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The addition of isocyanides to ReS_4^-: [3 + 1] cycloaddition to S=M=S

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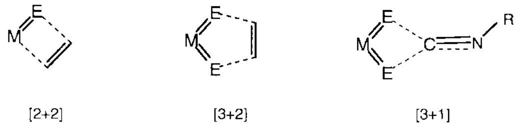
Received (in Irvine, CA, USA) 27th January 2000, Accepted 3rd May 2000
Published on the Web 8th June 2000

Isocyanides undergo [3 + 1] cycloadditions to ReS_4^- to give dithiocarboimidate derivatives, $Re(S)(S_4)(S_2CNR)^-$ and $Re_2S_5(S_2CNR)_2^{2-}$, which undergo S-atom transfer and, in the case of the monometallic species, *N*-alkylation.

Cycloadditions to oxo- and thio-metallates represent an important class of reactions related to atom transfer catalysis, *e.g.* by OsO_4.[1] In these transformations, the substrate adds wholly or in part to the main group atom, the metal playing a secondary role. Such cycloadditions to metal sulfides are relevant to catalyst–substrate interactions in hydrodesulfurization (HDS) catalysis.[2] Virtually all metal-based cycloadditions proceed *via* 2 + 2 or, more commonly, 3 + 2 pathways,[3,4] 3 + 1 pathways have not been observed.

Metal sulfides have been shown to catalyze the conversion of CO into thioesters and other biologically significant functionalities, although the mechanisms of such reactions are unclear.[5,6] The pathways for such reactions might be elucidated through studies on the interactions of isoelectronic analogues of CO with soluble metal sulfides under well defined conditions. Of all the soluble metal sulfides,[7] ReS_4^- **1** exhibits the greatest reactivity toward alkenes and alkynes.[8–11] Compound **1** was therefore selected for an investigation of the reactions of metal sulfides with isocyanides, which are isoelectronic with CO.



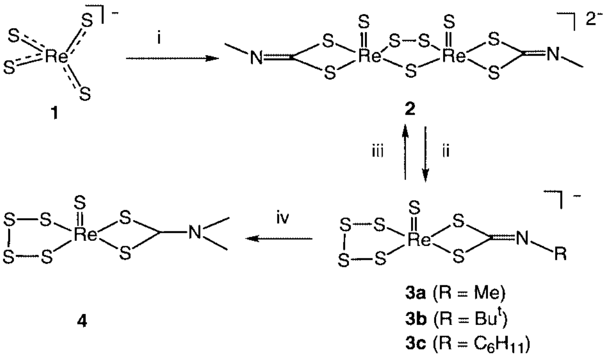
With rigorous exclusion of light and adventitious oxidants, solutions of **1**, as its NEt_4^+ or PPh_4^+ salts, are unreactive towards MeNC. The reaction of MeNC and **1**, however, proceeds briskly when in the presence of elemental sulfur. Addition of 1–2 equivalents of elemental sulfur to solutions of (PPh_4)**1** and MeNC afforded brown microcrystalline **2** whose (−)ESI-MS spectrum shows molecular ions at *m/z* 372 ($z = 2-$) and 743 ($z = 1-$) corresponding to $Re_2S_9(CNMe)_2^{2-}$ (isolated yield: 35%).† The IR spectrum of **2** exhibits peaks at 1586 and 526 cm^{-1} for $\nu_{C=N}$ and $\nu_{Re=S}$, respectively. The ^1H NMR spectrum in CD_3CN shows a PPh_4^+/Me ratio of 1; a pair of equally intense Me signals (δ 3.25 and 3.274) is attributed to the unsymmetrical environment of the square-pyramidal Re centers such that the Me can be *trans* to persulfide or sulfide (Scheme 1). In part due to its low solubility, $(PPh_4)_2$ **2** was not obtained as X-ray quality crystals.

The addition of further equivalents of S_8 to MeCN slurries of **2** gave $(PPh_4)[Re(S)(S_4)(S_2CNMe)]$ **3a** over the course of several hours at room temperature. In this reaction, the two isomers of **2** are consumed at comparable, but not identical rates. The new species can be more easily prepared by treatment of **1** with MeNC in the presence of an excess of sulfur, the yields being *ca.* 60%. The poorly soluble side products in this reaction absorb at *ca.* 1580 cm^{-1} ($\nu_{C=N}$); (−)ESI-MS of these solids revealed ions corresponding to $[ReS_4]_m[MeNC]_n^{m-}$ (where m and $n = 1$ and 2). The structure of **3a** was established by single crystal X-ray diffraction (Fig. 1).‡ The rhenium atom is square pyramidal; the square base is defined by the tetrasulfido bridge and the dithiocarboimidate ($MeNCS_2^{2-}$) ligands, a terminal sulfur atom occupying the apical position. The rhenium atom lies 0.4570 Å out of the plane formed by the basal sulfur ligands. The C=N distance is 1.24 Å, which is consistent with a double bond, and resembling previously described dithiocarbodimidate complexes.[12,13]

Analogues of **3** were prepared using *tert*-butyl isocyanide (Bu^tNC) and cyclohexyl isocyanide (CyNC) to give the corresponding derivatives **3b** and **3c**, respectively.§ No RNC exchange was observed when solutions of **3a** were treated with an excess of Bu^tNC or solutions of **3b** were exposed to MeNC. Warm solutions of **3a** react with **1** and 1 equiv. of MeNC to give **2**, indicating that intermetallic S-atom transfer is facile.

Methylation of **3a** with MeOTf gave the dithiocarbamate $Re(S)(S_4)(S_2CNMe_2)$ **4**, confirming the relationship between dithiocarboimidate and the more familiar dithiocarbamate ligands. Dithiocarbamate complexes are usually prepared from preformed dithiocarbamates or thiuram disulfides,[14] not by *N*-alkylation routes.

The mechanism by which **2** and **3** arise involves generation of a reactive derivative by the addition of sulfur atoms to **1** followed by trapping with RNC. We have previously shown that such solutions bind nitriles (*via* a 3 + 2 cycloaddition process[9]). Further work is underway to identify this reactive intermediate.



Scheme 1 *Reagents and conditions*: i, S_8, MeNC (25 °C); ii, excess S_8; iii, **1**, MeNC; iv, MeOTf.

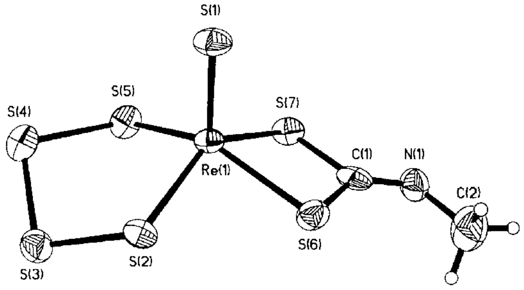


Fig. 1 Structure of **3a** with thermal ellipsoids drawn at the 50% probability level. Selected distances (Å) and angles (°): Re–S(1) 2.088(1), Re–S(2) 2.257(1), Re–S(5) 2.291(1), Re–S(6) 2.355(1), Re–S(7) 2.344(1), C(1)–S(7) 1.776(7), C(1)–S(6) 1.802(7), C(1)–N 1.248(8), N–C(2) 1.467(10); S(6)–C(1)–N 131.2(6), S(7)–C(1)–N 125.0(6), C(1)–N–C(2) 118.2(7), S(2)–Re–S(5) 92.41(7), S(6)–Re–S(7) 73.66(6).

DOI: 10.1039/b000932f

The important conclusion is that isocyanides add across the S=M=S functionality[7] *via* an unprecedented 3 + 1 cycloaddition process. Isocyanides have been shown to add to μ-S ligands in binuclear molybdenum compounds.[15]

This research was sponsored by the U.S. National Science Foundation.

Notes and references

† Satisfactory CHN analyses were obtained for **2**, **3a**–**c**, and **4**.

‡ *Crystallographic data* for **3a**: $C_{26}H_{23}NPReS_7$, M 791.12, T 193(2) K, monoclinic space group $P2_1/c$ a = 11.0148(7), b = 19.6065(13), c = 13.6281(9) Å, β = 98.89°, V = 2907.8(3) Å^3, Z = 4, μ = 4.755 mm^{-1}, 18817 reflections (R_{int} = 0.1019), 6944 independent reflections, for observed data R_1 = 0.0427, wR_2 = 0.0898, for all data R_1 = 0.0947, wR_2 = 0.1043.

CCDC 182/1636. See http://www.rsc.org/suppdata/cc/b0/b000932f/ for crystallographic files in .cif format.

§ **3b**: ^{1}H NMR (CD_3CN, 500 MHz): δ 1.43 (s). (−)ESI-MS: *m/z* 494. **3c**: ^{1}H NMR (CD_3CN, 500 MHz): δ 1.3–1.9(m). (−)ESI-MS: *m/z* 520.

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