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Ring-Opening Insertion of a Substituted Dithiazole-3-thione into the Re−Re Bond in a Dirhenium Carbonyl Complex

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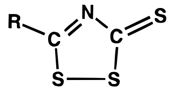
The reaction of the complex $Re_2(CO)_9(NCMe)$ with 5-((ethoxycarbonyl)amino)-1,2,4-dithiazole-3-thione (**1**) has yielded the series of complexes $Re(CO)_4[\mu\text{-}S_2CNC(N(H)CO_2Et)S]Re(CO)_5$ (**2**; 8% yield), $Re(CO)_4[\mu\text{-}S_2CNC(NHCO_2Et)S]Re(CO)_4$ (**3**; 14% yield), and $Re(CO)_4[\mu\text{-}S_2CNHC(NCO_2Et)S]Re(CO)_4$ (**4**; 27% yield) by the ring-opening insertion of **1** into the rhenium−rhenium bond of $Re_2(CO)_9(NCMe)$. The sulfur−sulfur bond in **1** was also cleaved. Two mononuclear rhenium complexes, $Re(CO)_4[S_2CNHCSNH(CO_2Et)]$ (**5**; 14% yield) and $Re(CO)_4[SCNC(NHCO_2Et)SCSN]$ (**6**; 6% yield), were also isolated and characterized. Compounds **3** and **4** are isomers that exist in an equilibrium at room temperature. The isomerization of **3** to **4** and vice versa is catalyzed by the presence of pyridine. Each of the complexes **2**−**6** as well as the starting material **1** was characterized by a single-crystal X-ray diffraction analysis.

Introduction

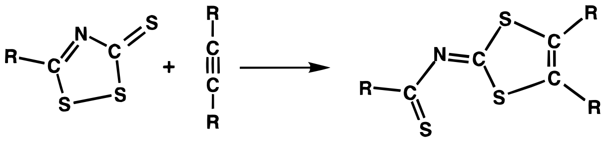
Although dithiazolethiones have been known for many years, the chemistry of these compounds has not been thoroughly investigated.[1] The lack of study of these compounds may have been due in part to their unavailability until recent years.[2]



5-R-1,2,4-dithiazole-3-thione

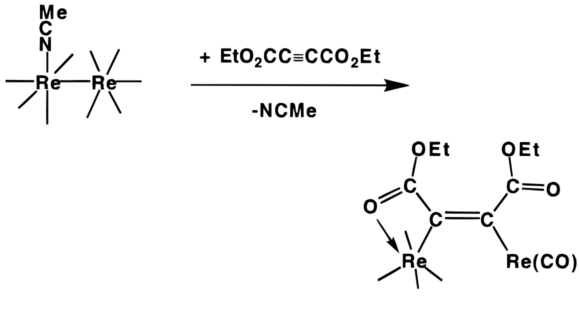
It is now known that they can be prepared by the sulfurization of carbonyl-substituted isothiocyanates[2] and, more simply, by combining the appropriate carbonyl[3] or thiocarbonyl chloride[4] with an alkali-metal isothiocyanate.

The sulfur−sulfur single bond in the five-membered ring of the dithiazole would seem to be a site susceptible to ring-opening cleavage reactions, but there are only a few examples where this reaction has been observed.[2a,5] For example, 5-substituted dithiazole-3-thiones have been found to react with alkynes, olefins, and dialkylcyanamides by a ring-opening cycloaddition to the thione sulfur atom and the sulfur atom at the 2-position in the ring (e.g. eq 1).[5] Studies of the coordination chemistry of dithiazole-3-thiones are very few.[6] 5-Amino-1,2,4-dithiazole-3-thione has been shown to chelate to bismuth via the thione sulfur atom and the ring nitrogen atom.[6] It has been reported that the reaction of 5-phenyl-1,2,4-dithiazole-3-thione with $Cp^*Co(CO)_2$ yields the complex $Cp^*\overline{Co[SNC(Ph)S}]$.[7]



(1)

In recent studies we have shown that carboxylate-substituted alkynes readily undergo addition with insertion into the rhenium−rhenium bond of $Re_2(CO)_9(NCMe)$ to produce dimetalated olefin complexes in which a carbonyl group becomes coordinated to one of the metal atoms (e.g. eq 2).[8]



(2)

We have now found that 5-((ethoxycarbonyl)amino)-1,2,4-dithiazole-3-thione (**1**) reacts with $Re_2(CO)_9(NCMe)$ by a ring-opening insertion into the Re−Re bond to yield the series of dirhenium complexes $Re(CO)_4[\mu\text{-}S_2CNC(N(H)CO_2Et)S]Re(CO)_5$ (**2**), $Re(CO)_4[\mu\text{-}S_2CNC(NHCO_2Et)S]Re(CO)_4$ (**3**), and $Re(CO)_4[\mu\text{-}S_2CNHC(NCO_2Et)S]Re(CO)_4$ (**4**) in which the S−S bond of the dithiazole ring has been cleaved. Two monorhenium side products, Re-

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$(CO)_4[S_2CNHCSNH(CO_2Et)]$ (**5**) and $Re(CO)_4[SCNC(NHCO_2Et)SCSN]$ (**6**), were also formed and were fully characterized.

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. 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. ^1H 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 run on a VG Model 70SQ mass spectrometer using electron impact ionization. $Re_2(CO)_9(MeCN)$[9] and 5-((ethoxycarbonyl)amino)-1,2,4-dithiazole-3-thione (**1**)[3] were prepared by reported procedures.

Reaction of $Re_2(CO)_9(MeCN)$ with 5-((Ethoxycarbonyl)amino)-1,2,4-dithiazole-3-thione (1). A 150.0-mg amount (0.225 mmol) of $Re_2(CO)_9(MeCN)$ and a 300.0-mg amount (1.350 mmol) of **1** were dissolved in 90 mL of CH_2Cl_2. The solution was heated to reflux for 17.5 h. The solvent was removed in vacuo, and the residue was separated by column chromatography on a silica gel to yield in order of elution: 52.3 mg of yellow $Re(CO)_4[\mu\text{-}S_2CNHC(NCO_2Et)S]Re(CO)_4$ (**4**), 27% yield; 13.9 mg of $Re_2(CO)_9(MeCN)$; 26.4 mg of yellow $Re(CO)_4[\mu\text{-}S_2CNC(NHCO_2Et)S]Re(CO)_4$ (**3**), 14% yield (eluted with a hexane/CH_2Cl_2 (4/1) solvent mixture); 33.2 mg of pale yellow $Re(CO)_4[S_2CNHCSNH(CO_2Et)]$ (**5**) in 14% yield (eluted with a hexane/CH_2Cl_2 (2/1) solvent mixture); 15.0 mg of yellow $Re(CO)_4[\mu\text{-}S_2CNC(N(H)CO_2Et)S]Re(CO)_5$ (**2**), 8% yield (eluted with a hexane/CH_2Cl_2 (1/1) solvent mixture); 12.4 mg of yellow $\mathrm{Re(CO)_4[S\overline{CNC(NHCO_2Et)SC{=}SN}]}$ (**6**), 6% yield (eluted with a hexane/CH_2Cl_2 (1/2) solvent mixture). Spectral data for **2**: IR (ν_{CO} in hexane, cm^{-1}) 2147 (w), 2103 (w), 2086 (w), 2045 (s), 2039 (s), 2005 (s), 2001 (s), 1992 (s), 1956 (s), 1778 (w, br), 1538 (w, br), 1521 (w, br); ^1H NMR (δ in $CDCl_3$, ppm) 9.49 (s, 1H, NH), 4.28 (q, $^3J_{H-H} = 7.1$ Hz, 2H, OCH_2Me), 1.33(t, $^3J_{H-H} = 7.1$ Hz, 3H, CH_3). Anal. Calcd (found): C, 19.86 (19.96); H, 0.71 (0.56); N, 3.31 (3.29). Spectral data for **3**: IR (ν_{CO} in hexane, cm^{-1}) 2113 (w), 2105 (w), 2014 (s), 2002 (s), 1993 (s), 1997 (s), 1964 (s), 1784 (w, br), 1501 (w, br); ^1H NMR (δ in $CDCl_3$, ppm) 11.18 (s, 1H, NH), 4.32 (q, $^3J_{H-H} = 7.1$ Hz, 2H, OCH_2Me), 1.35 (t, $^3J_{H-H} = 7.1$ Hz, 3H, CH_3). Anal. Calcd (found): C, 19.07 (19.38); H, 0.74 (0.64); N, 3.42 (3.37). Spectral data for **4**: IR (ν_{CO} in hexane, cm^{-1}) 2106 (m), 2012 (s), 1997 (s), 1964 (s), 1684 (w, br), 1517 (w, br); ^1H NMR (δ in $CDCl_3$, ppm) 13.17 (s, 1H, NH), 4.23 (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, 19.07 (19.17); H, 0.74 (0.75); N, 3.42 (3.29). Spectral data for **5**: IR (ν_{CO} in hexane, cm^{-1}) 2105 (w), 2008 (s), 1995 (s), 1959 (s), 1732 (w, br); ^1H NMR (δ in $CDCl_3$, ppm) 13.14 (s, br, 1H, NH), 8.06 (s, br, 1H, NH), 4.31 (q, $^3J_{H-H} = 7.1$ Hz, 2H, OCH_2Me), 1.35 (t, $^3J_{H-H} = 7.1$ Hz, 3H, CH_3). Anal. Calcd (found): C, 20.73 (20.78); H, 1.35 (1.58); N, 5.37 (5.16). Spectral data for **6**: IR (ν_{CO} in hexane, cm^{-1}) 2108 (w), 2007 (s), 2002 (s), 1964 (s), 1764 (w, br). ^1H NMR (δ in $CDCl_3$, ppm) 8.11 (s, br, 1H, NH), 4.34 (q, $^3J_{H-H} = 7.1$ Hz, 2H, OCH_2Me), 1.35 (t, $^3J_{H-H} = 7.1$ Hz, 3H, CH_3). The mass spectrum for **6** showed the parent ion *m/e* 547 and ions corresponding to the loss of each of four CO ligands. Anal. Calcd (found): C, 21.97 (21.69); H, 1.11 (1.15); N, 7.69 (7.00).

Decarbonylation of 2. A 10.0-mg amount (0.012 mmol) of **2** was dissolved in 15 mL of CH_2Cl_2. The solution was heated to reflux for 12 h. After the solvent was removed in vacuo, the residue was separated by TLC using a hexane/CH_2Cl_2 (2/1) solvent mixture. This yielded, in order of elution, 4.1 mg of **4** in 42% yield, 2.0 mg of **3** in 21% yield, and 1.5 mg of **2**.

Conversion of 3 to 4. (a) At 68 °C a 20.0-mg amount (0.024 mmol) of **3** was dissolved in 20 mL of hexane. The solution was heated to reflux for 6.5 h. After the solvent was removed in vacuo, the residue was separated by TLC to yield 7.8 mg of of **4** in 39% yield and 4.2 mg of unreacted **3**.

(b) A 5.0-mg amount of **3** in 0.5 mL of $CDCl_3$ was placed in a 5-mm NMR tube at 25 °C for 3 days. After this time there was no detectable formation of **4**.

Base-Catalyzed Conversion of 3 to 4. A 5.0-mg amount of **3**, 2 μL of pyridine, and 0.5 mL of $CDCl_3$ were placed in a 5-mm NMR tube at 25 °C, and the transformation was monitored by ^1H NMR spectroscopy. Compound **3** was slowly transformed to **4**. After 5 days the transformation appeared to be complete and the **4**/**3** ratio was 5.1/1.

Base-Catalyzed Conversion of 4 to 3. A 5.0-mg amount of **4**, 2 μL of pyridine, and 0.5 mL of $CDCl_3$ were placed in a 5-mm NMR tube at 25 °C, and the transformation was followed by ^1H NMR spectroscopy. Compound **4** was transformed partially back to **3**, and after 5 days the **4**/**3** ratio was 5.1/1. Since this is the same ratio found in the conversion of **3** to **4**, we accept this as the equilibrium constant for this transformation under these conditions.

Crystallographic Analyses. Crystals of **1** suitable for X-ray diffraction analysis were obtained by slow evaporation of solvent from a solution in a hexane/CH_2Cl_2 (1/1) solvent mixture at room temperature. Crystals of **2** were obtained by slow evaporation of solvent from a benzene solution at room temperature. Crystals of **3** were obtained by slow evaporation of solvent from a solution in a hexane/CH_2Cl_2 (1/1) solvent mixture at −4 °C. Crystals of **4** were obtained by slow evaporation of solvent from a solution in a MeOH/CH_2Cl_2 (1/10) solvent mixture at room temperature. Crystals of **5** were obtained by slow evaporation of solvent from a solution in a MeOH/CH_2Cl_2 (1/8) solvent mixture at room temperature. Crystals of **6** were obtained by slow evaporation of solvent from a solution in a benzene/CH_2Cl_2 (1/8) solvent mixture at room temperature. 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 Kα radiation. The 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) or a Silicon Graphics Indigo2 computer by using the TEXSAN Unix structure-solving program library 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] 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 $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$.

Compounds **1** and **3** crystallized in the monoclinic crystal system. The space groups $P2_1/n$ and $P2_1/a$, respectively, were established on the basis of the patterns of systematic absences observed during the collection of the intensity data. Both structures were solved by a combination of direct methods and difference Fourier syntheses. For **1** all non-hydrogen atoms were located in a three-dimensional E-map obtained by direct methods (MITHRIL). For **3** only the coordinates of the metal atoms were obtained in the first E-map. All remaining non-hydrogen atoms were subsequently obtained from a series of difference Fourier syntheses. In both analyses all non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of all hydrogen atoms in **1** were

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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) *Ibid.*, Table 2.3.1, pp 149−150.

Table 1. Crystallographic Data for Compounds 1−6

	compound		
	1	**2**	**3**
formula	$S_3O_2N_2C_5H_6$	$Re_2S_3O_{11}N_2C_{14}H_6 \cdot 0.5C_6H_6$	$Re_2S_3O_{10}N_2C_{13}H_6 \cdot 1.0CH_2Cl_2$
fw	222.29	885.86	903.72
cryst syst	monoclinic	triclinic	monoclinic
a (Å)	5.240(1)	14.305(3)	7.182(1)
b (Å)	21.878(4)	17.148(5)	30.321(7)
c (Å)	8.069(2)	11.848(2)	11.816(2)
α		99.879(2)	
β	105.00(1)	90.34(2)	103.06(1)
γ		70.61(2)	
V (Å^3)	893.5(3)	2696.6(11)	2506.4(8)
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/a$ (No. 14)
Z	4	4	4
ρ_{calcd} (g/cm^3)	1.65	2.18	2.40
μ(Mo Kα) (cm^{-1})	7.88	92.59	101.67
$2\theta_{max}$ (deg)	43	46	43
no. of obsd rflns ($I > 3\sigma$)	684	5937	2142
no. of variables	113	632	298
goodness of fit (GOF)[a]	1.22	2.44	2.13
max shift/error on final cycle	0.00	0.10	0.03
residuals: R; R_w[a]	0.029; 0.025	0.042; 0.046	0.038; 0.039
abs cor	empirical	DIFABS	empirical
transmissn coeff, max/min	1.00/0.86	1.00/0.44	1.00/0.19
largest peak in final diff map (e/Å^3)	0.19	1.72	1.05

	compound		
	4	**5**	**6**
formula	$Re_2S_3O_{10}N_2C_{13}H_6$	$ReS_3O_6N_2C_9H_7 \cdot 0.5H_2O$	$ReS_3O_6N_3C_{10}H_6 \cdot 0.5CH_2Cl_2$
fw	818.79	530.56	589.03
cryst syst	orthorhombic	monoclinic	monoclinic
a (Å)	21.986(9)	25.282(3)	16.248(2)
b (Å)	17.136(5)	19.544(3)	7.379(1)
c (Å)	11.280(3)	7.087(1)	17.143(2)
α (deg)	90.00	90.0	90.0
β (deg)	90.00	103.85(1)	116.73(1)
γ (deg)	90.00	90.0	90.0
V (Å^3)	4249.5(22)	3400.1(8)	1835.8(4)
space group	$Pcca$ (No. 54)	$C2/c$ (No. 15)	$P2/c$ (No. 13)
Z	8	8	4
ρ_{calcd} (g/cm^3)	2.56	2.07	2.13
μ(Mo Kα) (cm^{-1})	117.4	75.5	71.4
$2\theta_{max}$ (deg)	44	44	47
no. of obsd rflns	1811	1612	2092
no. of variables	275	194	227
goodness of fit (GOF)[a]	1.38	2.02	3.02
max shift/error on final cycle	0.07	0.07	0.02
residuals: R; R_w[a]	0.030; 0.028	0.034; 0.036	0.049; 0.054
abs cor	empirical	DIFABS	DIFABS
transmissn coeff, max/min	1.00/0.88	1.00/0.32	1.00/0.38
largest peak in final diff map (e/Å^3)	0.89	1.25	1.64

[a] $R = \sum_{hkl}(||F_o| - |F_c||/\sum_{hkl}|F_o|$; $R_w = [\sum_{hkl}w(|F_o| - |F_c|^2)/\sum_{hkl}wF_o^2]^{1/2}$, $w = 1/\sigma^2(F_o)$; GOF $= [\sum_{hkl}(|F_o| - |F_c|/\sigma(F_o))/(n_{data} - n_{vari})$.

calculated by assuming idealized geometries with C−H distances of 0.95 Å. The positions of hydrogen atoms on the ethyl group in **3** were also calculated by assuming idealized geometries. The hydrogen atom H(2) on the nitrogen atom N(2) was located and refined using an isotropic thermal parameter. One equivalent of CH_2Cl_2 from the crystallization solvent was located in the lattice of **3**. This was included in the calculations and was satisfactorily refined. The scattering contributions of all calculated hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Compound **2** 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 structure. The structure was solved by a combination of direct methods and difference Fourier syntheses. The compound crystallizes with two complete independent molecules of **2** in the asymmetric crystal unit. The coordinates of all metal atoms were obtained by direct methods (MITHRIL). All non-hydrogen atoms were subsequently obtained from difference Fourier syntheses, and all were refined with anisotropic thermal parameters. One equivalent of benzene from the crystallization solvent was located in the lattice and satisfactorily refined with 100% occupancy. The positions of all hydrogen atoms were calculated by assuming idealized geometries. The scattering contributions of the calculated hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Compound **4** crystallized in the orthorhombic crystal system. The space group *Pcca* was established uniquely on the basis of the patterns of systematic absences observed during the collection of the intensity data. The structure was 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 hydrogen atoms on the ethyl group were also calculated by assuming idealized geometries. The hydrogen atom H(1) on the nitrogen atom N(1) was located and refined on its positional parameters using a fixed thermal parameter. The scattering contributions of all calculated hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Compounds **5** and **6** crystallized in the monoclinic crystal system. For **5** the systematic absences were consistent with

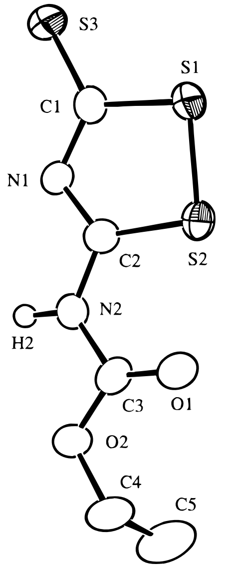

Figure 1. ORTEP diagram of 5-((ethoxycarbonyl)amino)-1,2,4-dithiazole-3-thione, $[\mathrm{S_2C{=}SNCN(H)CO_2Et}$ (**1**) showing 50% probability thermal ellipsoids**.** Selected interatomic distances (Å) and angles (deg) are as follows: S(1)−S(2) = 2.050(2), S(1)−C(1) = 1.751(4), S(2)−C(2) = 1.741(4), S(3)−C(1) = 1.651(4), C(1)−N(1) = 1.354(5), C(2)−N(1) = 1.304(5), C(2)−N(2) = 1.361(5); C(2)−S(2)−S(1) = 91.3(2), S(1)−C(1)−N(1) = 115.5(3), C(2)−N(1)−C(1) = 116.3(3), S(2)−C(2)−N(1) = 121.3(3).

either of the space groups *C*2/*c* and *Cc*, and for **6** the absences were consistent with the space groups *P*2/*c* and *Pc*. In both cases the structures were solved and refined in the higher symmetry centrosymmetric settings. Both structures were solved by a combination of direct methods and difference Fourier syntheses. For both analyses all non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of all hydrogen atoms in **5** were calculated by assuming idealized geometries. The positions of hydrogen atoms in **6** were also calculated by assuming idealized geometries, except for the hydrogen atom H(2) on the nitrogen atom N(2), which was located and refined using an isotropic thermal parameter. A molecule of water, probably obtained from the crystallization solvent, was found in the lattice of **5**. It was included in the calculations and satisfactorily refined at a 50% occupancy. In **6** a molecule of CH_2Cl_2 from the crystallization solvent was found in the lattice. This was included in the calculations and was satisfactorily refined at a 50% occupancy. The scattering contributions of all calculated hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Results

The reaction of 5-((ethoxycarbonyl)amino)-1,2,4-dithiazole-3-thione (**1**) with $Re_2(CO)_9(NCMe)$ has yielded five products: three dirhenium products identified as $Re(CO)_4[\mu\text{-}S_2CNC(N(H)CO_2Et)S]Re(CO)_5$ (**2**; 8% yield), $Re(CO)_4[\mu\text{-}S_2CNC(NHCO_2Et)S]Re(CO)_4$ (**3**; 14% yield), and $Re(CO)_4[\mu\text{-}S_2CNHC(NCO_2Et)S]Re(CO)_4$ (**4**; 27% yield) and the two mononuclear rhenium complexes $Re(CO)_4[S_2CNHCSNH(CO_2Et)]$ (**5**; 14% yield) and $Re(CO)_4[SCN(NHCO_2Et)SC{=}CN]$ (**6**; 6% yield). To characterize them unambiguously, each of the products as well as the starting material **1** was analyzed by a single-crystal X-ray diffraction analysis.

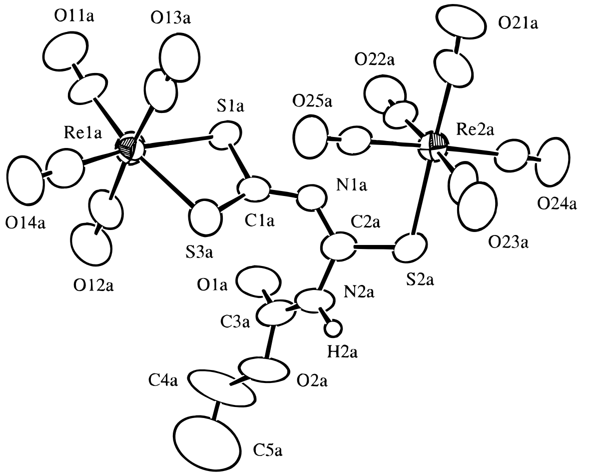

Figure 2. An ORTEP diagram of $Re(CO)_4[\mu\text{-}S_2CNHC(NCO_2Et)S]Re(CO)_5$ (**2**) showing 50% probability thermal ellipsoids.

Table 2. Intramolecular Distances (Å) for Compound 2[a]

Re(1b)−S(1b)	2.509(3)	S(3a)−C(1a)	1.72(1)
Re(1b)−S(3b)	2.501(4)	O(1a)−C(3a)	1.15(1)
Re(1b)−C(1b)	2.98(1)	O(1b)−C(3b)	1.20(1)
Re(1a)−S(1a)	2.494(3)	O(2b)−C(3b)	1.33(2)
Re(1a)−S(3a)	2.508(4)	O(2b)−C(4b)	1.39(4)
Re(1a)−C(1a)	2.98(1)	O(2a)−C(3a)	1.33(2)
Re(2b)−S(2b)	2.492(4)	O(2a)−C(4a)	1.46(2)
Re(2b)−N(1b)	3.40(1)	N(1a)−C(1a)	1.34(1)
Re(2b)−C(2b)	3.44(1)	N(1a)−C(2a)	1.30(2)
Re(2a)−S(2a)	2.490(4)	N(1b)−C(1b)	1.34(1)
Re(2a)−N(1a)	3.371(9)	N(1b)−C(2b)	1.29(1)
Re(2a)−C(2a)	3.40(1)	N(2a)−C(2a)	1.40(2)
S(1a)−S(3a)	2.879(5)	N(2a)−C(3a)	1.41(2)
S(1a)−C(1a)	1.71(1)	N(2b)−C(2b)	1.36(2)
S(1b)−C(1b)	1.71(1)	C(4a)−C(5a)	1.28(3)
S(2b)−C(2b)	1.74(1)	Re−C (av)	1.95(2)
S(2a)−C(2a)	1.72(1)	O−C (av)	1.14(1)
S(3b)−C(1b)	1.70(1)		

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

An ORTEP diagram of the molecular structure of **1** is shown in Figure 1. As expected, the molecule does indeed contain a five-membered 1,2,4-dithiazole ring with a thione grouping at the 3-position. The sulfur−sulfur bond distance S(1)−S(2) = 2.050(2) Å is similar to that found in other 1,2,4-dithiazole-3-thione molecules: $S_2C{=}SNCNH_2$, S−S = 2.052(4) Å[11a] and 2.063(5) Å;[11b] $S_2C{=}SNCN(Ph)C(NH_2)NPh$, S−S = 2.121(2) Å;[12] 2.054(4) Å in the bismuth complex $Bi(S_2C{=}SNCNH_2)_2(NCS)_4$.[6] The other bond distances and angles of **1** are also similar to the structures of the previously reported dithiazole-3-thiones.[6,11,12]

The product **2** crystallizes with two independent molecules in the asymmetric crystal unit. Both molecules are structurally similar, and an ORTEP diagram of the molecular structure of one of these is shown in Figure 2. Selected bond distances and angles for **2** are listed in Tables 2 and 3. The molecule contains $Re(CO)_4$ and $Re(CO)_5$ metal groupings that are linked by a $S_2CNC(N(H)CO_2Et)S$ ligand. This ligand contains a dithiocarboxylate grouping, CS_2, that is chelated to the $Re(CO)_4$ group at one end through the two sulfur atoms

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(11) (a) Stanford, R. H., Jr. *Acta Crystallogr.* **1963**, *16*, 1157. (b) Hordvik, A. *Acta Chem. Scand.* **1963**, *17*, 2575.

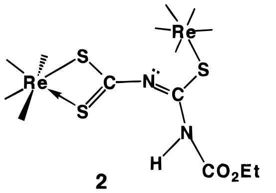
(12) Butler, A. R.; Glidewell, C.; Liles, D. C. *Acta Crystallogr.* **1978**, *B34*, 2570.

Table 3. Intramolecular Bond Angles (deg) for Compound 2[a]

S(1b)–Re(1b)–S(3b)	69.9(1)	S(1b)–C(1b)–N(1b)	119.7(9)
S(1a)–Re)(1a)–S(3a)	70.3(1)	S(3b)–C(1b)–N(1b)	125(1)
Re(1a)–S(1a)–C(1a)	88.2(4)	S(2b)–C(2b)–N(1b)	121(1)
Re(1b)–S(1b)–C(1b)	87.6(4)	S(2b)–C(2b)–N(2b)	113(1)
Re(2b)–S(2b)–C(2b)	107.2(5)	N(1b)–C(2b)–N(2b)	126(1)
Re(2a)–S(2a)–C(2a)	106.3(5)	S(2a)–C(2a)–N(1a)	122(1)
Re(1b)–S(3b)–C(1b)	87.9(4)	S(2a)–C(2a)–N(2a)	114(1)
Re(1a)–S(3a)–C(1a)	87.4(4)	N(1a)–C(2a)–N(2a)	124(1)
C(3b)–O(2b)–C(4b)	114(2)	O(1b)–C(3b)–O(2b)	125(1)
C(3a)–O(2a)–C(4a)	113(1)	O(1b)–C(3b)–N(2b)	126(1)
C(1a)–N(1a)–C(2a)	128(1)	O(2b)–C(3b)–N(2b)	109(1)
C(1b)–N(1b)–C(2b)	126(1)	O(1a)–C(3a)–O(2a)	127(1)
C(2a)–N(2a)–C(3a)	123(1)	O(1a)–C(3a)–N(2a)	127(1)
C(2b)–N(2b)–C(3b)	125(1)	O(2a)–C(3a)–N(2a)	106(1)
S(1a)–C(1a)–S(3a)	114.2(7)	O(2a)–C(4a)–C(5a)	114(2)
S(1a)–C(1a)–N(1a)	120.4(8)	O(2b)–C(4b)–C(5b)	117(4)
S(3a)–C(1a)–N(1a)	124(1)	Re–C–O (av)	177(1)
S(1b)–C(1b)–S(3b)	114.5(6)		

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

and a thioguanidine grouping N=CNR$_2$S at the other end which is coordinated to the Re(CO)$_5$ group through the sulfur atom alone. All Re–S distances span the narrow range 2.490(4)–2.509(3) Å and are very similar to those found in related compounds such as (OC)$_4$Re[μ-(*E*)-HC=C(CO$_2$Me)CS$_2$]Re(CO)$_4$ (**7**),[13] (OC)$_4$Re[μ-SC(H)C(CO$_2$Me)CS$_2$]Re(CO)$_4$ (**8**),[13] and (OC)$_4$Re[μ-C$_3$H$_2$(CO$_2$Me)(CO$_2$Et)CS]Re(CO)$_4$ (**9**).[13]



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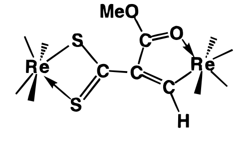

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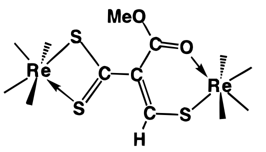

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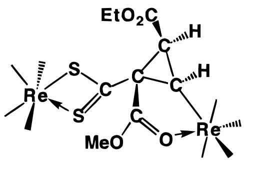

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The N(1)–C(2) distances (1.30(2) Å [1.29(1) Å]) are slightly shorter than the N(1) - C(1) distances (both 1.34(1) Å), indicating a greater C–N double-bond character at the N(1)–C(2) bond. Atom N(1) formally contains a lone pair of electrons, but there is no evidence for coordination of this atom to Re(2); Re(2)···N(1) = 3.40(1) Å [3.371(9) Å]. The ligand is not planar, and the dihedral angle between the planes S(1)–C(1)–S(3)–N(1) and C(2)–N(1)–S(2)–N(2) is 55.5° [53.0°]. The hydrogen atom on N(2) was not located crystallographically but was observed in the ^{1}H NMR spectrum at δ 9.49 ppm as a slightly broadened singlet. When hexane solutions of **2** were heated to reflux for 12 h, **2** was converted to a mixture of **3** and **4** in 21% and 42% yields, respectively.

An ORTEP diagram of the molecular structure of compound **3** is shown in Figure 3. This compound contains two Re(CO)$_4$ groupings that are linked by a S$_2$CNC(N(H)CO$_2$Et)S ligand similar to that in **2**. The principal difference between **2** and **3** is that the Re(CO)$_5$ group was converted into a Re(CO)$_4$ group and the nitrogen atom N(1) has become coordinated to the metal atom; Re(2)–N(1) = 2.20(1) Å. The rhenium–sulfur distances (Re(1)–S(1) = 2.516(5) Å, Re(1)–S(3) = 2.491(4) Å, and Re(2)–S(2) = 2.505(4) Å) are similar to those of **2**. The N(1)–C(2) distance (1.35(2) Å) has increased in length compared to that in **2**, which is probably a result of a weakening of the C–N π-bond by back-donation from the metal atom. The ligand is much closer to planarity than it was in **2**. The dihedral angle between the planes S(1)–C(1)–S(3)–N(1) and C(2)–N(1)–S(2)–N(2) is only 10.3°. In this case the hydrogen atom on N(2) was located and refined crystallographically and was observed in the ^{1}H NMR spectrum as a highly deshielded slightly broadened singlet at δ 11.18 ppm.

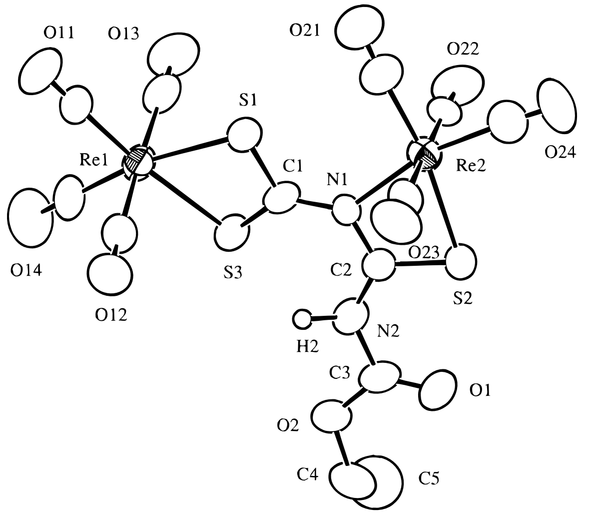

Figure 3. ORTEP diagram of Re(CO)$_4$[μ-S$_2$CNC(NHCO$_2$Et)S]Re(CO)$_4$ (**3**) showing 50% probability thermal ellipsoids. Selected intramolecular bond distances (Å) and angles (deg) are as follows: Re(1)–S(1) = 2.516(5), Re(1)–S(3) = 2.491(4), Re(2)–N(1) = 2.20(1), Re(2)–S(2) = 2.505(4), C(1)–S(1) = 1.73(1), C(1)–S(3) = 1.68(2), C(1)–N(1) = 1.36(2), C(2)–N(1) = 1.35(2), C(2)–N(2) = 1.35(2); Re(2)–N(1)–C(1) = 134(1), C(1)–N(1)–C(2) = 124(1).

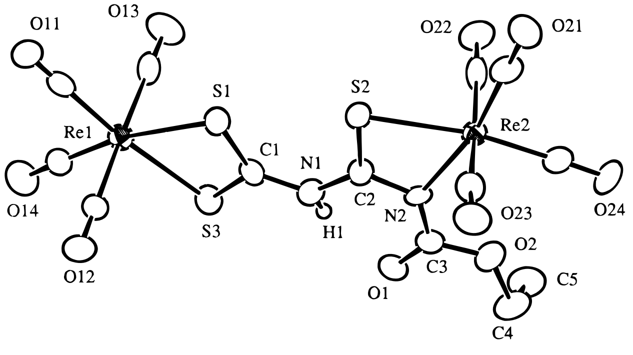

Figure 4. ORTEP diagram of Re(CO)$_4$[S$_2$CNHC(NCO$_2$Et)S]Re(CO)$_4$ (**4**) showing 35% probability thermal ellipsoids. Selected intramolecular bond distances (Å) and angles (deg) are as follows: Re(1)–S(1) = 2.525(4), Re(1)–S(3) = 2.508(4), Re(2)–N(2) = 2.21(1), Re(2)–S(2) = 2.528(4), C(1)–S(1) = 1.71(1), C(1)–S(3) = 1.68(1), C(1)–N(1) = 1.35(2), C(2)–N(1) = 1.38(2), C(2)–N(2) = 1.36(2); N(1)–C(2)–N(2) = 121(1), C(1)–N(1)–C(2) = 132(1), N(1)–C(2)–S(2) = 126(1).

Compound **4** is an isomer of **3**. An ORTEP diagram of the molecular structure of **4** is shown in Figure 4. This compound contains two Re(CO)$_4$ groupings that are linked by a S$_2$CN(H)C(NCO$_2$Et)S ligand. In this com-

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[13] Adams, R. D.; Chen, L.; Wu, W. *Organometallics* **1994**, *13*, 1257.

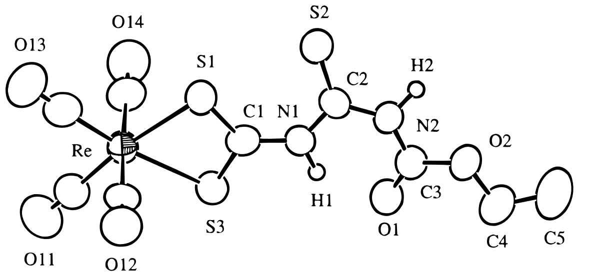


Figure 5. ORTEP diagram of $Re(CO)_4[S_2CNHCSNH(CO_2Et)]$ (**5**) showing 50% probability thermal ellipsoids. Selected intramolecular bond distances (Å) and angles (deg) are as follows: Re−S(1) = 2.500(3), Re−S(3) = 2.513(3), C(1)−S(1) = 1.69(1), C(1)−S(3) = 1.70(1), C(2)−S(2) = 1.63(1), C(1)−N(1) = 1.39(1), C(2)−N(1) = 1.37(1), C(2)−N(2) = 1.36(1); N(1)−C(2)−N(2) = 112.3(9), C(1)−N(1)−C(2) = 129.5(8), N(1)−C(2)−S(2) = 125.8(7), N(2)−C(2)−S(2) = 121.9(8).

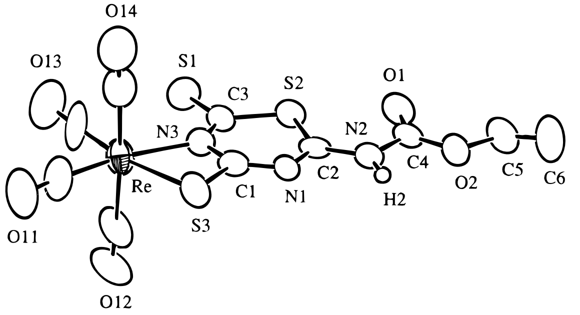


Figure 6. ORTEP diagram of $Re(CO)_4[SCNC(NHCO_2Et)SCSN]$ (**6**) showing 50% probability thermal ellipsoids. Selected intramolecular bond distances (Å) and angles (deg) are as follows: Re−S(3) = 2.517(4), Re−N(3) = 2.19(1), C(1)−S(3) = 1.63(1), C(3)−S(1) = 1.72(1), C(1)−N(3) = 1.40(1), C(1)−N(1) = 1.33(1), C(2)−N(1) = 1.32(1), C(2)−S(2) = 1.72(1), C(3)−S(2) = 1.76(1), C(3)−N(3) = 1.33(2); C(1)−N(1)−C(2) = 120(1), N(1)−C(2)−S(2) = 126(1), C(2)−S(2)−C(3) = 101.5(6), N(3)−C(3)−S(2) = 122(1), N(3)−C(3)−S(1) = 123(1), C(1)−N(3)−C(3) = 122(1).

pound the hydrogen atom is located on N(1), and it is even more deshielded in the ^1H NMR spectrum (δ 13.17 ppm), the C(2)−N(1) bond length has increased to 1.38(2) Å, and N(2) has become coordinated to Re(2) (Re(2)−N(2) = 2.21(1) Å). The other bond distances are similar to those in **2** and **3**. When a solution of **3** in hexane solvent was heated to reflux for 6.5 h, it was converted to **4** in 39% yield. Interestingly, the transformation was promoted by the presence of base. For example, a sample of **3** was transformed into a 5.1/1 **4**/**3** mixture in 3 days at 25 °C in the presence of pyridine, but in the absence of pyridine there was no evidence for any transformation of the **3** to **4** over a 5-day period at 25 °C. Conversely, samples of **4** were converted to a 5.1/1 **4**/**3** mixture in 5 days at 25 °C in the presence of pyridine. Accordingly, 5.1/1 is regarded as the **4**/**3** equilibrium constant under these conditions.

Products **5** and **6** were isolated in low yields, and each contains only one metal atom. Structural diagrams of **5** and **6** are shown in Figures 5 and 6, respectively. Each compound contains a $Re(CO)_4$ grouping. Compound **5** contains a thioamide-substituted dithiocarbamato ligand, $S_2CN(H)C[N(H)CO_2Et]{=}S$, that is chelated to the rhenium atom through the sulfur atoms of the dithiocarbamoyl grouping. The metal−sulfur and carbon−sulfur bond distances are similar to those observed in **2**−**4** and **7**−**9**.[13] Compound **5** is in fact very similar to **4**, and it could be viewed as a derivative of **4** by replacing the N-coordinated $Re(CO)_4$ grouping with a hydrogen atom. However, attempts to obtain **5** from **4** by reaction with H_2O were not successful. The nitrogen-bound hydrogen atoms in **5** were not located crystallographically but were observed spectroscopically at δ 13.14 (s, br, 1H) and 8.06 (s, br, 1H) in the ^1H NMR spectrum.

Compound **6** contains a $\overline{SCNC(NHCO_2Et)SC{=}SN}$ ligand which has a six-membered N−C−N−C−S−C ring. It is chelated to the rhenium atom through one of the nitrogen atoms and one of the thioketonic sulfur atoms.

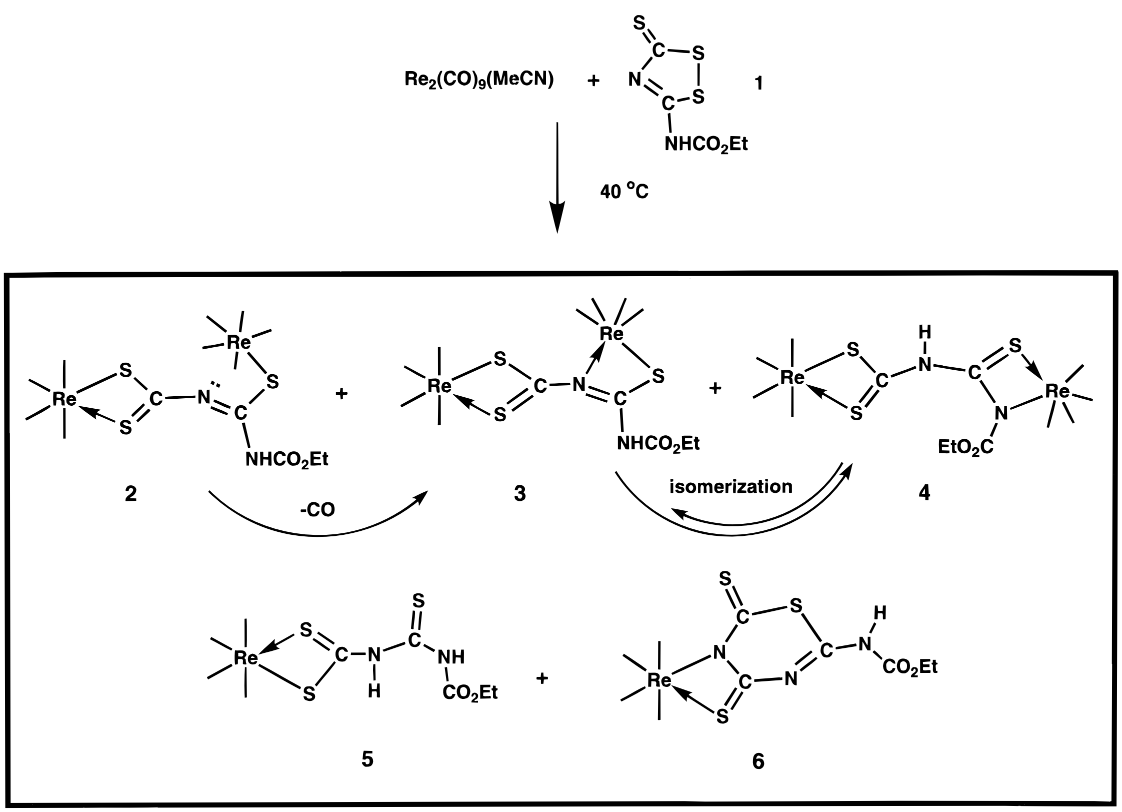
As confirmed by the parent ion of **6** in the mass spectrum (*m*/*e* 547), this ligand is heavier by the amount of one CN unit than those found in **2**−**4**. The source of this CN unit has not been identified, and attempts to prepare **6** by the reaction of **2** with $Et_4N[CN]$ were not successful; thus, it seems unlikely that this ligand was formed by the addition of a free CN^- unit to the ligand grouping in **2**. The Re−S and Re−N distances (Re−S(3) = 2.517(4) Å and Re−N(3) = 2.19(1) Å) are similar to those in **4**, (Re(2)−S(2) = 2.528(4) Å and Re(2)−N(2) = 2.21(1) Å). Except for the C(1)−N(3) bond of 1.40(1) Å, all the C−N bonds in the ring (C(1)−N(1) = 1.33(1) Å, C(2)−N(1) = 1.32(1) Å, and C(3)−N(3) = 1.33(2) Å) are short and indicative of significant delocalized π-bonding across the ring, even though formally the valences of all the atoms in the ring can be satisfied with only one internal π-bond in the six-membered ring. The hydrogen atom H(2) was located and refined crystallographically and observed in the ^1H NMR spectrum at δ 8.11 (s, br) ppm.

Discussion

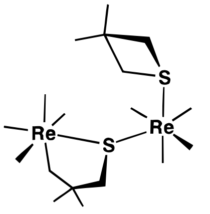
A summary of the results of this study is given in Scheme 1. Five products were isolated from the original reaction mixture. Three of these are the result of the addition and sequential transformation of the dithiazole-3-thione **1** to the original dirhenium complex. Compound **2** is clearly the product formed first, since it contains nine carbonyl ligands like the starting material $Re_2(CO)_9(NCMe)$. It was formed by the replacement of the acetonitrile ligand with the dithiazole-3-thione and a ring-opening insertion of the dithiazole-3-thione into the Re−Re bond. The driving force for the formation of **2** is clearly the formation of the three Re−S bonds. The energy of formation of these three bonds evidently exceeds that of the combination of the S−S bond in the dithiazole-3-thione molecule and the Re−Re and the Re−N bonds in the $Re_2(CO)_9(NCMe)$ molecule. From examination of the structure of **2** it is clear that it is the thione sulfur and the most closely positioned sulfur atom of the disulfide unit that have become the chelate grouping to the $Re(CO)_4$ group. The $Re(CO)_5$ was then shifted to the second sulfur atom of the disulfide grouping upon cleavage of the Re−Re bond.

In a somewhat related study, we have shown that one of the dimethylthietane ligands in the complex $Re_2(CO)_8(\overline{SCH_2CMe_2CH_2})_2$ undergoes a photoinduced ring-opening insertion into the rhenium−rhenium bond of the complex to yield the compound $Re(CO)_4(\mu\text{-}SCH_2CMe_2CH_2)Re(CO)_4(\overline{SCH_2CMe_2CH_2})$ (**10**) by cleavage of

Scheme 1



one of the carbon−sulfur bonds.[14]



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We have recently shown that the dirhenium−thietane complex $\mathrm{Re_2(CO)_9(\overline{SCH_2CH_2CH_2})}$ produces a ring-opening cyclooligomerization of thietane catalytically to yield polythioether macrocycles.[15] Our studies of the reactions of $\mathrm{Re_2(CO)_9(NCMe)}$ with carboxylate-substituted alkynes have shown that the alkynes can be inserted into the Re−Re bond intramolecularly with displacement of the NCMe ligand.[8] The resultant dimetalated olefin products undergo subsequent insertion reactions with a variety of other small molecules.[8] When $\mathrm{Mn_2(CO)_9(NCMe)}$ is used instead of $\mathrm{Re_2(CO)_9(NCMe)}$, these reactions have led to new routes to new organic molecules by multiple insertions and ring closures.[16]

Compound **3** is formed from **2** by loss of a CO ligand at the $\mathrm{Re(CO)_5}$ group and subsequent coordination of the imine nitrogen atom to that rhenium atom. The transformation of **3** to **4** involves a hydrogen shift from the carboxylate-substituted nitrogen atom to the coordinated nitrogen atom. This transformation is clearly base-catalyzed which indicates that it probably occurs by a deprotonation/reprotonation sequence. The pyridine may also assist in the decoordination of the imine nitrogen atom. In solution **3** and **4** exist in an equilibrium which lies heavily in favor of **4** at 25 °C. Compounds **5** and **6** are minor products, and we have not yet been able to obtain them from the compounds **2**−**4**; thus, the details of their formation are still unknown.

Our studies have shown for the first time that the rings of dithiazolethiones can be opened by cleavage of the sulfur−sulfur bond and insertion into a metal−metal bond. Given the large number of polynuclear metal complexes that have been characterized in recent years, it seems likely that additional examples of this reaction will be discovered. The ring-opened dimetalated dithiazoles should be susceptible to further modification. Studies of the reactions of dithiazolethiones with other metal cluster complexes are in progress.

Acknowledgment. This research was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy.

Supporting Information Available: Tables of atomic positional parameters, bond distances, bond angles, and anisotropic thermal parameters for all six structural analyses (38 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 ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

OM960016R

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[15] Adams, R. D.; Cortopassi, J. E.; Falloon, S. B. *Organometallics* **1995**, *14*, 1748.

[16] Adams, R. D.; Chen, L. *J. Am. Chem. Soc.* **1994**, *116*, 4467.