Ligand Exchange in Tungsten–Rhenium Acetylide Complexes $(C_5Me_5)WRe(\mu-X)(CCPh)(CO)_5$, $X = Br, I, SPh$, and O_2CMe , and the Conversion to Complexes $LWRe(\mu-SO_2Ph)(CCPh)(CO)_5$, $L = Cp$ and C_5Me_5 , Bearing a Sulfinate Bridge via Oxidation Using Hydrogen Peroxide

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Heterobimetallic acetylide compounds $(C_5Me_5)WRe(\mu-X)(CCPh)(CO)_5$, $X = I$ and Br (**1a,b**), were obtained in high yields from the combination of $(C_5Me_5)W(CO)_3(CCPh)$ and $Re(CO)_5X$, $X = Br$ and I . These complexes possess a nearly symmetrical halide bridge and an acetylide ligand, linked to the W atom via σ -bonding and to the Re atom via a π -interaction. The conversion to the corresponding thiolate and acetate complexes $LWRe(\mu-X)(CCPh)(CO)_5$ [$L = C_5Me_5$, $X = SPh$ (**2a**) and O_2CMe (**3**); $X = SPh$, $L = Cp$ (**2b**)] was realized by reactions of the halide complexes with thiophenol or with acetic acid, respectively, in the presence of triethylamine or pyridine. Related reactions of $(C_5Me_5)W(CO)_3(CCPh)$ with $[Re(CO)_4(\mu-SPh)]_2$ or with $[Re(CO)_4(\mu-O_2CMe)]_2$ afforded the identical thiolate and acetate complexes through a reaction sequence involving the dissociation of these dimeric starting materials. Reactions of **1–3** with $P(OMe)_3$ were also examined, and only the thiolate complex **2a** gave the isolated monosubstituted complex $(C_5Me_5)WRe(\mu-SPh)(CCPh)(CO)_4[P(OMe)_3]$ (**4**) in good yield. Oxidation of the bridging thiolate ligand in **2a,b** using 30% H_2O_2 solution yielded sulfinate complexes with the formula $LWRe(\mu-SO_2Ph)(CCPh)(CO)_5$, $L = C_5Me_5$ (**6**) and $L = Cp$ (**7, 8**). Two linkage isomers were characterized by single-crystal X-ray diffraction studies: One bears a μ - η^2 - SO_2Ph ligand with the bridging oxygen atom coordinated to the W atom, while in the second the bridging oxygen atom is coordinated to the Re atom. The isomerization caused by the interchange of the bridging and the terminal oxygen atom of the sulfinate group is discussed.

The reactions of acetylide complexes $LW(CO)_3(C\equiv CR)$, $L = Cp$ and C_5Me_5 , with carbonyl cluster complexes, such as $Os_3(CO)_{10}(NCMe)_2$ or $Ru_3(CO)_{12}$, have proved to be a general method for generating heterometallic compounds.¹ The formation of acetylide cluster compounds from these reactions provides mechanistic implications for substrate–metal interaction of small organic intermediates with metal surfaces.² Thus, thermolysis of the acetylide cluster $(C_5Me_5)WOS_3(CCPh)(CO)_{11}$, which was prepared from one of these reactions, afforded the carbido–alkylidyne cluster $(C_5Me_5)WOS_3(\mu_4-C)(\mu_3-CPh)(CO)_{10}$,³ while treatment of the WRu_2

analogues $LWRu_2(CCPh)(CO)_8$, $L = Cp$ and C_5Me_5 , with $Ru_3(CO)_{12}$ generated the high-nuclearity, square pyramidal $LWRu_4(\mu_5-C)(\mu-CPh)(CO)_{12}$ and the octahedral $LWRu_5(\mu_6-C)(\mu-CPh)(CO)_{14}$ cluster.⁴ These reactions represent some uncommon examples of reversible conversion from acetylide to carbide and alkylidyne ligands, through cleavage of carbon–carbon bonds.

In order to extend the range of this type of cluster building reaction, we turned our attention to the W–Re heterometallic system. The reactions of $(C_5Me_5)W(CO)_3(C\equiv CPh)$ with $Re_2(CO)_8(NCMe)_2$ have been systematically studied.⁵ Subsequent studies on WRe_2 acetylide clusters with various oxygen sources afforded new examples of oxo–carbonyl clusters.⁶ This provided an

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opportunity to investigate the influence of oxo ligands on the reactivity pattern of an acetylide ligand.⁷

In this paper, we describe the coupling reactions between $(C_5Me_5)W(CO)_3(C\equiv CPh)$ and $Re(CO)_5X$, $X = Br$ and I , which yield new complexes with the formula $(C_5Me_5)WRe(\mu-X)(CCPh)(CO)_5$. The conversion of the halide bridge in these complexes to bridging thiolate and acetate ligands was accomplished via direct exchange. Oxidation of the thiolate fragment gave the corresponding sulfinate complexes $LWRe(\mu-SO_2Ph)(CCPh)(CO)_5$, $L = Cp$ and C_5Me_5 .

Experimental Section

General Information and Materials. Infrared spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer. 1H , ^{13}C , and ^{31}P NMR spectra were recorded on a Bruker AM-400, AMX-300, or Varian Unity-400 instrument. Mass spectra were obtained on a JEOL-HX110 instrument operating in fast atom bombardment (FAB) mode. All reactions were performed under a nitrogen atmosphere using dried deoxygenated solvents. The reactions were monitored by analytical thin-layer chromatography (5735 Kieselgel 60 F₂₅₄, E. Merck), and the products were separated on commercially available preparative thin-layer chromatographic plates (Kieselgel 60 F₂₅₄, E. Merck). Elemental analyses were performed at the NSC Regional Instrumentation Center at National Cheng Kung University, Tainan, Taiwan.

The tungsten acetylide complexes $LW(CO)_3(CCPh)$, $L = Cp$ or C_5Me_5 , were prepared according to literature procedures.⁸ The rhenium complex $Re(CO)_5Br$ was prepared by addition of Br_2 to a solution of $Re_2(CO)_{10}$.⁹ The iodide derivative $Re(CO)_5I$ was prepared by the reaction of NaI with $[Re(CO)_5(NCMe)]PF_6$.¹⁰ The thiolate complex $[Re(CO)_4(\mu-SPh)]_2$ and the acetate complex $[Re(CO)_4(\mu-O_2CMe)]_2$ were prepared by photolysis of $PhSSPh$ with $Re_2(CO)_{10}$ and the reaction of $Re(CO)_5Br$ with sodium acetate, respectively.¹¹

Preparation of 1a,b. A toluene solution (35 mL) of $Re(CO)_5I$ (140 mg, 0.308 mmol) and $(C_5Me_5)W(CO)_3(CCPh)$ (155 mg, 0.308 mmol) was refluxed under nitrogen for 1 h, during which period the color changed from orange to red. After the solution was allowed to cool to room temperature, the solvent was removed, and the residue was dissolved in minimum amount of CH_2Cl_2 and separated by thin-layer chromatography (1:1 dichloromethane/hexane). Recrystallization from a solution of dichloromethane/heptane gave 185 mg of $(C_5Me_5)WRe(\mu-I)(CCPh)(CO)_5$ (**1a**, 0.211 mmol, 69%) as dark-red crystalline materials. The dark-red bromide complex $(C_5Me_5)WRe(\mu-Br)(CCPh)(CO)_5$ (**1b**) was prepared in a similar manner by the reaction of $(C_5Me_5)W(CO)_3(CCPh)$ with $Re(CO)_5Br$ in 44% yield.

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Spectral data for **1a**: MS (FAB, ^{184}W , ^{187}Re) m/z 874 (M^+); IR (C_6H_{12}) $\nu(CO)$ 2033 (vs), 1988 (m, br), 1941 (s, br), 1934 (m, sh), 1910 (vw) cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$, 294 K) δ 7.48 (d, 2H, $J_{HH} = 6$ Hz), 7.34 (t, 2H, $J_{HH} = 6$ Hz), 7.21 (t, 1H, $J_{HH} = 6$ Hz), 2.33 (s, 15H, C_5Me_5); ^{13}C NMR (75 MHz, $CDCl_3$, 294 K) δ 222.5, 220.3, 197.3, 195.2, and 195.1 (CO), 132.3 (2C, $o-C_6H_5$), 128.3 (2C, $m-C_6H_5$), 127.9 ($p-C_6H_5$), 127.6 ($i-C_6H_5$), 119.2 (CCPh), 104.9 (CCPh), 103.3 (C_5Me_5), 12.1 (C_5Me_5). Anal. Calcd for $C_{23}H_{20}O_5ReW$: C, 31.63; H, 2.31. Found: C, 31.37; H, 2.25.

Spectral data for **1b**: MS (FAB, ^{184}W , ^{187}Re) m/z 826 (M^+); IR (C_6H_{12}) $\nu(CO)$ 2034 (vs), 1989 (m, br), 1944 (s, br), 1936 (m, sh), 1913 (vw) cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$, 294 K) δ 7.55 (d, 2H, $J_{HH} = 6$ Hz), 7.38 (t, 2H, $J_{HH} = 6$ Hz), 7.26 (t, 1H, $J_{HH} = 6$ Hz), 2.27 (s, 15H, C_5Me_5); ^{13}C NMR (75 MHz, CD_2Cl_2 , 294 K) δ 226.2 ($J_{WC} = 139$ Hz), 223.5 ($J_{WC} = 157$ Hz), 198.5, 195.6, and 195.4 (CO), 132.3 (2C, $o-C_6H_5$), 128.6 (2C, $m-C_6H_5$), 128.2 ($p-C_6H_5$), 127.9 ($i-C_6H_5$), 121.7 (CCPh, $J_{WC} = 23$ Hz), 111.2 (CCPh, $J_{WC} = 104$ Hz), 104.4 (C_5Me_5), 11.5 (C_5Me_5). Anal. Calcd for $C_{23}H_{20}O_5BrReW$: C, 33.42; H, 2.44. Found: C, 33.30; H, 2.49.

Preparation of 2a,b. A toluene solution (30 mL) of **1b** (100 mg, 0.121 mmol), thiophenol (100 μ L, 0.982 mmol), and triethylamine (100 μ L) was refluxed under nitrogen for 1 h. After removal of the solvent and excess thiophenol and triethylamine under vacuum, the residue was redissolved in the minimum amount of CH_2Cl_2 and separated by thin-layer chromatography (2:1 dichloromethane/hexane); 90 mg of the red-orange compound $(C_5Me_5)WRe(\mu-SPh)(CCPh)(CO)_5$ (**2a**, 0.105 mmol, 87%) was obtained after recrystallization from a mixture of dichloromethane and hexane. Similarly, the Cp derivative $CpWRe(\mu-SPh)(CCPh)(CO)_5$ (**2b**) was prepared in 77% yield from the reaction of $CpW(CO)_3(CCPh)$ with $[Re(CO)_4(\mu-SPh)]_2$ in toluene at 110 $^\circ C$ for 30 min.

Spectral data for **2a**: MS (FAB, ^{184}W , ^{187}Re) m/z 857 (M^+); IR (C_6H_{12}) $\nu(CO)$ 2026 (vs), 1983 (m, br), 1940 (s, br), 1921 (m, br), 1910 (vw) cm^{-1} ; 1H NMR (400 MHz, CD_2Cl_2 , 294 K) δ 7.59 (d, 2H, $J_{HH} = 7.2$ Hz), 7.36–7.32 (m, 4H), 7.27 (t, 1H, $J_{HH} = 7.2$ Hz), 7.21–7.13 (m, 3H), 2.28 (s, 15H, C_5Me_5); ^{13}C NMR (100 MHz, CD_2Cl_2 , 294 K) δ 226.0, 225.2, 199.3, 197.5, and 196.8 (CO), 139.9 ($i-C_6H_5$), 133.1 (2C, $o-C_6H_5$), 132.7 (2C, $m-C_6H_5$), 128.8 (2C, $o-C_6H_5$), 128.6 (2C, $m-C_6H_5$), 128.2 ($p-C_6H_5$), 128.0 ($i-C_6H_5$), 127.2 ($p-C_6H_5$), 115.9 (CCPh), 104.1 (C_5Me_5), 101.5 (CCPh), 11.7 (C_5Me_5). Anal. Calcd for $C_{29}H_{25}O_5SReW$: C, 40.65; H, 2.94. Found: C, 40.59; H, 2.95.

Spectral data for **2b**: MS (FAB, ^{184}W , ^{187}Re) m/z 786 (M^+); IR (C_6H_{12}) $\nu(CO)$ 2032 (vs), 1992 (m, br), 1956 (s, br), 1927 (m, br), 1916 (vw) cm^{-1} ; 1H NMR (400 MHz, CD_2Cl_2 , 294 K) δ 7.52 (d, 2H, $J_{HH} = 7.5$ Hz), 7.37–7.16 (m, 8H), 5.86 (s, 5H, Cp); ^{13}C NMR (100 MHz, $CDCl_3$, 294 K) δ 219.6 ($J_{WC} = 142$ Hz), 218.9 ($J_{WC} = 144$ Hz), 198.0 (br), 196.0 (br), and 195.4 (br) CO, 139.5, 132.9 (2C), 132.2 (2C), 128.6 (4C), 128.4, 127.3, 127.2, 115.2 (CCPh, $J_{WC} = 22$ Hz), 90.1 (C_5H_5), 89.8 (CCPh). Anal. Calcd for $C_{24}H_{15}O_5SReW$: C, 36.70; H, 1.92. Found: C, 36.77; H, 1.94.

Preparation of 3. Method 1. A toluene solution (60 mL) of $[Re(CO)_4(\mu-O_2CMe)]_2$ (365 mg, 0.555 mmol) and $(C_5Me_5)W(CO)_3(CCPh)$ (140 mg, 0.278 mmol) was refluxed under nitrogen for 2 h, during which period the color changed from orange to red-orange. After the solvent was removed under vacuum, the residue was purified by thin layer chromatography (1:1 dichloromethane/hexane) and recrystallized from dichloromethane/heptane solution to yield 88 mg of $(C_5Me_5)WRe(\mu-O_2CMe)(C\equiv CPh)(CO)_5$ (**3**, 0.103 mmol, 37%) as a red crystalline material.

Method 2. A toluene solution (30 mL) of **1b** (94 mg, 0.114 mmol), acetic acid (2 mL), and triethylamine (2 mL) was refluxed under nitrogen for 2 h. Treatment as above gave 65 mg of **3** (0.081 mmol, 71%). The reaction of **1a** with acetic acid under similar conditions afforded complex **3** in only 59% yield.

Spectral data for **3**: MS (FAB, ^{184}W , ^{187}Re) m/z 806 (M^+). IR (C_6H_{12}) $\nu(\text{CO})$ 2030 (vs), 1978 (m, br), 1942 (s, br), 1927 (m, br), 1900 (vw) cm^{-1} ; ^1H NMR (300 MHz, CDCl_3 , 294 K) δ 7.56 (d, 2H, $J_{\text{HH}} = 7.5$ Hz), 7.37 (t, 2H, $J_{\text{HH}} = 7.5$ Hz), 7.26 (t, 1H, $J_{\text{HH}} = 7.5$ Hz), 2.14 (s, 15H, C_5Me_5), 1.74 (s, 3H, MeCO_2); ^{13}C NMR (75 MHz, CD_2Cl_2 , 294 K) δ 233.7 ($J_{\text{WC}} = 157$ Hz), 219.1 ($J_{\text{WC}} = 138$ Hz), 200.4, 198.9, and 196.5 (CO), 182.3 (MeCO_2), 133.9 (CCPh, $J_{\text{WC}} = 144$ Hz), 131.3 (2C, $o\text{-C}_6\text{H}_5$), 130.0 ($i\text{-C}_6\text{H}_5$), 128.5 (2C, $m\text{-C}_6\text{H}_5$), 127.7 (CPh, $J_{\text{WC}} = 28$ Hz), 127.5 ($p\text{-C}_6\text{H}_5$), 105.6 (C_5Me_5), 24.2 (Me), 10.7 (C_5Me_5). Anal. Calcd for $\text{C}_{25}\text{H}_{23}\text{O}_7\text{ReW}$: C, 37.22; H, 2.88. Found: C, 37.22; H, 2.85.

Attempted Reaction of 1a with P(OMe)₃. A toluene solution (30 mL) of **1a** (78 mg, 0.089 mmol) and P(OMe)_3 (42 μL , 0.355 mmol) was heated at reflux under nitrogen for 30 min, during which time the color changed rapidly from red to dark-green. After the solvent was removed under vacuum, the reaction mixture was separated by TLC (1:1 dichloromethane/hexane) to produce a trace amount of $(\text{C}_5\text{Me}_5)\text{W(CO)}_3(\text{CCPh})$ as determined by IR spectroscopy.

Reaction of 2a with P(OMe)₃. A toluene solution (30 mL) of **2a** (160 mg, 0.187 mmol) and trimethyl phosphite (100 μL , 0.93 mmol) was refluxed under nitrogen for 4 h. After removal of the solvent and excess phosphite under vacuum, the residue was separated by TLC (1:1 dichloromethane/hexane) to give 110 mg of $(\text{C}_5\text{Me}_5)\text{WRe}(\mu\text{-Sph})(\text{CCPh})(\text{CO})_4[\text{P(OMe)}_3]$ (**4**, 0.116 mmol, 62%).

Spectral data for **4**: MS (FAB, ^{184}W , ^{187}Re) m/z 952 (M^+); IR (CH_2Cl_2) $\nu(\text{CO})$ 1992 (vs), 1928 (vs, br), 1853 (m) cm^{-1} ; ^1H NMR (400 MHz, CD_2Cl_2 , 294 K) δ 7.50–7.12 (m, 10H, Ph), 3.36 (d, 9H, P(OMe)_3 , $J_{\text{PH}} = 11.7$ Hz), 2.21 (s, 15H, C_5Me_5); ^{13}C NMR (100 MHz, CD_2Cl_2 , 294 K) δ 227.9 ($J_{\text{WC}} = 141$ Hz), 227.5 ($J_{\text{WC}} = 178$ Hz), 203.1 (d, $J_{\text{PC}} = 13$ Hz), and 201.5 (d, $J_{\text{PC}} = 10$ Hz) (CO), 140.6 ($i\text{-C}_6\text{H}_5$), 133.5 (2C, $o\text{-C}_6\text{H}_5$), 132.9 (2C, $m\text{-C}_6\text{H}_5$), 130.1 ($i\text{-C}_6\text{H}_5$), 128.2 (2C, $o\text{-C}_6\text{H}_5$), 128.0 (2C, $m\text{-C}_6\text{H}_5$), 127.4 ($p\text{-C}_6\text{H}_5$), 126.7 ($p\text{-C}_6\text{H}_5$), 117.8 (CPh), 103.6 (C_5Me_5), 102.2 (CCPh, $J_{\text{WC}} = 144$ Hz), 52.0 (3C, OMe), 11.5 (C_5Me_5); ^{31}P NMR (121 MHz, CDCl_3 , 294 K) δ 138.2 (s). Anal. Calcd for $\text{C}_{31}\text{H}_{34}\text{O}_7\text{SPReW}$: C, 39.07; H, 3.60. Found: C, 38.86; H, 3.53.

Reaction of 4 with CO. To a 250 mL thick-wall pressure bottle were added 40 mL of toluene and 98 mg of **4** (0.103 mmol). The flask was charged with 100 psi of carbon monoxide and placed into an oil bath at 110 $^\circ\text{C}$ for 4 h. After the removal of solvent *in vacuo*, the residue was redissolved in CH_2Cl_2 and separated by TLC (1:1 dichloromethane/hexane). The final product was recrystallized from a solution of dichloromethane/hexane, giving 68 mg of **2a** (0.079 mmol, 77%).

Reaction of 3 with P(OMe)₃. A toluene solution (30 mL) of **3** (75 mg, 0.093 mmol) and P(OMe)_3 (44 μL , 0.372 mmol) was heated to reflux under nitrogen for 8 h, during which time the color changed gradually from red-orange to orange. After the solvent and excess phosphite were removed under vacuum, the residue was separated by TLC (1:1 dichloromethane/hexane), giving 10 mg of unreacted starting material **3** (0.013 mmol, 13%), 7 mg of $(\text{C}_5\text{Me}_5)\text{W(CO)}_3(\text{CCPh})$ (0.014 mmol, 15%), and approximately 2 mg of the red complex $(\text{C}_5\text{Me}_5)\text{WRe}(\mu\text{-O}_2\text{CMe})(\text{CCPh})(\text{CO})_4[\text{P(OMe)}_3]$ (**5**, 0.002 mmol, 2%).

Spectral data for **5**: MS (FAB, ^{184}W , ^{187}Re) m/z 902 (M^+); IR (C_6H_{12}) $\nu(\text{CO})$ 1992 (vs), 1937 (s), 1918 (br, vs), 1870 (br, s), 1864 (br, s) cm^{-1} ; ^1H NMR (400 MHz, CD_2Cl_2 , 294 K) δ 7.44 (d, 2H, $J_{\text{HH}} = 7.2$ Hz), 7.26 (d, 2H, $J_{\text{HH}} = 7.2$ Hz), 7.18 (t, 1H, $J_{\text{HH}} = 7.2$ Hz), 3.49 (d, 9H, P(OMe)_3 , $J_{\text{PH}} = 11.6$ Hz), 2.21 (s, 15H, C_5Me_5), 1.67 (s, 3H, O_2CMe).

Treatment of 2a with H₂O₂. To a toluene solution (45 mL) of **2a** (150 mg, 0.175 mmol) were added a mixture of 35% H_2O_2 (5 mL) and concentrated H_2SO_4 (0.15 mL). The solution was then stirred at room temperature for 16 h, during which time the color changed from yellow orange to red. After the reaction was completed, the solution was washed with deionized water three times (20 mL $\times$ 3) to remove excess H_2O_2 . The organic layer was separated and dried with Na_2SO_4 , and

the toluene solvent was removed under vacuum. The residue was taken up in a minimum amount of CH_2Cl_2 and separated by TLC (1:1 dichloromethane/hexane), giving 84 mg of $(\text{C}_5\text{Me}_5)\text{WRe}(\mu\text{-SO}_2\text{Ph})(\text{CCPh})(\text{CO})_5$ (**6**, 0.947 mmol, 54%). Crystals suitable for X-ray diffraction study were obtained from a layered solution of dichloromethane and hexane.

Selected spectral data for **6**: MS (FAB, ^{184}W , ^{187}Re) m/z 888 (M^+); IR (CH_2Cl_2) $\nu(\text{CO})$ 2033 (vs), 1983 (m, br), 1950 (s, br), 1936 (m, br) cm^{-1} ; ^1H NMR (400 MHz, CD_2Cl_2 , 294 K) δ 7.69–6.87 (m, 10H, $2\text{C}_6\text{H}_5$), 2.16 (s, C_5Me_5). ^{13}C NMR (100 MHz, CDCl_3 , 294 K): isomer **6a** (80%), δ 230.2 (W–CO, $J_{\text{WC}} = 158$ Hz), 224.0 (W–CO, $J_{\text{WC}} = 160$ Hz), 198.2 (Re–CO), 197.8 (Re–CO), 197.2 (Re–CO), 106.5 (C_5Me_5), 11.4 (C_5Me_5); isomer **6b** (20%), δ 232.9 (W–CO), 224.4 (W–CO), 198.2 (Re–CO), 197.8 (Re–CO), 197.1 (Re–CO), 106.9 (C_5Me_5), 11.7 (C_5Me_5). Anal. Calcd for $\text{C}_{29}\text{H}_{25}\text{O}_7\text{SReW}$: C, 39.24; H, 2.84. Found: C, 39.14; H, 2.88.

Treatment of 2b with H₂O₂. To a toluene solution (45 mL) of **2b** (150 mg, 0.190 mmol) were added a mixture of 35% H_2O_2 (5 mL) and concentrated H_2SO_4 (0.15 mL). This solution was then stirred at room temperature for 16 h, during which time the color changed from orange to red-orange. After the reaction was completed, the solution was washed with deionized water three times (20 mL $\times$ 3) to remove excess H_2O_2 . The organic layer was separated and dried with anhydrous Na_2SO_4 , and the toluene solvent was removed under vacuum. The residue obtained was then redissolved in a minimum amount of CH_2Cl_2 and separated by TLC (1:1 dichloromethane/hexane), giving 62 mg of orange-red (**7**) (0.076 mmol, 40%) and 8 mg of red (**8**) (0.010 mmol, 5%), both with the molecular formula $\text{CpWRe(CO)}_5(\mu\text{-SO}_2\text{Ph})(\text{CCPh})$. Crystals of complexes **7** and **8** were obtained from a layered solution of dichloromethane and hexane at room temperature.

Selected spectral data for **7**: MS (FAB, ^{184}W , ^{187}Re) m/z 818 (M^+); IR (CH_2Cl_2) $\nu(\text{CO})$ 2040 (vs), 2010 (m), 1949 (s, br), 1931 (m), 1902 (w, br) cm^{-1} ; ^1H NMR (400 MHz, CD_2Cl_2 , 294 K) δ 7.71–7.35 (m, 10H, $2\text{C}_6\text{H}_5$), 5.80 (s, **7b**, 24%, C_5H_5), 5.59 (s, **7a**, 76%, C_5H_5). ^{13}C NMR (100 MHz, CDCl_3 , 294 K): isomer **7a**, δ 225.2 (W–CO), 206.5 (W–CO), 198.9 (Re–CO), 197.9 (Re–CO), 196.0 (Re–CO), 92.5 (C_5H_5); isomer **7b**, δ 226.4 (W–CO), 206.7 (W–CO), 199.6 (Re–CO), 197.5 (Re–CO), 196.0 (Re–CO), 93.0 (C_5H_5). Anal. Calcd for $\text{C}_{24}\text{H}_{15}\text{O}_7\text{SReW}$: C, 35.26; H, 1.85. Found: C, 35.15; H, 1.84.

Selected spectral data for **8**: MS (FAB, ^{184}W , ^{187}Re) m/z 818 (M^+); IR (CH_2Cl_2) $\nu(\text{CO})$ 2040 (vs), 1997 (m, br), 1959 (s, br), 1942 (m) cm^{-1} ; ^1H NMR (400 MHz, CD_2Cl_2 , 294 K) δ 7.73–6.72 (m, 10H, $2\text{C}_6\text{H}_5$), 6.02 (s, **8b**, 27%, C_5H_5), 5.99 (s, **8a**, 73%, C_5H_5). ^{13}C NMR (100 MHz, CDCl_3 , 294 K): isomer **8a**, δ 225.8 (W–CO), 216.3 (W–CO), 196.8 (Re–CO), 195.9 (Re–CO), 195.3 (Re–CO), 92.1 (C_5H_5); isomer **8b**, δ 227.6 (W–CO), 216.1 (W–CO), 196.8 (Re–CO), 195.9 (Re–CO), 195.1 (Re–CO), 92.4 (C_5H_5). Anal. Calcd for $\text{C}_{24}\text{H}_{15}\text{O}_7\text{SReW}$: C, 35.26; H, 1.85. Found: C, 35.14; H, 1.85.

X-ray Crystallography. The X-ray diffraction measurements were carried out on a Nonius CAD-4 diffractometer at room temperature. For all experiments, the lattice parameters were determined from 25 randomly selected high-angle reflections. Three standard reflections were monitored every 3600 s. No significant change in intensities ($\leq 2\%$) was observed during the course of all data collection. Intensities of the diffraction signals were corrected for Lorentz, polarization, and absorption effects (ψ scans). The structure was solved by using the NRCC-SDP-VAX package. All the non-hydrogen atoms had anisotropic temperature factors, while the hydrogen atoms of the organic substituents were placed at the calculated positions with $U_{\text{H}} = U_{\text{C}} + 0.1$. The crystallographic refinement parameters of complexes **1a**, **6**, and **7** are given in Table 1, while their selected bond distances and angles are presented in Tables 2–4, respectively.

Table 1. Experimental Data for the X-ray diffraction Studies of **1a**, **6**, and **7a**

compd	1a	6	7
formula	C ₂₃ H ₂₀ IO ₅ ReW	C ₂₉ H ₂₅ O ₇ SReW	C ₂₄ H ₁₅ O ₇ SReW
mol wt	873.37	887.62	817.49
cryst system	monoclinic, <i>P</i> 2 ₁ / <i>n</i>	monoclinic, <i>P</i> 2 ₁ / <i>n</i>	triclinic, <i>P</i> $\bar{1}$
<i>a</i> (Å)	9.879(3)	10.682(4)	7.951(1)
<i>b</i> (Å)	18.401(3)	15.115(3)	11.077(1)
<i>c</i> (Å)	12.950(3)	18.004(4)	13.393(2)
α (deg)			90.55(1)
β (deg)	93.22(2)	98.36(3)	94.97(1)
γ (deg)			97.45(2)
<i>V</i> (Å ³)	2350(1)	2876(1)	1165.0(3)
<i>Z</i>	4	4	2
<i>D_c</i> (g/cm ³)	2.468	2.050	2.331
<i>F</i> (000)	1600	1672	756
cryst size (mm)	0.10 × 0.30 × 0.30	0.25 × 0.40 × 0.55	0.02 × 0.20 × 0.50
<i>h</i> , <i>k</i> , <i>l</i> ranges	−11/11, 0/21, 0/15	−12/12, 0/17, 0/21	−9/9, 0/13, −15/15
μ (cm ^{−1})	115.4	42.27	104.31
transm factors: max, min	0.348, 1.000	0.631, 1.000	0.366, 1.000
no. of unique data (<i>2</i> θ _{max})	4122 (50°)	5045 (50°)	4099 (50°)
no. of data with <i>I</i> > 2 σ (<i>I</i>)	3347	3955	3069
no. of params	281	353	308
max Δ/σ ratio	0.078	0.0047	0.011
<i>R_i</i> , <i>R_w</i>	0.039, 0.031	0.025, 0.025	0.026, 0.027
GOF	2.58	1.41	1.34
residual e-density (e/Å ³)	2.05/−2.95	0.85/−0.94	0.96/−0.75

^a Features common to all determinations: *T* = 297 K, λ (Mo K α) = 0.709 30 Å, *w* = 1/ σ^2 (*F_o*); GOF = [$\sum w|F_o - F_c|^2/(N_o - N_v)$]^{1/2} (*N_o* = number of observations; *N_v* = number of variables).

Table 2. Selected Bond Distances (Å) and Angles (deg) of **1a** (Esd's in Parentheses)

W–Re	2.906(1)	W–C(6)	2.09(1)
Re–C(6)	2.27(1)	Re–C(7)	2.46(1)
W–I	2.848(1)	Re–I	2.870(1)
W–C(4)	2.14(1)	W–C(5)	2.01(1)
Re–C(1)	1.91(1)	Re–C(2)	1.77(2)
Re–C(3)	1.90(2)	W–C(14)	2.33(1)
W–C(15)	2.35(1)	W–C(16)	2.32(1)
W–C(17)	2.29(1)	W–C(18)	2.28(1)
C(6)–C(7)	1.22(1)		
$\angle$ W–I–Re	61.10(2)	$\angle$ W–C(6)–C(7)	167.5(9)
$\angle$ C(6)–C(7)–C(8)	159(1)	$\angle$ W–C(4)–O(4)	172(1)
$\angle$ W–C(5)–O(5)	177(1)	$\angle$ Re–C(1)–O(1)	179(1)
$\angle$ Re–C(2)–O(2)	178(1)	$\angle$ Re–C(3)–O(3)	179(1)

Table 3. Selected Bond Distances (Å) and Angles (deg) of **6** (Esd's in Parentheses)

W–Re	2.9531(9)	W–C(6)	2.087(6)
Re–C(6)	2.250(6)	Re–C(7)	2.376(6)
W–O(6)	2.213(6)	Re–S	2.420(2)
S–O(6)	1.526(4)	S–O(7)	1.455(5)
W–C(4)	2.008(7)	W–C(5)	1.996(7)
Re–C(1)	1.901(7)	Re–C(2)	1.905(7)
Re–C(3)	1.936(7)	W–C(20)	2.308(6)
W–C(21)	2.279(6)	W–C(22)	2.306(6)
W–C(23)	2.361(6)	W–C(24)	2.389(6)
$\angle$ W–O(6)–S	111.6(2)	$\angle$ O(6)–S–O(7)	112.8(3)
$\angle$ Re–S–O(6)	103.9(2)	$\angle$ W–C(6)–C(7)	164.4(5)
$\angle$ C(6)–C(7)–C(14)	154.2(6)	$\angle$ W–C(4)–O(4)	173.6(6)
$\angle$ W–C(5)–O(5)	175.7(7)	$\angle$ Re–C(1)–O(1)	177.9(6)
$\angle$ Re–C(2)–O(2)	179.4(6)	$\angle$ Re–C(3)–O(3)	178.1(5)

Table 4. Selected Bond Distances (Å) and Angles (deg) of **7** (Esd's in Parentheses)

W–Re	3.0024(6)	W–C(6)	2.089(7)
Re–C(6)	2.251(6)	Re–C(7)	2.381(7)
W–S	2.506(2)	Re–O(6)	2.190(5)
S–O(6)	1.495(5)	S–O(7)	1.456(5)
W–C(4)	2.029(9)	W–C(5)	1.993(8)
Re–C(1)	1.902(8)	Re–C(2)	1.885(9)
Re–C(3)	1.911(8)	W–C(20)	2.288(8)
W–C(21)	2.290(8)	W–C(22)	2.337(7)
W–C(23)	2.353(8)	W–C(24)	2.335(8)
$\angle$ Re–O(6)–S	111.5(3)	$\angle$ O(6)–S–O(7)	113.1(3)
$\angle$ W–S–O(6)	105.3(2)	$\angle$ W–C(6)–C(7)	167.4(6)
$\angle$ C(6)–C(7)–C(8)	158.6(7)	$\angle$ W–C(4)–O(4)	176.4(7)
$\angle$ W–C(5)–O(5)	173.1(7)	$\angle$ Re–C(1)–O(1)	179.2(7)
$\angle$ Re–C(2)–O(2)	178.5(6)	$\angle$ Re–C(3)–O(3)	178.8(7)

red spectra showed ν (CO) stretching absorption in the range 2034–1913 cm^{−1}, indicating the presence of only terminal CO ligands. The ¹H NMR spectra gave rise to the signals expected for one phenyl group and a C₅Me₅ fragment. The ¹³C NMR spectra showed five downfield signals due to two W–CO and three Re–CO ligands, together with two signals; one appeared at δ 104.9 (**1a**) and 111.2 (**1b**) and the second at δ 119.2 (**1a**) and 121.7 (**1b**), assigned to the α - and the β -carbons of the bridging acetylide ligand in the μ - η^2 -bonding mode.¹² These data provided the preliminary identification for these complexes.

The X-ray diffraction study on **1a** was carried out to confirm the molecular geometry. As indicated in Figure 1, the molecule consists of a (C₅Me₅)W(CO)₂ fragment and a Re(CO)₃ unit linked by a short W–Re separation of 2.765 Å. The W–I bond length is 2.848(1) Å and is very close to that of the Re–I distance (2.870(1) Å). The acetylide ligand lies on a plane which is perpendicular to the triangle defined by the W, Re, and iodine atoms. The α -carbon C(6) is coordinated to the W atom via σ -bonding (W–C(6) = 2.09(1) Å) and the C₂ backbone linked to the Re atom via π -interaction. In addition,

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Results and Discussion

Synthesis of W–Re Acetylide Complexes. Treatment of the acetylide complex (C₅Me₅)W(CO)₃(CCPh) with Re(CO)₅I or Re(CO)₅Br in refluxing toluene (110 °C, 30 min) afforded the heterobimetallic acetylide complexes (C₅Me₅)WRe(μ -X)(CCPh)(CO)₅, X = I (**1a**) or X = Br (**1b**), via a 1:1 combination of starting materials (Scheme 1). These complexes were purified by thin-layer chromatography, and their structures were characterized by routine spectroscopic methods. The infra-

Scheme 1

from the C(6)–C(7) distance of 1.22(1) Å and the corresponding Re–C distances (Re–C(6) = 2.27(1) and Re–C(7) = 2.46(1) Å), it is apparent that the acetylide C–C triple bond uses only one set of the π -orbitals to coordinate to the Re atom.¹³ Therefore, complex **1a** provides a further example of the well established μ - η^2 -mode of coordination.¹⁴

The reactions of $(\text{C}_5\text{Me}_5)\text{W}(\text{CO})_3(\text{CCPh})$ with $[\text{Re}(\text{CO})_4(\mu\text{-SPh})]_2$ or with $[\text{Re}(\text{CO})_4(\mu\text{-O}_2\text{CMe})]_2$ were also examined, giving the thiolate- or acetate-bridged acetylide complexes $\text{LWRe}(\mu\text{-X})(\text{CCPh})(\text{CO})_5$ (**2a**, $\text{L} = \text{C}_5\text{Me}_5$, $\text{X} = \text{SPh}$; **2b**, $\text{L} = \text{Cp}$, $\text{X} = \text{SPh}$; **3**, $\text{L} = \text{C}_5\text{Me}_5$, $\text{X} = \text{O}_2\text{-CMe}$). These complexes were characterized by comparing their spectroscopic data with that of the halide complexes **1**. It is possible that the reactions proceed via a prior dissociation of the dimeric rhenium complexes to give the unsaturated mononuclear intermediates $[\text{Re}(\text{CO})_4(\text{SPh})]$ and $[\text{Re}(\text{CO})_4(\text{O}_2\text{CMe})]$, followed by coupling with the acetylide precursor $(\text{C}_5\text{Me}_5)\text{W}(\text{CO})_3(\text{CCPh})$ to afford the isolated heterometallic complexes.

Alternatively, both complexes **2** and **3** can be prepared in low yield from treatment of **1** with thiophenol (26%) or with acetic acid (8%) in refluxing toluene solution. On the basis of their molecular formulas, these transformations can be considered as ligand substitution reactions. Thus, the bridging halide ligands in **1** are replaced by the thiolate or acetate groups, with con-

Figure 1. Molecular structure and atomic labeling scheme of the complex $(\text{C}_5\text{Me}_5)\text{WRe}(\mu\text{-I})(\text{CCPh})(\text{CO})_5$ (**1a**) with thermal ellipsoids shown at the 30% probability level.

comitant release of a hydrogen halide molecule as indicated as follows:

As a result, introduction of a noncoordinated base would help the removal of the HX generated during the reaction and prevent unwanted decomposition. In fact, a dramatic improvement of the yields to 80%–58% was observed by addition of pyridine or triethylamine into the reaction mixture.

CO Substitution. Our results suggest that the reactivity of acetylide complexes **1**–**3** with phosphorus donor ligand depends not only on the nature of the bridging ligand X but also on the properties of the incoming phosphine ligands. Triphenylphosphine failed to react with any of the acetylide complexes. This result is presumably due to the greater cone angle for PPh_3 . On the other hand, trimethylphosphite, $\text{P}(\text{OMe})_3$, has a somewhat smaller cone angle than PPh_3 (107° vs 145°, respectively) and is also a significantly stronger π -acceptor ligand.¹⁵ We expected it to be more suitable for our study because of its expected higher reactivity.

Interestingly, the results for phosphite reactions varied according to the nature of the bridging ligands present in these W–Re complexes: Due to decomposition treatment of $\text{P}(\text{OMe})_3$ with **1a** produced only a small amount of $(\text{C}_5\text{Me}_5)\text{W}(\text{CO})_3(\text{CCPh})$. In contrast, complex **2a** reacted with $\text{P}(\text{OMe})_3$ to give a monosubstituted complex $(\text{C}_5\text{Me}_5)\text{WRe}(\mu\text{-SPh})(\text{CCPh})(\text{CO})_4[\text{P}(\text{OMe})_3]$ (**4**) in good yield, while the corresponding reaction between the acetate complex **3** and $\text{P}(\text{OMe})_3$ led to the formation of trace amount of the complexes $(\text{C}_5\text{Me}_5)\text{WRe}(\mu\text{-O}_2\text{CMe})(\text{CCPh})(\text{CO})_4[\text{P}(\text{OMe})_3]$ (**5**) and $(\text{C}_5\text{Me}_5)\text{W}(\text{CO})_3(\text{CCPh})$. The identification of **4** and **5** was achieved from spectroscopic data. For example, ^{13}C NMR data for **4** indicated the presence of only two Re–

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Figure 2. Molecular structure and atomic labeling scheme of the complex $(C_5Me_5)WRe(\mu-SO_2Ph)(CCPh)(CO)_5$ (**6**) with thermal ellipsoids shown at the 30% probability level.

CO and two W–CO ligands. Moreover, the ^{31}P NMR data exhibited a singlet at δ 138.2, confirming the attachment of the $P(OMe)_3$ ligand to the Re atom.

When the phosphite-substituted complex **4** was exposed to CO (45 psi), dissociation of phosphite was observed over a period of 1 h at 110 °C, suggesting that phosphite substitution at Re atom was reversible. Furthermore, when the above mentioned reactions were monitored by ^{31}P NMR spectroscopy in sealed tubes, no intermediate due to the transient coordination of phosphite on the acetylide ligand was observed. This result is in contrast to that observed with the thiolate-bridged acetylide complexes $Fe_2(\mu-SR)(CCR')(CO)_6$ ($R = 'Bu, Et, Ph; R' = 'Bu, Et, Ph, SiMe_3$)¹⁶ or the phosphido-bridged acetylide complexes $M_2(\mu-PPh_2)(CCR)(CO)_6$ ($M = Fe, Ru; R = 'Bu, 'Pr, Ph, etc.$)¹⁷ in which the acetylide ligand is highly electron deficient and reactive. Thus, the nucleophilic phosphines can attack at the C–C triple bond of the acetylide ligand, producing phosphonium, ylide-carbene complexes as the initial product, which then undergo facile conversion to the substitution products by decarbonylation and phosphine migration.

Sulfinate Complexes from Oxidation of Thiolate Complexes 2. The thiolate complex **2a** reacted with H_2O_2 to afford an orange sulfinate compound $(C_5Me_5)WRe(\mu-SO_2Ph)(CCPh)(CO)_5$ (**6**) in 54% yield. This complex was characterized by both spectroscopic and structural data. The ORTEP diagram of **6**, shown in Figure 2, indicates that the basic arrangement of the metal fragments and the acetylide ligand is essentially identical to that of the previously established structure

of **1a**, except that the bridging iodine atom is now replaced by a sulfinate functional group, $\mu-\eta^2-SO_2Ph$. One oxygen atom of the sulfinate group is coordinated to the W atom, while the second adopts a terminal mode and is located at a position *trans* to the acetylide ligand. To our knowledge, this complex is the first structurally characterized complex with a sulfinate ligand associated with a metal–metal edge. The S=O bond lengths (1.456(5) and 1.495(5) Å) are compatible with the μ -sulfinate complexes¹⁸ and η^2-SO_2 complexes (1.468–1.588 Å) reported in the literature.¹⁹

As indicated by the X-ray analysis, complex **6** exists in the solid state as only one isomer, while 1H and ^{13}C NMR studies indicate that two distinct isomers in a ratio of 4:1 are present in solution. The key evidence is the presence of two sets of two W–CO resonances in the region δ 232.9–224.0 and two signals at δ 106.5 and 106.9 for the inner carbon atoms of the C_5Me_5 ligand in the ^{13}C NMR spectrum, which allowed us to measure their relative ratio. Assignment of other ^{13}C NMR signals is ambiguous: Both the phenyl resonance signals of the acetylide and the sulfinate groups occur in the narrow region δ 132.7–122.0, which hindered the assignment of the acetylide C_α and C_β signals.

We speculate that such rapid tautomerization in solution is caused by a reversible exchange of the bridging and the terminal oxygen atom of the sulfinate group (Scheme 2). Alternatively, such a process can be viewed as a direct interchange of the phenyl substituent and the terminal oxygen atom on the sulfinate group. We favor the first exchange pathway, although our observations support both. A third mechanism involving $\sigma \rightarrow \pi$, $\pi \rightarrow \sigma$ interconversion²⁰ of the bridging acetylide ligand seems less probable due to unfavorable steric congestion between the C_5Me_5 ligand on W atom and the phenyl group of acetylide ligand. The last possibility, which involves reorientation of the $(C_5Me_5)W(CO)_2$ fragment with respect to the W–Re bond, is also unlikely, because similar isomerization for the respective thiolate and acetate complexes **2** and **3** was not observed in solution.

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Figure 3. Molecular structure and atomic labeling scheme of the complex $\text{CpWRe}(\mu\text{-SO}_2\text{Ph})(\text{CCPh})(\text{CO})_5$ (**7**) with thermal ellipsoids shown at the 30% probability level.

Scheme 3

The oxidation of the respective Cp complex $\text{CpWRe}(\mu\text{-SPh})(\text{CCPh})(\text{CO})_5$ (**2b**) was examined next. In this reaction, two air-stable complexes (**7** and **8**) with the identical molecular formula $\text{CpWRe}(\mu\text{-SO}_2\text{Ph})(\text{CCPh})(\text{CO})_5$ were isolated in 40% and 5% yields, respectively (Scheme 3). The structure of the minor red isomer **8** was easily deduced, as its IR $\nu(\text{CO})$ spectrum showed a pattern very similar to that of the C_5Me_5 complex **6** discussed earlier. In agreement with this assignment, two interconvertible isomers **8a,b** caused by the exchange of bridging and terminal oxygen atoms of the sulfinate ligand were also spotted in solution by the observation of two ^1H NMR Cp signals at δ 5.99 and 6.02 in a ratio of 3:1.

The identification of the major orange-red isomer **7** was based on the X-ray diffraction study. As depicted in Figure 3, the overall molecular arrangement of **7** resembles that of **6**, showing the expected $\text{CpW}(\text{CO})_2\text{-Re}(\text{CO})_3$ skeleton and the $\mu\text{-}\eta^2\text{-acetylide}$ group coordinated to the W atom via a σ -bond. The difference

between **6** and **7** is that the sulfinate oxygen atom is bonded to W atom in **6** and Re atom in **7**. In this respect, they form a novel pair of linkage isomers.

The solution behavior of **7** is similar to that of **8** (Scheme 3), showing two ^1H NMR Cp signals at δ 5.80 and 5.59, due to the isomers **7b** and **7a**. Furthermore, heating a solution of either **7** or **8** in NMR tubes slowly produces a mixture of both **7** and **8** along with some decomposition. These observations suggest that the proposed rotation of the bridging sulfinate group on the W–Re vector ($7 \leftrightarrow 8$) requires a much higher energy barrier than the exchange of bridging and terminal oxygen atoms ($7a \leftrightarrow 7b$ and $8a \leftrightarrow 8b$).

Summary. The W–Re acetylide complexes **1–3** bearing bridging halide, thiolate, or acetate ligands can be prepared by the combination of tungsten acetylide complexes and rhenium carbonyl complexes, such as $\text{Re}(\text{CO})_5\text{Br}$, $\text{Re}(\text{CO})_5\text{I}$, $[\text{Re}(\text{CO})_4(\mu\text{-SPh})]_2$, or $[\text{Re}(\text{CO})_4(\mu\text{-O}_2\text{-CMe})]_2$. The bridging halide ligand in **1** can be replaced by thiophenol or acetic acid to afford the bridging thiolate or acetate complexes **2** and **3**. Attempts to replace the thiolate ligand in **2** with the acetate ligand or *vice versa* were unsuccessful, indicating substantial kinetic stability. The acetylide ligand in these W–Re complexes is relatively inert, and the expected formation of phosphonium, ylide-carbene complexes was not observed from reaction with nucleophiles like phosphine or phosphite. We speculate that the unfavorable steric interaction on the tungsten atom and the electron releasing effect of the C_5Me_5 ligand are the two major factors that inhibit direct nucleophilic attack at the acetylide ligand.

The most unusual reaction for these series of W–Re acetylide complexes is the direct oxidation using an acidic H_2O_2 solution. In contrast to the halide- or acetate-bridged complexes **1** and **3**, where no stable product was isolated, the thiolate bridged counterparts **2** reacted to form $\mu\text{-}\eta^2\text{-sulfinate}$ bridged complexes. We initially believed that the H_2O_2 oxidation would occur at the oxophilic tungsten metal center, producing either an oxo or a peroxo ligand;²¹ however, the oxidation occurred at the bridging thiolate ligand. It is possible that the formation of these sulfinate complexes is via an intermediate bearing a partially oxidized, bridging sulfoxide ligand ($\mu\text{-SOPh}$).

The structure of the sulfinate products can be classified into two types. The first structure, exemplified by the complexes **6** and **8**, possesses a bridging sulfinate ligand with one oxygen atom coordinated to the W atom, while in the second, i.e. complex **7**, the bridging oxygen atom is linked to the Re atom. We speculate that the formation of **7** is due to a reduced steric interaction between the $\text{CpW}(\text{CO})_2$ fragment and the phenyl substituent on sulfinate ligand. This steric interaction would become more important if the Cp ligand were replaced by the bulky C_5Me_5 ligand; thus, no such structure with the C_5Me_5 complex **6** was observed. Moreover, rapid tautomerization due to the exchange of bridging and terminal oxygen atoms occurs in solution for both types of sulfinate complexes, producing the

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minor isomer **b**, in which the terminal oxygen atom of sulfinate group interchanges its position with the phenyl substituent.

Finally, the reactions described in this article are of interest as they provide a general route to bridging sulfinate ligands using hydrogen peroxide to oxidize a bridging thiolate ligand. A number of closely related sulfoxide, sulfinate, and sulfinyl complexes have been prepared from thiolate or sulfinyl complexes by using oxidants such as dimethyldioxirane or mCPBA;²² the

stronger oxidant H₂O₂ in acidic media was previously found to cause extensive degradation.²³

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Supporting Information Available: Tables of atomic coordinates and isotropic and anisotropic thermal parameters for complexes **1a**, **6**, and **7** (8 pages). Ordering information is given on any current masthead page.

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