Isocyanides undergo [3 + 1] cycloadditions to ReS₄⁻ to give dithiocarboximidate derivatives, Re(S(S₄)(S₂CNR)) and Re₂S₅(S₂CNR)₂²⁻, 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 OsO₄. 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. Virtually all metal-based cycloadditions proceed via 2 + 2 or, more commonly, 3 + 2 pathways,⁴ 3 + 1 pathways have not been observed.

Metal sulfides have been shown to catalyze the conversion of CO into thiocarbamates or thiocarbamates, which are isoelectronic with CO. With rigorous exclusion of light and adventitious oxidants, solutions of 1, as its NEt₄⁺ or PPh₄⁺ 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 PPh₄H and MeNC afforded brown microcrystalline 2 whose (~)ESI-MS spectrum shows molecular ions at m/z 572 (z = 2⁻) and 743 (z = 1⁻); corresponding to Re₂S₉(CNMe)₂⁻ (isolated yield: 35%). The IR spectrum of 2 exhibits peaks at 1586 and 526 cm⁻¹ for vC=O and vC≡N, respectively. The ¹H NMR spectrum in CD₂CN shows a PPh₄⁺/Me ratio of 1:1, 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). Re₃S₁⁵(CNMe)₂ was obtained as X-ray quality crystals.

The addition of further equivalents of S₈ to MeCN slurries of 2 gave (PPh₄)₂[Re₄(S₆)₂(S₄)CNMe] 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 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 are consumed at comparable, but not identical rates.

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 dithiocarboximidate (MeCN₂S₂⁻) 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 dithiocarboximidate complexes.¹² ¹³

Analogs of 3 were prepared using tert-butyl isocyanide (BuNC) 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 BuNC 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(S₄)(S₂CNMe)) 4, confirming the relationship between dithiocarboximidate 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)⁵. Further work is underway to identify this reactive intermediate.

The addition of isocyanides to ReS₄⁻: [3 + 1] cycloaddition to S=M=S

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

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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 = 98.89°, V = 2907.8(13) Å^3, Z = 4, μ = 4.735 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: 'H NMR (CD_3CN, 500 MHz): δ 1.43 (s). (--)ESI-MS: m/z 494. 3c: 'H NMR (CD_3CN, 500 MHz): δ 1.3–1.9 (m). (--)ESI-MS: m/z 520.