

Four-Electron Reduction of Metal Sulfides by Alkynes and the Reversible Formation of Persulfides

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We have recently reported that ReS_4^- (**1**) displays broad reactivity toward unsaturated organic compounds.^{1,2} In terms of its reactivity, **1** resembles the well-known oxidant OsO_4 but differs from ReO_4^- , which is unreactive toward unsaturated organic substrates.³ For example, in the presence of an amine oxide, both OsO_4 and **1** add 2 equiv of alkene to give square pyramidal d^2 derivatives of the type $\text{M}(\text{O})(\text{E}_2\text{C}_2\text{R}_4)_2^-$ ($\text{M} = \text{Re}, \text{E} = \text{S}; \text{M} = \text{Os}, \text{E} = \text{O}$).^{1,4} The reaction of alkynes and **1** have revealed a number of interesting processes including the ability of alkynes to induce S–S bond formation. Persulfides are well-known to form upon treatment of organic and inorganic thiolates (i.e., $\text{M}-\text{S}^-$ species) with oxidants (e.g., halogens, organic disulfides),⁵ but reducing agents such as alkynes were not known to cause S–S coupling. The present observations are relevant to the behavior of metal sulfide catalysts used in the processing of unsaturated organic compounds.⁶

The addition of an excess of bis(trimethylsilyl)acetylene, $(\text{TMS})_2\text{C}_2$, to a MeCN solution of **1** resulted in a rapid reaction, signaled by the loss of the violet color of the thioanion. In the case of the Ph_4P^+ salt of **1**, golden crystals of $(\text{PPh}_4)_2\mathbf{3}$ precipitate.⁷ Anion **3** was shown by single-crystal X-ray diffraction analysis to be a centrosymmetric binuclear dithiolene complex $\{\text{Re}_2\text{S}_4[\text{S}_2\text{C}_2(\text{TMS})_2]_2\}^{2-}$.⁸ The rhenium coordination sphere is square pyramidal, similar to that of $\text{Os}_2\text{O}_4(\text{O}_2\text{C}_2\text{Me}_4)_2$.⁹ In solution, **3** isomerizes to give a derivative with cis terminal sulfido atoms ($K_{\text{isom}} \approx 0.75$ at 20 °C). The isomer ratio was independent of concentration. The rate of isomerization is solvent dependent, being slower in DMSO than in MeCN.¹⁰

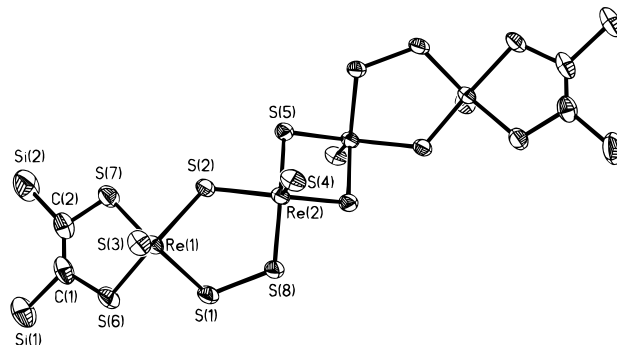


Figure 1. Structure of the anion in $(\text{Et}_4\text{N})_4\mathbf{4}$ with thermal ellipsoids drawn at the 50% probability level. Methyl groups on the dithiolene ligands have been omitted for clarity. Selected bond lengths (Å): Re1–S1, 2.252(2); Re1–S2, 2.349(2); Re1–S3, 2.113(2); Re1–S6, 2.309(2); Re1–S7, 2.294(3); Re2–S2, 2.324(2); Re2–S5, 2.345(2); Re2–S5A, 2.361(2); Re2–S8, 2.238(2); S1–S8, 2.134(2); C1–C2, 1.357(14).

A more detailed picture of the reaction pathway leading to **3** was obtained by a series of in situ ^1H NMR measurements on the Et_4N^+ salt of **1**. We observed the rapid formation of an initial adduct (**2**), which converts to **3** in a slower follow-up process. Given its stoichiometry ($\text{Et}_4\text{N}/(\text{TMS})_2\text{C}_2 = 1$) and its efficient conversion to **3**, **2** can be confidently assigned as $\text{ReS}_2[\text{S}_2\text{C}_2(\text{TMS})_2]^-$. By using excess ($\sim 5\times$) alkyne, the formation of **2** is nearly complete (i.e., $[\text{Et}_4\text{N}^+] = [(\text{TMS})_2\text{C}_2]_{\text{consumed}} = [\mathbf{2}]$) before its conversion to **3** occurs appreciably. Thus, the $[\text{R}_2\text{C}_2]$ affects the rate of formation of **2** but not the rate of conversion of **2** to **3**.

The reaction of **1** with substoichiometric amounts of the alkyne gave an unexpected result. Using 0.5 equiv of $(\text{TMS})_2\text{C}_2$, we again observe the initial formation of **2**. Subsequently, two new pairs of Me_3Si signals appear in addition to signals for the isomers of **3**. The new compound, **4**, has the stoichiometry $\text{R}_2\text{C}_2[\text{ReS}_4^-]_2$ based on integration values of $[\text{R}_2\text{C}_2]_{\text{consumed}}$ vs $[\text{Et}_4\text{N}^+]_0$ ($= [\text{ReS}_4^-]$).¹¹ In analogy to **3**, these new species are assigned as cis and trans isomers (see below). Although coproduction of **3** and **4** from **1** precluded isolation of analytically pure bulk samples of $(\text{Et}_4\text{N})_4\mathbf{4}$, we were able to grow single crystals of the new species. X-ray crystallographic analysis (Figure 1) revealed the

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(7) $(\text{Ph}_4\text{P})_2[\text{Re}_2\text{S}_4[\text{S}_2\text{C}_2(\text{TMS})_2]_2]$. To a stirred slurry of 0.65 g (1.0 mmol) of $\text{Ph}_4\text{P}(\text{ReS}_4)$ in 10 mL of MeCN was added 2.0 mL (9.0 mmol) of bis(trimethylsilyl)acetylene. The slurry immediately turned from violet to brown, and after ~ 1 min a crystalline precipitate appeared. After 18 h the crystals were collected, washed with Et_2O , and dried in vacuo. Yield: 0.56 g (69%). Anal. Calcd (found) for $\text{C}_{64}\text{H}_{76}\text{P}_2\text{Re}_2\text{S}_8\text{Si}_4$: C, 46.64 (46.64); H, 4.65 (4.64); P, 3.76 (3.48); Re, 22.59 (22.59); S, 15.56 (15.49); Si, 6.81 (6.71). ^1H NMR (500 MHz, CD_3CN): δ 0.43 (Me_3Si , cis), 0.50 (Me_3Si , trans), 7.64–7.92 (Ph_4P^+). IR (KBr): 423 ($\nu_{\text{Re-S}}$), 499 ($\nu_{\text{Re-S}}$), 616 ($\nu_{\text{C-S}}$), 625 ($\nu_{\text{C-S}}$), 833 ($\nu_{\text{Si-C}}$), 859 ($\nu_{\text{Si-C}}$) cm^{-1} . UV–vis (CH_2CN): 360, 388 nm.

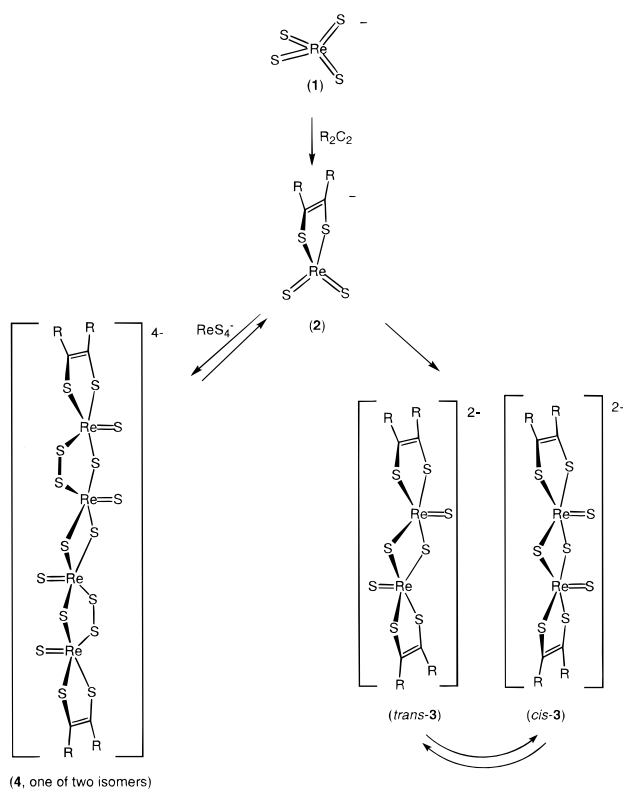
(8) Crystallographic results for $(\text{Ph}_4\text{P})_2\mathbf{3}$. The data crystal was obtained from a MeCN/ Et_2O solution: $P1$, $a = 11.2285(9)$ Å, $b = 11.3957(9)$ Å, $c = 17.4186(14)$ Å, $\alpha = 79.952(2)^\circ$, $\beta = 75.646(2)^\circ$, $\gamma = 74.310(1)^\circ$, $V = 2065.0(3)$ Å³, $Z = 1$, $D_{\text{calc}} = 1.451$ g cm^{-3} . The structure was solved by direct methods. All nonhydrogen atoms were refined anisotropically with the exception of one MeCN molecule and the disordered Et_2O . For 13 624 unique reflections (λ (Mo K α) = 0.710 73 Å, $[I > 2\sigma(I)]$) collected at 198(2) K for $2.42 < 2\theta < 56.58^\circ$, the final R_1 (on F^2) = 0.0477 ($wR_2 = 0.0879$).

(9) $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Re}_2\text{O}_4$: Herrmann, W. A.; Jung, K. A.; Herdtweck, E. *Chem. Ber.* **1989**, *122*, 2041. $\text{Os}_2\text{O}_4(\text{O}_2\text{C}_2\text{Me}_4)_2$: Phillips, F. L.; Skapski, A. C. *J. Chem. Soc., Dalton Trans.* **1975**, 2586.

(10) For the equilibrium of *trans-3* to *cis-3* at 20 °C: k_{forward} (s^{-1}) = 2.8×10^{-3} (CD_3CN), 1.3×10^{-3} ($(\text{D}_3\text{C}_2\text{SO})$); k_{reverse} (s^{-1}) = 3.7×10^{-3} (CD_3CN), 1.3×10^{-3} ($(\text{CD}_3)_2\text{SO}$).

(11) The reaction of alkynes and OsO_4 is proposed to lead to a polymer, see: Schröder, M.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* **1978**, 1599.

Scheme 1



tetrametallic salt, $(Et_4N)_4\{Re_4S_{12}[S_2C_2(TMS)_2]_2\}$.¹² The centrosymmetric anion can be described as a dimer of $\{ReS_2[S_2C_2(TMS)_2]\}ReS_4^{2-}$. As in **3**, each Re(V) atom is square pyramidal.

(12) Crystallographic results for $(Et_4N)_4\mathbf{4}$. The data crystal was obtained from a MeCN/Et₂O solution: $P2_1/c$, $a = 21.0659(2)$ Å, $b = 11.3603(1)$ Å, $c = 21.3777(2)$ Å, $\beta = 113.89^\circ$, $V = 4677.79(7)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.616$ g·cm⁻³. The structure was solved by direct methods. All nonhydrogen atoms were refined anisotropically with the exception of one Et₄N⁺ and one MeCN. For 11 156 unique reflections (λ (Mo K α) = 0.710 73 Å, $[I > 2\sigma(I)]$) collected at 198(2) K for $2.12 < 2\theta < 56.62^\circ$, the final R_1 (on F^2) = 0.0558 ($wR_2 = 0.0912$).

The persulfido group arises via a formal 1,3-addition of **1** to a Re=S moiety in **2** (Scheme 1). This produces a $[Re(V)]_2$ species, one Re of which would be tetrahedral, an apparently unstable geometry for this family of dithiolenes (cf. **2**).¹³ Dimerization of this Re_2 species, which is not directly observed, produces **4**.

In the conversion of **1** into **4**, the alkyne induces a 4 e⁻ reduction of two Re(VII) centers to two Re(V) centers. The 4 e⁻ derive from the conversion of the alkyne to a dithiolene (2 e⁻) and the coupling of two terminal sulfido ligands to a persulfide (2 e⁻). The S-S bond of 2.13 Å is ~5% longer than usually observed, which suggests that it would be labile. Indeed, additional $(TMS)_2C_2$ converts **4** to **3**. In this conversion, we observed an initially rapid growth of **2** followed by its disappearance and the formation of **3**. These results are consistent with the conversion of **4** to **3** via **2**, as summarized in the scheme.

The transformations discussed above also apply to 2-butyne, diphenylacetylene, and dimethylacetylenedicarboxylate (DMAD), as shown by ¹H NMR measurements, in situ UV-vis spectroscopy, and the isolation of analytically pure PPh_4^+ salt of $[Re_2S_4(S_2C_2Me_2)_2]^{2-}$, an analogue of **3**.¹⁴

Overall, the ready formation (**2** + **1**) and breakup (**4** + R_2C_2) of compound **4** highlight the relevance of S-S bond making and breaking in the processing of organic substrates by metal sulfides. These findings demonstrate that persulfide-sulfide equilibria should be considered in the reactions of metal sulfides with any substrate, not just those considered oxidizing.⁵

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Supporting Information Available: Tables giving X-ray crystallographic information, atomic parameters, bond lengths, angles, and torsion angle data for $(PPh_4)_2\mathbf{3}$ and $(Et_4N)_4\mathbf{4}$ (19 pages). Ordering information is given on any current masthead page.

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(13) Cis/trans isomers cannot arise for the Re_2 species, where only one Re center is square pyramidal.

(14) $(Ph_4P)_2[Re_2S_4(S_2C_2Me_2)_2]$: Anal. Calcd (found) for $C_{36}H_{52}P_2Re_2S_8 \cdot Et_2O$: C, 48.37 (48.03); H, 4.19 (4.25); Re, 24.99 (24.56); S, 17.22 (17.28). ¹H NMR (500 MHz, CD₃CN): δ 2.32 (Me), 2.68 (Me), 7.6–7.95 (Ph_4P^+).