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# Transformation of Alkenyl–*N*-Arylthioamido Ligands into Quinoline-2-thiolate Ligands in Dirhenium Carbonyl Complexes

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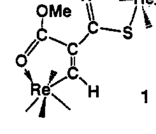
Irradiation of the alkenyl-*N*-arylthioamido complexes $Re(CO)_4[(E)\text{-}HC{=}C(CO_2Me)C{=}N(C_6H_4\text{-}p\text{-}R)S]Re(CO)_4$, **1a–c**, R = H, Me, Cl, in the presence of iodine yielded a mixture of four products: $Re_2(CO)_7[\mu\text{-}2\text{-}S\text{-}3\text{-}CO_2Me\text{-}6\text{-}RNC_9H_4](\mu\text{-}I)$, **2a–c**, R = H, Me, Cl; $Re(CO)_4[(E)\text{-}HC{=}C(CO_2Me)C{=}N(C_6H_4\text{-}p\text{-}R)S]Re_2(CO)_7(\mu\text{-}I)$, **3a–c**, R = H, Me, Cl; $Re(CO)_4[(E)\text{-}HC{=}C(CO_2Me)C(NHC_6H_4\text{-}p\text{-}R){=}S]Re(CO)_4(I)$, **4a–c**, R = H, Me, Cl; $Re(CO)_4(2\text{-}S\text{-}3\text{-}CO_2Me\text{-}6\text{-}RNC_9H_4)$, **5a–c**, R = H, Me, Cl, with compounds **5** being the major products. Compounds **2a–c**, **4a–c**, and **5a–c** are new. Compounds **4a–c** were also obtained from the reaction of **1a–c** with HI. UV irradiation of **1b** in the absence of iodine yielded the compounds $Re_2(CO)_8[\mu\text{-}2\text{-}S\text{-}3\text{-}CO_2Me\text{-}6\text{-}MeNC_9H_4](\mu\text{-}H)$, **6b**, $Re_2(CO)_7[\mu\text{-}2\text{-}S\text{-}3\text{-}CO_2Me\text{-}6\text{-}MeNC_9H_4](\mu\text{-}H)$, **7b**, and **5b**, while UV irradiation of **6b** yielded **7b** and **5b** plus $Re_3(CO)_{12}(\mu\text{-}H)_3$. UV irradiation of **2b** in the presence of CO yielded **5b** plus $Re_2(CO)_8(\mu\text{-}I)_2$. UV irradiation of **3b** also yielded **2b**, **5b**, and some **7b**. Treatment of **7b** with iodine yielded **2b**. Finally, from the UV irradiation of **5b** the dimer $[Re(CO)_3(2\text{-}S\text{-}3\text{-}CO_2Me\text{-}6\text{-}MeNC_9H_4)]_2$, **8b**, was obtained in 57% yield. Complexes **2b**, **4c**, **5b**, **6b**, **7b**, and **8b** were characterized by single crystal X-ray diffraction analyses. The compounds **2** and **5–8** all contain substituted quinoline-2-thiolate ligands formed by the coupling of one of the carbon atoms of the aryl ring to the hydrogen-substituted carbon atom of the alkenyl group. Crystal data: (for **2b·CH$_2$Cl$_2$**) space group = $P\bar{1}$, $a$ = 10.204(2) Å, $b$ = 13.733(6) Å, $c$ = 9.877(2) Å, $\alpha$ = 91.18(3)°, $\beta$ = 96.17(3)°, $\gamma$ = 74.78(3)°, $Z$ = 2, 2746 reflections, $R$ = 0.038; (for **4c**) space group = $P2_1/c$, $a$ = 7.027(2) Å, $b$ = 10.894(2) Å, $c$ = 34.470(4) Å, $\beta$ = 92.75(1)°, $Z$ = 4, 1762 reflections, $R$ = 0.028; (for **5b**) space group = $P\bar{1}$, $a$ = 11.250(2) Å, $b$ = 11.905(2) Å, $c$ = 7.312(1) Å, $\alpha$ = 107.23(1)°, $\beta$ = 106. 59(1)°, $\gamma$ = 67.73(1)°, $Z$ = 2, 1716 reflections, $R$ = 0.024; (for **6b**) space group = $P2_1/c$, $a$ = 18.603(3) Å, $b$ = 17.987(3) Å, $c$ = 7.223(1) Å, $\beta$ = 90.05(2)°, $Z$ = 4, 2099 reflections, $R$ = 0.025; (for **7b**) space group = $P\bar{1}$, $a$ = 11.877(2) Å, $b$ = 13.519(2) Å, $c$ = 7.876(1) Å, $\alpha$ = 98.14(1)°, $\beta$ = 103.79(1)°, $\gamma$ = 109.25(2)°, $Z$ = 2, 1677 reflections, $R$ = 0.030; (for **8b**) space group = $C2/c$, $a$ = 20.727(4) Å, $b$ = 10.669(2) Å, $c$ = 14.487(2) Å, $\beta$ = 106.76(1)°, $Z$ = 4, 1827 reflections, $R$ = 0.022.

## Introduction

Organic isothiocyanates have been shown to be useful reagents in organic synthesis,[1] but the organometallic chemistry of these molecules is not yet well developed.[2]

In recent studies we have found that aryl isothiocyanates react with the lightly stabilized dimetalated olefin complex $Re(CO)_4[trans\text{-}\mu\text{-}HC{=}C(CO_2Me)]Re(CO)_4(NCMe)$ by displacement of the NCMe ligand and insertion of the isothiocyanate molecule into the carboxylate substituted Re—C bond to yield the complexes $Re(CO)_4[(E)\text{-}HC{=}C(CO_2Me)C{=}N(C_6H_4\text{-}p\text{-}R)S]Re(CO)_4$, **1a–c**, R = H, Me, Cl, containing alkenyl–*N*-arylthioamido ligands.[3]



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We have now found that these complexes undergo a remarkable cyclization reaction in which the aryl ring is coupled at its ortho-position to the unsubstituted olefin carbon atom to yield complexes containing quinoline-2-thiolate ligands when they are irradiated in the presence of iodine. Quinoline-2-thiolates[4] and pyridine-2-thiolates[5] have recently attracted attention as ligands due to their ability to adopt several different multidentate coordination modes. A preliminary report of a portion of this work has been published.[6]

## Experimental Section

Unless specified otherwise, all reactions were carried out under an atmosphere of nitrogen. Hexane was freshly distilled over

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sodium under nitrogen before use. $CH_2Cl_2$ was dried over $CaH_2$. Traces of water in commerically obtained CP grade CO was removed by passing through a column of $P_2O_5$ before use. $I_2$ and HI (47% aqueous solution, 6.9 M) were purchased from Aldrich and were used without further purification. UV irradiations were performed by using an externally positioned 360-W high pressure mercury lamp purchased from Gates, Long Island, NY, on solutions in Pyrex glassware. TLC separations were performed in air by using silica gel (60 Å, $F_{254}$) on plates (Whatman, 0.25 mm). IR spectra were recorded on a Nicolet 5DXB FT-IR spectrophotometer. $^1$H NMR spectra were taken at 300 MHz on a Brüker AM-300 spectrometer. Mass spectra were run on a VG Model 70SQ mass spectrometer using electron impact ionization. Elemental analyses were performed by Desert Analytics, Tucson, AZ. The compounds Re(CO)$_4$[(*E*)-HC=C(CO$_2$Me)C=N(C$_6$H$_4$-*p*-R)S]Re(CO)$_4$, **1a–c**, R = H, Me, Cl,[3] and [Re(CO)$_4$($\mu$-I)]$_2$[7] were prepared by previously reported procedures.

**Reactions of 1a–1c with I$_2$ under UV Irradiation.** A 50.0-mg (0.061-mmol) amount of **1a** and a 50.0-mg (0.197-mmol) amount of $I_2$ were dissolved in 80 mL of hexane. The solution was exposed to UV at 25 °C for 15 min. After the solvent was removed under vacuum at 25 °C, the residue was separated using a hexane/$CH_2Cl_2$ 2/1 solvent mixture to give the following compounds in order of elution: 13.9 mg of starting material; 5.0 mg of Re(CO)$_4$[(*E*)-HC=C(CO$_2$Me)C=N(C$_6$H$_5$)S]Re$_2$(CO)$_7$($\mu$-I), **3a**,[3] 10%; 4.4 mg of yellow Re(CO)$_4$[(*E*)-HC=C(CO$_2$Me)C(NHC$_6$H$_5$)=S]Re(CO)$_4$(I), **4a**, 8%; 8.2 mg of yellow Re$_2$(CO)$_7$[$\mu$-2-S-3-CO$_2$MeNC$_9$H$_5$]($\mu$-I), **2a**, 1 5%; 10.3 mg of Re(CO)$_4$(2-S-3-CO$_2$MeNC$_9$H$_5$), **5a**, 33%; 2.6 mg of [Re(CO)$_4$($\mu$-I)]$_2$. IR ($\nu_{CO}$ in hexane, cm$^{-1}$): (for **4a**) 2106 (w), 2102 (m), 2013 (s), 2005 (s), 2001 (s), 1996 (s), 1958 (s), 1591 (w, br); (for **2a**) 2110 (m), 2035 (s), 2014 (s), 2004 (s), 1968 (s), 1959 (m), 1937 (s), 1926 (s), 1740 (w), 1733 (w); (for **5a**) 2106 (w), 2009 (s), 1992 (s), 1945 (s), 1746 (w), 1729 (w). $^1$H NMR ($\delta$ in CDCl$_3$, ppm): (for **4a**) 11.69 (s, br, 1H, N*H*), 11.06 (s, 1H, C*H*), 7.33 (m, 2H, C$_6$H$_5$), 7.26 (m, 1H, C$_6$*H*$_5$), 7.11 (m, 2H, C$_6$*H*$_5$), 3.53 (s, 3H, OC*H*$_3$); (for **2a**) 9.13 (s, 1H, C*H*), 8.20 (m, 1H, C$_6$H$_4$), 8.06 (m, 2H, C$_6$H$_4$), 7.77 (m, 1H, C$_6$*H*$_4$), 4.05 (s, 3H, OC*H*$_3$); (for **5a**) 8.69 (s, 1H, C*H*), 7.81 (m, 2H, C$_6$*H*$_4$), 7.64 (m, 1H, C$_6$*H*$_4$), 7.48 (m, 1H, C$_6$*H*$_4$), 3.98 (s, 3H, OC*H*$_3$). Mass spectrum: (for **2a** ($^{187}$Re)) $m/z = 915 - 28x$, $x = 0$–7 (M$^+$ – *x*CO); (for **4a** ($^{187}$Re)) $m/z = 945 - 28x$, $x = 0$–8 (M$^+$ – *x*CO); (for **5a** ($^{187}$Re)) $m/z = 517 - 28x$, $x = 0$–4 (M$^+$ – *x*CO).

When a 50.0-mg (0.060-mmol) amount of **1b** was allowed to react with a 50.0-mg (0.197-mmol) amount of $I_2$ in 80 mL of hexane under UV irradiation at 25 °C for 15 min, separation as described above gave the following compounds: 16.0 mg of starting material; 5.2 mg of Re(CO)$_4$[(*E*)-HC=C(CO$_2$Me)C=N(C$_6$H$_4$-*p*-Me)S]Re$_2$(CO)$_7$($\mu$-I), **3b**[3], 11.0%; 4.2 mg of yellow Re(CO)$_4$[(*E*)-HC=C(CO$_2$Me)C(NHC$_6$H$_4$Me-*p*)=S]Re(CO)$_4$(I), **4b**, 7%; 6.7 mg of yellow Re$_2$(CO)$_7$[$\mu$-2-S-3-CO$_2$Me-6-MeNC$_9$H$_4$]($\mu$-I), **2b**, 12%; 13.1 mg of Re(CO)$_4$(2-S-3-CO$_2$Me-6-MeNC$_9$H$_4$), **5b**, 41%; 2.0 mg of [Re(CO)$_4$($\mu$-I)]$_2$. IR ($\nu_{CO}$ in hexane, cm$^{-1}$): (for **4b**) 2106 (w), 2101 (m), 2013 (s), 2005 (s), 2000 (s), 1996 (s), 1958 (s), 1591 (w, br); (for **2b**) 2110 (m), 2035 (s), 2014 (s), 2003 (s), 1967 (s), 1958 (m), 1937 (s), 1925 (s), 1740 (w); (for **5b**) 2106 (w), 2008 (s), 1991 (s), 1944 (s), 1745 (w), 1728 (w). $^1$H NMR: (for **4b**) ($\delta$ in CDCl$_3$, ppm) 11.60 (s, br, 1H, N*H*), 11.02 (s, 1H, C*H*), 7.12 (d, $^3J_{H-H}$ = 8.3 Hz, 2H, C$_6$*H*$_4$), 6.99 (d, $^3J_{H-H}$ = 8.4 Hz, 2H, C$_6$*H*$_4$), 3.56 (s, 3H, OC*H*$_3$), 2.32 (s, 3H, C$_6$H$_4$C*H*$_3$); (for **2b**) ($\delta$ in CDCl$_3$, ppm) 9.04 (s, 1H, C*H*), 8.12 (d, $^3J_{H-H}$ = 8.0 Hz, 1H, C$_6$*H*$_3$), 7.89 (d, $^3J_{H-H}$ = 8.0 Hz, 1H, C$_6$*H*$_3$), 7.79 (s, 1H, C$_6$*H*$_3$), 4.04 (s, 3H, OC*H*$_3$), 2.63 (s, 3H, C$_6$H$_3$C*H*$_3$); (for **5b**) ($\delta$ in C$_6$D$_6$, ppm) 8.36 (s, 1H, C*H*), 8.05 (d, $^3J_{H-H}$ = 8.7 Hz, 1H, C$_6$*H*$_3$), 6.86 (d, $^3J_{H-H}$ = 8.7 Hz, 1H, C$_6$*H*$_3$), 6.68 (s, 1H, C$_6$*H*$_3$), 3.54 (s, 3H, O*Me*), 1.90 (s, 3H, C$_6$H$_3$*Me*). Mass spectrum: (for **4b** ($^{187}$Re)) $m/z = 959 - 28x$, $x = 0$–8 (M$^+$ – *x*CO). Anal. Calcd (found) for **5b** (ReSO$_6$NC$_{16}$H$_{10}$): C, 36.22 (36.14); H, 1.90 (1.86); N, 2.64 (3.12).

When a 50.0-mg (0.059-mmol) amount of **1c** was allowed to react with a 50.0-mg (0.197-mmol) amount of $I_2$ in 80 mL of hexane under UV irradiation at 25 °C for 15 min, separation as described above gave the following compounds: 17.7 mg of starting material; 5.0 mg of Re(CO)$_4$[(*E*)-HC=C(CO$_2$Me)C=N(C$_6$H$_4$-*p*-Cl)S]Re$_2$(CO)$_7$($\mu$-I), **3c**,[3] 10.0%; 4.8 mg of yellow Re(CO)$_4$[(*E*)-HC=C(CO$_2$Me)C(NHC$_6$H$_4$Cl-*p*)=S]Re(CO)$_4$(I), **4c**, 8%; 5.1 mg of yellow Re$_2$(CO)$_7$[$\mu$-2-S-3-CO$_2$Me-6-ClNC$_9$H$_4$]($\mu$-I), **2c**, 9%; 13.1 mg of Re(CO)$_4$(2-S-3-CO$_2$Me-6-ClNC$_9$H$_4$), **5c**, 45%; 3.0 mg of [Re(CO)$_4$($\mu$-I)]$_2$. IR ($\nu_{CO}$ in hexane, cm$^{-1}$): (for **2c**) 2110 (m), 2036 (s), 2015 (s), 2004 (s), 1969 (s), 1960 (m), 1940 (s), 1927 (s), 1741 (w), 1734 (w); (for **4c**) 2107 (w), 2101 (m), 2014 (s), 2007 (s), 2001 (s), 1997 (s), 1960 (s), 1591 (w, br); (for **5c**) 2107 (w), 2010 (s), 1994 (s), 1947 (s), 1747 (w), 1730 (w). $^1$H NMR: (for **2c**) ($\delta$ in CDCl$_3$, ppm) 9.02 (s, 1H, C*H*), 8.14 (d, $^3J_{H-H}$ = 9.1 Hz, 1H, C$_6$*H*$_3$), 8.02 (s, 1H, C$_6$*H*$_3$), 7.98 (d, $^3J_{H-H}$ = 9.1 Hz, 1H, C$_6$*H*$_3$), 4.05 (s, 3H, OC*H*$_3$); (for **4c**) ($\delta$ in C$_6$D$_6$, ppm) 11.93 (s, br, 1H, N*H*), 10.34 (s, 1H, C*H*), 6.80 (d, $^3J_{H-H}$ = 8.8 Hz, 2H, C$_6$*H*$_4$), 6.59 (d, $^3J_{H-H}$ = 8.8 Hz, 2H, C$_6$*H*$_4$), 2.40 (s, 3H, OC*H*$_3$); (for **5c**) ($\delta$ in CDCl$_3$, ppm): 8.58 (s, 1H, C*H*), 7.75 (d, $^3J$ H$_{-H}$ = 9.6 Hz, 1H, C$_6$*H*$_3$), 7.74 (s, 1H, C$_6$*H*$_3$), 7.57 (d, $^3J_{H-H}$ = 9.6 Hz, 1H, C$_6$*H*$_3$), 3.98 (s, 3H, OC*H*$_3$). Mass spectrum: (for **2c** ($^{187}$Re)) $m/z = 949 - 28x$, $x = 0$–7 (M$^+$ – *x*CO); (for **5c** ($^{187}$Re)) $m/z = 551 - 28x$, $x = 0$–4 (M$^+$ – *x*CO). Anal. Calcd (found) for **4c** (Re$_2$IClSO$_{10}$NC$_{19}$H$_9$): C, 23.33 (23.94); H, 0.92 (1.19); N, 1.43 (1.58).

**Reactions of 1a–c with HI.** To the solution of a 10.0-mg (0.012-mmol) amount of **1a** in 25 mL of hexane was added a 1.0-mL amount of 6.9 M HI aqueous solution. The reaction mixture was heated to reflux for 45 min. After cooling, the solvent was removed by vacuum. The residue was separated using a hexane/$CH_2Cl_2$ 2/1 solvent mixture to give the following compounds in order of elution: 1.1 mg of starting material; 5.6 mg of **4a**, 48% yield; 2.1 mg of [Re(CO)$_4$($\mu$-I)]$_2$. Compounds **4b** and **4c** were prepared similarly in 45% and 46% yields, respectively.

**Reaction of 2b with CO. (1) With UV Irradiation.** A solution of a 10.0-mg (0.011-mmol) amount of **2b** in 20 mL of hexane was exposed to UV irradiation at 25 °C in the presence of a CO purge through the solution for 15 min. After the solvent was evaporated at 25 °C, the residue was separated by TLC to yield 2.0 mg of starting material, 3.9 mg of **5b**, 69% yield, and 1.0 mg of [Re(CO)$_4$($\mu$-I)]$_2$.

**(2) Without UV Irradiation.** A solution of a 10.0-mg (0.011-mmol) amount of **2b** in 30 mL of hexane was purged with CO. No reaction was observed after 12 h at 25 °C or after 3 h at 68 °C.

**Reaction of 5b with [Re(CO)$_4$($\mu$-I)]$_2$.** A 10.0-mg (0.019-mmol) amount of **5b** and a 10.0-mg (0.012-mmol) amount of [Re(CO)$_4$($\mu$-I)]$_2$ were dissolved in 30 mL of hexane. The solution was irradiated with UV at 25 °C for 15 min. After the solvent was removed at 25 °C, the residue was separated using a hexane/$CH_2Cl_2$ 1/1 solvent mixture to give the following compounds in order of elution: 2.2 mg of **2b**, 22% yield; 2.9 mg of **5b**; 3.1 mg of [Re(CO)$_4$($\mu$-I)]$_2$.

**Photolysis of 3b.** A solution of 10.0 mg (0.019 mmol) of **3b** in 25 mL of hexane was exposed to UV at 25 °C for 15 min. The solvent was removed, and the residue was separated by TLC using a hexane/$CH_2Cl_2$ 2/1 solvent mixture to give the following compounds in order of elution: 0.8 mg of yellow Re$_2$(CO)$_7$[$\mu$-2-S-3-CO$_2$Me-6-MeNC$_9$H$_4$]($\mu$-H), **7b**, 12% yield; 1.3 mg of **2b**, 17% yield; 1.7 mg of **5b**, 39% yield; 0.2 mg of [Re(CO)$_4$($\mu$-I)]$_2$. Spectral data for **7b**: IR ($\nu_{CO}$ in hexane, cm$^{-1}$) 2105 (m), 2031 (s), 2009 (s), 1997 (s), 1967 (s), 1937 (s), 1928 (s), 1737 (w); $^1$H NMR ($\delta$ in CDCl$_3$, ppm) 8.72 (s, 1H, C*H*), 7.84 (d, $^3J_{H-H}$ = 8.9 Hz, 2H, C$_6$*H*$_3$), 7.78 (s, $^3J_{H-H}$ = 8.8 Hz, 2H, C$_6$*H*$_3$), 7.60 (s, 1H, C$_6$*H*$_3$), 4.07 (s, 3H, OC*H*$_3$), 2.55 (s, 3H, C$_6$H$_3$C*H*$_3$), −10.14 (s, 1H, Re$_2$($\mu$-*H*)). Anal. Calcd (found) for **7b** (Re$_2$SO$_9$NC$_{19}$H$_{11}$): C, 28.46 (28.68); H, 1.38 (1.33); N, 1.75 (1.90).

**Reaction of 7b with I$_2$.** A 10.0-mg (0.012-mmol) amount of **7b** in 20 mL of hexane was allowed to react with a 10.0-mg (0.039-mmol) amount of $I_2$ at 25 °C for 4 h. The solution was evaporated to dryness, and the residue was separated with a hexane/$CH_2Cl_2$ 2/1 solvent mixture to give 11.1 mg of **2b** in 97% yield.

**Reaction of 3b with I$_2$ under UV Irradiation.** A 10.0-mg (0.008-mmol) amount of **3b** and a 10.0-mg (0.039 mmol) amount

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**Table 1. Crystal Data for Compounds 2b and 4c–8b**

| compd | **2b**·$CH_2Cl_2$ | **4c** | **5b** | **6b** | **7b** | **8b** |
|---|---|---|---|---|---|---|
| formula | $Re_2ISO_9NC_{19}H_{10}\cdot CH_2Cl_2$ | $Re_2IClSO_{10}NC_{19}H_9$ | $ReSO_6NC_{16}H_{10}$ | $Re_2SO_{10}NC_{20}H_{11}$ | $Re_2SO_9NC_{19}H_{11}$ | $Re_2S_2O_{10}N_2C_{30}H_{20}$ |
| fw | 1012.60 | 978.11 | 530.53 | 829.78 | 801.77 | 1005.03 |
| cryst syst | triclinic | monoclinic | triclinic | monoclinic | triclinic | monoclinic |
| lattice params | | | | | | |
| $a$ (Å) | 10.204(4) | 7.027(2) | 11.250(2) | 18.603(3) | 11.877(2) | 20.727(4) |
| $b$ (Å) | 13.733(6) | 10.894(2) | 11.905(2) | 17.987(3) | 13.519(2) | 10.669(2) |
| $c$ (Å) | 9.877(2) | 34.470(4) | 7.312(1) | 7.223(1) | 7.876(1) | 14.487(2) |
| $\alpha$ (deg) | 91.18(3) | | 107.23(1) | | 98.14(1) | |
| $\beta$ (deg) | 96.17(3) | 92.75(1) | 106.59(1) | 90.05(2) | 103.79(1) | 106.76(1) |
| $\gamma$ (deg) | 74.78(3) | | 67.73(1) | | 109.25(2) | |
| V (Å$^3$) | 1328(2) | 2623(2) | 2128(1) | 817.5(7) | 1125.6(9) | 3067(2) |
| space group | $P\bar{1}$ (No. 2) | $P2_1/c$ (No. 14) | $P\bar{1}$ (No. 2) | $P2_1/c$ (No. 14) | $P\bar{1}$ (No. 2) | $C2/c$ (No. 15) |
| $Z$ value | 2 | 4 | 2 | 4 | 2 | 4 |
| $\rho_{calc}$ (g/cm$^3$) | 2.53 | 2.46 | 2.08 | 2.28 | 2.37 | 2.18 |
| $\mu$(Mo K$\alpha$) (cm$^{-1}$) | 107.11 | 106.89 | 74.03 | 102.79 | 110.29 | 81.83 |
| temp (°C) | 20 | 20 | 20 | 20 | 20 | 20 |
| $2\theta_{max}$ (deg) | 43.0 | 40.0 | 43.0 | 43.0 | 42.0 | 46.0 |
| no. obs ($I > 3\sigma$) | 2746 | 1762 | 1716 | 2099 | 1677 | 1827 |
| residuals: $R$; $R_w$ | 0.038; 0.057 | 0.028; 0.027 | 0.024; 0.026 | 0.025; 0.024 | 0.030; 0.030 | 0.022; 0.027 |

of $I_2$ were dissolved in 20 mL of hexane. The solution was irradiated with UV at 25 °C for 5 min. After the solvent was removed at room temperature, the residue was separated using a hexane/$CH_2Cl_2$ 1/1 solvent mixture to give the following compounds in order of elution: 1.9 mg of starting material; 4.0 mg of **2b**, 53% yield; 0.8 mg of **5b**, 19% yield; 1.6 mg of $[Re(CO)_4(\mu\text{-}I)]_2$.

**Photolysis of 1b. (1) Under Nitrogen.** A solution of 50.0-mg (0.060-mmol) of **1b** in 80 mL of hexane was exposed to UV at 25 °C for 15 min. After the solvent was removed at room temperature, separation of the residue using a hexane/$CH_2Cl_2$ 1/1 solvent mixture gave the following compounds in order of elution: 5.2 mg of starting material; 3.5 mg of yellow $Re_2(CO)_8[\mu\text{-}2\text{-}S\text{-}3\text{-}CO_2Me\text{-}6\text{-}MeNC_9H_4](\mu\text{-}H)$, **6b**, 7% yield; 3.7 mg of **7b**, 8% yield; 5.8 mg of **5b**, 18% yield. Spectral data for **6b**: IR ($\nu_{CO}$ in hexane, cm$^{-1}$) 2114 (w), 2091 (m), 2018 (s), 2000 (s), 1970 (s), 1742 (w). $^1H$ NMR ($\delta$ in $C_6D_6$, ppm): 8.09 (s, 1H, CH), 7.85 (d, $^3J_{H-H}$ = 8.5 Hz, 2H, $C_6H_3$), 7.06 (s, $^3J_{H-H}$ = 8.7 Hz, 2H, $C_6H_3$), 6.89 (s, 1H, $C_6H_3$), 3.65 (s, 3H, $OCH_3$), 2.00 (s, 3H, $C_6H_3CH_3$), −13.95 (s, 1H, $Re_2(\mu\text{-}H)$). Anal. Calcd (found) for **6b** ($Re_2SO_{10}NC_{20}H_{11}$): C, 28.95 (28.84); H, 1.34 (1.15); N, 1.69 (1.69).

**(2) Under CO.** When this reaction was performed in the presence of a CO purge at 25 °C for 2 h, the following products were obtained: 2.1 mg of starting material; 1.5 mg of **6b**, 3% yield; 2.6 mg of **5b**, 8% yield. No **7b** was isolated.

**Photolysis of 6b.** The solution of 10.0 mg (0.012 mmol) of **6b** in 20 mL of hexane was irradiated at 25 °C for 5 min. After the solvent was removed at 25 °C, the residue was separated using a hexane/$CH_2Cl_2$ 2/1 solvent mixture to give the following compounds in order of elution: 2.0 mg of starting material; 6.2 mg of **7b**, 62% yield; 1.1 mg of **5b**, 17% yield; 0.4 mg of $Re_3(CO)_{12}(\mu\text{-}H)_3$ ($\nu_{CO}$ in cyclohexane, cm$^{-1}$: 2093 (m), 2030 (vs), 2008 (s), 1983 (m)).[8]

**Transformations of 7b to 5b. (1) Under CO.** The solution of 10.0 mg (0.012 mmol) of **7b** in 20 mL of hexane was irradiated for 1 h in the presence of a slow purge with CO at 25 °C. After the solvent was removed at 25 °C, the residue was separated using a hexane/$CH_2Cl_2$ 2/1 solvent mixture to give the following compounds in order of elution: 0.8 mg of starting material; 4.8 mg of **5b**, 73% yield; 1.3 mg of $Re_3(CO)_{12}(\mu\text{-}H)_3$. No **6b** was formed in this reaction, and in the absence of UV irradiation no reaction was observed.

**(2) In the Absence of CO.** The solution of 10.0 mg (0.012 mmol) of **7b** in 20 mL of hexane was exposed to UV at 25 °C for 15 min. After the solvent was removed at 25 °C, the residue was separated using a hexane/$CH_2Cl_2$ 2/1 solvent mixture to give the following compounds in order of elution: 1.7 mg of starting material; 3.9 mg of **5b**, 60% yield; 0.5 mg of **8b**, 8% yield.

**Photolysis of 5b.** The solution of 10.0 mg (0.019 mmol) of **5b** in 20 mL of hexane was exposed to UV at 25 °C for 1 h, and then evaporated to dryness at room temperature. Separation of the residue using a hexane/$CH_2Cl_2$ 1/1 solvent mixture to give 0.8 mg of starting material and 5.4 mg of yellow $[Re(CO)_3(2\text{-}S\text{-}3\text{-}CO_2Me\text{-}6\text{-}MeNC_9H_4)]_2$, **8b**, 57% yield. Spectral data for **8b**: IR ($\nu_{CO}$ in $CH_2Cl_2$, cm$^{-1}$) 2036 (s), 2019 (s), 1937 (m), 1915 (s, br), 1734 (w), 1719 (w); $^1H$ NMR ($\delta$ in $CDCl_3$, ppm) 7.86 (s, 2H, C*H*), 7.79 (d, $^3J_{H-H}$ = 8.5 Hz, 4H, $C_6H_3$), 7.70 (s, $^3J_{H-H}$ = 8.6 Hz, 4H, $C_6H_3$), 7.37 (s, 2H, $C_6H_3$), 3.85 (s, 6H, $OCH_3$), 1.56 (s, 6H, $C_6H_3CH_3$). Anal. Calcd (found) for **8b** ($Re_2S_2O_{10}N_2C_{30}H_{20}$): C, 35.85 (36.14); H, 2.01 (1.86); N, 2.79 (3.12).

**Crystallographic Analyses.** Crystals of **2b**·$CH_2Cl_2$ were grown from solution in $CH_2Cl_2$ solvent by cooling to −14 °C. Crystals of **4c**, **5b**, and **7b** were grown from solution in a hexane/$CH_2Cl_2$ 1/1 solvent mixture by slow evaporation of solvent at −3 °C. Compound **6b** was crystallized from solution in a hexane/$CH_2Cl_2$ 2/1 solvent mixture by slow evaporation of the solvent at −3 °C. Crystals of **8b** were grown from solution in a hexane/$CH_2Cl_2$ 1/2 solvent mixture by slow evaporation of the solvent at 25 °C. All crystals used in diffraction analyses were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S automatic diffractometer by using graphite-monochromated Mo K$\alpha$ radiation. Unit cells were determined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table 1. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN structure solving program library (version 5.0) obtained from the Molecular Structure Corp., The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures.[9a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[9b] Full matrix least-squares refinements minimized the function: $\sum_{hkl} w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$. All structures were solved by a combination of direct methods and difference Fourier syntheses.

Compounds **2b**, **5b**, and **7b** crystallized in the triclinic crystal system. The centrosymmetric space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structures. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms were calculated by assuming idealized geometries and using observed positions whenever possible for both analyses. The position of the hydride ligand in **7b** was calculated by the energy minimization program HYDEX at a distance of 1.90 Å.[10] The scattering

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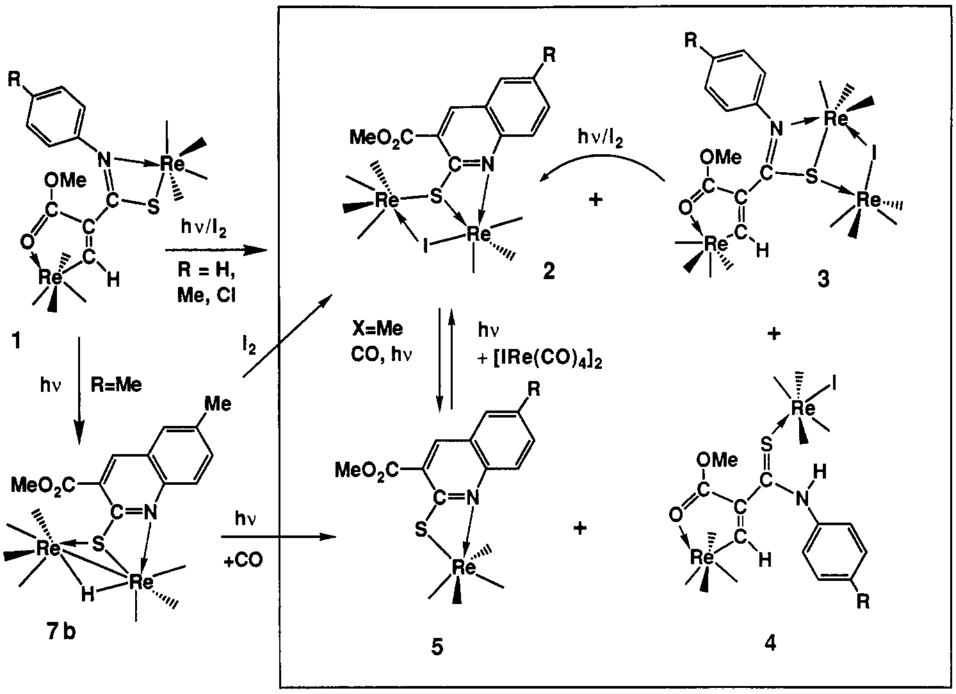
[8] Andrews, M. A.; Kirtley, S. W.; Kaesz, H. D. *Inorg. Synth.* **1977**, *17*, 66.

[9] (a) *International Tables for X-ray Crystallography*; Vol. IV, Kynoch Press: Birmingham, England, 1975; Table 2.2B, pp 99–101. (b) *Ibid.*, Table 2.3.1, pp 149–150.

[10] Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509.

**Scheme 1**



contributions of the calculated hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Compounds **4c** and **6b** crystallized in the monoclinic crystal system. The space group $P2_1/c$ was established for both of these structures on the basis of the patterns of systematic absences observed during the collection of the intensity data. All non-hydrogen atoms were refined with anisotropic thermal parameters. For **4c** the hydrogen atoms H and H(1) were located and refined. For **6b** the bridging hydride ligand was located and refined. The positions of all other hydrogen atoms for both of these analyses were calculated by assuming idealized geometries and using observed positions whenever possible for both analyses. The scattering contributions of the calculated hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Compounds **8b** crystallized in the monoclinic crystal system. The patterns of systematic absences observed during the collection of the intensity data were consistent with either of the space groups $C2/c$ or $Cc$. The centrosymmetric space group $C2/c$ was selected initially and was confirmed by the successful solution and refinement of the structure. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms H(3), H(23), H(25) and H(26) were located and refined. The positions of the hydrogen atoms on the methyl groups were calculated by assuming idealized geometries and using observed positions whenever possible for both analyses. The scattering contributions of the calculated hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

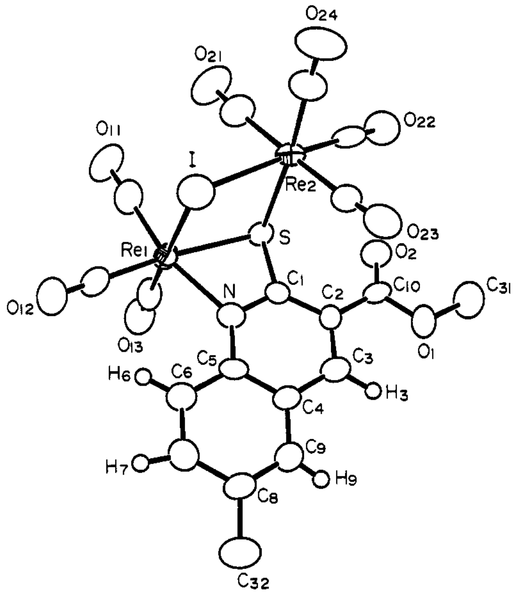


**Figure 1.** ORTEP diagram of $Re_2(CO)_7[\mu\text{-}2\text{-}S\text{-}3\text{-}CO_2Me\text{-}6\text{-}MeNC_9H_4](\mu\text{-}I)$, **2b**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are as follows: Re(1)···Re(2) = 3.933(4), Re(1)–N = 2.20(1), Re(1)–S = 2.519(4), Re(2)–S = 2.533(4), Re(1)–I = 2.785(3), Re(2)–I = 2.803(3), C(1)–C(2) = 1.41(2), C(2)–C(3) = 1.40(2), C(1)–N = 1.33(1), C(1)–S = 1.76(1), C(3)–C(4) = 1.41(2); Re(1)–I–Re(2) = 89.49(8), Re(1)–S–Re(2) = 102.3(1) S–C(1)–N = 109.8(8).

## Results

Irradiation of the complexes $Re(CO)_4[(E)\text{-}HC{=}C(CO_2Me)C{=}N(C_6H_4\text{-}p\text{-}R)S]Re(CO)_4$, **1a–c**, R = H, Me, Cl, in the presence of iodine yielded a mixture of four products: $Re_2(CO)_7[\mu\text{-}2\text{-}S\text{-}3\text{-}CO_2Me\text{-}6\text{-}RNC_9H_4](\mu\text{-}I)$, **2a–c**, R = H, Me, Cl; $Re(CO)_4[(E)\text{-}HC{=}C(CO_2Me)C{=}N(C_6H_4\text{-}p\text{-}R)S]\text{-}Re_2(CO)_7(\mu\text{-}I)$, **3a–c**, R = H, Me, Cl; $Re(CO)_4[(E)\text{-}HC{=}C(CO_2Me)C(NHC_6H_4\text{-}p\text{-}R){=}S]Re(CO)_4(I)$, **4a–c**, R = H, Me, Cl; $Re(CO)_4(2\text{-}S\text{-}3\text{-}CO_2Me\text{-}6\text{-}RNC_9H_4)$, **5a–c**, R = H, Me, Cl (see Scheme 1). Compounds **5a–c** were the major products obtained in yields ranging from 33% for R = H to 45% for R = Cl. Compounds **3a–c** were obtained previously from the reactions of **1a–c** with $Re_2(CO)_8(\mu\text{-}I)_2$.[3] Compounds **2a–c**, **4a–c**, and **5a–c** are new. All new compounds were characterized by IR and $^1H$ NMR spectroscopy and by a single crystal X-ray diffraction analysis of a representative member **2b**, **4c**, and **5b** from each series.

An ORTEP diagram of the molecular structure of **2b** is shown in Figure 1. Final fractional atomic coordinates are listed in Table 2. The complex contains two rhenium atoms bridged by an iodo ligand and the sulfur atom of

**Table 2. Positional Parameters and *B*(eq) for 2b**

| atom | *x* | *y* | *z* | *B*(eq) (Å$^2$) |
|---|---|---|---|---|
| Re(1) | 0.71456(6) | 0.17483(4) | −0.06870(5) | 3.01(3) |
| Re(2) | 0.68017(6) | 0.09823(4) | 0.30479(5) | 3.02(3) |
| I | 0.89907(11) | 0.10644(9) | 0.16016(11) | 4.96(6) |
| Cl(1) | 1.1045(9) | 0.3089(8) | 0.5970(8) | 13.1(7) |
| Cl(2) | 0.9644(5) | 0.3790(4) | 0.3340(5) | 7.3(3) |
| S | 0.5429(3) | 0.2018(2) | 0.1031(3) | 2.7(2) |
| O(1) | 0.3931(10) | 0.4756(7) | 0.3708(9) | 4.2(6) |
| O(2) | 0.3828(10) | 0.3242(8) | 0.3087(9) | 4.2(6) |
| O(11) | 0.7175(14) | −0.0412(9) | −0.1546(14) | 7.0(8) |
| O(12) | 0.9450(14) | 0.1685(9) | −0.2427(14) | 7.0(8) |
| O(13) | 0.5104(12) | 0.2509(9) | −0.3156(11) | 5.7(7) |
| O(21) | 0.6470(14) | −0.0953(10) | 0.1473(14) | 7.2(9) |
| O(22) | 0.4229(12) | 0.1059(9) | 0.4459(13) | 5.8(7) |
| O(23) | 0.7257(14) | 0.2784(9) | 0.4822(10) | 6.0(8) |
| O(24) | 0.8615(13) | −0.0348(10) | 0.5326(13) | 6.8(8) |
| N | 0.6719(10) | 0.3233(7) | 0.0296(9) | 2.6(5) |
| C(1) | 0.5846(12) | 0.3184(9) | 0.1185(11) | 2.5(6) |
| C(2) | 0.5292(13) | 0.3988(9) | 0.2041(11) | 2.8(7) |
| C(3) | 0.5739(13) | 0.4861(9) | 0.1967(12) | 3.0(7) |
| C(4) | 0.6647(13) | 0.4949(9) | 0.1018(12) | 2.8(7) |
| C(5) | 0.7150(12) | 0.4115(9) | 0.0203(11) | 2.5(6) |
| C(6) | 0.8009(13) | 0.4183(10) | −0.0792(13) | 3.4(7) |
| C(7) | 0.8403(15) | 0.5074(11) | −0.0887(14) | 3.9(8) |
| C(8) | 0.7950(13) | 0.5921(9) | −0.0018(13) | 3.1(7) |
| C(9) | 0.7086(14) | 0.5844(10) | 0.0873(12) | 3.1(7) |
| C(10) | 0.4278(14) | 0.3924(10) | 0.2960(12) | 2.9(7) |
| C(11) | 0.7161(16) | 0.0395(13) | −0.1218(15) | 5(1) |
| C(12) | 0.8635(15) | 0.1715(10) | −0.1778(16) | 4.0(8) |
| C(13) | 0.5873(16) | 0.2218(11) | −0.2216(14) | 3.8(8) |
| C(21) | 0.6567(16) | −0.0249(13) | 0.1981(18) | 5(1) |
| C(22) | 0.5193(16) | 0.1019(9) | 0.3945(14) | 3.7(8) |
| C(23) | 0.7066(16) | 0.2156(11) | 0.4122(14) | 3.8(8) |
| C(24) | 0.7958(17) | 0.0118(12) | 0.4474(16) | 4(1) |
| C(31) | 0.2950(17) | 0.4749(13) | 0.4630(17) | 6(1) |
| C(32) | 0.8367(14) | 0.6859(11) | −0.0207(16) | 4.2(8) |
| C(101) | 1.082(2) | 0.2869(15) | 0.419(2) | 7(1) |

a 3-carbomethoxy-6-methyl-quinoline-2-thiolate ligand, Re(1)–I = 2.785(3) Å, Re(2)–I = 2.803(3) Å and Re(1)–S = 2.519(4) Å, Re(2)–S = 2.533(4) Å. The rhenium–sulfur distances are slightly longer than those found in the complexes [PPN][$Re_3(CO)_{10}(\mu\text{-}SCH_2CMe_2CH_2Cl)(\mu\text{-}H)_3$], 2.478(3) Å, and $Re_3(CO)_{10}(\mu\text{-}SCH_2CH_2CH_2NMe_3)(\mu\text{-}H)_3$, 2.472(5) and 2.471(4) Å, which contain edge bridging thiolato ligands.[11] The rhenium–rhenium distance is too long to permit the existence of any significant metal–metal bonding interactions, Re(1)···Re(2) = 3.933(4) Å. The nitrogen atom of the quinoline grouping is also coordinated to one of the rhenium atoms, Re(1)–N = 2.20(1) Å. Rhenium Re(1) contains three linear terminal carbonyl ligands, rhenium Re(2) has four, and both metal atoms obey the 18 electron rule. The aromatic hydrogen atoms appear as a pair of doublets, 8.12 (d), 7.89 ppm, (d), $^3J_{H-H}$ = 8.0 Hz, and two singlets, 9.04 (s), 7.79 ppm, (s), in the $^1H$ NMR spectrum, as expected on the basis of their proximities. Compounds **2a** and **2c** are believed to be structurally similar to **2b**.

The $^1H$ NMR spectrum of compound **4a** exhibits highly deshielded resonances that must be attributed to seven hydrogen atoms on the basis of intensities: 11.69 (s, br, 1H, N*H*), 11.06 (s, 1H, C*H*), 7.33 (m, 2H, $C_6H_5$), 7.26 (m, 1H, $C_6H_5$), 7.11 ppm (m, 2H, $C_6H_5$). Five of these are aromatic, which indicates that the phenyl ring was not transformed in the reaction. A single crystal X-ray diffraction analysis of **4c** was performed to establish the structures. An ORTEP diagram of the molecular structure of **4c** is shown in Figure 2. Final fractional atomic coordinates are listed in Table 3. The complex contains two rhenium atoms bridged by alkenyl-*N*-(*p*-chlorophenyl)thioformamide ligand. The molecule appears to have been derived from **1c** by the simple addition of HI, and this was subsequently confirmed by an independent reaction of **1c** with HI that gave **4c** in a 46% yield. Compounds **4a,b** were also obtained from **1a,b**, respec-

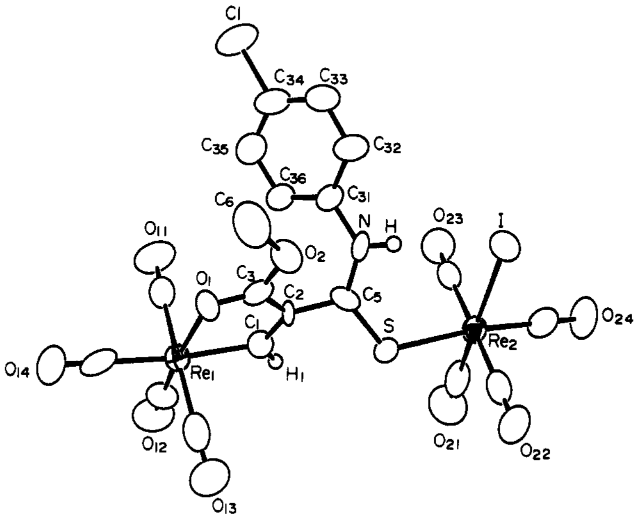


**Figure 2.** ORTEP diagram of $Re(CO)_4[(E)\text{-}HC{=}C(CO_2Me)C(NHC_6H_4\text{-}p\text{-}Cl){=}S]Re(CO)_4(I)$, **4c**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are as follows: Re(1)—C(1) = 2.14(2), Re(1)—O(1) = 2.21(1), Re(2)—I = 2.814(1), Re(2)—S = 2.491(3), C(1)—C(2) = 1.32(2), C(2)—C(3) = 1.46(2), C(5)—N = 1.33(2), C(5)—S = 1.66(2), C(2)—C(5) = 1.44(2); C(5)—S—Re(2) = 118.5(6), C(1)—C(2)—C(5) = 124(1), S—C(5)—N = 124(1).

**Table 3. Positional Parameters and *B*(eq) for 4c**

| atom | *x* | *y* | *z* | *B*(eq) (Å$^2$) |
|---|---|---|---|---|
| Re(1) | 0.29480(9) | 0.20342(7) | 0.051863(18) | 3.49(3) |
| Re(2) | −0.18250(9) | −0.38725(6) | 0.117025(18) | 3.30(3) |
| I | −0.21880(15) | −0.31876(11) | 0.19502(3) | 4.38(6) |
| Cl | 0.7913(7) | 0.0419(6) | 0.25545(14) | 7.4(3) |
| S | −0.0918(5) | −0.1786(4) | 0.09485(11) | 3.6(2) |
| O(1) | 0.1898(14) | 0.2268(10) | 0.1108(3) | 3.5(5) |
| O(2) | 0.0735(13) | 0.1260(10) | 0.1613(3) | 3.9(6) |
| O(11) | 0.7010(17) | 0.1397(14) | 0.0860(4) | 7.3(8) |
| O(12) | 0.4462(17) | 0.1362(14) | −0.0267(4) | 7.4(8) |
| O(13) | −0.1050(18) | 0.2385(14) | 0.0094(4) | 7.0(8) |
| O(14) | 0.393(2) | 0.4813(13) | 0.0449(4) | 7.4(9) |
| O(21) | −0.135(2) | −0.4731(14) | 0.0340(4) | 7.8(9) |
| O(22) | −0.5886(16) | −0.2815(12) | 0.0967(3) | 5.4(7) |
| O(23) | 0.2247(17) | −0.4810(12) | 0.1402(4) | 6.5(8) |
| O(24) | −0.3505(18) | −0.6352(12) | 0.1407(4) | 7.6(9) |
| N | 0.1460(17) | −0.1394(11) | 0.1553(4) | 3.0(7) |
| C(1) | 0.2030(20) | 0.0246(16) | 0.0686(4) | 3.4(9) |
| C(2) | 0.1402(18) | 0.0148(13) | 0.1039(4) | 2.3(7) |
| C(3) | 0.1362(20) | 0.1306(17) | 0.1252(5) | 3(1) |
| C(5) | 0.0732(19) | −0.1018(15) | 0.1208(4) | 3.3(8) |
| C(6) | 0.093(3) | 0.2373(16) | 0.1844(5) | 6(1) |
| C(11) | 0.552(2) | 0.1656(16) | 0.0739(5) | 4(1) |
| C(12) | 0.383(2) | 0.1629(17) | 0.0025(5) | 5(1) |
| C(13) | 0.039(3) | 0.2304(16) | 0.0260(5) | 4(1) |
| C(14) | 0.361(2) | 0.380(2) | 0.0471(5) | 5(1) |
| C(21) | −0.152(2) | −0.4440(19) | 0.0642(6) | 6(1) |
| C(22) | −0.438(2) | −0.3209(16) | 0.1044(4) | 4(1) |
| C(23) | 0.079(3) | −0.4427(16) | 0.1315(4) | 4(1) |
| C(24) | −0.286(2) | −0.5431(18) | 0.1313(5) | 5(1) |
| C(31) | 0.301(2) | −0.0935(14) | 0.1787(4) | 3.2(8) |
| C(32) | 0.2994(20) | −0.1015(16) | 0.2185(4) | 4(1) |
| C(33) | 0.449(2) | −0.0607(16) | 0.2425(4) | 4(1) |
| C(34) | 0.599(2) | −0.0082(18) | 0.2255(5) | 5(1) |
| C(35) | 0.610(2) | 0.0034(16) | 0.1867(5) | 5(1) |
| C(36) | 0.460(2) | −0.0433(15) | 0.1625(4) | 3.5(8) |

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[11] Adams, R. D.; Cortopassi, J. E.; Falloon, S. B. *Organometallics* **1992**, *11*, 2404.

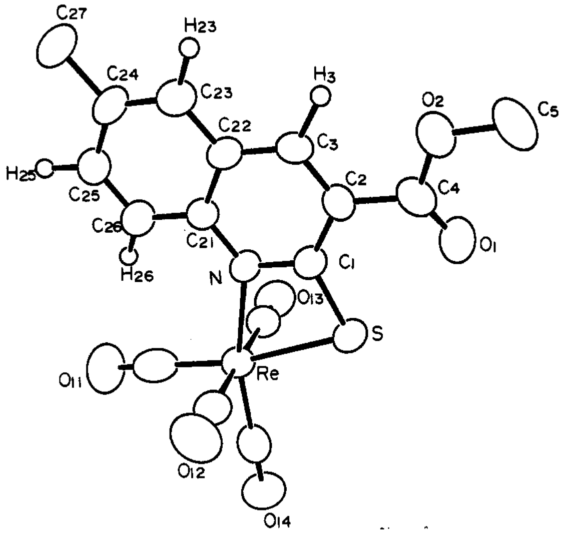


**Figure 3.** ORTEP diagram of Re(CO)$_4$(2-S-3-CO$_2$Me-6-MeNC$_9$H$_4$), **5b**, showing 50% probability thermal ellipsoids. Selected intramolecular bond distances (Å) and angles (deg) are as follows: Re–N = 2.196(5), Re–S = 2.505(2), C(1)–C(2) = 1.42(1), C(2)–C(3) = 1.37(1), C(1)–N = 1.345(9), C(21)–N = 1.383(9), C(1)–S = 1.731(7); S–Re–N = 64.9(2), S–C(1)–N = 110.3(5).

tively, in yields of 48% and 45% by reaction with HI. The alkenyl group C(1)–C(2) contains a normal C–C double bond, 1.32(2) Å. The rhenium–carbon distance, Re(1)–C(1) = 2.14(2) Å, compared favorably with that found in **1b**, 2.149(9) Å.[3] The C–S bond in **4c** should have multiple character and the C(5)–S distance of 1.66(2) Å is significantly shorter than that found for the thioformamido ligand found in **1b**, 1.717(9) Å.[3] As in the compounds 1, the ketonic oxygen atom of the carboxylate group is coordinated to the metal atom that is bonded to the alkenyl carbon C(1), Re(1)–O(1) = 2.21 (1) Å. The deshielded resonances 11.93 (s, br, N*H*) and 10.34 ppm (s, C*H*), observed in **4c** are attributed to the NH and alkenyl CH hydrogen atoms, respectively. The alkenyl hydrogen atom in **1c** also exhibits a very similar deshielded resonance shift, 10.53 ppm.[3]

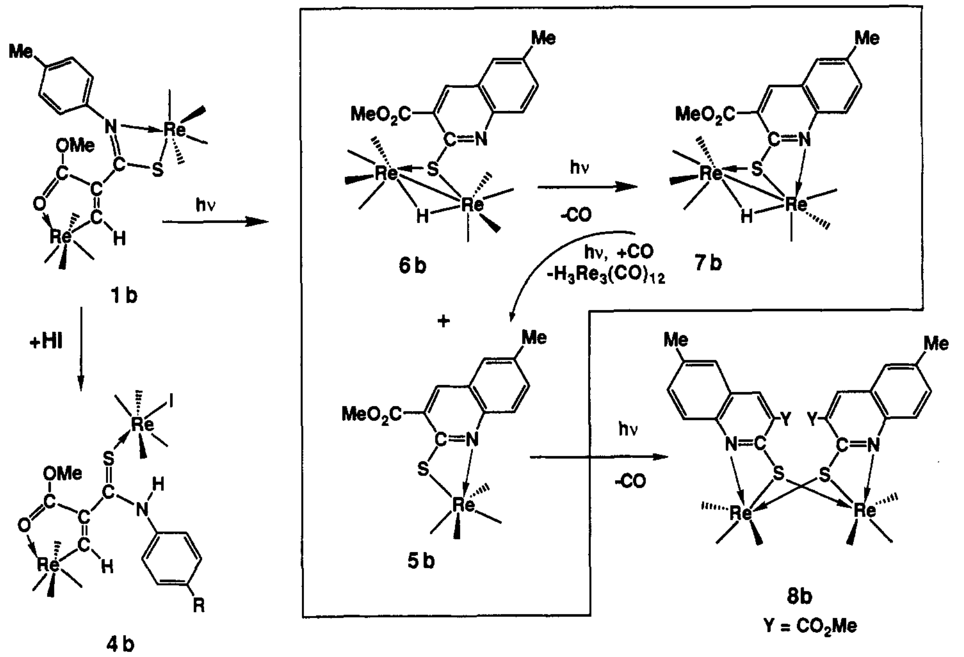
The structures of the mononuclear metal complexes **5a–c** were established by a single crystal X-ray diffraction analysis of **5b**. An ORTEP diagram of the molecular structure of **5b** is shown in Figure 3. Final fractional atomic coordinates are listed in Table 4. The complex contains a six coordinate rhenium atom with four linear terminal carbonyl ligands and a chelated 3-carbomethoxy-6-methylquinoline-2-thiolate ligand. The metal–nitrogen and metal–sulfur distances are similar to those of the S-bridged quinoline-2-thiolate ligand found in **2b**: Re–N = 2.196(5) Å, Re–S = 2.505(2) Å. The S–Re–N angle is fairly acute due to the chelating form of the ligand, S–Re–N = 64.9(2)°. The quinoline-2-thiolate ligand serves as a three-electron donor, and the rhenium atom thus has an 18-electron configuration. The resonances of the aromatic hydrogen atoms of the quinoline-2-thiolate ligand consist of a pair of doublets, 8.05 (d), 6.86 ppm (d), $^3J_{H-H}$ = 8.7 Hz, and two singlets, 8.36 (s), 6.68 ppm (s), similar to that found for the quinoline-2-thiolate ligand in **2b**. The spectra of **5a** and **5c** indicate that they are structurally similar to **5b**. Irradiation of compound **5b** in the presence of [Re(CO)$_4$($\mu$-I)]$_2$ for 1 h resulted in the formation of compound **2b** in 22% yield. Conversely, irradiation of **2b** in the presence of CO regenerated **5b** in 69% yield plus [Re(CO)$_4$($\mu$-I)]$_2$.

**Table 4. Positional Parameters and *B*(eq) for 5b**

| atom | *x* | *y* | *z* | *B*(eq) (Å$^2$) |
|---|---|---|---|---|
| Re | 0.90380(3) | 0.23113(3) | 0.37267(5) | 3.74(2) |
| S | 0.88776(19) | 0.44508(18) | 0.5743(3) | 4.0(1) |
| O(1) | 0.7542(7) | 0.7152(5) | 0.6731(10) | 6.4(4) |
| O(2) | 0.5400(6) | 0.8022(5) | 0.5836(9) | 5.8(3) |
| O(11) | 0.8731(7) | –0.0094(6) | 0.0855(11) | 7.7(4) |
| O(12) | 0.8192(7) | 0.1711(6) | 0.6938(11) | 6.6(4) |
| O(13) | 0.9849(6) | 0.3012(6) | 0.0541(9) | 6.0(4) |
| O(14) | 1.1913(6) | 0.0911(6) | 0.5276(11) | 7.0(4) |
| N | 0.7110(5) | 0.3722(5) | 0.3187(8) | 3.2(3) |
| C(1) | 0.7288(7) | 0.4763(6) | 0.4418(10) | 3.1(4) |
| C(2) | 0.6259(7) | 0.5912(6) | 0.4538(10) | 3.3(4) |
| C(3) | 0.5043(7) | 0.5931(6) | 0.3427(10) | 3.2(4) |
| C(4) | 0.6510(9) | 0.7066(7) | 0.5812(12) | 4.1(5) |
| C(5) | 0.5533(11) | 0.9165(8) | 0.7102(15) | 7.1(6) |
| C(11) | 0.8824(8) | 0.0844(9) | 0.1969(15) | 5.6(5) |
| C(12) | 0.8500(8) | 0.1934(7) | 0.5764(13) | 4.6(5) |
| C(13) | 0.9587(8) | 0.2755(7) | 0.1706(13) | 4.5(5) |
| C(14) | 1.0840(10) | 0.1427(8) | 0.4693(14) | 5.5(6) |
| C(21) | 0.5896(7) | 0.3735(6) | 0.2032(10) | 3.1(4) |
| C(22) | 0.4820(7) | 0.4859(7) | 0.2187(10) | 3.1(4) |
| C(23) | 0.3566(7) | 0.4830(7) | 0.1074(11) | 3.6(4) |
| C(24) | 0.3380(7) | 0.3764(8) | –0.0137(11) | 3.9(5) |
| C(25) | 0.4470(8) | 0.2688(7) | –0.0331(12) | 4.3(5) |
| C(26) | 0.5714(8) | 0.2654(7) | 0.0731(11) | 4.0(4) |
| C(27) | 0.2021(8) | 0.3735(8) | –0.1231(12) | 5.1(5) |

To establish the importance of iodine in the reactions, the irradiation of **1b** in the absence of iodine was studied. This reaction yielded a series of dirhenium complexes in low yields, Re$_2$(CO)$_8$[$\mu$-2-S-3-CO$_2$Me-6-MeNC$_9$H$_4$]($\mu$-H), **6b**, 7% yield, and Re$_2$(CO)$_7$[$\mu$-2-S-3-CO$_2$Me-6-MeNC$_9$H$_4$]($\mu$-H), **7b**, 8% yield, that contain a 3-carbomethoxy-6-methylquinoline-2-thiolate ligand and the mononuclear complex **5b** described above in 18% yield (see Scheme 2). Compounds **6b** and **7b** were both characterized crystallographically, and ORTEP diagrams of the molecular structures of these compounds are shown in Figures 4 and 5, respectively. Final fractional atomic coordinates for these structures are listed in Tables 5 and 6, respectively. The structures of both compounds are very similar. Both contain a pair of rhenium atoms bridged by a hydride ligand and the sulfur atom of 3-carbomethoxy-6-methylquinoline-2-thiolate ligand. The principal difference is **6b** contains eight carbonyl ligands while **7b** has only seven and the nitrogen atom of the quinoline grouping is coordinated to one of the metal atoms in **7b**. Thus, **7b** is analogous to **2b**, but has a bridging hydride ligand instead of a bridging iodide ligand. Since bridging iodide ligands serve as three-electron donors and hydride ligands can donate no more than one electron, a metal–metal bond is formed in complexes **6b** and **7b** in order to maintain the 18-electron configurations at the metal atoms. Accordingly, the metal–metal internuclear distance is much shorter in **6b** and **7b** than in **2b**, Re–Re = 3.0854(8) Å in **6b** and 3.119(1) Å in **7b**. When irradiated, compound **6b** was converted to **7b** in 62% yield in 5 min. Some **5b**, 17% yield, and Re$_3$(CO)$_{12}$($\mu$-H)$_3$ was also formed in this reaction. When **7b** was irradiated under an atmosphere of CO at 25 °C, compound **5b** was obtained in 73% yield together with a small amount of Re$_3$(CO)$_{12}$($\mu$-H)$_3$. In fact, **5b** can also be obtained in a good yield (69%) together with some [Re(CO)$_4$($\mu$-I)]$_2$ from **2b** irradiation in the presence of a CO. Even in the absence of CO, **5b** was obtained in a 60% yield from irradiated solutions of **7b**, but a small amount of yet another compound [Re(CO)$_3$(2-S-3-CO$_2$Me-6-MeNC$_9$H$_4$)]$_2$, **8b**, in 8% yield was also obtained. It was

**Scheme 2**



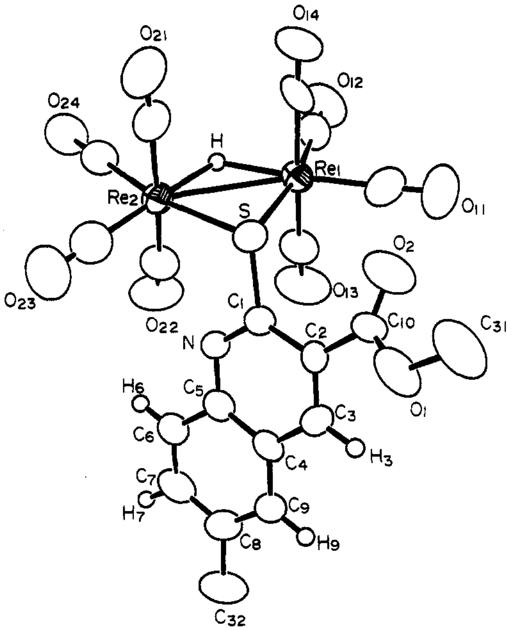


**Figure 4.** ORTEP diagram of $Re_2(CO)_8[\mu\text{-}2\text{-}S\text{-}3\text{-}CO_2Me\text{-}6\text{-}MeNC_9H_4](\mu\text{-}H)$, **6b**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are as follows: Re(1)–Re(2) = 3.0854(8), Re(1)–S = 2.488(3), Re(2)–S = 2.474(2), C(1)–C(2) = 1.43(1), C(2)–C(3) = 1.37(1), C(1)–N = 1.30(1), C(1)–S = 1.806(9), C(3)–C(4) = 1.41(1); Re(1)–S–Re(2) = 76.90(7), S–C(1)–N = 116.8(6).

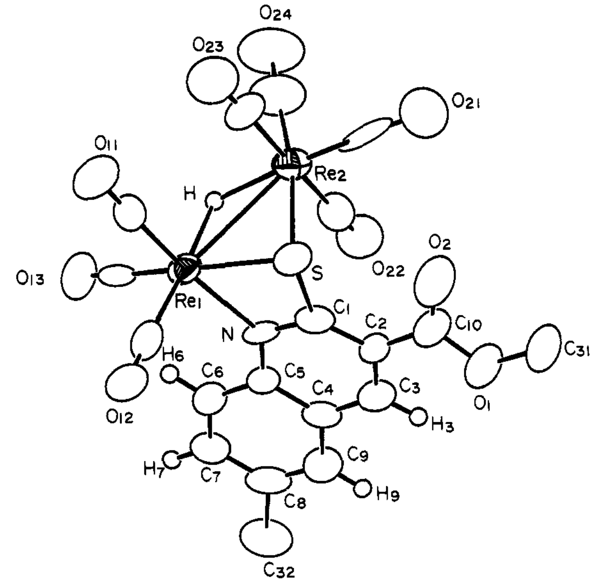


**Figure 5.** ORTEP diagram of $Re_2(CO)_7[\mu\text{-}2\text{-}S\text{-}3\text{-}CO_2Me\text{-}6\text{-}MeNC_9H_4](\mu\text{-}H)$, **7b**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are as follows: Re(1)–Re(2) = 3.119(1), Re(1)–N = 2.22(1), Re(1)–S = 2.477(4), Re(2)–S = 2.497(4), C(1)–C(2) = 1.38(2), C(2)–C(3) = 1.36(2), C(1)–N = 1.34(2), C(1)–S = 1.81(1), C(3)–C(4) = 1.40(2); Re(1)–S–Re(2) = 77.7(1), S–C(1)–N = 108(1 ).

subsequently found that **8b** can be obtained in 57% yield by the photodecarbonylation of **5b**.

Compound **8b** was characterized by a single crystal X-ray diffraction analysis, and an ORTEP diagram of its molecular structure is shown in Figure 6. Final fractional atomic coordinates are listed in Table 7. The molecule contains a crystallographic 2-fold rotation axis and can be viewed as a dimer of a decarbonylated form of **5b**. The two rhenium atoms are bridged by the sulfur atoms of two 3-carbomethoxy-6-methylquinoline-2-thiolate ligands which have a *cis* geometry. The rhenium–rhenium distance is long, Re···Re = 3.695(1) Å, and indicative no direct metal–metal bonding, as expected on the basis of electron counting considerations. The other distances Re–N = 2.195(5) Å, Re–S = 2.521(2) Å, Re′–S = 2.530(2) Å, and C(1)–S = 1.768(6) Å are similar to those found in compounds **2b**, **5b**, and **6b**, and **7b**.

Compound **3b** was also irradiated in the absence of iodine. This reaction yielded **5b** as the major product (39% yield) with small amounts of **7b**, 12% yield, **2b**, 17% yield, and $[Re(CO)_4(\mu\text{-}I)]_2$.

## Discussion

We have found that the alkenyl-*N*-arylthioamido ligands in complexes **1a–c** are transformed into substituted

**Table 5. Positional Parameters and *B*(eq) for 6b**

| atom | *x* | *y* | *z* | *B*(eq) (Å$^2$) |
|---|---|---|---|---|
| Re(1) | 0.34525(2) | 0.05350(2) | 0.79982(6) | 3.83(2) |
| Re(2) | 0.20236(2) | 0.10300(2) | 0.97798(6) | 3.81(2) |
| S | 0.28761(14) | 0.00710(13) | 1.0882(03) | 3.7(1) |
| O(1) | 0.3751(4) | –0.1976(5) | 1.2967(12) | 7.7(5) |
| O(2) | 0.4068(5) | –0.1014(5) | 1.1485(16) | 10.2(6) |
| O(11) | 0.4818(5) | –0.0431(5) | 0.7876(14) | 8.8(6) |
| O(12) | 0.3941(5) | 0.1341(5) | 0.4475(12) | 7.8(6) |
| O(13) | 0.2714(5) | –0.0662(5) | 0.5548(12) | 9.2(6) |
| O(14) | 0.4281(4) | 0.1749(4) | 1.0272(12) | 6.7(5) |
| O(21) | 0.2810(5) | 0.2155(5) | 1.2342(14) | 9.2(6) |
| O(22) | 0.1123(5) | 0.0115(4) | 0.6904(12) | 7.8(6) |
| O(23) | 0.0881(5) | 0.0715(5) | 1.2682(14) | 9.0(7) |
| O(24) | 0.1207(4) | 0.2381(4) | 0.8274(13) | 7.5(5) |
| N | 0.1837(4) | –0.0862(4) | 0.9903(10) | 3.3(4) |
| C(1) | 0.2496(5) | –0.0841(5) | 1.0515(13) | 3.4(5) |
| C(2) | 0.2900(5) | –0.1487(5) | 1.1020(13) | 3.4(5) |
| C(3) | 0.2570(5) | –0.2160(5) | 1.0733(13) | 3.6(5) |
| C(4) | 0.1861(5) | –0.2217(5) | 1.0043(12) | 3.2(5) |
| C(5) | 0.1509(5) | –0.1538(5) | 0.9622(13) | 3.7(5) |
| C(6) | 0.0793(5) | –0.1561(5) | 0.9043(13) | 4.0(5) |
| C(7) | 0.0460(5) | –0.2229(6) | 0.8820(14) | 4.7(6) |
| C(8) | 0.0809(6) | –0.2910(5) | 0.9160(13) | 4.2(6) |
| C(9) | 0.1504(5) | –0.2913(5) | 0.9756(13) | 3.6(5) |
| C(10) | 0.3628(6) | –0.1450(6) | 1.1802(17) | 4.7(6) |
| C(11) | 0.4293(7) | –0.0075(6) | 0.7935(16) | 5.6(7) |
| C(12) | 0.3758(6) | 0.1031(6) | 0.5804(17) | 5.3(6) |
| C(13) | 0.2968(6) | –0.0209(6) | 0.6469(16) | 5.6(7) |
| C(14) | 0.3972(5) | 0.1312(6) | 0.9490(16) | 4.6(6) |
| C(21) | 0.2545(6) | 0.1729(6) | 1.1397(18) | 5.5(7) |
| C(22) | 0.1470(6) | 0.0400(6) | 0.7983(18) | 5.6(7) |
| C(23) | 0.1322(7) | 0.0839(6) | 1.1603(19) | 6.2(7) |
| C(24) | 0.1513(6) | 0.1873(6) | 0.8806(17) | 5.3(6) |
| C(31) | 0.4443(7) | –0.2010(8) | 1.382(2) | 9(1) |
| C(32) | 0.0415(7) | –0.3632(6) | 0.8940(15) | 6.1(7) |

**Table 6. Positional Parameters and *B*(eq) for 7b**

| atom | *x* | *y* | *z* | *B*(eq) (Å$^2$) |
|---|---|---|---|---|
| Re(1) | 0.31220(6) | 0.38215(5) | 0.69112(8) | 3.48(3) |
| Re(2) | 0.20813(7) | 0.16842(6) | 0.39301(10) | 4.30(3) |
| S | 0.0958(4) | 0.2451(3) | 0.5718(5) | 4.0(2) |
| O(1) | –0.2485(10) | 0.2462(10) | 0.1655(15) | 5.8(5) |
| O(2) | –0.1533(12) | 0.1534(11) | 0.306(2) | 9.3(7) |
| O(11) | 0.4412(12) | 0.2885(11) | 0.9752(18) | 7.7(6) |
| O(12) | 0.2807(11) | 0.5277(11) | 0.9963(15) | 6.3(6) |
| O(13) | 0.5692(11) | 0.5456(11) | 0.7171(15) | 6.0(5) |
| O(21) | –0.0188(15) | –0.0356(13) | 0.198(2) | 8.6(7) |
| O(22) | 0.1458(12) | 0.2739(10) | 0.0713(17) | 6.4(6) |
| O(23) | 0.3046(14) | 0.0689(11) | 0.702(2) | 9.3(7) |
| O(24) | 0.3800(16) | 0.0940(13) | 0.215(2) | 11.1(9) |
| N | 0.1821(11) | 0.4260(10) | 0.4909(15) | 3.3(5) |
| C(1) | 0.0728(15) | 0.3414(12) | 0.4429(20) | 3.4(6) |
| C(2) | –0.0357(14) | 0.3343(12) | 0.3203(19) | 3.3(6) |
| C(3) | –0.0313(16) | 0.4219(15) | 0.2512(19) | 4.2(7) |
| C(4) | 0.0775(15) | 0.5154(13) | 0.3023(19) | 3.5(6) |
| C(5) | 0.1865(14) | 0.5141(14) | 0.4252(18) | 3.5(6) |
| C(6) | 0.2964(14) | 0.6074(14) | 0.472(2) | 4.2(6) |
| C(7) | 0.3001(15) | 0.6989(13) | 0.415(2) | 4.6(7) |
| C(8) | 0.1908(18) | 0.6987(15) | 0.298(2) | 4.6(7) |
| C(9) | 0.0821(16) | 0.6094(15) | 0.2403(20) | 4.5(7) |
| C(10) | –0.1484(16) | 0.2360(16) | 0.268(2) | 4.7(7) |
| C(11) | 0.3940(15) | 0.3257(13) | 0.865(2) | 4.5(7) |
| C(12) | 0.2966(14) | 0.4768(14) | 0.882(2) | 4.1(7) |
| C(13) | 0.4725(18) | 0.4876(14) | 0.7128(20) | 3.7(7) |
| C(21) | 0.085(2) | 0.055(2) | 0.278(2) | 7(1) |
| C(22) | 0.1663(15) | 0.2360(14) | 0.190(2) | 4.6(7) |
| C(23) | 0.2607(16) | 0.1012(15) | 0.591(3) | 5.9(8) |
| C(24) | 0.3168(19) | 0.1260(15) | 0.287(3) | 7(1) |
| C(31) | –0.3632(16) | 0.1530(16) | 0.104(3) | 6.6(8) |
| C(32) | 0.1942(18) | 0.8046(14) | 0.247(2) | 6.6(9) |

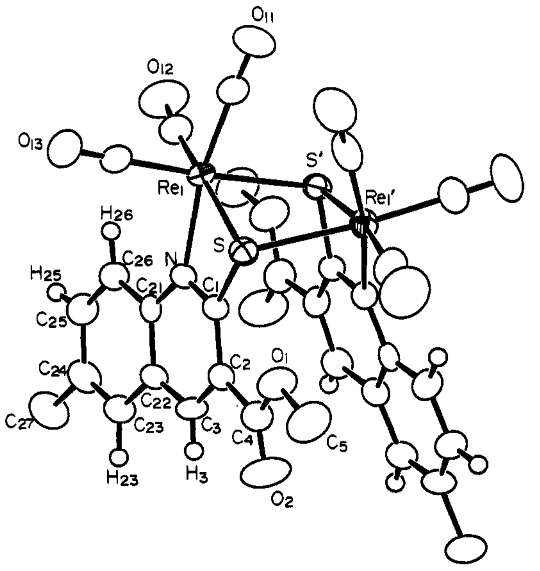


**Figure 6.** ORTEP diagram of $[Re(CO)_3(2\text{-}S\text{-}3\text{-}CO_2Me\text{-}6\text{-}MeNC_9H_4)]_2$, **8b**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are as follows: Re···Re = 3.70(1), Re–N = 2.195(5), Re–S = 2.521(2), Re′–S = 2.530(2), C(1)–C(2) = 1.441(9), C(2)–C(3) = 1.35(1), C(1)–N = 1.327(8), C(1)–S = 1.768(6); Re(1)–S–Re(2) = 94.04(6), S–Re–S = 81.75(6), S–C(1)–N = 108.8(4).

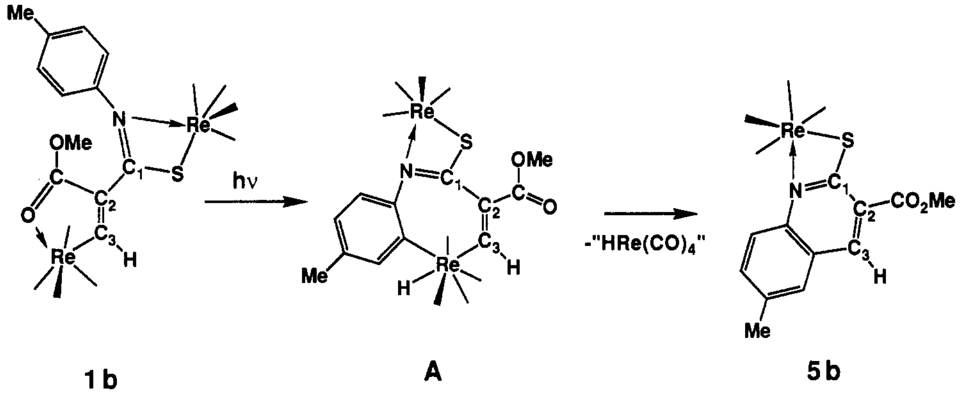
**Table 7. Positional Parameters and *B*(eq) for 8b**

| atom | *x* | *y* | *z* | *B*(eq) (Å$^2$) |
|---|---|---|---|---|
| Re | 0.434507(14) | 0.16886(2) | 0.132348(18) | 2.49(1) |
| S | 0.55897(9) | 0.21410(15) | 0.19380(12) | 2.51(6) |
| O(1) | 0.6728(2) | 0.3909(5) | 0.2497(4) | 4.1(2) |
| O(2) | 0.6661(3) | 0.5983(5) | 0.2457(5) | 5.6(3) |
| O(11) | 0.4231(4) | –0.1031(5) | 0.1935(5) | 6.8(3) |
| O(12) | 0.2810(3) | 0.1606(6) | 0.0803(5) | 6.6(3) |
| O(13) | 0.4292(3) | 0.0892(6) | –0.0721(4) | 5.8(3) |
| N | 0.4638(3) | 0.3638(4) | 0.1177(4) | 2.3(2) |
| C(1) | 0.5294(3) | 0.3683(5) | 0.1627(4) | 2.2(3) |
| C(2) | 0.5667(3) | 0.4841(6) | 0.1772(4) | 2.5(3) |
| C(3) | 0.5323(3) | 0.5895(6) | 0.1409(5) | 2.7(3) |
| C(4) | 0.6397(3) | 0.4988(7) | 0.2279(5) | 3.2(3) |
| C(5) | 0.7448(4) | 0.4032(9) | 0.2939(7) | 5.3(4) |
| C(11) | 0.4278(4) | –0.0039(8) | 0.1688(5) | 4.2(4) |
| C(12) | 0.3391(4) | 0.1673(7) | 0.0975(5) | 4.0(3) |
| C(13) | 0.4315(4) | 0.1202(7) | 0.0046(5) | 3.5(3) |
| C(21) | 0.4290(3) | 0.4698(6) | 0.0761(4) | 2.2(3) |
| C(22) | 0.4636(3) | 0.5868(6) | 0.0873(5) | 2.4(3) |
| C(23) | 0.4269(4) | 0.6952(6) | 0.0433(5) | 2.9(3) |
| C(24) | 0.3604(4) | 0.6881(6) | –0.0076(5) | 3.1(3) |
| C(25) | 0.3285(4) | 0.5697(7) | –0.0167(5) | 2.9(3) |
| C(26) | 0.3611(3) | 0.4634(7) | 0.0237(5) | 2.7(3) |
| C(27) | 0.3224(4) | 0.8019(7) | –0.0530(6) | 4.2(4) |

quinoline-2-thiolate ligands when irradiated in the presence of iodine to yield the complexes **2a–c** and **5a–c**. The reactions were studied for three different substituents at the para position of the *N*-aryl ring, R = H, Me, and Cl. Compounds **3a–c** and **4a–c** do not contain quinoline-2-thiolate ligands, and an explanation of the formation of these side products will be described below. From studies on complex **1b**, it was shown that related products containing quinoline-2-thiolate ligands are also formed when **1b** is irradiated even in the absence of iodine, but the yields are significantly lower. This observation demonstrates that the quinoline ring forming process does not require iodine.

A possible mechanism for transformation of **1b** to **5b** is presented in Scheme 3. In brief, these transformations must include (1) a cleavage of the Re–O bond, (2) a *cis–trans* isomerization of the stereochemistry at the olefin site C(2)–C(3), (3) the activation of one of the aryl CH bonds at a position ortho to the nitrogen atom, (4) the formation of a carbon–carbon bond between the olefin carbon C(3) and the ortho carbon in the phenyl ring, and (5) the elimination of a $HRe(CO)_4$ grouping. The sequence

**Scheme 3**



of these events has not been established experimentally, but clearly, the Re–O bond cleavage must precede the *cis–trans* isomerization at the olefin site C(2)–C(3) and these steps must precede the cyclization process. We propose that the irradiation process provides the energy for the combination of the first two steps. This results in the formation of a vacant coordination site on the rhenium atom which contains C(3) and shifts the aryl ring to a position from which ortho-metalation could occur. This could produce an intermediate species such as **A** shown in Scheme 3. A reductive elimination involving C(3) and the metalated aryl carbon would lead to the formation of the heterocyclic ring, the elimination of a $HRe(CO)_4$ fragment, and the formation of the major product **5b**. It is possible that some of the unsaturated $HRe(CO)_4$ fragments might recombine with **5b** by addition at the lone pair of electrons on the sulfur atom and yield the minor product **6b** which in turn yields **7b** by decarbonylation.

We suspect that the iodine might facilitate these reactions by reacting with the hydride containing intermediate and converting it to an iodide homolog with a simultaneous formation of HI. The iodide homolog might eliminate a "$Re(CO)_4I$" grouping more easily to yield the compounds **5**. An additional driving force might also be the combination of two "$Re(CO)_4I$" groupings to yield $[Re(CO)_4(\mu\text{-}I)]_2$ which was also observed in these reactions. An "$Re(CO)_4I$" grouping or $[Re(CO)_4(\mu\text{-}I)]_2$ could also combine with **5b** to yield **2b**. The latter possibility was established by an independent reaction. The formation of the side products **3** could occur by the reaction of unreacted 1 with $[Re(CO)_4(\mu\text{-}I)]_2$. This was also established through independent reactions.[3] Finally, the HI formed in the reaction of **A** with $I_2$ could react with unreacted 1 to yield the other side product **4**. This reaction was also verified independently. Interestingly, when **5b** was photodecarbonylated, it combined with a similar fragment to yield the dimer **8b**.

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**Supplementary Material Available:** Tables of hydrogen atom positional parameters, interatomic distances, interatomic bond angles, and anisotropic thermal parameters for all six structural analyses (33 pages). Ordering information is given on any current masthead page.

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