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Novel Nucleophilic Reactivity of Disulfido Ligands Coordinated Parallel to M–M (M = Rh, Ir) Bonds

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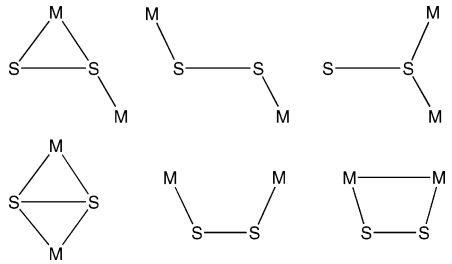
Reaction of *trans*-[(MCp*)$_2$(μ-CH$_2$)$_2$Cl$_2$] (M = Rh, Ir; Cp* = η^5-C$_5$Me$_5$) with Li$_2$S$_2$ afforded the disulfido complexes [(MCp*)$_2$(μ-CH$_2$)$_2$(μ-S$_2$-*S*:*S*′)] which were easily oxidized by O$_2$ to give the oxygenated complexes [(MCp*)$_2$-(μ-CH$_2$)$_2$(μ-SSO$_2$-*S*:*S*′)]. Although [(RhCp*)$_2$(μ-CH$_2$)$_2$(μ-S$_2$-*S*:*S*′)] gave a complicated mixture when reacted with CH$_2$Cl$_2$ or CHCl$_3$, [(IrCp*)$_2$(μ-CH$_2$)$_2$(μ-S$_2$-*S*:*S*′)] reacted with both CH$_2$Cl$_2$ and CHCl$_3$ to give the dithioformato complex [(IrCp*)$_2$(μ-CH$_2$)$_2$(μ-S$_2$CH-*S*:*S*′)]Cl and the cyclotetrasulfido complex [{(IrCp*)$_2$(μ-CH$_2$)$_2$}$_2$(μ-S$_4$-*S*:*S*′:*S*″:*S*‴)]Cl$_2$. The oxygenated complexes [(RhCp*)$_2$(μ-CH$_2$)$_2$(μ-SSO$_2$-*S*:*S*′)] reacted with hydrocarbyl halides to afford bridging hydrocarbyl thiolato complexes accompanied by the generation of SO$_2$ gas. These complexes have been characterized by NMR spectroscopy, ESI-MS, and X-ray diffraction.

Introduction

Being able to adopt a wide range of oxidation states from −2 to +6, sulfur has rich redox chemistry and is involved in many important biological, mineralogical, and industrial processes.[1] Disulfide, an oxidized form of sulfide (S^{2-}), is a π donor ligand and adopts a variety of bridging modes when coordinated to two metal ions, Scheme 1, and several examples have been reported.[2] There are two possible coordination modes in which the disulfido ligand is parallel to the M···M axis: with and without a formal M−M bond.

Scheme 1



Matsumoto and co-workers reported a Ru complex, [{RuCl$_2$-[P(OMe)$_3$]$_2$}$_2$(μ-S$_2$)(μ-Cl)(μ-N$_2$H$_4$)]$^+$, without an M−M bond,[3] in which the disulfido ligand undergoes oxygenation to give an S$_2$O$_5$ ligand. Only a small number of complexes with a disulfido ligand parallel to an M−M bond have been reported.[2] The M−M bond creates a more rigid structure reducing the possible coordination modes that the S−S ligand can adopt, and therefore, parallel coordinated disulfido ligands are expected to have different reactivity compared to complexes without an M−M bond.

In our studies, we have been examining both the oxidation and oxygenation of inorganic sulfur compounds coordinated to a methylene bridged dirhodium unit with a Rh−Rh single bond, {(RhCp*)$_2$(μ-CH$_2$)$_2$} with each Rh ion having only

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one coordination site available. In most cases, the dinuclear structure is maintained during reactions involving the ligands except under certain conditions.[4] For example, $[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SH)]^+$ ($Cp^* = \eta^5\text{-}C_5Me_5$)[5] is oxidized by S_8 or O_2 with excess H_2S to give the cyclotetrasulfido complex $[\{(RhCp^*)_2(\mu\text{-}CH_2)_2\}_2(\mu\text{-}S_4\text{-}S:S':S'':S''')]^{2+}$.[6] $[\{(RhCp^*)_2(\mu\text{-}CH_2)_2\}_2(\mu\text{-}S_4\text{-}S:S':S'':S''')]^{2+}$ is reduced with $NaBH_4$ to give $[\{(RhCp^*)_2(\mu\text{-}CH_2)_2\}_2(\mu\text{-}S_2\text{-}S:S')]$ (**1**).[7] In this paper, we report the direct synthesis of the Rh (**1**) and the corresponding Ir (**2**) disulfido complexes using Li_2S_2 and their reactivity with oxygen and alkyl halides, including C−H activation by the Ir complex. In addition, the reactivity of the oxygenated species with electrophiles is also reported.[8]

Experimental Section

Materials. All solvents were purchased from Nacalai Tesque for the reactions and from Sigma-Aldrich Japan or Merck for the measurements. MeOH was distilled from Mg and I_2 under Ar, and toluene was distilled from Na and benzophenone under Ar. Other solvents were used without further purification. The dichloro dirhodium complex, *trans*-$[(RhCp^*)_2(\mu\text{-}CH_2)_2Cl_2]$[9], and Li_2S_2[10] were synthesized by literature procedures. The dichloro diiridium complex, *trans*-$[(IrCp^*)_2(\mu\text{-}CH_2)_2Cl_2]$, was synthesized by modifying the procedure for the corresponding Rh analogue.[9] All other reagents were used as received.

General Procedure. All reactions were performed in a dry glovebox filled with N_2 or using standard Schlenk techniques under Ar. NMR spectra were recorded on JEOL Lambda300 and 400 and Bruker AVANCE600 FT-NMR spectrometers, and chemical shifts were referenced to tetramethylsilane. Fast atom bombardment (FAB) and electrospray ionization (ESI) mass spectrometry were performed on JEOL JMS-700T and Applied Biosystem Mariner spectrometers, respectively. IR spectra were measured on a JASCO FT/IR-420 spectrometer. Elemental analyses were performed by the Analytical Research Service Center at Osaka City University on Perkin-Elmer 240C or FISONS Instrument EA108 elemental analyzers.

Preparation of $[(MCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2\text{-}S:S')]$ (M = Rh (1), Ir (2)). A suspension of *trans*-$[(IrCp^*)_2(\mu\text{-}CH_2)_2Cl_2]$ (120 mg, 0.16 mmol) in MeOH (50 mL) was added to a solution of Li_2S_2 (24 mg, 0.31 mmol) in MeOH (10 mL) under N_2. After stirring the reaction mixture for 4 h, the solvent was removed under reduced pressure to give crude $[(IrCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2\text{-}S:S')]$ (**2**) as a brown residue. Toluene (30 mL) was added to the crude product and the insoluble matter was filtered off. Pure **2** was obtained as a brown solid by evaporation of the solvent. Yield 46 mg, 39%. Single crystals suitable for X-ray diffraction studies were obtained from a solution of **2** in α,α′,α″-trifluorotoluene by slow evaporation of the solvent. ^1H NMR (300 MHz, CD_3OD): δ 8.01 (2H, s, μ-CH_2), 7.64 (2H, s, μ-CH_2), 1.87 (30H, s, Cp*). ^{13}C NMR (75 MHz, CD_3OD): δ 107.7 (μ-CH_2), 97.3 (s, C_5Me_5), 10.6 (C_5Me_5). HRMS (ESI+): *m*/*z* calcd for $^{12}C_{22}{}^1H_{35}{}^{191}Ir_2{}^{32}S_2$ ($[M + H]^+$): 745.1392. Found: 745.1405.

Complex **1** was prepared in a similar manner using *trans*-$[(RhCp^*)_2(\mu\text{-}CH_2)_2Cl_2]$ (90 mg, 0.16 mmol) instead of *trans*-$[(IrCp^*)_2(\mu\text{-}CH_2)_2Cl_2]$, and the reaction was stirred for only 1 h. Yield: 51 mg, 58%. ^1H NMR (CD_3OD): δ 9.92 (dt, $^2J_{H-H} = 3.8$ Hz, $^2J_{H-Rh} = 1.9$ Hz, 2H, μ-CH_2), 9.10 (dt, $^2J_{H-H} = 3.8$ Hz, $^2J_{H-Rh} = 1.5$ Hz, 2H, μ-CH_2), 1.74 (s, 30H, Cp*). MS (FAB+): *m*/*z* = 569 ($[M + H]^+$).

Due to the high reactivity of **1** and **2** with O_2, accurate elemental analyses for the disulfido complexes have not been obtained.

Preparation of $[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SSO\text{-}S:S')]$ (3) and $[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SSO_2\text{-}S:S')]$ (4). A mixture of *trans*-$[(RhCp^*)_2(\mu\text{-}CH_2)_2Cl_2]$ (58 mg, 0.10 mmol) and Li_2S_2 (16 mg, 0.20 mmol) in MeOH (50 mL) was stirred for 1 h under N_2 then exposed to air. After stirring for 10 min, the solvent was removed under reduced pressure to give a dark reddish brown solid. A mixture of **3** and **4** (first fraction, 45 mg) was obtained via silica gel column chromatography (ϕ 2.5 cm × 30 cm) using CH_2Cl_2/MeOH (49:1) as the eluent. These complexes were separated by silica gel column chromatography (ϕ 2.5 cm × 30 cm) using CH_2Cl_2/MeCN/MeOH (4:6:1) as the eluent. The first and second fractions contained **3** and **4**, respectively. Yield: 23 mg, 39% for **3**; 13 mg, 22% for **4** based on Rh. Single crystals for X-ray diffraction studies were obtained by diffusion of Et_2O for **3** or AcOEt for **4** into a solution of each in CH_2Cl_2. Complex **3**. ^1H NMR (400 MHz, $CDCl_3$): δ 9.53 (m, 2H, μ-CH_2), 8.45 (m, 2H, μ-CH_2), 1.81 (s, 15H, Cp*), 1.74 (s, 15H, Cp*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3 (dd, $^1J_{C-Rh} = 24$ and 30 Hz, μ-CH_2), 161.8 (t, $^1J_{C-Rh} = 25$ Hz, μ-CH_2), 101.8 (s, C_5Me_5), 100.3 (d, $^1J_{C-Rh} = 4$ Hz, C_5Me_5), 9.9 (C_5Me_5), 9.6 (C_5Me_5). MS (FAB+): *m*/*z* = 556 ($[M + H]^+$). Anal. Calcd for **3**: C, 45.21; H, 5.86. Found: C, 44.34; H, 5.68. Complex **4**. ^1H NMR (400 MHz, $CDCl_3$): δ 9.72 (m, 2H, μ-CH_2), 8.90 (m, 2H, μ-CH_2), 1.82 (s, 15H, Cp*), 1.73 (s, 15H, Cp*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.0 (t, $^1J_{C-Rh} = 25$ Hz, μ-CH_2), 102.6 (d, $^1J_{C-Rh} = 6$ Hz, C_5Me_5), 101.3 (d, $^1J_{C-Rh} = 6$ Hz, C_5Me_5), 9.7 (C_5Me_5). MS (FAB+): *m*/*z* = 601 ($[M + H]^+$). Anal. Calcd for **4**: C, 44.01; H, 5.71. Found: C, 43.73; H, 5.40.

Preparation of $[(IrCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SSO_2\text{-}S:S')]$ (5). A suspension of *trans*-$[(IrCp^*)_2(\mu\text{-}CH_2)_2Cl_2]$ (120 mg, 0.16 mmol) in MeOH (50 mL) was added to a solution of Li_2S_2 (24 mg, 0.31 mmol) in MeOH (10 mL) under N_2. The reaction mixture was stirred for 4 h and then exposed to air. After the mixture was stirred for another 18 h, the solvent was removed under reduced pressure to give an orange solid. CH_2Cl_2 (20 mL) was added to the solid and the insoluble material was filtered off. Removal of the solvent gave **5** as an orange solid (yield 83 mg, 69% based on Ir). Single crystals suitable for X-ray structure analysis were obtained by diffusion of hexane into a solution of **5** in CH_2Cl_2. ^1H NMR (300 MHz, $CDCl_3$): δ 7.97 (2H, s, μ-CH_2), 7.58 (2H, s, μ-CH_2), 1.93 (15H, s, Cp*), 1.83 (15H, s, Cp*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 108.5 (μ-CH_2), 97.5 (C_5Me_5), 95.7 (C_5Me_5), 9.6 (C_5Me_5), 9.5 (C_5Me_5). MS (FAB+): *m*/*z* (% relative intensity) = 777 (4), 778 (1.6), 779 (13), 780 (4), 781 (11), 782 (4), 783 (1.5), 784 (0.6) ($[M + H]^+$); 799 (8), 800 (2), 801 (28), 802 (9), 803 (31), 804 (7), 805 (3), 806 (1) ($[M + Na]^+$). Anal. Calcd for **5**: C, 33.92; H, 4.40. Found: C, 33.90; H, 4.31.

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Preparation of [(RhCp*)$_2$(μ-CH$_2$)$_2$(μ-SMe)](BPh$_4$) (6). Methyl iodide (4.7 μL, 0.075 mmol) was added to a solution of **4** (30 mg, 0.050 mmol) in 5 mL of MeOH under N_2. After the mixture was stirred for 14 h, a solution of $NaBPh_4$ (50 mg, 0.146 mmol) in 5 mL of MeOH was added to the reaction mixture to give a red precipitate of **6**, which was collected by filtration. Yield 27 mg, 63%. Single crystals suitable for X-ray crystallography were obtained by diffusion of toluene into a solution of **6** in CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (1H, m, μ-CH$_2$), 7.82 (1H, m, μ-CH$_2$), 7.73 (1H, m, μ-CH$_2$), 7.49 (1H, m, μ-CH$_2$), 7.41 (8H, m, *o*-H−Ph$_4$B), 7.03 (8H, t, J_{H-H} = 7.3 Hz, *m*-H−Ph$_4$B), 6.88 (4H, t, J_{H-H} = 7.2 Hz, *p*-H−Ph$_4$B), 1.73 (30H, s, Cp*), 1.34 (3H, t, $^3J_{H-Rh}$ = 1.7 Hz, MeS). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7 (t, J_{C-Rh} = 25 Hz, μ-CH$_2$), 164.2 (q, J_{C-B} = 49 Hz, BPh$_4$), 164.1 (t, J_{C-Rh} = 24 Hz, μ-CH$_2$), 136.3 (BPh$_4$), 125.3 (q, $^3J_{C-B}$ = 2.5 Hz, BPh$_4$), 121.5 (BPh$_4$), 101.8 (C_5Me$_5$), 10.0 (C$_5$*Me*$_5$), 7.5 (SMe). MS (FAB+): *m*/*z* = 551 ([M]$^+$). Anal. Calcd for **6**: C, 64.84; H, 6.60. Found: C, 64.54; H, 6.57.

Preparation of [(RhCp*)$_2$(μ-CH$_2$)$_2$(μ-SCH$_2$CHCH$_2$)](BPh$_4$) (7). Complex **7** was synthesized in a manner similar to **6** using allyl iodide (6.8 μL, 0.075 mmol) instead of methyl iodide. Yield: 30 mg, 69%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (1H, m, μ-CH$_2$), 7.75 (1H, m, μ-CH$_2$), 7.71 (1H, m, μ-CH$_2$), 7.51 (1H, m, μ-CH$_2$), 7.41 (8H, m, *o*-H−Ph$_4$B), 7.03 (8H, t, J_{H-H} = 7.3 Hz, *m*-H−Ph$_4$B), 6.88 (4H, t, J_{H-H} = 7.1 Hz, *p*-H−Ph$_4$B), 5.54 (1H, m, CH$_2$═C*H*CH$_2$S), 5.08 (1H, d, J_{H-H} = 15.6 Hz, CH*H* = CHCH$_2$S), 5.05 (1H, d, J_{H-H} = 10.0 Hz, CH*H* = CHCH$_2$S), 2.58 (2H, d, J_{H-H} = 7.1 Hz, CH$_2$═CHC*H*$_2$S), 1.73 (30H, s, Cp*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8 (t, J_{C-Rh} = 21 Hz, μ-CH$_2$), 164.5 (t, J_{C-Rh} = 25 Hz, μ-CH$_2$), 164.2 (q, J_{C-B} = 48 Hz, BPh$_4$), 136.3 (BPh$_4$), 134.2 (SCH$_2$C*H*CH$_2$), 125.4 (q, $^3J_{C-B}$ = 2.7 Hz, BPh$_4$), 121.5 (BPh$_4$), 118.1 (SCH$_2$CH*C*H$_2$), 102.1 (C_5Me$_5$), 28.2 (S*C*H$_2$CHCH$_2$), 10.2 (C$_5$*Me*$_5$). MS (FAB+): *m*/*z* = 577 ([M]$^+$). Anal. Calcd for **7**: C, 65.64; H, 6.63. Found: C, 65.43; H, 6.59.

Preparation of [{(RhCp*)$_2$(μ-CH$_2$)$_2$}$_2$(μ,μ-SCH$_2$CH$_2$CH$_2$S)](BPh$_4$)$_2$ (8). A mixture of **4** (25 mg, 0.041 mmol) in 15 mL of MeOH and 1,3-diiodopropane (2.6 μL, 0.022 mmol) was refluxed for 14 h under Ar. After the reaction mixture was cooled to room temperature, a solution of $NaBPh_4$ (50 mg, 0.146 mmol) in 5 mL of MeOH was added to give a red precipitate which was collected by filtration. Yield: 11 mg, 31%. Single crystals suitable for X-ray crystallography were obtained by diffusion of Et_2O into a solution of **8** in CH_2Cl_2. ^{1}H NMR (600 MHz, CD_2Cl_2): δ 8.51 (2H, s, μ-CH$_2$), 7.86 (2H, s, μ-CH$_2$), 7.84 (2H, s, μ-CH$_2$), 7.63 (2H, s, μ-CH$_2$), 7.34 (16H, m, *o*-H−Ph$_4$B), 7.04 (16H, t, J_{H-H} = 7.4 Hz, *m*-H−Ph$_4$B), 6.89 (8H, t, J_{H-H} = 7.2 Hz, *p*-H−Ph$_4$B), 1.96 (4H, t, J_{H-H} = 7.3 Hz, SC*H*$_2$CH$_2$C*H*$_2$S), 1.81 (60H, s, Cp*), 1.41 (2H, q, J_{H-H} = 7.3 Hz, SCH$_2$C*H*$_2$CH$_2$S). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 165.6 (t, J_{C-Rh} = 25 Hz, μ-CH$_2$), 164.7 (t, J_{C-Rh} = 26 Hz, μ-CH$_2$), 164.4 (q, J_{C-B} = 49 Hz, BPh$_4$), 136.3 (BPh$_4$), 126.0 (q, $^3J_{C-B}$ = 2.8 Hz, BPh$_4$), 122.1 (BPh$_4$), 102.5 (C_5Me$_5$), 34.4 (SCH$_2$*C*HCH$_2$S), 24.5 (S*C*H$_2$CH*C*H$_2$S), 10.4 (C$_5$*Me*$_5$). MS (ESI+): *m*/*z* = 1433 ([M + BPh$_4$]$^+$), *m*/*z* = 557 ([M]$^{2+}$). Anal. Calcd for **8**·CH$_2$Cl$_2$: C, 62.73; H, 6.36. Found: C, 62.39; H, 6.32.

Preparation of [{(RhCp*)$_2$(μ-CH$_2$)$_2$}$_2${*p*-(μ-SCH$_2$)$_2$(C$_6$H$_4$)}](BPh$_4$)$_2$ (9). A mixture of **4** (13 mg, 0.022 mmol) and α,α'-dibromoxylene (3 mg, 0.011 mmol) in 3 mL of MeOH was stirred for 48 h under N_2. After cooling the reaction mixture to room temperature, a solution of $NaBPh_4$ (30 mg, 0.088 mmol) in **3** mL of MeOH was added to give a red precipitate which was collected by filtration. Yield: 12 mg, 61%. Single crystals suitable for X-ray structure analysis were obtained by diffusion of MeOH into the solution of **9** in CH_2Cl_2. ^{1}H NMR (600 MHz, CD_2Cl_2): δ 8.67 (2H, s, μ-CH$_2$), 7.91 (2H, s, μ-CH$_2$), 7.78 (2H, s, μ-CH$_2$), 7.63 (2H, s, μ-CH$_2$), 7.33 (16H, m, *o*-H−Ph$_4$B), 7.09 (4H, s, SCH$_2$-(C$_6$*H*$_4$)CH$_2$S), 7.03 (16H, t, J_{H-H} = 7.4 Hz, *m*-H−Ph$_4$B), 6.88 (8H, t, J_{H-H} = 7.2 Hz, *p*-H−Ph$_4$B), 3.13 (4H, s, SC*H*$_2$(C$_6$H$_4$)C*H*$_2$S), 1.76 (60H, s, Cp*). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 166.5 (t, J_{C-Rh} = 25 Hz, μ-CH$_2$), 164.5 (t, J_{C-Rh} = 23 Hz, μ-CH$_2$), 164.5 (q, J_{C-B} = 49 Hz, BPh$_4$), 138.2 (SCH$_2$(*C*$_6$H$_4$)CH$_2$S), 136.3 (BPh$_4$), 129.6 (SCH$_2$(*C*$_6$H$_4$)CH$_2$S), 126.0 (q, $^3J_{C-B}$ = 2.8 Hz, BPh$_4$), 122.1 (BPh$_4$), 102.6 (*C*$_5$Me$_5$), 29.9 (SCH$_2$(C$_6$H$_4$)*C*H$_2$S), 10.4 (C$_5$*Me*$_5$). MS (ESI+): *m*/*z* = 588 ([M]$^{2+}$). Anal. Calcd for **9**·CH$_2$Cl$_2$: C, 63.84; H, 6.26. Found: C, 64.04; H, 6.20.

Reaction of [(RhCp*)$_2$(μ-CH$_2$)$_2$(μ-SSO$_2$-*S*:*S*′)] (4) with 1,2-Diiodoethane. To a solution of **3** (10 mg, 0.017 mmol) in 2.5 mL of MeOH was added 1,2-diiodoethane, and the reaction mixture was refluxed for 2 h under Ar to give a purple solid of *trans*-[(RhCp*)$_2$(μ-CH$_2$)$_2$I$_2$] which was filtered off. Upon addition of $NaBPh_4$ (20 mg, 0.058 mmol) to the filtrate, a red precipitate formed and was determined to be the tetrasulfido complex [{(RhCp*)$_2$-(μ-CH$_2$)$_2$}$_2$(μ-S$_4$-*S*:*S*′:*S*″:*S*‴)] by the ^{1}H NMR and FAB mass spectra.

Formation of [(IrCp*)$_2$(μ-CH$_2$)$_2$(μ-S$_2$CH-*S*:*S*′)]Cl (10a) and [{(IrCp*)$_2$(μ-CH$_2$)$_2$}$_2$(μ_4-S$_4$-*S*:*S*′:*S*″:*S*‴)]Cl$_2$ (11a). Complex **2** was dissolved in 10 mL of $CHCl_3$ or CH_2Cl_2 to give an orange solution. After stirring for several hours, the solution changed to green. After 18 h, the solvent was removed under reduced pressure to give a mixture of **10a** and **11a**. Toluene (30 mL) was added to the mixture and the insoluble solid, most of which was complex **11a**, was filtered off. The solvent was removed from the filtrate to give crude **10a**. Complexes **10a** and **11a** were purified as the BPh_4 salts (**10b** and **11b**, respectively) by adding a solution of $NaBPh_4$ in MeOH to solutions of the crude complexes in MeOH. Single crystals of both **10a** and **11a** suitable for X-ray diffraction study were obtained concomitantly by diffusion of hexane into the reaction mixture. Complex **10b**. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.81 (1H, s, μ-S$_2$CH), 8.44 (2H, s, μ-CH$_2$), 7.54 (2H, s, μ-CH$_2$), 7.42 (8H, m, *o*-H−Ph$_4$B), 7.02 (8H, t, μ-H−Ph$_4$B), 6.87 (4H, t, *p*-H−Ph$_4$B), 1.76 (30H, s, Cp*). ^{13}C NMR (150 MHz, $CDCl_3$): δ 197.75 (μ-S$_2$*C*H), 102.3 (μ-CH$_2$), 99.9 (*C*$_5$Me$_5$), 9.3 (C$_5$*Me*$_5$). MS (ESI$^+$): *m*/*z* (% relative intensity) = 757 (15), 758 (4), 759 (63), 760 (19), 761 (62), 762 (17), 763(9), 764 (2) ([M]$^+$). Anal. Calcd for [(IrCp*)$_2$-(μ-CH$_2$)$_2$(μ-S$_2$CH)](BPh$_4$)·1/3toluene: C, 53.38; H, 5.24. Found: C, 53.40; H, 5.20. Complex **11b**. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.86 (2H, μ-CH$_2$), 7.68 (2H, d, μ-CH$_2$), 7.36 (2H, s, μ-CH$_2$), 6.49 (2H, s, μ-CH$_2$), 1.77 (60H, s, Cp*). ^{13}C NMR (150 MHz, $CDCl_3$): δ 112.0 (μ-CH$_2$), 110.9 (μ-CH$_2$), 100.0 (*C*$_5$Me$_5$), 10.1 (C$_5$*Me*$_5$). MS (ESI+): *m*/*z* (% relative intensity) = 744 (24), 745 (8), 746 (100), 747 (28), 748 (85), 749 (23), 750 (8), 751 (2) ([M]$^+$). Anal. Calcd for C$_{92}$H$_{108}$B$_2$Ir$_4$S$_4$: C, 51.81; H, 5.10. Found: C, 51.71; H, 5.04.

Reaction of [(IrCp*)$_2$(μ-CH$_2$)$_2$(μ-S$_2$-*S*:*S*′)] (2) with 1,1-Dichloroethane. Complex **2** (5 mg, 6.7 mmol) was dissolved in 1,1-dichloroethane (1 mL) and the mixture was stirred for 1 h. ESI mass spectrometry was performed on a portion of the reaction mixture, diluted with MeOH, to show the formation of [(IrCp*)$_2$-(μ-CH$_2$)$_2$(μ-S$_2$CCH$_3$-*S*:*S*′)]Cl (**12**) and the tetrasulfido complex **11a**. Complex **12**. MS (ESI+): *m*/*z* (% relative intensity) = 771 (23), 772 (8), 773 (91), 774 (28), 775 (100), 776 (25), 777 (24), 778 (7), 779(12) ([M]$^+$).

X-ray Crystallography. Diffraction data were collected on Rigaku AFC-5S (**3**, **4**), AFC-7S (**6**), and AFC7/CCD Mercury (**2**, **5**−**9**, **10a**, **11a**) diffractometers. The Data for **3**, **4**, and **6** were collected using the ω-2θ scan technique and the data for the others were collected by using a rotation method with a 0.3 (**5**, **7**−**9**, **11a**) or 0.5 (**2**, **10a**) frame width and with a 5-s (**7**), 10-s (**2**, **5**, **9**, **10a**,

Table 1. Crystallographic Data for Complexes **2**−**5**

	2	**3**	**4**	**5**
formula	$C_{22}H_{34}Ir_2S_2$	$C_{22}H_{34}OS_2Rh_2$	$C_{22}H_{34}O_2S_2Rh_2$	$C_{22}H_{34}O_2S_2Ir_2$
fw	747.07	584.44	600.44	779.07
cryst syst	monoclinic	monoclinic	monoclinic	tetragonal
space group	*C*2/*c* (No. 15)	*C*2/*c* (No. 15)	*P*2$_1$/*n* (No. 14)	$P\bar{4}2_1c$ (No. 114)
a (Å)	12.093(7)	11.696(3)	8.517(6)	23.013(1)
b (Å)	12.303(6)	12.930(4)	14.367(6)	= *a*
c (Å)	15.621(9)	15.816(5)	19.674(5)	8.8481(5)
α (deg)	90	90	90	90
β (deg)	105.36(1)	105.40(2)	96.30(1)	90
γ (deg)	90	90	90	90
V (Å^3)	2241(2)	2305(1)	2392(2)	4686.0(4)
Z	4	4	4	8
D_{calcd} (g/cm^3)	2.214	1.683	1.667	2.208
diffractometer	AFC-7/Mercury CCD	AFC-5S	AFC-5S	AFC-7/Mercury CCD
temp (K)	193	293	293	193
reflns collected	10651	3669	7679	37065
independent reflns	2523 (R_{int} = 0.065)	3370 (R_{int} = 0.067)	6974 (R_{int} = 0.075)	5353 (R_{int} = 0.054)
μ (mm^{-1})	12.087	1.619	1.565	11.573
$T_{min}-T_{max}$	0.339−0.684	0.697−1.000	0.630−0.811	0.355−0.561
data/params	2519/114	3370/195	6974/253	5353/267
R_1 [$I > 2\sigma(I)$]	0.0777	0.0415	0.0757	0.0380
wR_2 (all data)	0.1704	0.1132	0.1572	0.0781
GOF	1.840	1.126	1.182	0.964

Table 2. Crystallographic Data for Complexes **6**−**9**

	6	**7**	**8**	**9**·2CH_2Cl_2
formula	$C_{47}H_{57}BSRh_2$	$C_{49}H_{59}BSRh_2$	$C_{95}H_{114}B_2S_2Rh_4$	$C_{102}H_{120}B_2Cl_4S_2Rh_4$
fw	870.65	896.69	1753.31	1985.24
cryst syst	triclinic	orthorhombic	monoclinic	triclinic
space group	$P\bar{1}$ (No. 2)	*Pna*2$_1$ (No. 33)	*P*2$_1$/*n* (No. 14)	$P\bar{1}$ (No. 2)
a (Å)	12.519(1)	29.931(2)	16.868(2)	11.5491(8)
b (Å)	14.582(1)	8.7984(7)	17.464(2)	12.315(1)
c (Å)	11.842(1)	16.809(1)	29.355(3)	17.291(1)
α (deg)	98.007(9)	90	90	79.146(9)
β (deg)	95.297(7)	90	92.869(5)	83.98(1)
γ (deg)	85.428(8)	90	90	87.84(1)
V (Å^3)	2126.6(3)	4426(1)	8637(1)	2401.6(3)
Z	2	4	4	1
D_{calcd} (g/cm^3)	1.360	1.345	1.348	1.373
diffractometer	AFC-7S	AFC-7/Mercury CCD	AFC-7/Mercury CCD	AFC-7/Mercury CCD
temp (K)	296	293	293	293
reflns collected	12918	33920	66101	19067
independent reflns	12389 (R_{int} = 0.024)	8303 (R_{int} = 0.072)	19186 (R_{int} = 0.082)	10536 (R_{int} = 0.040)
μ (mm^{-1})	0.854	0.822	0.841	0.873
$T_{min}-T_{max}$	0.805−0.920	0.839−0.907	0.778−0.998	0.863−0.962
data/params	12389/460	8303/478	19186/952	10536/531
R_1 [$I > 2\sigma(I)$]	0.0348	0.0417	0.0708	0.0810
wR_2 (all data)	0.0589	0.0566	0.1310	0.1941
GOF	1.133	0.929	0.969	1.074

11a), or 15 s (**8**) exposure time per frame. The data collected on the CCD diffractometer were integrated, scaled, sorted, and averaged using the CrystalClear[11] software. Absorption corrections were applied using an empirical *ψ* scan (**3**), Tompa analytical (**4**, **6**), multiscan (**5**, **8**), or Coppens numerical (**2**, **7**, **9**, **10a**, **11a**) method. The structures were solved using DIRDIF94−PATTY[12] for **3** and **10a** or SIR92[13] for the others and refined with teXsan[14] for **2** or SHELX-97[15] for the others. Crystallographic data are summarized in Tables 1−3. All non-hydrogen atoms were refined anisotropically except for one of the C atoms in **2** which was refined isotropically because thermal parameters became negative when it refined anisotropically.

Results and Discussion

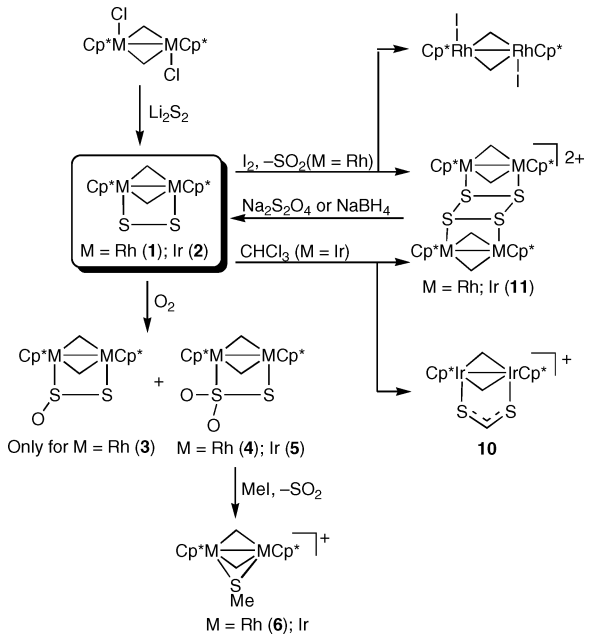
Disulfido Complexes. [(RhCp*)$_2$(*μ*-CH_2)$_2$(*μ*-S_2-*S*:*S*′)] (**1**) was first obtained by reducing the tetrasulfido tetrarhodium complex [{(RhCp*)$_2$(*μ*-CH_2)$_2$}$_2$(*μ*$_4$−S_4-*S*:*S*′:*S*″:*S*‴)]$^{2+}$ with $Na_2S_2O_4$ and NaOH in water or with $NaBH_4$ in MeOH. Complex **1** can also be synthesized by reacting *trans*-[(RhCp*)$_2$(*μ*-CH_2)$_2$$Cl_2$] with Li_2S_2 in MeOH, and the Ir analogue [(IrCp*)$_2$(*μ*-CH_2)$_2$(*μ*-S_2-*S*:*S*′)] (**2**) was first prepared from the corresponding Ir dichloro complex using the same method. The synthesis and reactivity of complexes **1** and **2** are summarized in Scheme 2. In an inert atmosphere, both

(11) *CrystalClear*. Rigaku Corp.: Woodlands, TX, 1999.
(12) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *The DIRDIF-94 Program System*; Technical Report; Crystallography Laboratory, University of Nijmegen, The Netherlands, 1994.
(13) Altomare, A.; Burla, M. C.; Camalli, G.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Cryst.* **1994**, *27*, 435.
(14) *TeXsan, Crystal Structure Analysis Package*; Molecular Structure Corp.: Houston, TX, 1985 and 1992.
(15) Sheldrick, G. M. *SHELX-97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

Table 3. Crystallographic Data for Complexes **10a** and **11a**

	10a·CH_2Cl_2	**11a**
formula	$C_{24}H_{37}Cl_3Ir_2S_2$	$C_{46}H_{72}Cl_6Ir_4S_4$
fw	880.48	1734.91
cryst syst	monoclinic	monoclinic
space group	*P*2/*m* (No. 11)	*P*2$_1$/*n* (No. 14)
a (Å)	10.989(2)	8.681(3)
b (Å)	9.809(2)	12.564(4)
c (Å)	13.058(2)	24.512(8)
α (deg)	90	90
β (deg)	91.252(4)	98.255(4)
γ ()	90	90
V (Å^3)	1407.2(4)	2645(1)
Z	2	2
D_{calcd} (g/cm^3)	2.078	2.177
diffractometer	AFC-7/Mercury CCD	AFC-7/Mercury CCD
temp (K)	153	193
reflns collected	13790	21094
independent reflns	3366 (R_{int} = 0.039)	5982 (R_{int} = 0.036)
μ (mm^{-1})	9.918	10.547
$T_{min}-T_{max}$	0.372−0.699	0.369−0.568
data/params	3366/163	5982/271
R_1 [$I > 2\sigma(I)$]	0.0305	0.0379
wR_2 (all data)	0.0629	0.0657
GOF	0.942	1.078

Scheme 2



1 and **2** are stable in MeOH and toluene but react with halogenated solvents such as $CHCl_3$ and CH_2Cl_2. Even though complex **1** reacts with $CHCl_3$ or CH_2Cl_2 to give an intractable mixture, complex **2** reacts with $CHCl_3$ resulting in the incorporation of a C atom into the S−S bond (vide infra). Complexes **1** and **2** readily react in MeOH with atmospheric O_2, in which case the disulfido ligands became oxygenated. In the case of complex **1**, a mixture of the monooxygenated [(RhCp*)$_2$(μ-CH_2)$_2$(μ-SSO-*S:S*′)] (**3**) and dioxygenated [(RhCp*)$_2$(μ-CH_2)$_2$(μ-SSO_2-*S:S*′)] (**4**) complexes was obtained. However, only the dioxygenated complex [(IrCp*)$_2$-(μ-CH_2)$_2$(μ-SSO_2-*S:S*′)] (**5**) formed when complex **2** was exposed to O_2. The disulfido ligand in most monomeric complexes is relatively stable toward O_2 and typically needs stronger oxidizing agents to become oxygenated. For example, [Ir(dppe)$_2$(S_2)]$^+$ and [Mo(S_2)(S_2CNEt_2)$_3$] are oxygenated using IO_4^- or *m*-chloroperbenzoic acid to give the corresponding SSO complexes [Ir(dppe)$_2$(SSO)]$^+$[16] and [Mo(SSO)(S_2CNEt_2)$_3$],[17] respectively. To the best of our knowledge, there have been no reports involving the oxygenation of a disulfide ligand which is coordinated parallel to an M−M bond.

Table 4. Selected Bond Lengths (Å) and Angles (°) for Complexes **2**−**5**

	2	**3**	**4**	**5**
M−M	2.642(1)	2.6053(7)	2.6137(9)	2.6373(6)
M−S	2.353(5)	2.324(1)[a]	2.346(3)	2.290(4)[a]
M−S(O)			2.311(3)	2.304(3)[a]
M−C(μ-CH_2)	2.06(2)	2.020(5)	2.020(9)	2.049(9)
	2.08(2	2.056(4)	2.031(9)	2.056(10)
S−S	2.126(10)	2.107(3)	2.102(4)	2.173(7)
S−O		1.436(10)	1.441(9)	1.22(3), 1.55(2)
			1.455(10)	1.30(2), 1.63(4)
M−S−S	96.2(1)			95.3(2)[a]
M−S−S(O)		96.05(4)[a]	94.2(1)	96.3(2)[a]
M−S(O)−S			98.5(1)	
M−C(μ-CH_2)−M	79.1(7)	79.5(1)	80.3(3)	79.8(3)
			80.6(3)	80.0(3)
M−M−S	83.7(1)	83.76(4)[a]	84.63(8)	84.1(1)[a]
M−M−S(O)			82.73(8)	84.3(1)[a]
S−S−O		110.3(5)[a]	107.0(4)	106(1), 112(1)
			109.8(4)	107(1), 115.6(10)
O−S−O			112.0(5)	105(1)
				114(1)

[a] These values were calculated using the S atoms that are bound to disordered oxygen atoms.

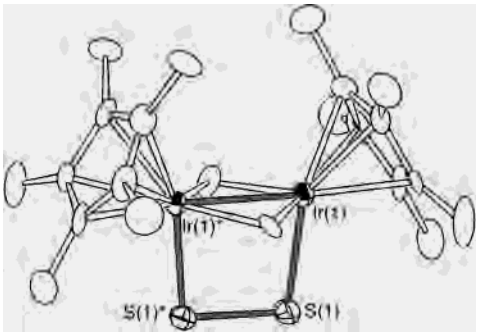


Figure 1. ORTEP drawing of [(IrCp*)$_2$(μ-CH_2)$_2$(μ-S_2-*S:S*′)] (**2**) with 65% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Structures of Disulfido and Oxygenated Complexes. The structures of **2**−**5** were determined by X-ray diffraction and the crystal data for these complexes are summarized in Table 1. Selected bond lengths and angles are listed in Table 4. The disulfido ligand in **2** is coordinated parallel to the Ir−Ir single bond (2.642(1) Å), Figure 1. The S−S bond length (2.126(10) Å) is the longest among those observed for similar disulfido complexes with M−M bonds (2.023(7)−2.117(2) Å)[3] and lies in the range of those without M···M bonds (1.963(7)−2.159(2) Å).[18]

Complex **3** has a crystallographic C_2 axis bisecting the M−M and S−S bonds, Figure 2. Existence of the C_2 axis indicates either that the oxygen atom of the SSO ligand in **3** is disordered into two positions with $^1/_2$ occupancies or that the single crystal contains both the disulfido complex **1** and

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(17) Halcrow, M. A.; Huffman, J. C.; Christou, G. *Inorg. Chem.* **1994**, *33*, 3639.

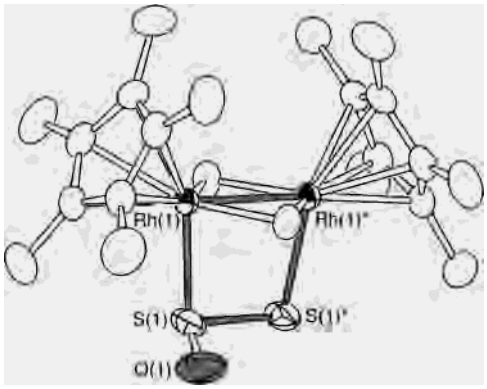


Figure 2. ORTEP drawing of $[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SSO\text{-}S{:}S')]$ (**3**) with 50% probability ellipsoids. Hydrogen atoms and half of the disordered oxygen atoms are omitted for clarity.

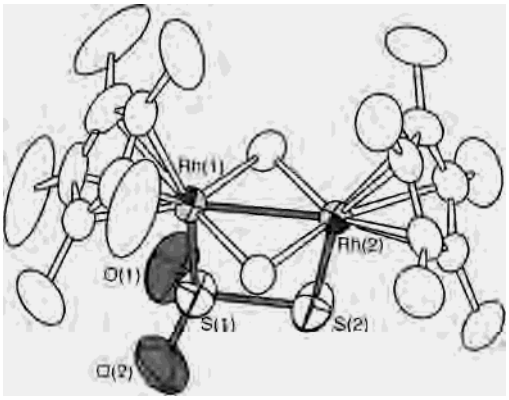


Figure 3. ORTEP drawing of $[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SSO_2\text{-}S{:}S')]$ (**4**) with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

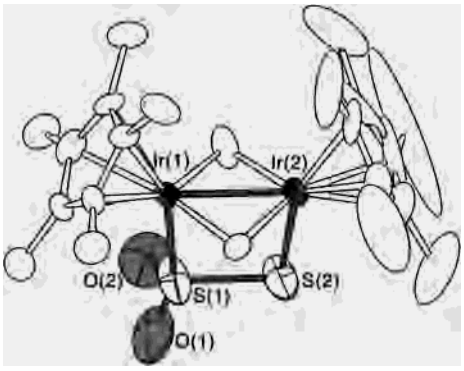
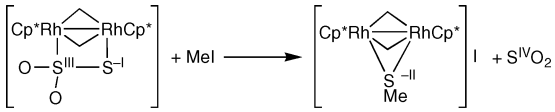


Figure 4. ORTEP drawing of $[(IrCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SSO_2\text{-}S{:}S')]$ (**5**) with 50% probability ellipsoids. Hydrogen atoms and half of the disordered oxygen atoms are omitted for clarity.

the O−S−S−O complex. The ^{1}H NMR spectrum of **3** has two Cp* methyl signals, meaning that the complex is not symmetric, and no signals corresponding to **1** were observed. The disordered structure has an averaged Rh−S bond with no difference between the Rh−S(oxygenated) and Rh−S(unoxygenated) bonds.

Most thiosulfito ligands bridge via the non-oxygenated S atom.[19] *S:S′* coordination of the thiosulfito ligand is quite rare and only one structure of $[\{Co(CN)_5\}_2(\mu\text{-}SSO_2\text{-}S{:}S')]^{6-}$ has been reported.[20] However, the metal atoms are arranged in a trans fashion about the S−S bond. Complexes **4** (Figure 3) and **5** (Figure 4) are the first examples of a thiosulfito ligand that is coordinated parallel to a M−M bond. The Rh−S(oxygenated) (2.311(3) Å) and Rh−S(unoxygenated) (2.346(3) Å) bonds in **4** are different in lengths. The oxygen atoms in the Ir analogue **5** are disordered into four positions, and the Ir−S bond lengths in **5** appear to be average values of the Ir−S(oxygenated) and Ir−S(unoxygenated) bond lengths, Table 4. The oxygenated S atoms form shorter bonds to the metal ions than the unoxygenated S atoms and these Ir−S bonds are clearly shorter than those in **2**. The S−S bond distance in **5** (2.173(7) Å) becomes slightly longer than that in **2** (2.126(10) Å) upon oxygenation. A similar trend was observed for $[\{Co(CN)_5\}_2(\mu\text{-}SSO_2\text{-}S{:}S')]^{6-}$ (Co−S(oxygenated) = 2.255(2) Å; Co−S(unoxygenated) = 2.297(2) Å).

Scheme 3



4 **6**

Reaction of Thiosulfito Complexes with Hydrocarbyl Halides. The two S atoms in the thiosulfito ligand of both **4** and **5** have different formal oxidation states, −1 for ***S***SO_2 and +3 for S***S***O_2, and their reactivity toward electrophiles reflects this difference. For instance, complex **4** reacts with MeI to give the bridging methyl thiolato complex $[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SMe\text{-}S{:}S')](BPh_4)$ (**6**) accompanied by the release of SO_2 gas, which was verified using a gas detector tube (Gastec Corporation). Unlike complex **4**, when complex **1** reacts with MeI, $[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SSMe\text{-}S{:}S')]$ is formed and S−S bond cleavage does not occur. C−S bond formation in complex **4** leads to the redistribution of charge in the SSO_2 ligand resulting in S−S bond cleavage (Scheme 3). The S atoms in the μ-SMe ligand and SO_2 have formal oxidation states of −2 and +4, respectively.

Hydrocarbyl dihalides, such as 1,3-diiodopropane, react with the thiosulfito complexes similar to the reaction with MeI to give a dimer of the dinuclear complexes bridged by dithiolato ligands. The reaction of **4** with 1,3-diiodopropane gives a 1-iodopropane-3-thiolato bridged dirhodium complex,

(18) (a) Brunner, H.; Janietz, N. J.; Meier, W.; Sergeson, G.; Wachter, J.; Zhan, T.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1060. (b) Nishio, M.; Matsuzaka, H.; Mizobe, Y.; Hidai, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1872. (c) Yamada, M.; Tobita, H.; Inomata, S.; Ogino, H. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 861. (d) Mizobe, Y.; Hosomizu, M.; Kawabata, J.; Hidai, M. *Chem. Commun.* **1991**, 1226. (e) Matsumoto, T.; Matsumoto, K. *Chem. Lett.* **1992**, 559. (f) Roberts, S. A.; Young, C. G.; Cleland, W. E., Jr.; Yamanouchi, K.; Oitega, R. B.; Enemark, J. H. *Inorg. Chem.* **1988**, *27*, 2647. (g) Kawano, M.; Hoshino, S.; Matsmoto, K. *Inorg. Chem.* **1992**, *31*, 5158. (h) Goodman, J. T.; Rauchfuss, T. B. *Inorg. Chem.* **1998**, *37*, 5040. (i) Yoshioka, K.; Kikuchi, H.; Mizutani, J.; Matsumoto, K. *Inorg. Chem.* **2001**, *40*, 2234. (j) Rauchfuss, T. B.; Rodgers, D. P. S.; Wilson, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 3114. (k) Matsumoto, K.; Matsumoto, T.; Kawano, M.; Ohnuki, H.; Shichi, Y.; Nishide, T.; Sato, T. *J. Am. Chem. Soc.* **1996**, *118*, 3597. (l) Mizobe, Y.; Hosomizu, M.; Kubota, Y.; Hidai, M. *J. Organomet. Chem.* **1996**, *507*, 179. (m) Mizobe, Y.; Hosomizu, M.; Kuwata, S.; Kawabata, J.; Hidai, M. *J. Organomet. Chem.* **1996**, *513*, 231. (n) Weberg, R. T.; Haltiwanger, R. C.; Dubois, M. R. *Organometallics* **1985**, *4*, 1315.

(19) (a) Kubas, J. K.; Wasserman, H. J.; Ryan, R. R. *Organometallics* **1985**, *4*, 419. (b) Kubas, J. K.; Ryan, R. R.; Kubat-Martin, K. A. *J. Am. Chem. Soc.* **1989**, *111*, 7823. (c) Hoser, E. J.; Krautscheid, H.; T. B. Rauchfuss, Wilson, S. R. *Chem. Commun.* **1994**, 1283.

(20) Fronczek, F. R.; Marsh, R. E.; Schaefer, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 3382.

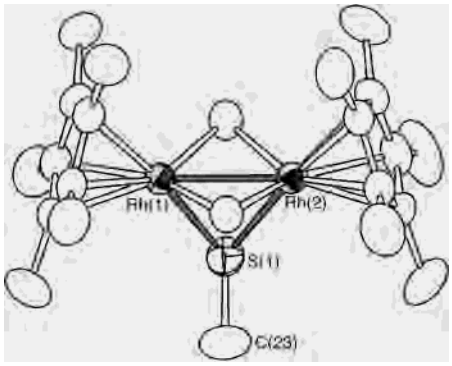
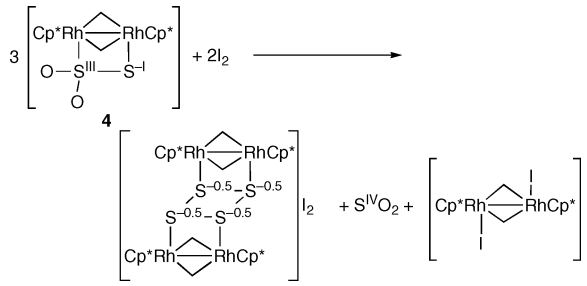


Figure 5. ORTEP drawing of the cationic moiety of $[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SMe)](BPh_4)$ (**6**) with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Scheme 4



confirmed by ESI-MS. This complex then reacts further with another molecule of **4** to give the dimer of the dirhodium complexes $[\{(RhCp^*)_2(\mu\text{-}CH_2)_2\}_2(\mu,\mu\text{-}SCH_2CH_2CH_2S)](BPh_4)_2$ (**8**). Alkyl dibromides such as α,α′-dibromo-*p*-xylene also react with **4** to give the corresponding dimer of the dirhodium complexes, $[\{(RhCp^*)_2(\mu\text{-}CH_2)_2\}_2\{p\text{-}(\mu\text{-}SCH_2)_2(C_6H_4)\}](BPh_4)_2$ (**9**). In the case of the iridium thiosulfito complex **5**, reaction with α,α′-dibromo-*p*-xylene only affords $[(IrCp^*)_2(\mu\text{-}CH_2)_2\{\mu\text{-}(p\text{-}SCH_2C_6H_4CH_2Br)\}]^+$ reflecting the lower reactivity of the iridium analogue.

The reaction of **4** with 1,2-diiodoethane does not give the corresponding dimer of the dirhodium complexes but gives *trans*-$[(RhCp^*)_2(\mu\text{-}CH_2)_2I_2]$ and $[\{(RhCp^*)_2(\mu\text{-}CH_2)_2\}_2(\mu\text{-}S_4\text{-}S{:}S'{:}S''{:}S''')]^{2+}$ through reaction with I_2, formed from the decomposition of 1,2-diiodoethane. In fact, **4** reacts with I_2 to give *trans*-$[(RhCp^*)_2(\mu\text{-}CH_2)_2I_2]$ and $[\{(RhCp^*)_2(\mu\text{-}CH_2)_2\}_2(\mu\text{-}S_4\text{-}S{:}S'{:}S''{:}S''')]^{2+}$ accompanied by the release of SO_2 gas. I_2 oxidizes both of the S atoms of the SSO_2 ligand to generate the S_4^{2-} ligand and SO_2 gas, and the formal oxidation numbers change from −1 for ***S***$SO_2$and +3 for S***S***O_2 to +0.5 for the S_4^{2-} and +4 for SO_2 gas, Scheme 4.

Structures of Bridging Thiolato Complexes. X-ray structure analyses were performed for complexes **6**−**9** and ORTEP drawings of each complex are shown in Figures 5−8. Crystal data are summarized in Table 2 and selected bond lengths and angles are listed in Table 5. Because the sulfur atoms in **8** and **9**, the carbon atoms of the 1,3-propanedithiolato ligand in **8**, and the μ-CH_2 carbon atoms in **9** are disordered, bond lengths and angles calculated using atoms with larger occupancies are used for discussion. All four complexes have almost the same geometry as the thiolato bridged dirhodium unit, $\{(Cp^*Rh)_2(\mu\text{-}CH_2)_2(\mu\text{-}SR)\}$. The acute Rh−S−Rh angles (64.27(7)−64.70(4)°) observed in **6**−**9** are similar to those of other μ-CH_2 dirhodium thiolato complexes with a Rh−Rh single bond, such as $[(Cp^*Rh)_2(\mu\text{-}CH_2)_2\{\mu\text{-}SC(COOMe){=}CH(COOMe)\}]^+$ (63.53(3)°)[4c] and $[(Cp^*Rh)_2(\mu\text{-}CH_2)_2(\mu\text{-}SH)]^+$ (64.3(1)°).[5] The μ-CH_2 complexes with a shorter Rh−Rh bond lengths tend to have smaller Rh−S−Rh angles.

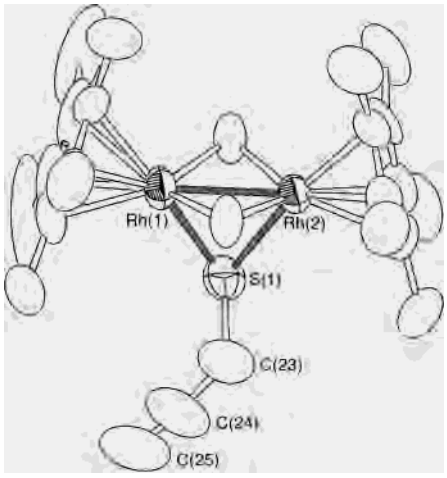


Figure 6. ORTEP drawing of the cationic moiety of $[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SCH_2CHCH_2)](BPh_4)$ (**7**) with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

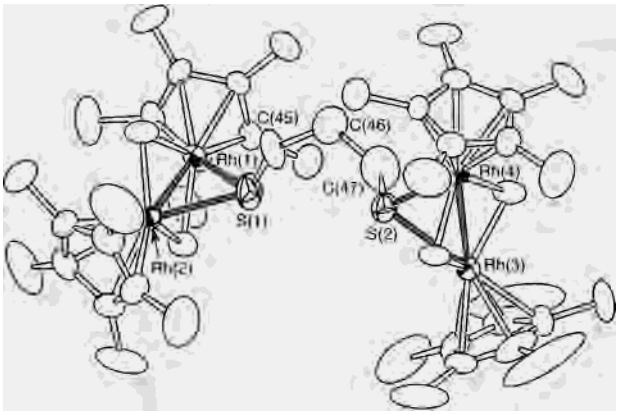


Figure 7. ORTEP drawing of the cationic moiety $[\{(RhCp^*)_2(\mu\text{-}CH_2)_2\}_2(\mu,\mu\text{-}SCH_2CH_2CH_2S)](BPh_4)_2$ (**8**) with 50% probability ellipsoids. Hydrogen atoms and half of the disordered carbon and sulfur atoms are omitted for clarity.

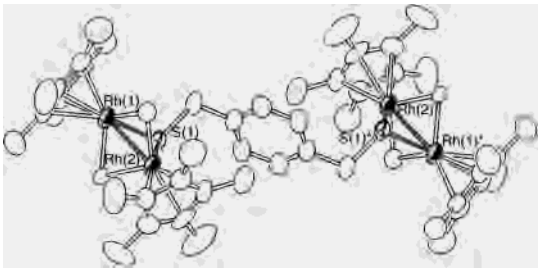


Figure 8. ORTEP drawing of the cationic moiety of $[\{(RhCp^*)_2\{p\text{-}(\mu\text{-}SCH_2)_2(C_6H_4)\}](BPh_4)_2$ (**9**) with 50% probability ellipsoids. Hydrogen atoms and half of the disordered sulfur atoms are omitted for clarity.

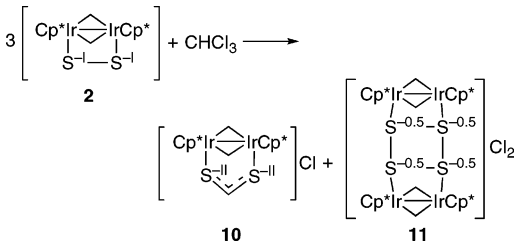
Reaction of Disulfido Complex 2 with Di- or Trichloroalkanes. When complex **2** reacts with either CH_2Cl_2 or $CHCl_3$ at room temperature, CH incorporation into the S−S bond occurs giving a dithioformato complex $[(IrCp^*)_2$-

Table 5. Selected Bond Lengths (Å) and Angles (°) for Complexes **6**−**9**[a]

	6	**7**	**8**	**9**
M−M	2.5447(3)	2.5479(5)	2.5623(8) 2.5637(8)	2.5549(8)
M−S	2.3712(9) 2.3897(8)	2.374(2) 2.388(2)	2.416(3), 2.402(3) 2.396(4), 2.411(4) [2.22(2), 2.38(2) 2.35(2), 2.30(3)]	2.387(2) 2.413(2) [2.564(9) 2.55(1)]
M−C(μ-CH_2)	2.027(2) 2.028(3) 2.035(3) 2.046(3)	2.021(4) 2.023(6) 2.037(4) 2.039(6)	2.034(8), 2.036(7) 2.011(7), 2.042(7) 2.049(7), 2.038(7) 2.055(7), 2.043(8)	1.997(9), 2.097(10) 1.97(1), 2.116(8) [2.38(3), 1.71(4), 2.30(3), 1.71(4)]
S−C	1.824(4)	1.801(8)	1.80(2), 1.76(2) [1.42(3), 1.49(2), 1.51(3)]	1.842(9) [1.77(1)]
M−S−M	64.62(2)	64.70(4)	64.27(7), 64.5(1) [67.5(5), 66.8(7)]	64.31(6) [60.0(2)]
M−C(μ-CH_2)−M	77.15(10) 77.75(9)	77.7(2) 77.8(2)	77.9(2), 78.6(3) 77.3(3), 77.8(3)	80.3(4), 74.7(3) [66.1(9), 96(2)]
M−M−S	57.34(2) 58.04(2)	57.38(4) 57.92(4)	57.60(6), 58.13(7), 58.0(1), 57.49(8) [59.3(5), 53.2(5), 55.6(6), 57.6(6)]	58.33(6) [59.7(2)]
M−S−C	111.3(1) 111.9(1)	110.4(3) 114.2(3)	115.4(5), 115.4(5) 117.4(6), 124.8(6) [129.2(9), 131(1), 148(1), 132(1), 133(1), 153(1)]	109.6(3) 114.7(3) [104.8(5), 111.4(6)]

[a] Values in [ ] were calculated using other sets of disordered atoms.

Scheme 5



(μ-CH_2)$_2$(μ-S_2CH-*S*:*S*′)]Cl (**10a**) accompanied by the formation of a cyclotetrasulfido complex, [{(IrCp*)$_2$(μ-CH_2)$_2$}$_2$(μ-S_4-*S*:*S*′:*S*″:*S*‴)]Cl_2 (**11a**), Scheme 5. The formal oxidation state of the S atoms goes from −1 in complex **2** to −2 in **10a** and −0.5 in **11a**.

Formation of **10a** occurs via either dechlorination for $CHCl_3$ or C−H activation and dechlorination for CH_2Cl_2 and in both cases incorporation of a CH moiety into the S−S bond then occurs. For $CHCl_3$, which only undergoes C−Cl bond activation, the reaction proceeds with a product molar ratio (**10a**:**11a**) of 1:1, as confirmed by ^{1}H NMR spectroscopy. The proton of the dithioformato ligand at δ 8.81 (see Experimental Section) was observed in the ^{1}H NMR spectrum when $CDCl_3$ was used. However, H−D exchange occurs in CD_3OD, confirmed by ESI-MS.

When 1,1-Cl_2CHCH_3 is used, [(IrCp*)$_2$(μ-CH_2)$_2$(μ-S_2-CCH_3-*S*:*S*′)]Cl (**12**) and **11a** are generated via a pathway similar to the reaction with CH_2Cl_2. Three sets of peaks were observed in the ESI mass spectrum of this reaction, Figure 9. The peaks at m/z = 773 and 746 correspond to [(IrCp*)$_2$(μ-CH_2)$_2$(μ-S_2CCH_3-*S*:*S*′)]$^+$ and [(IrCp*)$_2$(μ-CH_2)$_2S_2$]$^+$, which is from the cleavage of **11a** (Scheme 6), respectively. The third set of peaks at m/z = 761 corresponds to [{(IrCp*)$_2$(μ-CH_2)$_2S_2$}$_2$($CHCH_3$)]$^{2+}$, and this complex may be an intermediate in this reaction.

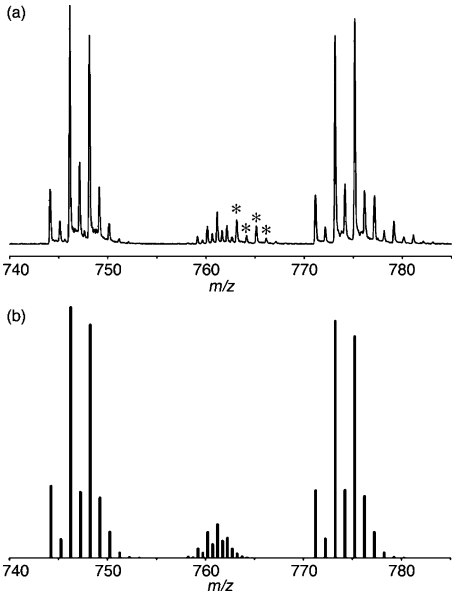
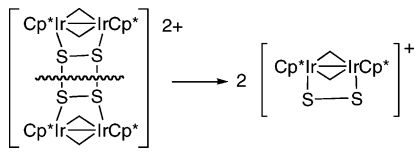


Figure 9. (a) ESI mass spectrum recorded 18 h after mixing of [(IrCp*)$_2$(μ-CH_2)$_2$(μ-S_2-*S*:*S*′)] (**2**) and 1,1-Cl_2CHCH_3. (b) Simulated spectrum. Peaks marked with * are from an unknown monocation.

Scheme 6



A possible structure of the intermediate is shown in Scheme 7. The proposed structure is based on [(RhCp*)$_2$(μ-CH_2)$_2$(μ-S_2Me-*S*:*S*′)] from the reaction of MeI with complex **1**.[2]

Structures of Dithiocarboxylato and Tetrasulfido Complexes. Crystals of **10a** and **11a** were obtained directly from

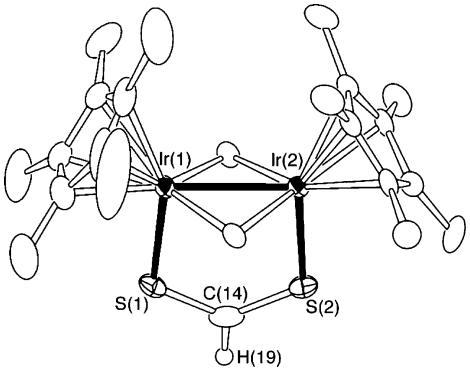


Figure 10. ORTEP drawing of the cationic moiety of $[(IrCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}S_2CH\text{-}S:S')]Cl$ (**10a**) with 50% probability ellipsoids. Hydrogen atoms except for that of the dithioformate are omitted for clarity.

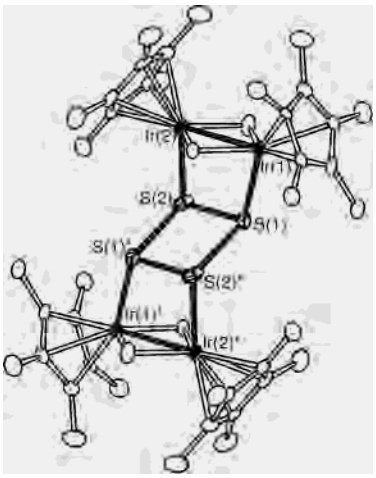
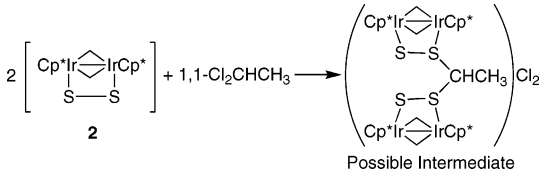


Figure 11. ORTEP drawing of the cationic moiety of $[\{(IrCp^*)_2(\mu\text{-}CH_2)_2\}_2(\mu_4\text{-}S_4\text{-}S:S':S'':S''')]Cl_2$ (**11a**) with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Scheme 7



the reaction mixture, and their structures are shown in Figures 10 and 11, respectively. Crystal data are summarized in Table 3 and selected bond lengths and angles are listed in Table 6. The hydrogen atom of the dithioformato ligand was found in the difference Fourier map (the C−H bond distance is 0.92 Å). The C−S bond distances in the dithioformato ligand (1.648(9) and 1.664(10) Å) in **10a** are consistent with a bond order of 1.5. The bond lengths and the S−C−S angle (129.4(5)°) are similar to those of analogous dithioformato Os complexes (1.62(3)−1.71(3) Å and 129.9(4)−132(2)°).[21]

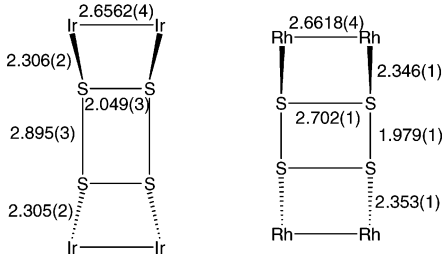
Like the Rh analogue $[\{(RhCp^*)_2(\mu\text{-}CH_2)_2\}_2(\mu\text{-}S_4\text{-}S:S':S'':S''')]^{2+}$,[6] complex **11a** has a chairlike structure with the cyclotetrasulfido ligand bound between two iridium dinuclear moieties. The cyclotetrasulfido ligand has two short S−S bonds (2.049(3) Å) which have nearly double bond character and two long S−S bonds (2.895(3) Å) which have

(21) Adams, R. D.; Selegue, J. P. *J. Organomet. Chem.* **1980**, *195*, 223.

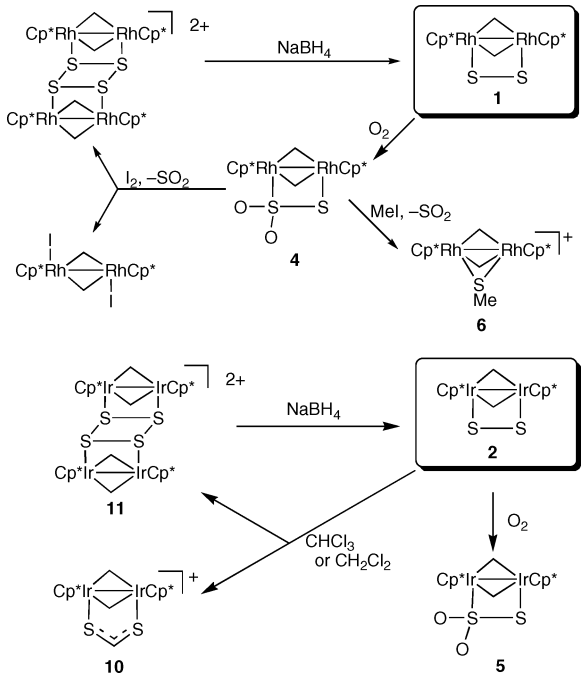
Table 6. Selected Bond Lengths (Å) and Angles (°) for Complexes **10a** and **11a**

	10a	**11a**
M−M	2.6555(7)	2.6561(4)
M−S	2.309(2), 2.320(2)	2.306(2), 2.305(2)
M−C(μ-CH_2)	2.062(5)	2.079(7), 2.064(6)
		2.075(7), 2.066(6)
S−C	1.648(9), 1.664(10)	
S−S (parallel to M−M)		2.049(3)
S−S (perpendicular to M−M)		2.894(3)
M−S−S (parallel to M−M)		97.25(9), 97.88(9)
M−S−S (perpendicular to M−M)		109.70(7), 109.44(7)
M−C(μ-CH_2)−M	80.2(2)	79.5(2), 80.1(2)
M−M-S	94.49(5), 93.90(6)	82.66(5), 82.21(5)
M−S−C	111.2(3), 111.0(3)	
S−C−S	129.4(5)	
S−S−S		90.08(9), 89.92(9)

Scheme 8



Scheme 9



less than single bond character. The longer S−S bonds are significantly shorter than the sum of the van der Waals radii of S atoms (3.60 Å) and similar S−S distances are reported for the trans annular S−S bonds in S_8^+ (2.86(3) Å).[22] The shorter S−S bonds lie parallel to the Ir−Ir bonds and the longer ones lie perpendicular to the Ir dinuclear backbone. In the corresponding Rh complex, the longer bonds are parallel to the Rh−Rh bonds and the shorter ones are

(22) Davies, C. G.; Gillespie, R. J.; Park, J. J.; Passmore, J. *Inorg. Chem.* **1971**, *10*, 2781.

perpendicular to the Rh dinuclear backbone, Scheme 8. This implies that the S_4 ligand in **11a** has a different electronic structure from that in the Rh complex, in which the S_4 moiety was determined to have a net −1 charge based on theoretical calculations.[23] Further, the structure of **11a** is maintained in solution, verified by ^{1}H NMR spectroscopy, even though it has weak S−S bonds.

Conclusions

Disulfido ligands coordinated parallel to M−M bonds have high reactivity toward O_2 and alkyl halides. When exposed to O_2, these complexes are readily converted to a disulfur monoxide for the dirhodium complex and a thiosulfito complex for both the dirhodium and diiridium complexes. The disulfido ligand in the Ir complex is also susceptible to electrophilic attack by di- or trichloroalkanes. This attack causes the incorporation of C−R (R = H or Me) into the S−S bond to produce dithiocarboxylato complexes. The cyclotetrasulfido complex **11a** also forms during this reaction. The thiosulfito ligand reacts with hydrocarbyl halides to release SO_2 gas and affords an alkylthiolato ligand bridging the two metal ions in the dimetallic unit. All of the reactions summarized in Scheme 9 occur through redox processes involving the sulfur atoms and reflect a variety of oxidation states of sulfur atoms.

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Supporting Information Available: Crystallographic data in CIF format for complexes **2**−**11a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) Mebel, A. M.; Morokuma, K.; Isobe, K. *Inorg. Chem.* **1995**, *34*, 1208.