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Studies of the Insertion of an Organic Isothiocyanate into a Rhenium−Rhenium Single Bond and a New Mode of Metal-Promoted Coupling of Isothiocyanates

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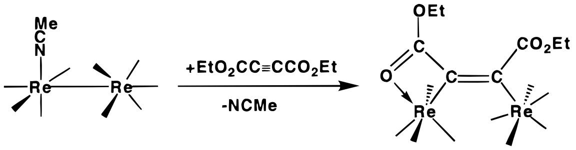
Five new compounds were obtained from the reaction of $Re_2(CO)_9(MeCN)$ with $EtO_2CN{=}C{=}S$ in a hexane solution at reflux (68 °C). These were identified as $Re(CO)_4[s\text{-}trans\text{-}\mu\text{-}C,S\text{-}EtO_2CN{=}CS]Re(CO)_5$ (**2**, 7% yield), $Re(CO)_4[\mu\text{-}C,S,N\text{-}EtO_2CN{=}CS]Re(CO)_4$ (**3**, 40% yield), $Re(CO)_4[\mu\text{-}C,N,S_2\text{-}(EtO_2C)_2NC{=}NCS_2]Re(CO)_4$ (**4**, 17% yield), $Re(CO)_4[\mu\text{-}C,N,S_2\text{-}(EtO_2C)_2NC{=}NCS_2]Re(CO)_3(NCMe)$ (**5**, 5% yield), and trace $Re(CO)_4[\mu\text{-}C,N,S_2\text{-}(EtO_2C)(H)NC{=}NCS_2]Re(CO)_4$ (**6**). All five products have been characterized crystallographically. Compounds **2** and **3** can be described as dimetalated thioimidate complexes formed by the insertion of one $EtO_2CN{=}C{=}S$ molecule into the Re−Re bond of **1**. Compounds **4** and **5** contain a $(EtO_2C)_2NC{=}NCS_2$ ligand that was formed by the insertion and rearrangement of two isothiocyanate molecules in the Re−Re bond of **1**. Compound **6** is similar to **5** but contains a bridging $(EtO_2C)(H)NC{=}NCS_2$ ligand instead. The reaction of $Re(CO)_4(PMe_2Ph)Re(CO)_4(NCMe)$ with $EtO_2CN{=}C{=}S$ yielded two isomeric products, $trans\text{-}Re(CO)_4(PMe_2Ph)[\mu\text{-}(EtO_2C)N{=}CN(CO_2Et)CS_2]Re(CO)_4$ (**8**) and $cis\text{-}Re(CO)_4(PMe_2Ph)[\mu\text{-}EtO_2C)N{=}CN(CO_2Et)CS_2]Re(CO)_4$ (**9**), plus a small amount of the dimetalated thioimidate compound $Re_2(CO)_8(PPhMe_2)(\mu\text{-}EtO_2CNCS)$ (**10**). Compounds **8** and **9** contain a bridging $(EtO_2C)N{=}CN(CO_2Et)CS_2$ ligand that was also formed by the coupling and rearrangement of two isothiocyanate molecules. This ligand is considered to be an intermediate en route to the $(EtO_2C)_2NC{=}NCS_2$ ligand as found in **4**, since **8** and **9** can be transformed into the complex $Re(CO)_4[\mu\text{-}C,N,S_2\text{-}(EtO_2C)_2NC{=}NCS_2]Re(CO)_3(PMe_2Ph)$ (**11**), a phosphine derivative of **4**. A small amount of the complex $Re(CO)_3(PPhMe_2)(\mu\text{-}S_2C{=}NCO_2Et)Re(CO)_3(PPhMe_2)$ (**12**) was also formed from **8** and **9**. Compound **12** contains a dithiocarbimato ligand in a novel tetradentate bridging coordination mode. A mechanism for the formation of the $(EtO_2C)_2NC{=}NCS_2$ ligand is presented and discussed.

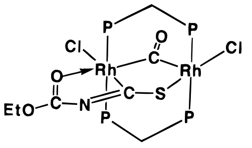
Introduction

Recently, we have shown that carboxylate-substituted alkynes undergo facile insertion into the metal−metal bonds of activated dimanganese and dirhenium complexes to yield dimetalated olefin complexes.[1] A strong tendency for coordination of a carbonyl oxygen atom of a carboxylate group was observed (e.g., eq 1).[2]

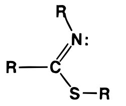


(1)

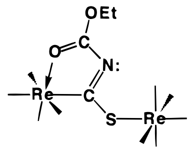
Organic isothiocyanates are useful reagents in organic synthesis,[3] but the organometallic chemistry of these molecules in polynuclear metal complexes has not yet been well studied.[4−6] In one case the reaction of $EtO_2CN{=}C{=}S$ with $Rh_2Cl_2(\mu\text{-}CO)(dpm)_2$ is proposed to yield the product $Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}EtO_2CNCS)(dpm)_2$, containing a C,S-coordinated bridging isothiocyanate ligand:[6]



We have now found that $EtO_2CN{=}C{=}S$ undergoes a facile insertion into the rhenium−rhenium bond in $Re_2(CO)_9(NCMe)$ (**1**) to yield dimetalated thioimidate complexes [e.g., $Re(CO)_4[s\text{-}trans\text{-}\mu\text{-}C,S\text{-}EtO_2CN{=}CS]Re(CO)_5$ (**2**)].[7] We have also observed products formed by a new coupling/rearrangement process involving two isothiocyanate molecules:



thioimidate



dirheniathioimidate-2

Details of this study are reported here.

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Experimental Section

Unless specified otherwise, all reactions were carried out under an atmosphere of nitrogen. All solvents were appropriately dried and degassed prior to use. Ethoxycarbonyl isothiocyanate (98%) and dimethylphenylphosphine were purchased from Aldrich. 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 400 MHz on a Bruker AM-400 spectrometer. Elemental analyses were performed by Desert Analytics (Tucson, AZ). Mass spectra were carried out on a VG Model 70SQ mass spectrometer (direct inlet, electron impact ionization). $Re_2(CO)_9(MeCN)$ (**1**) was prepared by the literature method.[8]

Reaction of 1 with EtO_2CNCS. (a) A 20.0-mg amount (0.030 mmol) of $Re_2(CO)_9(MeCN)$ and a 10.6-μL amount (0.09 mmol) of $EtO_2CN{=}C{=}S$ were dissolved in 40 mL of hexane. The solution was heated to reflux for 1 h and 50 min. After the solvent was removed in vacuo, the residue was separated by TLC using a 9/2 hexane/CH_2Cl_2 solvent mixture. This yielded, in order of elution, 0.4 mg of $Re_2(CO)_{10}$, 8.8 mg of colorless $Re(CO)_4[\mu\text{-}C,S,N\text{-}EtO_2CN{=}CS]Re(CO)_4$ (**3**) in 40% yield, 1.5 mg of $Re(CO)_4[s\text{-}trans\text{-}\mu\text{-}C,S\text{-}EtO_2CN{=}CS]Re(CO)_5$ (**2**) in 7% yield, 0.5 mg of unreacted **1**, 4.3 mg of red orange $Re(CO)_4[\mu\text{-}C,N,S_2\text{-}(EtO_2C)_2NC{=}NCS_2]Re(CO)_4$ (**4**) in 17% yield, 1.3 mg of red $Re(CO)_4[\mu\text{-}C,N,S_2\text{-}(EtO_2C)_2NC{=}NCS_2]Re(CO)_3(NCMe)$ (**5**) in 5% yield, and trace amount of yellow $Re(CO)_4[\mu\text{-}C,N,S_2\text{-}(EtO_2C)(H)NC{=}NCS_2]Re(CO)_4$ (**6**). Spectral data for **2**: IR (ν_{CO} in hexane, cm^{-1}) 2139(w), 2097(w), 2076(w), 2037(vs), 2034(vs), 1995(vs), 1991(vs), 1953(s), 1524(w, br); ^{1}H NMR (δ in $CDCl_3$, ppm) 4.36 (q, $^3J_{H-H} = 7.1$ Hz, 2H, OCH_2Me), 1.36 (t, $^3J_{H-H} = 7.1$ Hz, 3H, CH_3). Anal. Calcd (Found): C, 20.66 (20.79); H, 0.67 (0.57); N, 1.85 (1.85). Spectral data for **3**: IR (ν_{CO} in hexane, cm^{-1}) 2099(m), 2011(vs), 1993(s), 1964(s), 1957(s), 1554(w, br); ^{1}H NMR (δ in $CDCl_3$, ppm) 4.34 (q, $^3J_{H-H} =$ 7.2 Hz, 2H, OCH_2Me), 1.40 (t, $^3J_{H-H} = 7.1$ Hz, 3H, CH_3). Anal. Calcd (Found): C, 19.81 (19.70); H, 0.69 (0.89); N, 1.92 (1.91). Spectral data for **4**: IR (ν_{CO} in hexane, cm^{-1}) 2104(m), 2028(s), 2016(s), 1998(s), 1969(s), 1964(s), 1956(sh, w), 1780(w, br); ^{1}H NMR (δ in $CDCl_3$, ppm) 4.40 (q, $^3J_{H-H} = 7.1$ Hz, 4H, OCH_2Me), 1.37 (t, $^3J_{H-H} = 7.1$ Hz, 6H, CH_3). Anal. Calcd (Found): C, 22.38 (22.24); H, 1.17 (1.00); N, 3.26 (3.19). Spectral data for **5**: IR (ν_{CO} in hexane, cm^{-1}) 2102(w), 2036(s), 2019(m), 2009(s), 1964(s), 1941(s), 1936(sh), 1927(m), 1780(w, br); ^{1}H NMR (δ in $CDCl_3$, ppm) 4.37 (q, $^3J_{H-H} = 7.1$ Hz, 4H, OCH_2Me), 2.34 (s, 3H, Me), 1.36 (t, $^3J_{H-H} = 7.1$ Hz, 6H, CH_3). Anal. Calcd (Found): C, 23.42 (23.33); H, 1.50 (1.70); N, 4.82 (4.48). Spectral data for **6**: IR (ν_{CO} in hexane, cm^{-1}) 2102(m), 2020(vs), 2013(sh), 2000(s), 1976(m), 1949(m), 1779(w, br); ^{1}H NMR (δ in $CDCl_3$, ppm) 8.32 (s, br, 1H, NH), 4.41 (q, $^3J_{H-H} = 7.2$ Hz, 2H, OCH_2Me), 1.41 (t, $^3J_{H-H} = 7.2$ Hz, 3H, CH_3); MS parent ion $m/e = 786$ and ions corresponding to the loss of each of the eight carbonyl ligands.

(b) A 20.0-mg amount (0.030 mmol) of $Re_2(CO)_9(MeCN)$ and a 106.0-μL amount (0.90 mmol) of EtO_2CNCS were dissolved in 40 mL of hexane. The solution was heated to reflux for 1 h and 50 min. After the solvent was removed in vacuo, the residue was separated by TLC using a 9/2 hexane/CH_2Cl_2 solvent mixture. This yielded, in order of elution, 0.3 mg of $Re_2(CO)_{10}$, 0.6 mg of **3** in 3% yield, 0.1 mg of **2**, 8.0 mg of **4** in 31% yield, and 1.2 mg of **5** in 5% yield.

Conversion of 2 to 3. A 10.0-mg amount (0.013 mmol) of **2** was dissolved in 15 mL of hexane. The solution was heated to reflux for 2 h. After the solvent was removed in vacuo, the residue was separated by TLC using a 4/1 hexane/CH_2Cl_2 solvent mixture. This yielded, in order of elution, 7.8 mg of colorless **3** in 81% yield and 1.8 mg of unreacted starting material.

Attempted Reaction of 2 with EtO_2CNCS. A 10.0-mg amount (0.013 mmol) of **2** and a 32.0-μL amount (0.28 mmol) of EtO_2CNCS were dissolved in 20 mL of hexane. The solution was heated to 50 °C for 21 h. After the solvent was removed in vacuo, the residue was separated by TLC using a 3/1 hexane/CH_2Cl_2 solvent mixture. This yielded, in order of elution, 6.4 mg of **3** and 2.6 mg of unreacted **2**.

Attempted Reaction of 3 with EtO_2CNCS. A 11.0-mg amount (0.015 mmol) of **3** and a 25.0-μL amount (0.21 mmol) of EtO_2CNCS were dissolved in 25 mL of hexane. The solution was heated to reflux for 24 h. After the solvent was removed in vacuo, the residue was separated by TLC using a 3/1 hexane/CH_2Cl_2 solvent mixture. **3** (7.6 mg) was recovered plus several products all in trace amounts.

Conversion of 4 to 5. A 20.0-mg amount (0.023 mmol) of **4** and a 12.5-μL amount (0.23 mmol) of MeCN were dissolved in 25 mL of hexane, and the solution was then heated to reflux for 4 h. After cooling and removal of the solvent in vacuo, the residue was separated by TLC using a 2/1 hexane/CH_2Cl_2 solvent mixture. This yielded, in order of elution, 2.7 mg of starting material and 16.4 mg of **5** in 80% yield.

Carbonylation of Compound 3. A 100.0-mg amount (0.020 mmol) of **3** was dissolved in 5 mL of CH_2Cl_2 and placed in a Parr high-pressure reaction vessel. The vessel was pressurized with 1100 psi of CO, and the solution was stirred at 25 °C for 35 h. After venting, the solvent was removed in vacuo and the residue was separated by TLC using a 4/1 hexane/CH_2Cl_2 solvent mixture. This yielded, in order of elution, 30.2 mg of starting material and 70.7 mg of colorless $Re(CO)_5[\mu\text{-}C,S,N\text{-}(EtO_2C)N{=}CS]Re(CO)_4$ (**7**) in 68% yield. Spectral data for **7**: IR (ν_{CO} in hexane, cm^{-1}) 2143(w), 2101(w), 2076(w), 2038(vs), 2006(s), 1999(s), 1989(s), 1952(s), 1701(w, br); ^{1}H NMR (δ in $CDCl_3$, ppm) 4.16 (q, $^3J_{H-H} = 7.1$ Hz, 2H, OCH_2Me), 1.34 (t, $^3J_{H-H} = 7.1$ Hz, 3H, CH_3). Anal. Calcd (Found): C, 20.66 (20.73); H, 0.67 (0.60); N, 1.85 (1.77).

Decarbonylation of 7. A 10.0-mg amount (0.013 mmol) of **7** was dissolved in 15 mL of hexane. The solution was heated to reflux for 30 min. IR spectra indicated that all of the starting material was converted to compound **3**. After the solvent was removed in vacuo, the residue was separated by TLC using a 4/1 hexane/CH_2Cl_2 solvent mixture. This yielded 9.1 mg of colorless **3** in 95% yield.

Attempted Reaction of 7 with EtO_2CNCS. A 10.0-mg amount (0.013 mmol) of **7** and a 1.9-μL amount (0.016 mmol) of EtO_2CNCS were dissolved in 15 mL of hexane. The solution was heated to reflux for 30 min. After the solvent was removed, the residue was separated by TLC using a 4/1 hexane/CH_2Cl_2 solvent mixture. This yielded 9.0 mg of **3** in 94% yield.

Reaction of $Re_2(CO)_8(PPhMe_2)(NCMe)$ with EtO_2CNCS. $Re_2(CO)_8(PPhMe_2)(NCMe)$ was prepared in situ by the reaction of $Re_2(CO)_9(PPhMe_2)$ with Me_3NO in the presence of NCMe by the procedure used by Coville.[9] A 250-mL three-neck flask containing a 150.0-mg amount (0.20 mmol) of $Re_2(CO)_9(PPhMe_2)$ and a 17.5-mg amount (0.23 mmol) of Me_3NO in 100 mL of MeCN was stirred at 25 °C for 30 min. The solvent was removed under vacuum, and 200 mL of hexane was introduced into the flask. A 71.0-μL amount (0.59 mmol) of newly distilled EtO_2CNCS was then added via syringe, and the mixture was stirred at 25 °C for 8 h. The solvent was removed via rotary evaporation, and the residue was separated by TLC using a 1/4 hexane/CH_2Cl_2 solvent mixture. This yielded, in order of elution, 6.5 mg of pale yellow $Re_2(CO)_8(PPhMe_2)(\mu\text{-}EtO_2CNCS)$ (**10**) in 4% yield, 62.3 mg of orange *cis*-$Re_2(CO)_8(PPhMe_2)(EtO_2CNCS)_2$ (**9**) in 32% yield, and 71.3 mg of orange *trans*-$Re_2(CO)_8(PPhMe_2)(EtO_2CNCS)_2$ (**8**) in 36% yield. Spectral data for **8**: IR (ν_{CO} in CH_2Cl_2, cm^{-1}) 2098(m), 2045(w), 2003(vs), 1992(vs), 1948(s), 1768(w, br), 1705(w, br), 1582(w, br); ^{1}H NMR (δ in $CDCl_3$, ppm) 7.49 (m, 5H, C_6H_5), 4.44 (q, $^3J_{H-H} = 7.2$ Hz, 2H, OCH_2Me), 4.22 (q, $^3J_{H-H} = 7.2$ Hz, 2H, OCH_2Me), 2.02 (d, $^3J_{P-H} = 9.0$ Hz, 6H, P$(CH_3)_2$), 1.38

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(t, $^3J_{\mathrm{H-H}} = 7.2$ Hz, 3H, CH_3), 1.31 (t, $^3J_{\mathrm{H-H}} = 7.2$ Hz, 3H, CH_3). Anal. Calcd (Found): C, 28.91 (29.14); H, 2.12 (1.86); N, 2.79 (2.79). Spectral data for **9**: IR (ν_{CO} in CH_2Cl_2, cm^{-1}) 2107(m), 2099(m), 2021(sh), 2007(vs), 1965(sh), 1951(s), 1770(w, br), 1710(w, br), 1584(w, br); ^{1}H NMR (δ in $CDCl_3$, ppm) 7.47 (m, 5H, C_6H_5), 4.43 (q, $^3J_{\mathrm{H-H}} = 7.2$ Hz, 2H, OCH_2Me), 4.22 (q, $^3J_{\mathrm{H-H}} = 7.2$ Hz, 2H, OCH_2Me), 2.02 (d, $^3J_{\mathrm{P-H}} = 9.0$ Hz, 6H, $P(CH_3)_2$), 1.38 (t, $^3J_{\mathrm{H-H}} = 7.2$ Hz, 3H, CH_3), 1.31 (t, $^3J_{\mathrm{H-H}} = 7.2$ Hz, 3H, CH_3). Anal. Calcd (Found): C, 28.91 (28.87); H, 2.12 (2.06); N, 2.79 (2.71). Spectral data for **10**: IR (ν_{CO} in hexane, cm^{-1}) 2100(m), 2089(m), 2029(w), 2020(sh), 2016(m), 1995(s), 1985(s), 1949(s), 1516(w, br); ^{1}H NMR (δ in $CDCl_3$, ppm) 7.48 (m, 5H, C_6H_5), 4.41 (q, $^3J_{\mathrm{H-H}} = 7.2$ Hz, 2H, OCH_2Me), 2.02 (d, $^3J_{\mathrm{P-H}} = 8.9$ Hz, 6H, $P(CH_3)_2$), 1.34 (t, $^3J_{\mathrm{H-H}} = 7.1$ Hz, 3H, CH_3); MS parent ion $m/e = 867$ (for ^{187}Re) and ions corresponding to the loss of each of the eight carbonyl ligands.

Pyrolysis of 9. A 50.0-mg amount (0.050 mmol) of **9** was dissolved in 80 mL of heptane and heated to reflux for 2 h. After the solvent was removed via rotary evaporation, the residue was separated by TLC using a 1/1 hexane/CH_2Cl_2 solvent mixture to yield, in order of elution, 4.0 mg of yellow $Re(CO)_3(PPhMe_2)(\mu\text{-}S_2CNCO_2Et)Re(CO)_3(PPhMe_2)$ (**12**) in 8% yield, 25.1 mg of dark red $Re(CO)_4[\mu\text{-}C,N,S_2\text{-}(EtO_2C)_2\text{-}NC{=}NCS_2]Re(CO)_3(PMe_2Ph)$ (**11**) in 52% yield, 0.8 mg of **4**, and 1.9 mg of unreacted **9**. Spectral data for **11**: IR (ν_{CO} in hexane, cm^{-1}) 2104(w), 2032(s), 2022(s), 2014(s), 2008(s), 1964(s), 1961(s), 1946(s), 1925(m), 1919(m), 1779(w, br); ^{1}H NMR (δ in $CDCl_3$, ppm) 7.44 (m, 5H, C_6H_5), 4.42 (br, 2H, OCH_2Me), 4.28 (q, br, $^3J_{\mathrm{H-H}} = 7.2$ Hz, 2H, OCH_2Me), 1.80 (d, $^3J_{\mathrm{P-H}} = 9.3$ Hz, 3H, PCH_3), 1.74 (d, $^3J_{\mathrm{P-H}} = 9.3$ Hz, 3H, PCH_3), 1.33 (t, $^3J_{\mathrm{H-H}} = 7.1$ Hz, 6H, CH_3). Anal. Calcd (Found): C, 28.51 (28.73); H, 2.19 (2.08); N, 2.89 (2.86). Spectral data for **12**: IR (ν_{CO} in hexane, cm^{-1}) 2032(m), 2021(s), 1941(s), 1926(m), 1912(vs), 1591(w, br); ^{1}H NMR (δ in $CDCl_3$, ppm) 7.38 (m, 10H, C_6H_5), 3.29 (dq, $^3J_{\mathrm{H-H}} = 7.2$ Hz, 1H, $OCHHMe$), 2.96 (dq, $^3J_{\mathrm{H-H}} = 7.2$ Hz, 1H, $OCHHMe$), 1.92 (d, $^3J_{\mathrm{P-H}} = 8.4$ Hz, 3H, PCH_3), 1.89 (d, $^3J_{\mathrm{P-H}} = 8.4$ Hz, 3H, PCH_3), 1.82 (d, $^3J_{\mathrm{P-H}} = 8.4$ Hz, 3H, PCH_3), 1.80 (d, $^3J_{\mathrm{P-H}} = 8.4$ Hz, 3H, PCH_3), 0.98 (t, $^3J_{\mathrm{H-H}} = 7.2$ Hz, 3H, CH_3). Anal. Calcd (Found): C, 31.87 (31.89); H, 2.78 (2.73); N, 1.43 (1.48).

Crystallographic Analyses. Crystals of **2** suitable for X-ray diffraction analysis were obtained by slow evaporation of solvent from a solution in a 2/1 hexane/CH_2Cl_2 solvent mixture at 25 °C. Crystals of **3**, **5**, **7**, and **8** were obtained similarly from a solution in a 1/1 hexane/CH_2Cl_2 solvent mixture. Crystals of **4**, **9**, and **11** were each obtained by slow evaporation of solvent from solutions in diethyl ether at −14 °C. Crystals of **6** suitable for X-ray diffraction analysis were obtained by slow evaporation of solvent from a solution in benzene solvent at room temperature. Crystals of **12** were obtained by slow evaporation of solvent from solutions in hexane at room temperature. The crystals used in intensity measurements were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromated Mo Kα radiation. The unit cells were determined and refined from 15 randomly selected reflections obtained by using the AFC6S automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of these analyses are listed in Table 1. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer or an SGI Indigo2 computer by using the TEXSAN structure-solving program libraries obtained from the Molecular Structure Corp. (The Woodlands, TX). Neutral atom scattering factors were calculated by the standard procedures.[10a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[10b] Lorentz polarization (Lp) and absorption corrections were applied in each analysis. Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(|F_o| - |F_c|)^2$,

Table 1. Crystallographic Data for Compounds 2−8, 9, 11, and 12[a]

	2	3	4	5	6	7	8	9	11	12
formula	Re_2SO_{11}-$NC_{13}H_5$	Re_2SO_{10}-$NC_{12}H_5$	$Re_2S_2O_{12}$-$N_2C_{16}H_{10}$	$Re_2S_2O_{11}$-$N_3C_{17}H_{13}$	$Re_2S_2O_{10}$-$N_2C_{13}H_6$	Re_2SO_{11}-$NC_{13}H_5$	$Re_2S_2PO_{12}$-$N_2C_{24}H_{21}$	$Re_2S_2PO_{12}$-$N_2C_{24}H_{21}$	$Re_2S_2PO_{11}$-$N_2C_{23}H_{21}$	$Re_2S_2P_2O_8$-$NC_{26}H_{27}$
formula weight	755.66	727.65	858.80	871.84	786.73	755.66	996.94	996.94	968.93	979.98
crystal system	triclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	triclinic	monoclinic
lattice parameters										
a (Å)	10.476(2)	10.132(2)	10.703(3)	9.181(1)	6.452(1)	6.820(1)	12.805(2)	12.546(2)	11.796(2)	11.082(2)
b (Å)	14.386(2)	10.417(2)	12.365(4)	17.066(2)	16.784(4)	23.550(4)	13.499(2)	11.010(2)	14.084(2)	21.450(3)
c (Å)	6.865(1)	9.994(1)	10.271(3)	16.384(2)	19.007(2)	25.091(4)	10.530(2)	24.312(5)	10.365(2)	13.861(2)
α (deg)	91.68(1)	98.06(1)	108.46(2)	90.0	90.0	90.0	98.46(1)	90.0	91.18(1)	
β (deg)	92.19(1)	94.38(1)	109.44(2)	97.73(1)	90.79(1)	93.94(1)	92.72(1)	99.55(1)	113.21(1)	94.78(1)
γ (deg)	109.30(1)	62.03(1)	89.84(3)	90.0	90.0	90.0	65.57(1)	90.0	102.40	
V (Å^3)	974.7(2)	922.4(3)	1207.8(6)	2543.8(5)	2057.8(5)	4020.4(9)	1638.9(5)	3311.6(8)	1535.1(5)	3283.2(7)
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
Z	2	2	2	4	4	8	2	4	2	4
ρ_{calcd} (g/cm^3)	2.57	2.62	2.36	2.28	2.54	2.50	2.02	2.00	2.10	1.98
μ (Mo Kα) (cm^{-1})	125.75	132.80	102.52	97.35	120.14	121.96	76.17	75.4	81.27	76.40
temperature (°C)	20	20	20	20	20	20	20	20	20	20
$2\theta_{\max}$ (deg)	45	45	47	44	43	43	47	40	44	44
no. obs. ($I > 3\sigma$)	2252	2087	2825	2043	1820	3194	4145	2541	3251	3171
goodness of fit	2.40	2.99	2.15	1.33	2.05	2.05	2.44	3.42	1.82	1.68
residuals R; R_w	0.027; 0.034	0.035; 0.042	0.034; 0.036	0.024; 0.024	0.030; 0.021	0.044; 0.042	0.034; 0.040	0.053; 0.063	0.024; 0.027	0.028; 0.029
abs. cor.	empirical	empirical	empirical	empirical	empirical	empirical	empirical	DIFABS	empirical	empirical
largest peak in final diff. map (e/Å^3)	1.54	1.42	1.06	0.46	0.90	1.93	1.09	1.17	0.74	0.72

[a] $R = \sum_{hkl}(||F_{\mathrm{obs}}| - |F_{\mathrm{calc}}||)/\sum_{hkl}|F_{\mathrm{obs}}|$; $R_w = [\sum_{hkl} w(|F_{\mathrm{obs}}| - |F_{\mathrm{calc}}|^2)/\sum_{hkl} wF_{\mathrm{obs}}^2]^{1/2}$, $w = 1/\sigma^2(F_{\mathrm{obs}})$; GOF $= [\sum_{hkl}(w(|F_{\mathrm{obs}}| - |F_{\mathrm{calc}}|)^2)/(n_{\mathrm{data}} - n_{\mathrm{vari}})]^{1/2}$.

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(10) (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, Table 2.2B, pp 99−101. (b) Reference 10a, Table 2.3.1, pp 149−150.

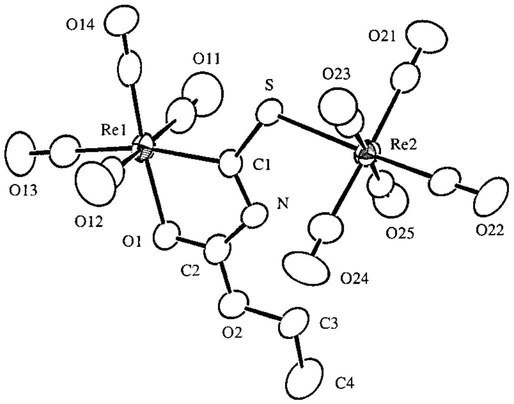


Figure 1. ORTEP diagram of $Re(CO)_4$[*s-trans*-*μ*-*C*,*S*-$EtO_2CN{=}CS$]$Re(CO)_5$ (**2**) showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): Re(1)–O(1) = 2.148(6), Re(1)–C(1) = 2.146(9), Re(2)–S = 2.497(3), Re(2)···N = 3.423(7), C(1)–S = 1.720(9), C(1)–N = 1.33(1), C(2)–N = 1.35(1); N–C(1)–S = 118.8(7), Re(2)–S–C(1) = 109.9(3), Re(1)–C(1)–S = 123.0(5), Re(1)–C(1)–N = 118.2(6).

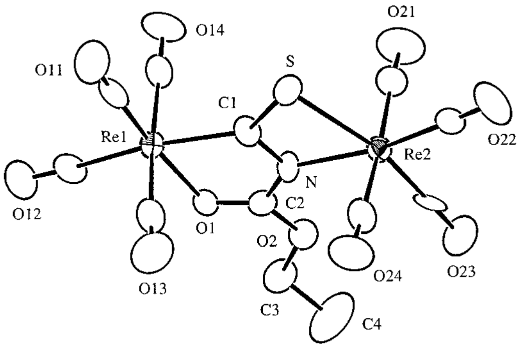


Figure 2. ORTEP diagram of $Re(CO)_4$[*μ*-*C*,*S*,*N*-$EtO_2CN{=}CS$]$Re(CO)_4$ (**3**) showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): Re(1)–O(1) = 2.178(8), Re(1)–C(1) = 2.13(1), Re(2)–S = 2.534(3), Re(2)–N = 2.172(9), C(1)–S = 1.69(1), C(1)–N = 1.38(2), C(2)–N = 1.37(2); N–C(1)–S = 109.0(8), Re(2)–S–C(1) = 82.5(4), Re(1)–C(1)–S = 137.3(7), Re(1)–C(1)–N = 113.(8).

where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$.

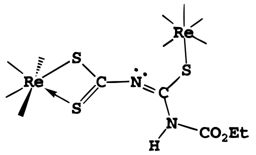
Compounds **2**, **3**, **4**, **8**, and **11** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed in each case by the successful solution and refinement of the structures. The structures were solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms on the ligands were calculated by assuming idealized geometries with all C–H distances at 0.95 Å. Their contributions were added to the structure factor calculations, but their positions were not refined.

Compounds **5**, **6**, **7**, **9**, and **12** crystallized in the monoclinic crystal system. On the basis of the patterns of systematic absences observed during the collection of data, the space group $P2_1/n$ was established for compounds **5**, **6**, and **12** and $P2_1/c$ for **7** and **9**. The structures were solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms on the ligands were calculated by assuming idealized geometries with all C–H distances at 0.95 Å. Except for the amino hydrogen atom H(2) in the structure of compound **6**, which was located and refined, the contributions of the hydrogen atoms were added to the structure factor calculations without refinement.

Results

Five new compounds were obtained from the reaction of $Re_2(CO)_9(MeCN)$ with $EtO_2CN{=}C{=}S$ in a hexane solution at reflux (68 °C). These were identified as $Re(CO)_4$[*s-trans*-*μ*-*C*,*S*-$EtO_2CN{=}CS$]$Re(CO)_5$ (**2**, 7% yield), $Re(CO)_4$[*μ*-*C*,*S*,*N*-$EtO_2CN{=}CS$]$Re(CO)_4$ (**3**, 40% yield), $Re(CO)_4$[*μ*-*C*,*N*,*S*$_2$-$(EtO_2C)_2NC{=}NCS_2$]$Re(CO)_4$ (**4**, 17% yield), $Re(CO)_4$[*μ*-*C*,*N*,*S*$_2$-$(EtO_2C)_2NC{=}NCS_2$]$Re(CO)_3(NCMe)$ (**5**, 5% yield), and $Re(CO)_4$[*μ*-*C*,*N*,*S*$_2$-$(EtO_2C)(H)NC{=}NCS_2$]$Re(CO)_4$ (**6**, trace). All five products have been characterized by a combination of IR, ^1H NMR, and elemental and single-crystal X-ray diffraction analyses.

An ORTEP diagram of the molecular structure of compound **2** is shown in Figure 1. The complex can be viewed as a dirhenium thioimidate formed by the displacement of the NCMe ligand in **1** and the insertion of the isothiocyanate molecule into the rhenium–rhenium bond. One rhenium atom is bonded to the carbon atom of the isothiocyanate ligand and the other is bonded to the sulfur atom, Re(1)–C(1) = 2.146(9) Å and Re(2)–S = 2.497(3) Å. The Re–S distance is very similar to the S–$Re(CO)_5$ bond length [2.492(4) vs 2.490(4) Å] observed for the structurally related compound $Re(CO)_4$[*μ*-$S_2CNC(N(H)CO_2Et)S$]$Re(CO)_5$ (**13**), which we obtained recently from the reaction of **1** with *N*-(ethoxycarbonyl)-5-amino-1,2,4-dithiazole-3-thione.[11] There is a *trans* conformation at the C–S bond in **2**. The C–S bond length is slightly shorter than a C–S single bond (1.80 Å), C(1)–S = 1.720(9) Å. The oxygen atom of the carbonyl group of the isothiocyanate is coordinated to the rhenium atom Re(1), Re(1)–O(1) = 2.148(6) Å, while the nitrogen atom is uncoordinated, Re(2)···N = 3.423(7) Å. There is considerable multiple bond character across the C–N–C grouping, C(1)–N = 1.33(1) Å and C(2)–N = 1.35(1) Å (C=N double bonds are typically 1.30 Å in length, while C–N single bonds are about 1.47 Å).[12]



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An ORTEP diagram of the molecular structure of compound **3** is shown in Figure 2. The complex is a simple decarbonylation product of **2**. A CO ligand was eliminated from the $Re(CO)_5$ group in **2** and a bond was then formed between the rhenium atom and the nitrogen atom of the isothiocyanate ligand. The rhenium to nitrogen distance is then reduced from 3.423(7) Å in **2** to Re(2)–N = 2.172(9) Å in **3**. The rhenium–oxygen and rhenium–carbon bond distances to the isothiocyanate ligand are similar to those in **2**, Re(1)–O(1) = 2.178(8) Å, Re(1)–C(1) = 2.13(1) Å; however, the rhenium–sulfur distance is a little longer, Re(2)–S = 2.534(3) Å, and the carbon–sulfur distance, C(1)–S = 1.69(1) Å, is a little shorter.

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(11) Adams, R. D.; Huang, M. *Organometallics* **1996**, *15*, 2125.

(12) Sandorfy, C. In *The Chemistry of the Carbon-Nitrogen Double Bond*; Patai, S., Ed.; Interscience: New York, 1970; Chapter 1.

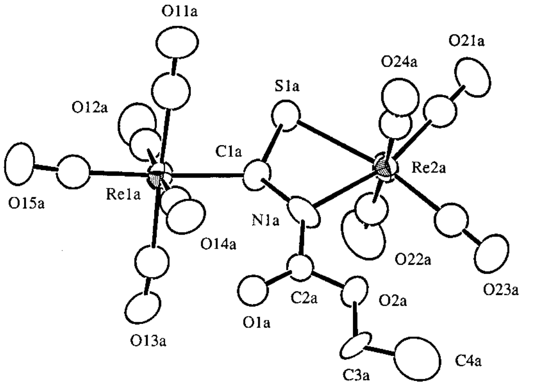


Figure 3. ORTEP diagram of Re(CO)$_5$[μ-*C*,*S*,*N*-(EtO$_2$C)N=CS]Re(CO)$_4$ (**7**) showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): Re(1a)−C(1a) = 2.17(2), Re(1b)−C(1b) = 2.19(2), Re(2a)−S(1a) = 2.472(7), Re(2b)−S(1b) = 2.484(7), Re(2a)−N(1a) = 2.20(1), Re(2b)−N(1b) = 2.19(1), C(1a)−S(1a) = 1.71(2), C(1b)−S(1b) = 1.71(2), C(1a)−N(1a) = 1.34(3), C(1b)−N(1b) = 1.32(3), C(2a)−N(1a) = 1.40(2), C(2b)−N(1b) = 1.41(2); N(1a)−C(1a)−S(1a) = 106(1), N(1b)−C(1b)−S(1b) = 107(2), Re(2a)−S(1a)−C(1a) = 85.0(8), Re(2b)−S(1b)−C(1b) = 83.6(8), Re(1a)−C(1a)−S(1a) = 119(1), Re(1b)−C(1b)−S(1b) = 118(1), Re(1a)−C(1a)−N(1a) = 135(1), Re(1b)−C(1b)−N(1b) = 134(1).

Compound **3** was obtained independently from **2** in 81% yield simply by heating a solution of **2** in hexane to reflux for 2 h. Interestingly, the addition of CO to **3** at 1100 psi at 25 °C did not result in the regeneration of **2**, but instead resulted in the formation of a new compound Re(CO)$_5$[μ-*C*,*S*,*N*-(EtO$_2$C)N=CS]Re(CO)$_4$ (**7**) in 68% yield. The molecular structure of **7** was also established crystallographically. Compound **7** crystallizes with two independent molecules in the asymmetric crystal unit. Both molecules are structurally similar, and an ORTEP diagram of one of these is shown in Figure 3. Compound **7** is an isomer of **2**. The principal difference is that the Re(CO)$_5$ group is attached to the carbon atom of the isothiocyanate in **7** rather than the sulfur atom in **2**. The rhenium−carbon distance is slightly longer than that in **2**, Re(1)−C(1) = 2.17(2) Å [2.19(2) Å], and the rhenium−sulfur distance is slightly shorter, Re(2)−S(1) = 2.472(7) Å [2.484(7) Å]. In both cases this may be due to chelation effects, with bond shortening occurring in the presence of chelation. The rhenium−nitrogen, carbon−sulfur, and carbon−nitrogen distances are not significantly different: Re(2)−N(1) = 2.20(1) Å [2.19(1) Å], C(1)−S(1) = 1.71(2) Å [1.71(2) Å], C(1)−N(1) = 1.34(3) Å [1.32(3) Å], and C(2)−N(1) = 1.40(2) Å [1.41(2) Å]. The transformation of **3** to **7** is fairly easy to explain: it involves simply the displacement of the coordinated oxygen atom of the carbonyl group in **3** and the addition of CO to that site. When heated to 68 °C in hexane solvent, compound **7** loses CO and is transformed back into **3** in high yield.

An ORTEP diagram of the molecular structure of compound **4** is shown in Figure 4. This complex contains a (EtO$_2$C)$_2$NC=NCS$_2$ ligand inserted between two Re(CO)$_4$ groups. One Re(CO)$_4$ group is chelated by an N−C−S group to form a four-membered ring, Re(2)−S(1) = 2.516(3) Å, Re(2)−N(1) = 2.201(8) Å, C(1)−S(1) = 1.68(1) Å, and C(1)−N(1) = 1.43(1) Å, while the other is chelated by a C−N−C−S group to form a five-membered ring, Re(1)−S(2) = 2.472(3) Å, Re(1)−C(2) = 2.13(1) Å, C(1)−S(2) = 1.67(1) Å, and C(2)−N(1) = 1.28(1) Å. Both rings have the C(1)−N(1) bond in common. The bonding in **4** could be represented by any of the resonance structures: **4a**,**b** or the zwitterion **4c**. The carbon C(2) could be viewed as a carbene center (**4a** form), but on the basis of observed bond distances the **4c** structure seems to be the best representation.

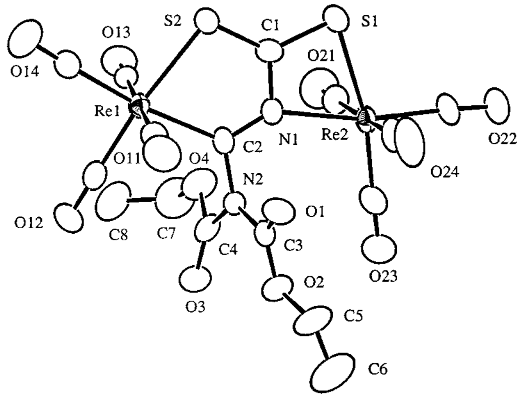
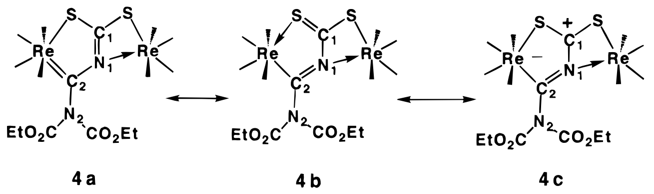


Figure 4. ORTEP diagram of Re(CO)$_4$[μ-*C*,*N*,*S*$_2$-(EtO$_2$C)$_2$-NC=NCS$_2$]Re(CO)$_4$ (**4**) showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): Re(1)−S(2) = 2.472(3), Re(1)−C(2) = 2.13(1), Re(2)−S(1) = 2.516(3), Re(2)−N(1) = 2.201(8), C(1)−S(1) = 1.68(1), C(1)−S(2) = 1.67(1), C(1)−N(1) = 1.43(1), C(2)−N(1) = 1.28(1), C(2)−N(2) = 1.47(1); S(1)−C(1)−S(2) = 128.5(7), N(1)−C(1)−S(1) = 109.9(7), N(1)−C(1)−S(2) = 121.6(8), Re(2)−N(1)−C(2) = 140.7(8), Re(1)−C(2)−N(2) = 124.7(6).



The planarity of the nitrogen atom N(2) can be attributed to π-interactions of the lone pair of electrons on that nitrogen atom with the two carboxylate groups; the C(2)−N(2) bond is single [1.47(1) Å]. However, the plane of the amino group is twisted 75.6° from the plane of the NC=NCS$_2$ group. This is probably a result of steric interactions with the proximate CO ligands C(12)−O(12) and C(23)−O(23) on the metal atoms.

The composition of the (EtO$_2$C)$_2$NC=NCS$_2$ ligand is equivalent of two formula units of EtO$_2$CN=C=S. However, considerable rearrangement was required to produce the final result. In particular, the nitrogen atom N(2) contains two CO$_2$Et groups, N(1) has no CO$_2$Et groups, and carbon C(1) contains two sulfur atoms. Interestingly, however **4** was not obtained when solutions of **2** or **3** were allowed to react with a second equivalent of EtO$_2$CN=C=S. The mechanism of the formation of the (EtO$_2$C)$_2$NC=NCS$_2$ ligand will be described in the following.

Compounds **5** and **6** are closely related to **4**. ORTEP diagrams of the molecular structures of these two products are shown in Figures 5 and 6, respectively. Compound **5** differs from **4** by the presence of a NCMe ligand coordinated to rhenium atom Re(2) in the place of a carbonyl ligand. Interestingly, compound **5** is readily obtained from **4** in 80% yield by reaction with NCMe in a hexane solution at reflux for 4 h. There are

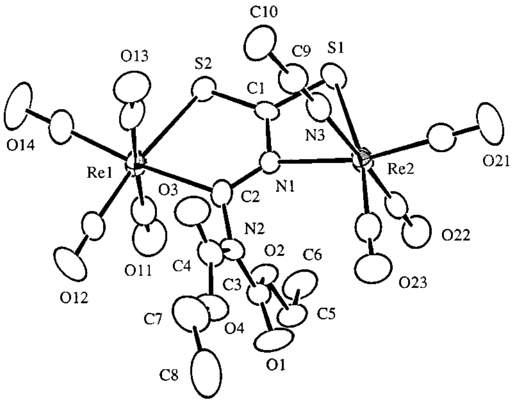


Figure 5. ORTEP diagram of Re(CO)$_4$[μ-*C*,*N*,*S*$_2$-(EtO$_2$C)$_2$NC=NCS$_2$]Re(CO)$_3$(NCMe) (**5**) showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): Re(1)−S(2) = 2.473(3), Re(1)−C(2) = 2.14(1), Re(2)−S(1) = 2.508(3), Re(2)−N(1) = 2.195(7), C(1)−S(1) = 1.69(1), C(1)−S(2) = 1.68(1), C(1)−N(1) = 1.39(1), C(2)−N(1) = 1.30(1), C(2)−N(2) = 1.46(1); S(1)−C(1)−S(2) = 127.3(6), N(1)−C(1)−S(1) = 110.0(7), N(1)−C(1)−S(2) = 122.7(7), Re(2)−N(1)−C(2) = 139.2(7), Re(1)−C(2)−N(2) = 124.4(7).

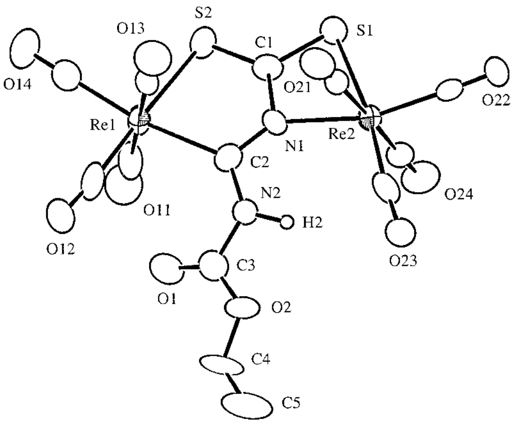


Figure 6. ORTEP diagram of Re(CO)$_4$[μ-*C*,*N*,*S*$_2$-(EtO$_2$C)(H)NC=NCS$_2$]Re(CO)$_4$ (**6**) showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): Re(1)−S(2) = 2.473(3), Re(1)−C(2) = 2.19(1), Re(2)−S(1) = 2.500(3), Re(2)−N(1) = 2.225(9), C(1)−S(1) = 1.70(1), C(1)−S(2) = 1.68(1), C(1)−N(1) = 1.40(1), C(2)−N(1) = 1.32(1), C(2)−N(2) = 1.37(1); S(1)−C(1)−S(2) = 125.2(7), N(1)−C(1)−S(1) = 110.4(9), N(1)−C(1)−S(2) = 124.4(9), Re(2)−N(1)−C(2) = 140.6(9), Re(1)−C(2)−N(2) = 130(1).

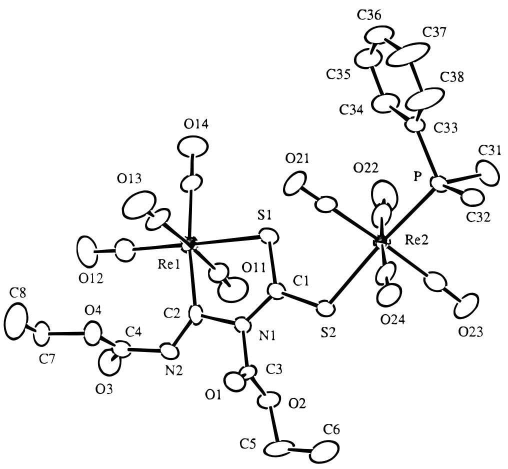


Figure 7. ORTEP diagram of *trans*-Re(CO)$_4$[μ-*C*,*N*,*S*$_2$-(EtO$_2$C)N=CN(CO$_2$Et)CS$_2$]Re(CO)$_5$ (**8**) showing 50% probability thermal ellipsoids. Selected itneratomic distances (Å) and angles (deg): Re(1)−S(1) = 2.466(2), Re(1)−C(2) = 2.16(1), Re(2)−S(2) = 2.493(2), N(1)−C(1) = 1.36(1), Re(2)−P = 2.411(2), N(1)−C(2) = 1.46(1), S(1)−C(1) = 1.69(1), S(2)−C(1) = 1.709(8), N(2)−C(2) = 1.30(1); S(1)−Re(1)−C(2) = 79.8(2); S(1)−C(1)−N(1) = 119.8(6), S(2)−Re(2)−P = 174.88(7), S(2)−C(1)−N(1) = 115.7(6), Re(1)−S(1)−C(1) = 101.2(3), Re(1)−C(2)−N(1) = 116.8(6), Re(2)−S(2)−C(1) = 114.1(3), Re(1)−C(2)−N(2) = 133.9(6), N(1)−C(2)−N(2) = 109.0(8), C(1)−N(1)−C(2) = 121.5(7), C(1)−N(1)−C(3) = 120.6(7), C(2)−N(1)−C(3) = 117.1(7), C(2)−N(2)−C(4) = 120.3(8), S(1)−C(1)−S(2) = 124.5(5).

no significant differences between any of the corresponding bond distances in **4** and **5**.

Compound **6** is a trace product. The only difference between **4** and **6** is that **6** has only one CO$_2$Et group bonded to the nitrogen atom N(2). This change has resulted in some changes in the bond distance parameters in bonds proximate to N(2). In particular, the distances Re(1)−C(2) = 2.19(1) Å and C(2)−N(1) = 1.32(1) Å have increased significantly in length, while the C(2)−N(2) distance of 1.37(1) Å is significantly shorter than that in **4** and **5**. This can be explained by a release of π-electron density from the nitrogen atom into the C(2)−N(1) bond when one of the carboxylate groups in **4** is replaced by the hydrogen atom. This leads to an increase in the C(2)−N(2) bond order and in turn a decrease in the bond order of other bonds involving C(2), as indicated by the larger bond distances to this atom. This also leads to a significant rotation of the N(H)CO$_2$Et relative to the NC=NCS$_2$ plane. The dihedral angle between these two planes is reduced to 18.4° in this case. The hydrogen atom H(2) on the nitrogen atom N(2) was located and refined in the structural analysis. It exhibits a characteristic deshielded and broad resonance in the ^{1}H NMR spectrum (δ 8.32).

To try to obtain further information about the character of these reactions, we have investigated the reaction of the phosphine derivative of **1**, Re(CO)$_4$(PMe$_2$Ph)Re(CO)$_4$(NCMe), with EtO$_2$CN=C=S. Two isomeric products, *trans*-Re(CO)$_4$(PMe$_2$Ph)[μ-(EtO$_2$C)N=CN(CO$_2$Et)CS$_2$]Re(CO)$_4$ (**8**) and *cis*-Re(CO)$_4$(PMe$_2$Ph)[μ-(EtO$_2$C)N=CN(CO$_2$Et)CS$_2$]Re(CO)$_4$ (**9**), were obtained in 36% and 32% yields, respectively, plus a small amount of the compound Re$_2$(CO)$_8$(PPhMe$_2$)(μ-EtO$_2$CNCS) (**10**) in 4% yield. Compounds **8** and **9** were characterized by single-crystal X-ray diffraction analysis. ORTEP diagrams of the molecular structures of these two products are shown in Figures 7 and 8, respectively. Both compounds contain Re(CO)$_4$(PMe$_2$Ph) and Re(CO)$_4$ groups linked by a (EtO$_2$C)N=CN(CO$_2$Et)CS$_2$ ligand. In both cases, one sulfur atom is terminally coordinated to the Re(CO)$_4$(PMe$_2$Ph) in a manner similar to that observed in **2** and **13**. The Re−S distances are similar in all four cases, with Re(1)−S(1) = 2.466(2) Å in **8** and Re(1)−S(1) = 2.478(5) Å in **9**. The Re(CO)$_4$ group is chelated by a group of four atoms C−N−C−S to form a five-membered metallacycle similar to that found in compounds **4**−**6**. The major difference between compounds **8** and **9** and compounds **4**−**6** is that both nitrogen atoms in **8** and **9** contain one CO$_2$Et group, whereas in **4**−**6** the coordinated nitrogen atom has none and the uncoordinated nitrogen atom has two CO$_2$Et groups. The C(2)−N(2) bonds in **8** and **9** are double, C(2)−N(2) = 1.30(1) and 1.27(2) Å, respectively, and are significantly

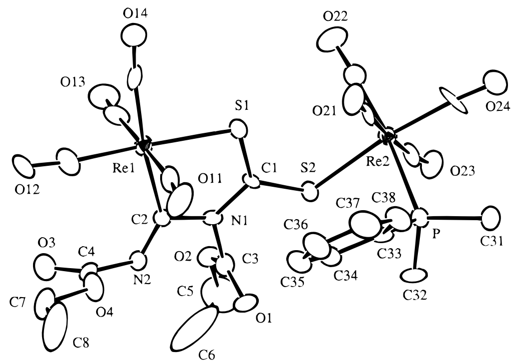


Figure 8. ORTEP diagram of *cis*-Re(CO)$_4$[μ-*C*,*N*,*S*$_2$-(EtO$_2$C)N=CN(CO$_2$Et)CS$_2$]Re(CO)$_4$(PMe$_2$Ph) (**9**) showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): Re(1)−S(1) = 2.478(5), Re(1)−C(2) = 2.16(2), Re(2)−S(2) = 2.499(5), N(1)−C(1) = 1.36(2), Re(2)−P = 2.471(6), N(1)−C(2) = 1.45(2), S(1)−C(1) = 1.69(2), S(2)−C(1) = 1.69(2), N(2)−C(2) = 1.27(2); S(1)−Re(1)−C(2) = 79.6(5); S(1)−C(1)−N(1) = 118(1), S(2)−Re(2)−P = 83.4(2), S(2)−C(1)−N(1) = 117(1), Re(1)−S(1)−C(1) = 101.6(6), Re(1)−C(2)−N(1) = 115(1), Re(2)−S(2)−C(1) = 115.8(6), Re(1)−C(2)−N(2) = 136(1), N(1)−C(2)−N(2) = 109(2), C(1)−N(1)−C(2) = 124(1), C(1)−N(1)−C(3) = 119(2), C(2)−N(1)−C(3) = 116(2), C(2)−N(2)−C(4) = 122(2), S(1)−C(1)−S(2) = 125(1).

shorter than those in **4**, **5**, and even **6**, while C(2)−N(1) is double in **4**−**6** [1.28(1) Å in **4**] and significantly shorter than those in **8** and **9**, which are single, C(2)−N(1) = 1.46(1) and 1.45(2) Å, respectively. The principal difference between **8** and **9** is the position of the phosphine ligand relative to the sulfur atom. In **8** it is *trans* to the Re−S bond, while in **9** it is *cis*. The Re−P bond distance in **8** is much shorter than that in **9**, Re(2)−P = 2.411(2) Å vs Re(2)−P = 2.471(6) Å, probably due to a steric effect in **9**.

When heated to 97 °C in heptane solution, compound **9** was transformed into two new compounds: Re(CO)$_4$[μ-*C*,*N*,*S*$_2$-(EtO$_2$C)$_2$NC=NCS$_2$]Re(CO)$_3$(PMe$_2$Ph) (**11**) in 52% yield and Re(CO)$_3$(PPhMe$_2$)(μ-S$_2$C=NCO$_2$Et)Re(CO)$_3$(PPhMe$_2$) (**12**) in 8% yield. Both compounds were characterized crystallographically. An ORTEP drawing of the molecular structure of **11** is shown in Figure 9. Compound **11** is simply a phosphine derivative of **4**. The phosphine is coordinated to the rhenium atom that is chelated by the nitrogen and sulfur atoms of the (EtO$_2$C)$_2$NC=NCS$_2$ ligand, Re(2), in a site that is *cis* to both the nitrogen and sulfur atoms. There are no significant differences between the interatomic bond distances and angles within the (EtO$_2$C)$_2$NC=NCS$_2$ ligand in **4** and **11**. Structurally, the carboxylate groups on the nitrogen atom N(2) are inequivalent. Spectroscopically, however, only one methyl resonance is observed in the ^{1}H NMR spectrum (δ 1.33). We attribute this to the existence of a dynamical exchange process involving a rotation of the N(CO$_2$Et)$_2$ grouping about the C(2)−N(2) single bond, which averages these resonances on the NMR time scale.

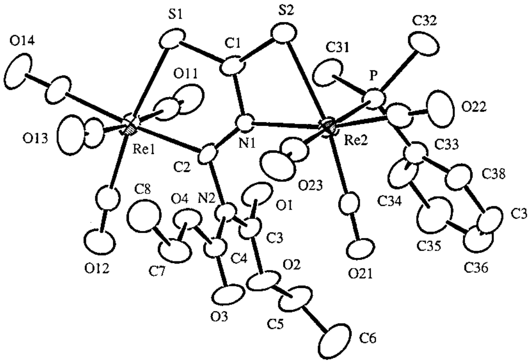


Figure 9. ORTEP diagram of Re(CO)$_4$[μ-*C*,*N*,*S*$_2$-(EtO$_2$C)$_2$NC=NCS$_2$]Re(CO)$_3$(PMe$_2$Ph) (**11**) showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): Re(1)−S(1) = 2.474(2), Re(1)−C(2) = 2.141(6), Re(2)−S(2) = 2.528(2), Re(2)−N(1) = 2.207(5), C(1)−S(1) = 1.697(7), C(1)−S(2) = 1.677(7), C(1)−N(1) = 1.421(7), C(2)−N(1) = 1.290(8), C(2)−N(2) = 1.476(7); S(1)−C(1)−S(2) = 127.6(4), N(1)−C(1)−S(1) = 121.1(5), N(1)−C(1)−S(2) = 111.3(5), Re(2)−N(1)−C(2) = 141.2(4), Re(1)−C(2)−N(2) = 123.7(4).

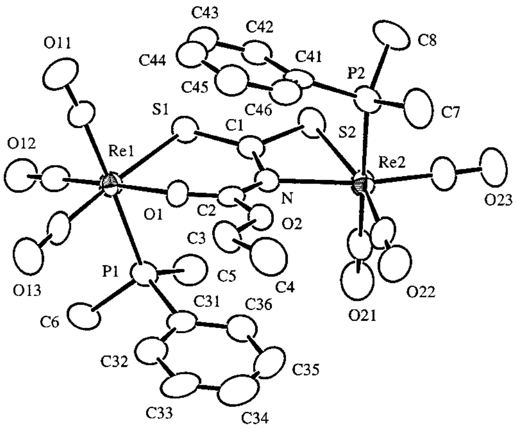
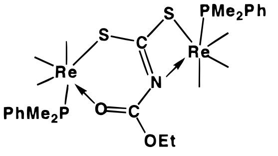
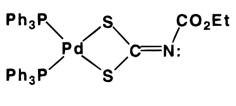


Figure 10. ORTEP diagram of Re(CO)$_3$(PPhMe$_2$)(μ-S$_2$CNCO$_2$Et)Re(CO)$_3$(PPhMe$_2$) (**12**) showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): Re(1)−S(1) = 2.476(2), Re(1)−O(1) = 2.165(5), Re(2)−S(2) = 2.522(2), Re(2)−N = 2.210(6), C(1)−S(1) = 1.686(8), C(1)−S(2) = 1.715(8), C(1)−N = 1.36(1), C(2)−N = 1.37(1); S(1)−C(1)−S(2) = 119.5(5), N−C(1)−S(1) = 131.4(6), N(1)−C(1)−S(2) = 109.1(6), Re(2)−N−C(2) = 130.0(5).

An ORTEP drawing of the molecular structure of **12** is shown in Figure 10. Compound **12** is a new member of this family of compounds. It contains a dithiocarbimato ligand S$_2$C=NCO$_2$Et in a novel tetradentate bridging coordination mode between two Re(CO)$_3$(PMe$_2$Ph) groups. The nitrogen atom and one of the sulfur atoms are chelated to one rhenium atom to form a four-membered ring, and the carbonyl oxygen of the carboxylate group and the other sulfur atom are chelate to the other sulfur atom to form a six-membered ring: Re(1)−S(1) = 2.476(2) Å, Re(1)−O(1) = 2.165(5) Å, Re(2)−S(2) = 2.522(2) Å, Re(2)−N = 2.210(6) Å. The C(1)−N and C(2)−N bonds are equal in length, 1.36(1) and 1.37(1) Å, within error, indicating the delocalization of C−N π-bonding over both C−N bonds.



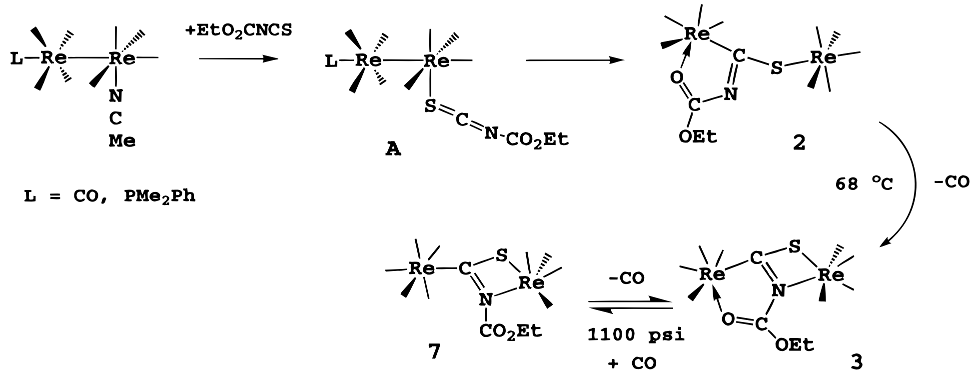
12



14

There are not many examples of complexes containing dithiocarbimato ligands. One was structurally charac-

Scheme 1



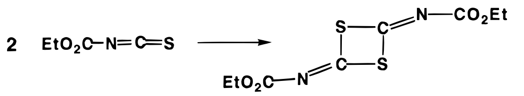
terized in the complex $Pd(S_2C{=}NCO_2Et)(PPh_3)_2$ (**14**).[13] In **14** the dithiocarbimato ligand is chelated to the palladium atom through the two sulfur atoms. The nitrogen atom is uncoordinated, and the C=N double bond is much shorter in length [1.282(5) Å].

Discussion

The reactions of **1** and $Re(CO)_4(PMe_2Ph)Re(CO)_4(NCMe)$ with $EtO_2CN{=}C{=}S$ can be understood within the framework of two competing reaction pathways. The existence of two independent product-forming pathways is implied by the observation that neither **2** nor **3** reacts with $EtO_2CN{=}C{=}S$ under the original reaction conditions to yield **4**−**6**.

The first pathway involves the interaction of 1 equiv of the dirhenium complex with 1 equiv of $EtO_2CN{=}C{=}S$ (see Scheme 1). One could imagine an intermediate **A** containing a terminally coordinated sulfur-bound isothiocyanate ligand, but compound **2** is the first isolable product, and this is a result of an insertion of the isothiocyanate into the rhenium−rhenium bond. Following the insertion the sulfur atom is bonded to the $Re(CO)_5$ grouping and the carbon atom is bonded to the $Re(CO)_4$ group. Both atoms can be viewed formally as one-electron donors. In this case, however, the $Re(CO)_4$ group needs two additional electrons to meet its 18-electron requirement. This requirement is met through the coordination of the carbonyl oxygen atom of the CO_2Et group. When heated, CO is eliminated from the $Re(CO)_5$ group and the nitrogen atom becomes coordinated to yield **3**. Interestingly, when CO is added to **3**, it occurs by displacement of the carbonyl oxygen atom to yield **7** rather than reverting back to **2**.

The second reaction pathway involves the interaction of 1 equiv of the dirhenium complex with 2 equiv of $EtO_2CN{=}C{=}S$. The coupling of the two isothiocyanate molecules must occur before the insertion step, perhaps at the stage of the intermediate **A**. This is not unreasonable since there is already evidence to indicate that carboxylate-substituted isothiocyanates can couple spontaneously in the absence of metal atoms in a manner analogous to the self-coupling of ketenes (e.g., eq 2).[14]



(2)

We believe that a similar coupling process could explain the formation of compounds **8** and **9** and, subsequently, compounds **4**−**6**. Coupling of a free isothiocyanate to the isothiocyanate ligand in compound **A** could lead to a species such as **B** containing a four-membered C−N−C−S ring (see Scheme 2). One might envisage coordination of the sulfur atom in the four-membered ring to the second rhenium atom with a concomitant cleavage of the metal−metal bond. Opening of the ring followed by bond rotation and closure by the formation of a rhenium−carbon bond would lead to the metallacyclic complexes **8** or **9**.

Subsequent decarbonylation of **8** or **9** would allow the ring nitrogen to coordinate to the 16-electron rhenium center and also activate the attached ester carbonyl group toward nucleophilic attack by the neighboring nitrogen atom (Scheme 3). Fragmentation of the resultant four-membered ring intermediate would lead to **11**. A similar process could be imagined for the formation of **4** from a fully carbonylated homolog of **8**. Moreover, the minor product **6** could also arise during this process. If the four-membered ring were to eliminate ethoxide (as in transesterifications), the resulting $N(CO_2Et)CO_2H$ moiety could readily lose CO_2 to yield **6**. Not only does this sequence of transformations provide strong support for the **B** to **4** transformation but it also establishes the chronology of some of the particular steps.

It is relevant to contrast the rearrangements that we have observed with those of Cowie and co-workers, who have shown that $EtO_2CN{=}C{=}S$ molecules undergo coupling by a sequence of reactions with the complex $Rh_2Cl_2(\mu\text{-}CO)(dpm)_2$.[6] In this case, one $EtO_2CN{=}C{=}S$ becomes coordinated to the metal atoms as a bridging ligand in the complex $Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}EtO_2CNCS)(dpm)_2$ (**15**). The second isothiocyanate is then coupled to the first via an initial coordination and formation of a carbon−nitrogen bond (Scheme 4). Via a sequence of rearrangements similar to that described above, the carboxylato group on the bridging isothiocyanate ligand is then shifted to the second nitrogen atom to yield the product $Rh_2Cl_2(\mu\text{-}CO)[\mu\text{-}(EtO_2C)_2NC{=}SNCS](dpm)_2$ (**16**). This coupled ligand is quite different from those observed in our study.

Compound **5** is derived from **4** by reaction with the NCMe that was introduced into the reaction mixture via compound **1**. The **4** to **5** transformation was confirmed independently. The formation of **12** from **8** and **9** is a side reaction and could occur by cleavage of

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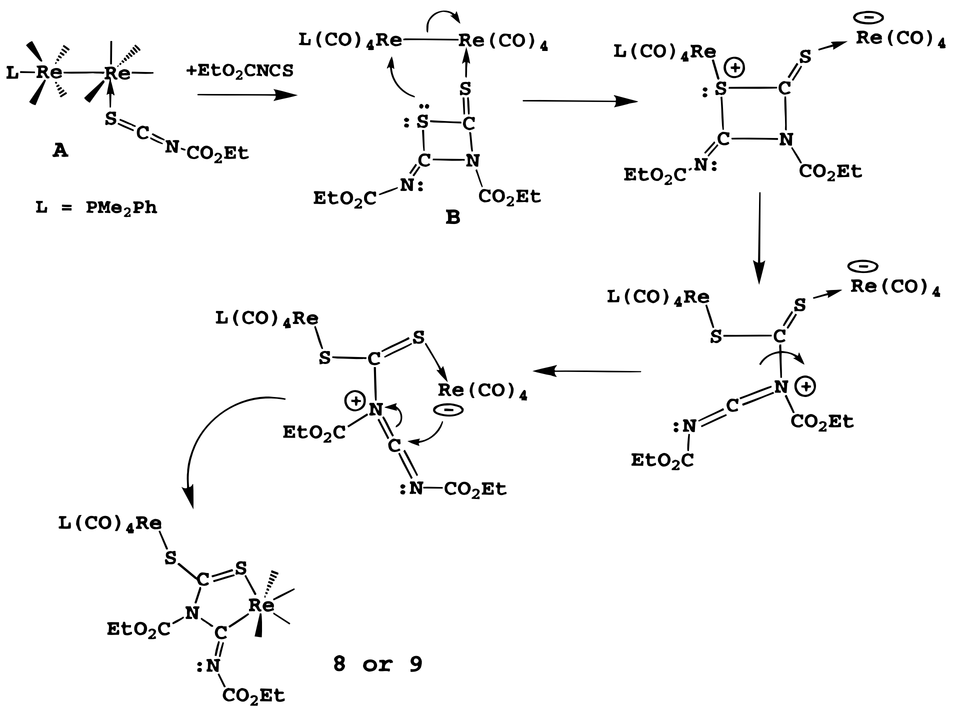
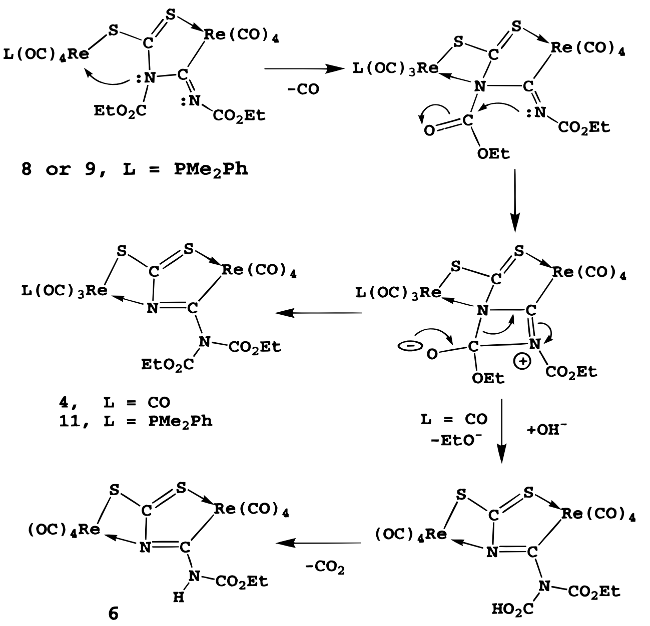
[13] Ahmed, J.; Itoh, K.; Matsuda, I.; Ueda, F.; Ishii, Y.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 620.

[14] (a) Goerdeler, J. *Q. Rep. Sulfur Chem.* **1970**, *5*, 169. (b) Ho, C. H. Diplomarbeit, Bonn, 1969.

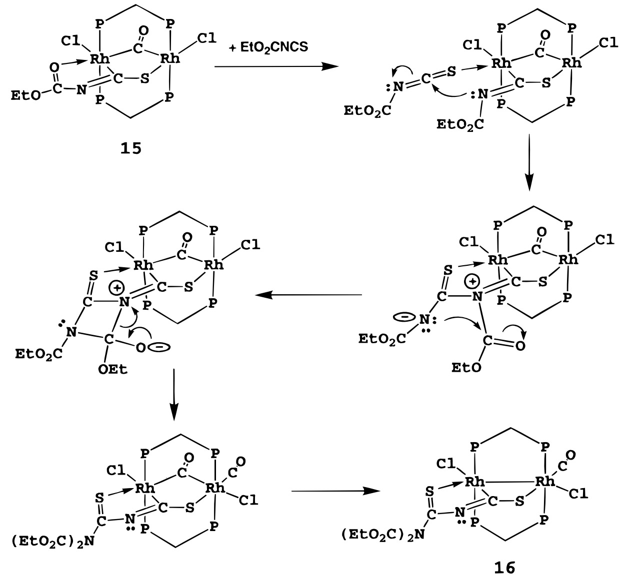
Scheme 2



Scheme 3



Scheme 4



the C−N bond in the five-membered metallacyclic ring with elimination of the (EtO$_2$C)NC grouping and the substitution of one CO ligand by a PMe$_2$Ph ligand. The (EtO$_2$C)NC group may be expelled in the form of an isocyanide, but this isocyanide, which would have been present only in very small amounts, was not detected in this reaction.

Our results demonstrate that the insertion of small molecules into the Re−Re bond of dirhenium carbonyl complexes is more general than we originally observed[1] and can lead to a variety of new metalated ligand complexes that can be transformed still further. The reactions of other dinuclear metal complexes with M−M single bonds can be anticipated to proceed similarly. Also, it seems likely that dimetalated thioimidate complexes should be susceptible to reaction with other small molecules and lead to other new ligands and new organic molecules.

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Supporting Information Available: Tables of atomic positional parameters, bond distances, bond angles, and anisotropic thermal parameters for all 10 structural analyses (77 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the American Chemical Society, and can be downloaded from the Internet. See any current masthead page for ordering information and Internet access instructions.

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