The Synthesis of Stabilized Dimetallated Thioimidate Complexes by the Insertion of Ethoxycarbonylisothiocyanate into a Rhenium−Rhenium Bond

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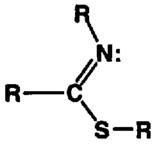
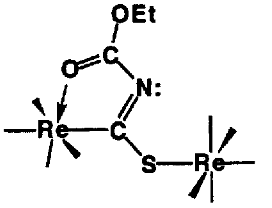
Molecules containing dimetallated hydrocarbyl groupings are of great chemical interest[1−3]. These groupings often represent intermediates in important catalytic processes[4]. Recently, we have shown that substituted dimetallated olefins can be formed by alkyne insertion into the metal−metal bonds of certain dinuclear complexes[2,5]. Complexes having dimetallated hydrocarbyl groups combined with heteroatoms are quite rare[6]. Herein is described the formation of a dimetallathioimidate grouping by the insertion of an organic isothiocyanate into an unsupported metal−metal bond. Organic isothiocyanates are useful reagents in organic synthesis[7], but the organometallic chemistry of these molecules is not yet well developed[8].

The reaction of $EtO_2CN{=}C{=}S$ with $Re_2(CO)_9(NCMe)$ (**1**) yielded three products: $Re(CO)_4$[*s-trans*-μ-*C*,*S*-$EtO_2CN{=}CS$]$Re(CO)_5$ (**2**), $Re(CO)_4$[*s-trans*-μ-*C*,*S*,*N*-$EtO_2CN{=}CS$]$Re(CO)_4$ (**3**), and $Re(CO)_4$[μ-*C*,*N*,*S*$_2$-$(EtO_2C)_2N{=}CNCS_2$]$Re(CO)_4$ (**4**) as shown by a combination of IR, ^{1}H-NMR and single crystal X-ray diffraction analyses (see Experimental and ref.[8]). The molecular structures of **2** and **3** were established by single crystal X-ray diffraction analyses (see Figures 1 and 2). Compound **2** can be viewed as a dirheniathioimidate complex with an *s-trans* conformation at the C−S bond.



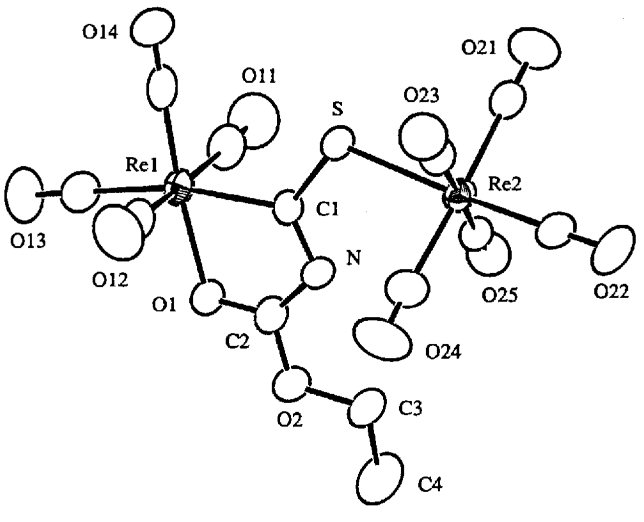
thioimidate



dirheniathioimidate-2

It was formed by the insertion of the isothiocyanate molecule into the rhenium−rhenium bond in **1**, although the mechanism of this insertion has not yet been established. An $Re(CO)_5$ group is bonded to the sulfur atom, and the carbon atom C(1) and the oxygen atom of the carbonyl group are coordinated to a $Re(CO)_4$ group to form a five membered ring. The nitrogen atom is not bonded to the $Re(CO)_5$ group [Re(2)···N = 3.423(7)]. Compound **3** was derived from **2** by the loss of CO from the $Re(CO)_5$ and coordination of the lone pair of electrons on the nitrogen atom to the rhenium atom. The Re(2)−N distance was reduced to 2.172(9) Å. Compound **3** was obtained independently in 81% yield by refluxing solutions of **2** in hexane for 2 h.

Figure 1. An 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 [°] are: 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)



The molecular structure of compound **4** was also established crystallographically, and its structure is shown in Figure 3. Compound **4** was formed by the addition and coupling of two molecules of $EtO_2C{-}N{=}C{=}S$ to **1**. Compound **4** contains a novel bridging $S_2CNCN(CO_2Et)_2$ grouping inserted between two $Re(CO)_4$ groups. The central carbon C(1) contains two sulfur atoms each of which is bound to a different rhenium atom [C(1)−S(1) = 1.68(1) Å, C(1)−S(2) = 1.67(1) Å, Re(1)−S(2) = 2.472(3) Å and Re(2)−S(1) = 2.516(3) Å]. Nitrogen N(1) is bonded to Re(2) to form a four membered Re−N−C−S ring. The bonding in **4** can be represented by the resonance structures **4a** or the zwitterion **4b**. On the basis of observed bond distances, the latter seems to be the more appropriate structure. N(1) is also bonded to the carbon C(2) that can be viewed as a carbene center (**4a** form) [Re(1)−C(2) = 2.13(1) Å], and there is a $N(CO_2Et)_2$ group bonded to N(2) [C(2)−N(2) = 1.47(1) Å].

The $S_2CNCN(CO_2Et)_2$ grouping appears to be derived from two molecules of $EtO_2C{-}N{=}C{=}S$. It seems that the sulfur atom from

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Figure 2. An ORTEP diagram of $Re(CO)_4[s$-*trans*-μ-*C,S,N*-$EtO_2CN{=}CS]Re(CO)_4$ (**3**) showing 50% probability thermal ellipsoids; selected interatomic distances [Å] and angles [°] are: 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)

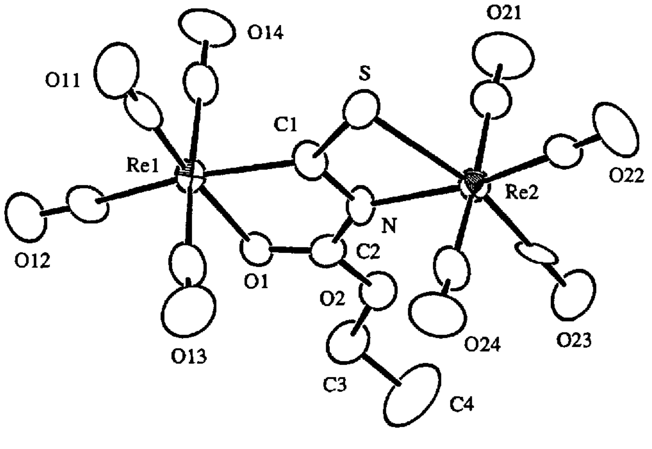
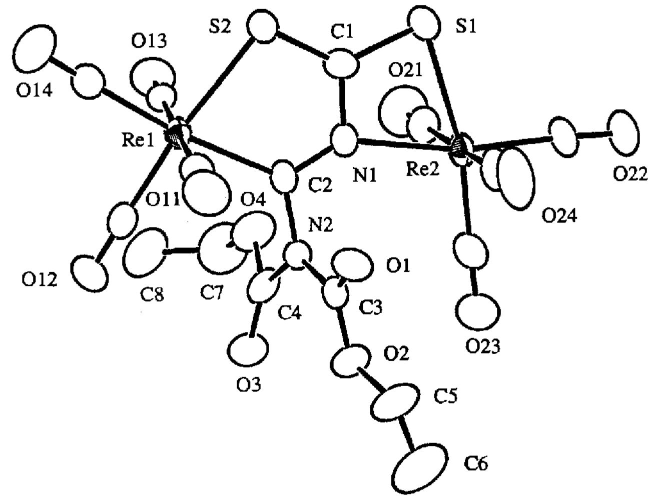
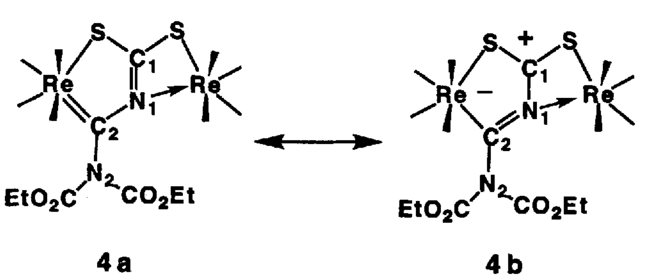


Figure 3. An ORTEP diagram of $Re(CO)_4[μ$-*C,N,S*$_2$-$(EtO_2C)_2N{=}CNCS_2]Re(CO)_5$ (**4**) showing 50% probability thermal ellipsoids; selected interatomic distances [Å] and angles [°] are: Re(1)–S(2) = 2.472(3), Re(1)–C(2) = 2.13(1), Re(2)–S(1) = 2.516(3), Re(2)–N(1) = 2.201(8), C(1)–S(1) = 1.68(1), 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)–N(1)–C(1) = 101.6(6)





4a **4b**

one isothiocyanate molecule was transferred to the carbon of the other isothiocyanate and that the CO_2Et grouping from the second isothiocyanate was transferred back to the nitrogen atom of the first isothiocyanate. The coupling of isothiocyanates in the presence of metal atoms is well known[8,9]. Recently, Cowie has reported an example of a carboxylate shift in the addition of isothiocyanates, $R{-}N{=}C{=}S$, to a bridging $EtO_2C{-}N{=}C{=}S$ ligand[6a].

It can be anticipated that the dimetallated thioimidates such as **2** and **3** can be further modified by coupling to other unsaturated organic molecules to yield new ligands and new organic molecules[2]. The insertion of heterocumulenes into metal–metal bonds may prove to be a general method for the activation of these molecules.

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Experimental

A solution containing 20.0 mg (0.030 mmol) of $Re_2(CO)_9$-(MeCN), and 10.6 μl (0.09 mmol) of EtO_2CNCS in 40 ml of hexane was heated to reflux for 1 h, 50 min. The products were separated by TLC on silica gel using a hexane: CH_2Cl_2, 9:2, solvent mixture to yield in order of elution: 0.4 mg of $Re_2(CO)_{10}$; 8.8 mg of colorless **3**, 40% yield; 1.5 mg of **2**, 7% yield; 0.5 mg of $Re_2(CO)_9$-(MeCN); and 4.3 mg of red-orange **4**, 17% yield. Spectral data for **2**: IR (hexane): $\tilde{\nu}_{CO}$ (cm^{-1}) = 2139 (w), 2097 (w), 2076 (w), 2037 (vs), 2034 (vs), 1995 (vs), 1991 (vs), 1953 (s), 1524 (w, br.). ^1H NMR ($CDCl_3$): δ = 4.36 (q, $^3J_{H-H}$ = 7.1 Hz, 2H, OCH_2Me), 1.36 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_3); for **3**: IR (hexane): $\tilde{\nu}_{CO}$ (cm^{-1}) = 2099 (m), 2011 (vs), 1993 (s), 1964 (s), 1957 (s), 1554 (w, br.). ^1H NMR ($CDCl_3$): δ = 4.34 (q, $^3J_{H-H}$ = 7.2 Hz, 2H, OCH_2Me), 1.40 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_3); for **4**: IR (hexane): $\tilde{\nu}_{CO}$ (cm^{-1}) = 2104 (m), 2028 (s), 2016 (s), 1998 (s), 1969 (s), 1964 (s), 1956 (sh, w), 1780 (w, br.). ^1H NMR ($CDCl_3$): δ = 4.40 (q, $^3J_{H-H}$ = 7.1 Hz, 4H, OCH_2Me), 1.37 (t, $^3J_{H-H}$ = 7.1 Hz, 6H, CH_3). – Analytical data: **2**: $C_{13}H_5NO_{11}Re_2S$ (755.7): calcd. C 20.66, H 0.67, N 1.85; found: C 20.79, H 0.57, N 1.85; **3**: $C_{12}H_5NO_{10}Re_2S$ (727.7): calcd. C 19.81, H 0.69, N 1.92; found C 19.70, H 0.89, N 1.91; **4**: $C_{16}H_{10}N_2O_{12}Re_2S_2$ (858.8): calcd. C 22.38, H 1.17, N 3.26; found C 22.24, H 1.00, N 3.19.

X-ray Structure Analyses: For **2**: $Re_2SO_{11}NC_{13}H_5$, M_r = 755.66, triclinic, space group = $P\bar{1}$, a = 10.476(2) Å, b = 14.386(2) Å, c = 6.865(1) Å, α = 91.68(1)°, β = 92.19(1)°, γ = 109.30(1)°, Z = 2, $\mu(Mo_{K\alpha})$ = 125.75 cm^{-1}, T = 293 K, 2252 independent reflections, R = 0.027, R_w = 0.034; for **3**: $Re_2SO_{10}NC_{12}H_5$, M_r = 727.65, triclinic, space group = $P\bar{1}$, a = 10.132(2) Å, b = 10.417(2) Å, c = 9.994(1) Å, α = 98.06(1)°, β = 94.38(1)°, γ = 62.03(1)°, Z = 2, $\mu(Mo_{K\alpha})$ = 132.80 cm^{-1}, T = 293 K, 2087 independent reflections, R = 0.035, R_w = 0.042; for **4**: $Re_2S_2O_{12}N_2C_{16}H_{10}$, M_r = 858.80, triclinic, space group = $P\bar{1}$, a = 10.703(3) Å, b = 12.365(4) Å, c = 10.271(3) Å, α = 108.46(2)°, β = 109.44(2)°, γ = 89.84(3)°, Z = 2, $\mu(Mo_{K\alpha})$ = 102.52 cm^{-1}, T = 293 K, 2825 independent reflections, R = 0.034, R_w = 0.036. Empirical absorption corrections (psi scans). All structures were solved by direct methods (MITHRIL). Further details of the crystal structure analyses are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository number CSD-59264.

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