complexes [M(SR)$_3$(PMe$_2$Ph)$_2$] (M = Ru, Os; R = C$_6$F$_4$H-4, C$_6$F$_5$) were prepared as published.[21,22] CS$_2$ (Aldrich) was used as received. The products were separated by passage through an aluminum oxide or silica gel chromatographic column with 4:1 hexanes−dichloromethane as eluent.

Melting points were obtained on a Fisher-Johns melting point apparatus.

Infrared spectra were recorded on a 750 Nicolet Fourier transform Magna-IR spectrometer.

Elemental analyses were determined by Galbraith Laboratories Inc.

^{19}F and ^{31}P{^{1}H} nuclear magnetic resonance spectra were recorded on a Varian Unity INOVA-300 spectrometer. Chemical shifts are in ppm relative to CFCl$_3$ (for ^{19}F) and H$_3$PO$_4$ (for ^{31}P) at 0 ppm.

FAB$^+$ mass spectra were performed on a JEOL JMS−SX102A mass-spectrometer using Xe gas, with 3-nitrobenzyl alcohol as matrix.

[Ru(S$_2$CSC$_6$F$_4$H-4)$_2$(PMe$_2$Ph)$_2$] (1) and *trans*-Thiolates [Ru(SC$_6$F$_4$H-4)$_2$(S$_2$CSC$_6$F$_4$H-4)(PMe$_2$Ph)$_2$] (2). In a Schlenk flask, [Ru(SC$_6$F$_4$H-4)$_3$(PMe$_2$Ph)$_2$] (0.184 g, 0.2 mmol) was dissolved in acetone (10 mL), carbon disulfide (0.7 mL, 11.6 mmol) was added, and the mixture was stirred at room temperature for 30 min. The blue-green solution became brown. The solution was evaporated to dryness under reduced pressure, and the solid residue was separated by passage through an aluminum oxide chromatographic column with 4:1 hexanes−dichloromethane as eluent, giving an orange fraction of **1** and a green fraction of **2**. The eluent was removed under vacuum.

Recrystallization of [Ru(S$_2$CSC$_6$F$_4$H-4)$_2$(PMe$_2$Ph)$_2$] (**1**) from hot hexanes gave orange crystals (0.050 g, 28%). Anal. Calcd for C$_{30}$H$_{24}$F$_8$P$_2$RuS$_6$: C, 40.40; H, 2.71; S, 21.57. Found: C, 40.36; H, 2.82; S, 21.02. Mp: 122−124 °C dec. IR (KBr, cm^{-1}): $\nu_{\mathrm{CS(S2CS)}}$ 1004(m); $\nu_{\mathrm{SR\ (thioxanthato)}}$ 1493(vs), 1436(w), 1180(m), 907(s); $\nu_{\mathrm{(phosphine)}}$ 1294(w), 1280(w), 929(s), 907(s), 746(m). ^{19}F NMR (CDCl$_3$): δ −131.15 (m, 1F^2, C$_6$F$_4$H), −137.47 (m, 1F^3, C$_6$F$_4$H). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 14.82 (s, PMe$_2$Ph). FAB$^+$-MS {*m*/*z* (%) [fragment]}: 892 (42) [M$^+$], 816 (4) [M$^+$ − (CS$_2$)], 740 (30) [M$^+$ − 2(CS$_2$)], 602 (15) [M$^+$ − 2(CS$_2$) − (PMe$_2$Ph)], 559 (18) [M$^+$ − (S$_2$CSC$_6$F$_4$H) − (CS$_2$)].

Green solid of *trans*-thiolates [Ru(SC$_6$F$_4$H-4)$_2$(S$_2$CSC$_6$F$_4$H-4)(PMe$_2$Ph)$_2$] (**2**) was obtained (0.012 g, 6%). Anal. Calcd for

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$C_{35}H_{25}F_{12}P_2RuS_5$: C, 42.17; H, 2.53; S, 16.08. Found: C, 41.95; H, 2.48; S, 16.01. Mp: 156−158 °C dec. IR (KBr, cm^{-1}): $\nu_{CS(S2CS)}$ 1012(w); $\nu_{SR(thiolate)}$ 1481(vs), 1428(m), 1171(m), 907(vs); $\nu_{SR(thioxanthato)}$ 1496(vs), 1436(w), 1181(w), 920(s); $\nu_{(phosphine)}$ 1297(w), 1282(w), 947(m), 907(vs), 742(w) . FAB$^+$-MS {*m*/*z* (%) [fragment]}: 997 (35) [M^+], 920 (17) [$M^+ - Ph$], 859 (4) [$M^+ - (PMe_2Ph)$], 816 (11) [$M^+ - (SC_6F_4H)$], 740 (23) [$M^+ - (S_2CSC_6F_4H)$], 602 (4) [$M^+ - (S_2CSC_6F_4H) - (PMe_2Ph)$], 559 (12) [$M^+ - (S_2CSC_6F_4H) - (SC_6F_4H)$].

$Ru(S_2CSC_6F_5)_2(PMe_2Ph)_2]$ (3) and *trans*-Thiolates $[Ru(SC_6F_5)_2(S_2CSC_6F_5)(PMe_2Ph)_2]$ (4). In a Schlenk flask, $[Ru(SC_6F_5)_3(PMe_2Ph)_2]$ (0.195 g, 0.2 mmol) was dissolved in acetone (10 mL), carbon disulfide (0.7 mL, 11.6 mmol) was added, and the mixture was stirred at room temperature for 30 min. The blue-green solution became brown. The solution was evaporated to dryness under reduced pressure, and the solid residue was separated by passage through an aluminum oxide chromatographic column with 4:1 hexanes−dichloromethane as eluent, giving an orange fraction of **3** and a green fraction of **4**.

The eluent was removed under vacuum giving **$[Ru(S_2CSC_6F_5)_2(PMe_2Ph)_2]$** (**3**) as an orange solid (0.046 g, 25%). Anal. Calcd for $C_{30}H_{22}F_{10}P_2RuS_6$: C, 38.83; H, 2.39; S, 20.73. Found: C, 38.65; H, 2.45; S, 20.21. Mp: 122−124 °C dec. IR (KBr, cm^{-1}): $\nu_{CS(S2CS)}$ 1001(s); $\nu_{SR(thioxanthato)}$ 1509(vs), 1491(vs), 1091(s), 980(s), 862(s); $\nu_{(phosphine)}$ 1290(w), 1280(w), 940(m), 915(s), 737(m). ^{19}F NMR ($CDCl_3$): δ −130.21 (m, 2F^2, C_6F_5), −148.50 (m, 1F^4, C_6F_5), −160.33 (m, 2F^3, C_6F_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 14.80 (s, PMe_2Ph). FAB$^+$-MS {*m*/*z* (%) [fragment]}: 928 (45) [M^+], 852 (10) [$M^+ - (CS_2)$], 776 (65) [$M^+ - 2(CS_2)$], 638 (30) [$M^+ - 2(CS_2) - (PMe_2Ph)$], 577 (55) [$M^+ - (S_2CSC_6F_4H) - (CS_2)$].

Green solid of *trans*-Thiolates $[Ru(SC_6F_5)_2(S_2CSC_6F_5)(PMe_2Ph)_2]$ (**4**) was obtained (0.021 g, 10%). Anal. Calcd for $C_{35}H_{22}F_{15}P_2RuS_5$: C, 40.00; H, 2.11; S, 15.25. Found: C, 39.85; H, 2.19; S, 15.40. Mp: 188−190 °C dec. IR (KBr, cm^{-1}): $\nu_{CS(S2CS)}$ 1011(m); $\nu_{SR(thiolate)}$ 1509(vs), 1476(vs), 1080(vs), 973(vs), 851(vs); $\nu_{SR(thioxanthato)}$ 1489(vs), 1096(m); $\nu_{(phosphine)}$ 1298(w), 1282(w), 950(m), 909(vs), 743(m). FAB$^+$-MS {*m*/*z* (%) [fragment]}: 1051 (35) [M^+], 974 (1) [$M^+ - Ph$], 913 (6) [$M^+ - (PMe_2Ph)$], 852 (24) [$M^+ - (SC_6F_5)$], 776 (42) [$M^+ - (S_2CSC_6F_5)$], 638 (5) [$M^+ - (S_2CSC_6F_5) - (PMe_2Ph)$], 577 (14) [$M^+ - (S_2CSC_6F_5) - (SC_6F_5)$].

***trans*-Thiolates $[Os(SC_6F_4H\text{-}4)_2(S_2CSC_6F_4H\text{-}4)(PMe_2Ph)_2]$ (5) and *trans*-Thiolate−Phosphine $[Os(SC_6F_4H\text{-}4)_2(S_2CSC_6F_4H\text{-}4)(PMe_2Ph)_2]$ (6).** In a Schlenk flask, $[Os(SC_6F_4H\text{-}4)_3(PMe_2Ph)_2]$ (0.202 g, 0.2 mmol) was dissolved in acetone (10 mL), carbon disulfide (0.7 mL, 11.6 mmol) was added, and the mixture was stirred at room temperature for 30 min. The purple solution became green. The solution was evaporated to dryness under reduced pressure, and the solid residue was separated by passage through a silica gel chromatographic column with 4:1 hexanes−dichloromethane as eluent, giving a blue fraction of **5** and a green fraction of **6**. The eluent was removed under vacuum.

Recrystallization of *trans*-Thiolates $[Os(SC_6F_4H\text{-}4)_2(S_2CSC_6F_4H\text{-}4)(PMe_2Ph)_2]$ (**5**) from an acetone−ethanol solution gave blue crystals (0.024 g, 11%). Anal. Calcd for $C_{35}H_{25}F_{12}OsP_2S_5$: C, 38.71; H, 2.32; S, 14.76. Found: C, 38.49; H, 2.31; S, 14.90. Mp: 188−190 °C. IR (KBr, cm^{-1}): $\nu_{CS(S2CS)}$ 1006(w); $\nu_{SR(thiolate)}$ 1478(vs), 1428(m), 1170(m), 906(vs); $\nu_{SR(thioxanthato)}$ 1496(s); $\nu_{(phosphine)}$ 1298(w), 1282(w), 938(m), 906(vs), 742(w). FAB$^+$-MS {*m*/*z* (%) [fragment]}: 1087 (38) [M^+], 949 (64) [$M^+ - (PMe_2Ph)$], 906 (50) [$M^+ - (SC_6F_4H)$], 830 (14) [$M^+ - (S_2CSC_6F_4H)$], 692 (8) [$M^+ - (S_2CSC_6F_4H) - (PMe_2Ph)$].

Green solid of *trans*-Thiolate−Phosphine $[Os(SC_6F_4H\text{-}4)_2(S_2CSC_6F_4H\text{-}4)(PMe_2Ph)_2]$ (**6**) was obtained (0.113 g, 52%). Anal. Calcd for $C_{35}H_{25}F_{12}OsP_2S_5$: C, 38.71; H, 2.32; S, 14.76. Found: C, 38.69; H, 2.48; S, 15.11. Mp: 143−144 °C. IR (KBr, cm^{-1}): $\nu_{CS(S2CS)}$ 1002(w); $\nu_{SR(thiolate)}$ 1480(vs), 1428(m), 1170(m), 908(vs); $\nu_{SR(thioxanthato)}$ 1494(s); $\nu_{(phosphine)}$ 1298(w), 1282(w), 944(m), 908(vs), 742(w). FAB$^+$-MS {*m*/*z* (%) [fragment]}: 1087 (13) [M^+], 949 (100) [$M^+ - (PMe_2Ph)$], 906 (42) [$M^+ - (SC_6F_4H)$], 830 (15) [$M^+ - (S_2CSC_6F_4H)$], 692 (9) [$M^+ - (S_2CSC_6F_4H) - (PMe_2Ph)$].

***trans*-Thiolates $[Os(SC_6F_5)_2(S_2CSC_6F_5)(PMe_2Ph)_2]$ (7) and *trans*-Thiolate−Phosphine $[Os(SC_6F_5)_2(S_2CSC_6F_5)(PMe_2Ph)_2]$ (8).** In a Schlenk flask, $[Os(SC_6F_5)_3(PMe_2Ph)_2]$ (0.213 g, 0.2 mmol) was dissolved in acetone (10 mL), carbon disulfide (0.7 mL, 11.6 mmol) was added, and the mixture was stirred at room temperature for 30 min. The purple solution became green. The solution was evaporated to dryness under reduced pressure, and the solid residue was separated by passage through a silica gel chromatographic column with 4:1 hexanes−dichloromethane as eluent, giving a blue fraction of **7** and a green fraction of **8**.

The eluent was removed under vacuum giving a blue solid ***trans*-thiolates $[Os(SC_6F_5)_2(S_2CSC_6F_5)(PMe_2Ph)_2]$** (**7**) (0.027 g, 12%). Anal. Calcd for $C_{35}H_{22}F_{15}OsP_2S_5$: C, 36.88; H, 1.95; S, 14.06. Found: C, 36.95; H, 1.99; S, 14.04. Mp: 209−213 °C dec. IR (KBr, cm^{-1}): $\nu_{CS(S2CS)}$ 1004(w); $\nu_{SR(thiolate)}$ 1508(vs), 1476(vs), 1078(s), 974(vs), 848(s); $\nu_{SR(thioxanthato)}$ 1490(vs), 1098(m); $\nu_{(phosphine)}$ 1296(w), 1282(w), 942(m), 902(s), 744(m). FAB$^+$-MS {*m*/*z* (%) [fragment]}: 1141 (39) [M^+], 1003 (88) [$M^+ - (PMe_2Ph)$], 942 (48) [$M^+ - (SC_6F_5)$], 866 (25) [$M^+ - (S_2CSC_6F_5)$], 728 (16) [$M^+ - (S_2CSC_6F_5) - (PMe_2Ph)$].

Recrystallization of ***trans*-Thiolate−Phosphine $[Os(SC_6F_5)_2(S_2CSC_6F_5)(PMe_2Ph)_2]$** (**8**) from an acetone−ethanol solution gave green crystals (0.130 g, 57%). Anal. Calcd for $C_{35}H_{22}F_{15}OsP_2S_5$: C, 36.88; H, 1.95; S, 14.06. Found: C, 36.75; H, 1.85; S, 14.54. Mp: 140−141 °C. IR (KBr, cm^{-1}): $\nu_{CS(S2CS)}$ 1010(w); $\nu_{SR(thiolate)}$ 1508(vs), 1476(vs), 1080(s), 972(vs), 850(m); $\nu_{SR(thioxanthato)}$ 1490(vs), 1096(m); $\nu_{(phosphine)}$ 1296(w), 1282(w), 942(m), 914(s), 744(w). FAB$^+$-MS {*m*/*z* (%) [fragment]}: 1141 (10) [M^+], 1003 (100) [$M^+ - (PMe_2Ph)$], 942 (38) [$M^+ - (SC_6F_5)$], 866 (15) [$M^+ - (S_2CSC_6F_5)$], 728 (9) [$M^+ - (S_2CSC_6F_5) - (PMe_2Ph)$].

Additional Experiments. The reaction of $[Ru(SC_6F_5)_3(PMe_2Ph)_2]$ and excess of CS_2 (58 molar excess), in acetone under Ar, was followed by TLC with the following outcome: After 5 min, $[Ru(S_2CSC_6F_5)_2(PMe_2Ph)_2]$, **3**, $[Ru(SC_6F_5)_2(S_2CSC_6F_5)(PMe_2Ph)_2]$, **4**, $F_5C_6SSC_6F_5$, and starting material are detected. After 10 min, we found the same species, but the concentration of the starting material is substantially lower. After 20 min, we found the same species, but **3** seems to be more abundant and the starting material has been almost consumed out.

The reaction between $[Ru(SC_6F_5)_3(PMe_2Ph)_2]$ and an equimolar quantity of CS_2 in acetone under Ar, followed by TLC, afforded compounds $[Ru(S_2CSC_6F_5)_2(PMe_2Ph)_2]$, **3**, $[Ru(SC_6F_5)_2(S_2CSC_6F_5)(PMe_2Ph)_2]$, **4**, and $F_5C_6SSC_6F_5$ along with unreacted starting material.

Reacting pure $[Ru(SC_6F_5)_2(S_2CSC_6F_5)(PMe_2Ph)_2]$, **4**, with CS_2 (174 molar excess) in acetone under Ar yields a mixture of $[Ru(S_2CSC_6F_5)_2(PMe_2Ph)_2]$, **3**, $[Ru(SC_6F_5)_2(S_2CSC_6F_5)(PMe_2Ph)_2]$, **4**, and $F_5C_6SSC_6F_5$ as shown by TLC compared with pure samples of each compound. Therefore, $[Ru(SC_6F_5)_2(S_2CSC_6F_5)(PMe_2Ph)_2]$, **4**, is precursor of $[Ru(S_2CSC_6F_5)_2(PMe_2Ph)_2]$, **3**. $F_5C_6SSC_6F_5$ was detected by TLC, comparing the reaction product with an authentic sample. The reaction of $[Ru(SC_6F_5)_2(S_2CSC_6F_5)(PMe_2Ph)_2]$, **4**, with

Table 1. X-ray Parameters

	1	4	5	8
chem formula	$C_{30}H_{24}F_8P_2RuS_6$	$C_{35}H_{22}F_{15}P_2RuS_5$	$C_{35}H_{25}F_{12}OsP_2S_5$	$C_{35}H_{22}F_{15}OsP_2S_5$
fw	891.86	1050.84	1086	1139.97
space group	$P2/c$	$C2/c$	$P\bar{1}$	$P2_1/a$
a/Å	10.2185(7)	18.7424(18)	11.590(2)	13.046(2)
b/Å	11.2170(7)	19.721(2)	12.764(3)	25.712(5)
c/Å	16.0894(12)	21.8899(16)	13.828(2)	13.187(3)
α/deg			102.28(10)	
β/deg	106.075(5)	93.764(4)	96.27(10)	117.420(10)
γ/deg			91.56(2)	
V/Å^3	1772.1(2)	8073.3(13)	1984.2(6)	3926.5(13)
Z	2	8	2	4
μ/mm^{-1}	0.951	0.823	3.640	3.695
R indices $[I > 2\sigma(I)]$[a]	R1 = 3.91% wR2 = 7.56%	R1 = 4.64% wR2 = 9.77%	R1 = 3.98% wR2 = 8.09%	R1 = 5.55% wR2 = 13.36%
R indices (all data)[a]	R1 = 7.97% wR2 = 9.44%	R1 = 8.48% wR2 = 11.23%	R1 = 10.84% wR2 = 9.94%	R1 = 23.62% wR2 = 20.25%
D_{obsd}/g cm^{-3}	1.671	1.729	1.818	1.928
T/°C	25(2)	25(2)	25(2)	25(2)
λ/Å	0.71073	0.71073	0.71073	0.71073

[a] $$\mathrm{R1} = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad \mathrm{wR2} = \sqrt{\frac{\sum w(F_o^{\,2} - F_c^{\,2})^2}{\sum w(F_o^{\,2})^2}}$$

CS$_2$ in the presence of a radical scavenger, 1,4-quinone, in acetone under Ar, does not favor the formation of [Ru(S$_2$CSC$_6$F$_5$)$_2$(PMe$_2$Ph)$_2$], **3**.

X-ray Diffraction Data. Air stable single crystals of complexes **1**, **4**, **5**, and **8** were obtained by fast (**1**) and slow (**4**, **5**, and **8**) evaporation of solutions as described above. Pertinent crystal data and other crystallographic parameters are listed in Table 1. The diffraction data were collected at room temperature on a Bruker P4 diffractometer[31] for **1** and **4** (work done in Puebla) and on an Enraf CAD4 diffractometer for **5** and **8** (work done in Barcelone) using graphite monochromated Mo *K*α radiation (λ = 0.71073 Å) and $\theta/2\theta$ or ω scan mode with variable scan speed. Structures were solved and refined using routine procedures[32] on the basis of absorption-corrected data (ψ-scans). Structures **1** and **4** were refined without restraints, while in the case of **5** and **8**, phenyl rings of the phosphine ligands were refined as idealized flat hexagons. H atoms were placed on idealized positions, and final least-squares cycles were carried-out using anisotropic displacement parameters for non-H atoms. Refinement corresponding to complex **8** is somewhat worse when compared to the other compounds, probably because of the limited thickness of the single-crystal, ca. 0.02 mm. Complete crystallographic data have been deposited in the CIF format.

Selected geometric parameters for **1**, **4**, **5**, and **8** are listed in Tables 2, 3, 4, and 5, respectively.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**[a]

Ru1−P1	2.2991(10)	Ru1−P1′	2.2991(10)
Ru1−S2	2.3808(9)	Ru1−S2′	2.3808(9)
Ru1−S1	2.4664(10)	Ru1−S1′	2.4664(10)
P1−Ru1−P1′	97.25(5)	P1′−Ru1−S2	97.17(4)
P1−Ru1−S2	93.99(3)	P1′−Ru1−S2′	93.99(3)
P1−Ru1−S2′	97.17(4)	S2−Ru1−S2′	163.08(5)
P1′-Ru1−S1′	165.24(3)	P1−Ru1−S1′	87.82(4)
S2−Ru1−S1′	96.28(4)	S2′−Ru1−S1′	71.56(3)
P1′-Ru1−S1	87.82(4)	P1−Ru1−S1	165.24(3)
S2−Ru1−S1	71.56(3)	S2′−Ru1−S1	96.28(4)
S1′-Ru1−S1	90.70(5)		

[a] Primed atoms are generated through operator $-x, y, -z + {}^1/_2$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **4**

Ru1−S5	2.3336(13)	Ru1−S4	2.3366(13)
Ru1−P1	2.3609(13)	Ru1−P2	2.3705(12)
Ru1−S2	2.4289(12)	Ru1−S1	2.4625(11)
S5−Ru1−S4	171.07(5)	S5−Ru1−P1	87.75(5)
S4−Ru1−P1	90.56(5)	S5−Ru1−P2	87.28(4)
S4−Ru1−P2	84.18(4)	P1−Ru1−P2	96.19(5)
S5−Ru1−S2	94.68(4)	S4−Ru1−S2	94.17(4)
P1−Ru1−S2	93.30(4)	P2−Ru1−S2	170.38(4)
S5−Ru1−S1	91.62(4)	S4−Ru1−S1	92.39(4)
P1−Ru1−S1	164.15(5)	P2−Ru1−S1	99.60(4)
S2−Ru1−S1	70.95(4)		

Results and Discussion

The reactions between [M(SR)$_3$(PMe$_2$Ph)$_2$] and CS$_2$ were monitored by TLC. The blue complex [Ru(SR)$_3$(PMe$_2$Ph)$_2$] (R = C$_6$F$_4$H-4 or C$_6$F$_5$) readily reacts with CS$_2$ in acetone to give an orange-brown solution from which the orange diamagnetic thioxanthato ruthenium(II) complex [Ru(S$_2$CSR)$_2$(PMe$_2$Ph)$_2$] (R = C$_6$F$_4$H-4 **1**, C$_6$F$_5$ **3**), in 28% (**1**) or 25% (**3**) yield, respectively, and the green paramagnetic thiolate−thioxanthato ruthenium(III) complex *trans*-thiolates [Ru(SR)$_2$(S$_2$CSR)(PMe$_2$Ph)$_2$] (R = C$_6$F$_4$H-4 **2**, C$_6$F$_5$ **4**), in 6% (**2**) or 10% (**4**) yield, respectively, have been isolated by passage through a chromatographic column (Scheme 1).

The orange complexes [Ru(S$_2$CSR)$_2$(PMe$_2$Ph)$_2$] (R = C$_6$F$_4$H-4, **1**; C$_6$F$_5$, **3**) decompose readily in solution, but they are relatively stable in the solid state necessitating their isolation. These ruthenium(II) complexes were characterized by elemental analyses, FAB$^+$-spectrometry, and spectroscopy. The ^{31}P{^{1}H} and ^{19}F NMR studies also suggest that two CS$_2$ molecules had been incorporated into Ru−SR bonds while one SR ligand had been lost. This was confirmed by the X-ray structure determination of **1** shown in Figure 1.

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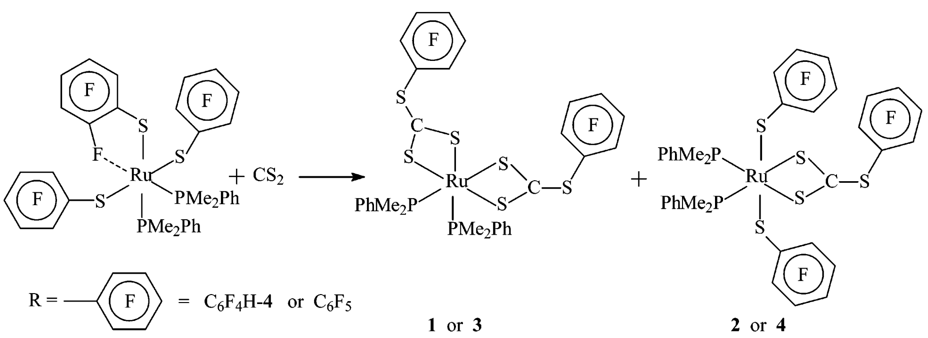
(31) *XSCAnS (release 2.21) Users Manual*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1996.

(32) Sheldrick, G. M. *SHELXTL-plus*, release 5.10; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1998. Sheldrick, G. M. *SHELX97 Users Manual*; University of Göttingen: Göttingen, Germany 1997.

Scheme 1



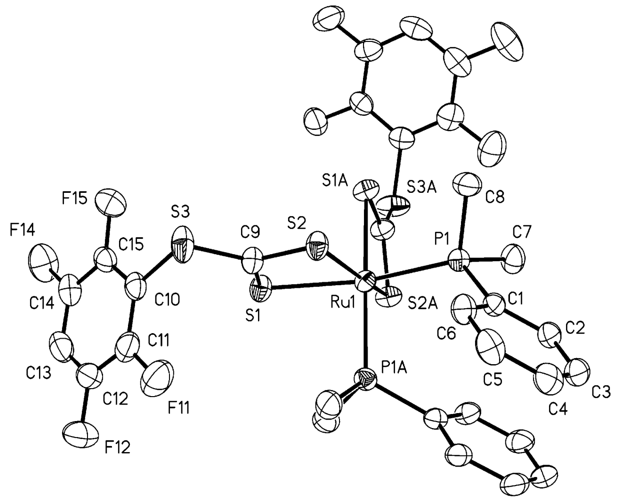


Figure 1. Structure of complex **1** showing thermal displacement parameters at the 30% probability level. H atoms are omitted for clarity. Atoms labeled as A are generated through the following operator: $-x$, y, $-z + {}^{1}/_{2}$.

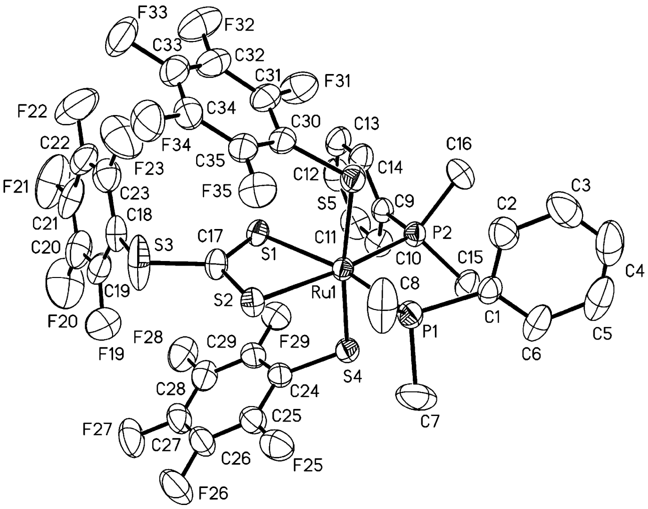


Figure 2. Structure of complex **4** showing thermal displacement parameters at the 30% probability level. H atoms are omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **5**

Os−S1	2.4555(12)	Os−S2	2.4279(13)
Os−S10	2.3459(14)	Os−S20	2.3476(14)
Os−P30	2.3706(13)	Os−P40	2.3422(13)
P40−Os−S10	86.79(5)	P40−Os−S20	86.30(5)
S10−Os−S20	172.64(5)	P40−Os−P30	95.70(5)
S10−Os−P30	88.23(5)	S20−Os−P30	89.95(5)
P40−Os−S2	94.90(5)	S10−Os−S2	92.02(5)
S20−Os−S2	91.08(5)	P30−Os−S2	169.39(4)
P40−Os−S1	165.79(4)	S10−Os−S1	92.67(5)
S20−Os−S1	94.65(5)	P30−Os−S1	98.48(4)
S2−Os−S1	70.91(4)		

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **8**

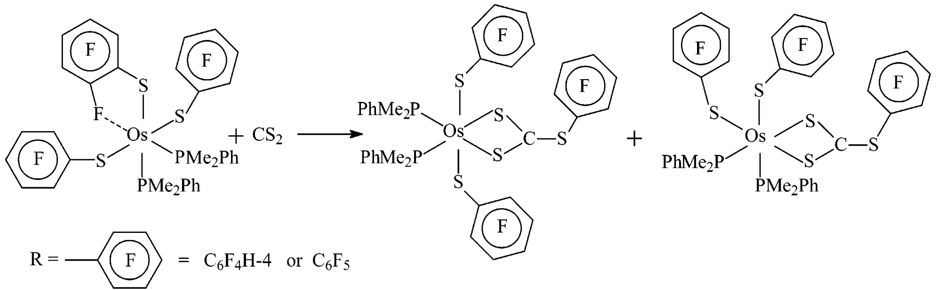
Os−S1	2.448(2)	Os−S2	2.402(2)
Os−S10	2.334(2)	Os−S20	2.395(2)
Os−P30	2.339(2)	Os−P40	2.406(2)
S10−Os−P30	86.19(9)	S10−Os−S20	94.92(9)
P30−Os−S20	85.26(8)	S10−Os−S2	169.11(9)
P30−Os−S2	104.37(8)	S20−Os−S2	88.70(8)
S10−Os−P40	91.93(9)	P30−Os−P40	92.31(8)
S20−Os−P40	172.55(9)	S2−Os−P40	85.08(8)
S10−Os−S1	98.54(9)	P30−Os−S1	174.11(7)
S20−Os−S1	90.81(8)	S2−Os−S1	71.09(8)
P40−Os−S1	91.04(9)		

The structure of **1** consists of discrete essentially octahedral molecules with two chelating thioxanthato ligands and *cis*-phosphine groups. These Ru(II) complexes are the bis-insertion products, and their formation should furthermore involve reduction of the ruthenium(III) center while RSSR is probably the oxidized species. The monoinsertion products of reaction 1, the green *trans*-thiolates $[Ru(SR)_2(S_2CSR)(PMe_2Ph)_2]$ (R = C_6F_4H-4, **2**; C_6F_5, **4**) are more stable in solution. These ruthenium(III) complexes were characterized by elemental analyses, FAB$^+$-spectrometry, and spectroscopic properties. The paramagnetism of these Ru(III) d^5 species gives rise to broad uninformative NMR spectra, but fortunately, single crystals of **4** were obtained and the X-ray structure determination, shown in Figure 2, confirms that only one CS_2 molecule had been incorporated into a Ru−SR bond giving an octahedral molecule with a chelating thioxanthato group, *trans*-thiolates and *cis*-phosphines.

The purple complex $[Os(SR)_3(PMe_2Ph)_2]$ (R = C_6F_4H-4 or C_6F_5) also reacts readily with CS_2 in acetone, giving a green solution from which a blue paramagnetic osmium(III) complex *trans*-thiolates $[Os(SR)_2(S_2CSR)(PMe_2Ph)_2]$ (R = C_6F_4H-4, **5**; C_6F_5, **7**), in 11% (**5**) or 12% (**7**) yield, and a green paramagnetic osmium(III) complex *trans*-thiolate−phosphine $[Os(SR)_2(S_2CSR)(PMe_2Ph)_2]$ (R = C_6F_4H-4, **6**; C_6F_5, **8**), in 52% (**6**) or 57% (**8**) yield, have been isolated by passage through a chromatographic column (Scheme 2).

These osmium(III) complexes were characterized by elemental analyses, FAB$^+$-spectrometry, and spectroscopic properties. As for **2** and **4**, the paramagnetism of these d^5 species of osmium(III) precluded NMR structural studies in solution, but single crystals of one *trans*-thiolates isomer (**5**) and a *trans*-thiolate−phosphine isomer (**8**) were obtained. Their X-ray crystal structures as shown in Figures 3 and 4,

Scheme 2



5 or **7** **6** or **8**

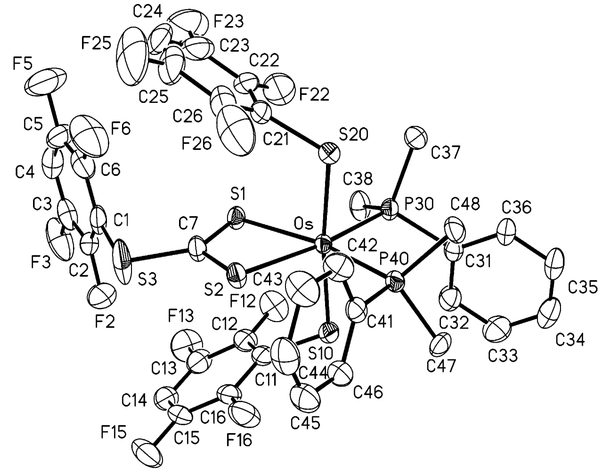


Figure 3. Structure of complex **5** showing thermal displacement parameters at the 30% probability level. H atoms are omitted for clarity.

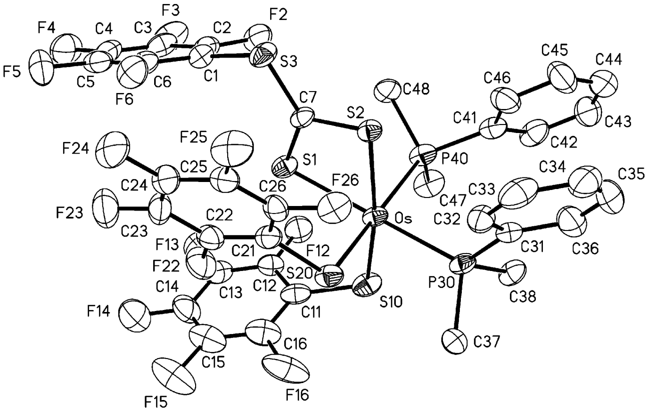


Figure 4. Structure of complex **8** showing thermal displacement parameters at the 30% probability level. H atoms are omitted for clarity.

respectively, confirm that only one CS$_2$ molecule had been incorporated into an Os−SR bond giving octahedral molecules with a chelating thioxanthato group, *trans*-thiolates and *cis*-phosphines in **5** or a chelating thioxanthato group, a pair of *trans*-thiolate-phosphine ligands, and another pair of *cis*-thiolate-phosphine ligands in **8**.

The four structurally characterized complexes are mononuclear species with six-coordinated metals (M = Ru, Os) in distorted octahedral geometry with two phosphine ligands in a *cis* arrangement. In the case of **1**, the asymmetric unit contains half of the molecule, which is completed through the *c* glide plane of the space group (Figure 1). As expected, the *trans* influence of the phosphine ligands is reflected in the significantly largest distance Ru1−S1 2.4664(10) Å (*trans* to P1), compared to Ru1−S2 2.3808(9) Å (*trans* to S2′), despite the severe distortion from an idealized octahedral geometry for the metal center, apparent for instance from the angle S1−Ru1−P1 = 165.24(3)°. This distortion seems to arise from symmetry imposed restraints rather than steric hindrance or electronic effects.

In complex **4** (Figure 2), where the thioxanthato is symmetrically coordinated with respect to phosphine ligands, both bond lengths Ru1−S1 and Ru1−S2 are very similar, within the standard uncertainty. For complexes **1** and **4**, the thioxanthato ligands have the same geometry: the bite angles are almost identical, S1−C9−S2 = 115.1(2)° for **1** and S1−C17−S2 = 116.2(3)° for **4**. The SC$_6$F$_4$H group bonded to the thioxanthato ligand in **1** and **4** seems to be flexible in its orientation. The angle observed for **1** is C9−S3−C10 = 100.88(18)°, significantly different from that observed in **4**, C(18)−S(3)−C(17) = 106.6(2)°, where the ligand is sandwiched by the C$_6$F$_5$ groups of thiolate ligands S4 and S5. No significant π−π interactions are observed between the aromatic moieties within the complex.

The structure of complex **5** (Figure 3) is similar to that of **4**, with M = Os instead of M = Ru and the thiolate ligand substituted by C$_6$F$_4$H group instead of C$_6$F$_5$. The substitution of a F atom by an H atom in the *para* position of the perfluorophenyl groups does not modify substantially the overall structure. For example, the geometry of the thioxanthato moiety remains close to that observed in the previous cases, with a bite angle S1−C7−S2 = 115.4(3)° and an angle around S3 of 104.4(3)°.

Finally, in contrast to the structures of complexes **4** and **5**, in complex **8** (M = Os) the two thiolate ligands adopt a *cis* configuration, with an angle S10−Os−S20 = 94.92(9)° (Figure 4). The *trans* influence of phosphine P30 is reflected in the different bond lengths Os−S(thioxanthato): Os−S1, 2.448(2) Å (*trans* to phosphine) and Os−S2, 2.402(2) Å (*trans* to thiolate). The phosphine P40 also induces a difference in Os−S(thiolate) distances: Os−S10, 2.334(2) Å (*trans* to thioxanthato) and Os−S20, 2.395(2) Å (*trans* to phosphine). These differences show the greater *trans* influence of the phosphine ligand compared to the thiolate and thioxanthato ligands. These features result in a more distorted geometry for **8** than for the previous complexes. However, potential steric hindrance arising from this arrangement is avoided because of the free rotation of the phenyl groups at the periphery of the molecule. As a consequence, the geometry of the thioxanthato ligand is unaffected compared to complexes **1**, **4**, and **5**: the bite angle S1−C7−S2 is 113.8(5)°, and the angle for S3 is C1−S3−C7 = 103.8(4)°.

In the four structures, the bond lengths from the central C atom of the thioxanthato group are asymmetric: two short bonds for the S atoms bonded to the metal center and one long bond length for the S atom bonded to the fluorophenyl group. The C−S bond distances involving the chelated S atoms are also shorter than those involving the thiolate sulfur atoms attached to the metal. This reflects the partial double bond character on the first two C−S bonds. Furthermore, of the three bond angles S−C−S around the central carbon atom in the thioxanthato ligands, the largest one is that on the side occupied by the fluorophenyl group of the thioxanthato ligand, suggesting that this distortion is required to accommodate fluorinated moiety.

As expected, in the structures of **1**, **4**, **5**, and **8**, the S−Os−S angle of the thioxanthato ligands is larger than the corresponding S−Os−O[28] and O−Os−O[26] angles found on thiocarboxylate[28] and carboxylate[26] related derivatives.

It is worth noting that complexes **1** and **4** are Ru(II) and Ru(III) species, respectively, and that one should expect shorter Ru−P bond lengths for **4** than for **1**. However, an opposite situation is observed: Ru−P = 2.2991(19) Å for **1** versus Ru−P = 2.3609(13) and 2.3705(12) Å for **4**, although in both complexes the phosphorus atom is *trans* to a sulfur atom of a S_2CSR ligand. This discrepancy may be attributed to a strong back-bonding in the $Ru^{II}P_2$ fragment, while Ru(III) in $Ru^{III}P_2$ fragment is a poor π-donor and back-bonding in the latter may be expected to be weak, as observed by Chakravorty et al.[33,34] in thioxanthato complexes of Ru(II), Ru(III),[33] Os(II), and Os(III),[34] with triphenylphosphine. Thus, the influence of the oxidation state in these Ru−P distances is more than offset by the higher back-bonding ability of Ru(II) compared to Ru(III).

There have been qualitative observations regarding the mechanism of CS_2 insertion into metal−thiolate bonds, and two processes for the initial interaction of the metal complex with the incoming CS_2 have been suggested:[20,35] precoordination of CS_2 at the metal center, which will be favored on coordinatively unsaturated compounds, or attack by free CS_2 on the sulfur atom of the thiolate ligand. Complexes $[M(SR)_3(PMe_2Ph)_2]$ react with CS_2 probably via a cleavage of the weak M−F−C interaction, thus enabling the precoordination of CS_2 to the metal atom, followed by electrophilic attack of the CS_2 ligand on the sulfur atom of a thiolate ligand to give $[M(SR)_2(S_2CSR)(PMe_2Ph)_2]$ complexes.

The well-known kinetic inertness of osmium systems is consistent with the failure to observe reduction in these systems.

Thiolate groups are well-known as reducing species so an additional loss of one SR^- anion group from $[Ru(SR)_2(S_2CSR)(PMe_2Ph)_2]$, attack by a second CS_2 molecule with formation of a second thioxanthato ligand, and reduction of the ruthenium center are required to rationalize the formation of bisthioxanthato complexes $[Ru(S_2CSR)_2(PMe_2Ph)_2]$ and RSSR.

Searching for clues for the possible mechanisms outlined above, the following experiments were carried out.

The reaction of $[Ru(SC_6F_5)_3(PMe_2Ph)_2]$ and excess of CS_2 afforded $[Ru(S_2CSC_6F_5)_2(PMe_2Ph)_2]$, **3**, $[Ru(SC_6F_5)_2(S_2CSC_6F_5)(PMe_2Ph)_2]$, **4**, $F_5C_6SSC_6F_5$, and starting material, as shown by TLC compared with pure samples of each compound. A few minutes later, the same species are detected, but **3** seems to be more abundant, and the starting material has been almost consumed out.

The reaction between $[Ru(SC_6F_5)_3(PMe_2Ph)_2]$ and an equimolar quantity of CS_2 also afforded compounds $[Ru(S_2CSC_6F_5)_2(PMe_2Ph)_2]$, **3**, $[Ru(SC_6F_5)_2(S_2CSC_6F_5)(PMe_2Ph)_2]$, **4**, and $F_5C_6SSC_6F_5$ along with unreacted starting material, although compound **4** could be expected as the only product from this reaction.

On the other hand, reacting pure $[Ru(SC_6F_5)_2(S_2CSC_6F_5)(PMe_2Ph)_2]$, **4**, with excess of CS_2 yields a mixture of $[Ru(S_2CSC_6F_5)_2(PMe_2Ph)_2]$, **3**, $[Ru(SC_6F_5)_2(S_2CSC_6F_5)(PMe_2Ph)_2]$, **4**, and $F_5C_6SSC_6F_5$. Therefore, $[Ru(SC_6F_5)_2(S_2CSC_6F_5)(PMe_2Ph)_2]$, **4**, is the precursor of $[Ru(S_2CSC_6F_5)_2(PMe_2Ph)_2]$, **3**. The reaction of $[Ru(SC_6F_5)_2(S_2CSC_6F_5)(PMe_2Ph)_2]$, **4**, with CS_2 in the presence of a radical scavenger does not favor the formation of $[Ru(S_2CSC_6F_5)_2(PMe_2Ph)_2]$, **3**.

In conclusion, a free radical mechanism seems very unlikely since the presence of a radical scavenger does not alter the outcome of the overall reaction. The experiments described are consistent with the mechanism suggested above for the formation of **1**/**3** from **2**/**4**, but other reactions paths cannot be ruled out and, in fact, are suggested by the described experimental observations.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structures **2**, **3**, **5**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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