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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 $M(O)(E_2C_2R_4)_2^z$ (M = Re, E = S; M = Os, E = 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., $M-S^-$ 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, $(TMS)_2C_2$, 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 $(PPh_4)_2$**3** precipitate.[7] Anion **3** was shown by single-crystal X-ray diffraction analysis to be a centrosymmetric binuclear dithiolene complex $\{Re_2S_4[S_2C_2(TMS)_2]_2\}^{2-}$.[8] The rhenium coordination sphere is square pyramidal, similar to that of $Os_2O_4(O_2C_2Me_4)_2$.[9] In solution, **3** isomerizes to give a derivative with cis terminal sulfido atoms ($K_{isom} \approx 0.75$ 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]

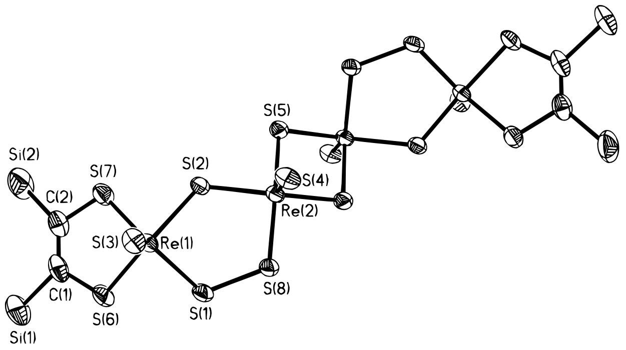

Figure 1. Structure of the anion in $(Et_4N)_4$**4** with thermal ellipsoids drawn at the 50% probability level. Methyl groups on the dithiolene ligands have been omitted for clarity. Selected bond lengths (Å): Re1−S1, 2.252(2); Re1−S2, 2.349(2); Re1−S3, 2.113(2); Re1−S6, 2.309(2); Re1−S7, 2.294(3); 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 ($Et_4N/(TMS)_2C_2 = 1$) and its efficient conversion to **3**, **2** can be confidently assigned as $ReS_2[S_2C_2(TMS)_2]^-$. By using excess (∼5×) alkyne, the formation of **2** is nearly complete (i.e., $[Et_4N^+] = [(TMS)_2C_2]_{consumed} = [\mathbf{2}]$) before its conversion to **3** occurs appreciably. Thus, the $[R_2C_2]$ affects the rate of formation of **2** but not the rate of conversion of **2** to **3**.

The reaction of **1** with *sub*stoichiometric amounts of the alkyne gave an unexpected result. Using 0.5 equiv of $(TMS)_2C_2$, 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 $R_2C_2[ReS_4^-]_2$ based on integration values of $[R_2C_2]_{consumed}$ vs $[Et_4N^+]_o$ ($= [ReS_4^-]$).[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 $(Et_4N)_4$**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) $(Ph_4P)_2\{Re_2S_4[S_2C_2(TMS)_2]_2\}$. To a stirred slurry of 0.65 g (1.0 mmol) of $Ph_4P(ReS_4)$ 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 $C_{64}H_{76}P_2Re_2S_8Si_4$: 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*$_3$Si, cis), 0.50 (*Me*$_3$Si, trans), 7.64 − 7.92 (Ph_4P^+). IR (KBr): 423 (ν_{Re-S}), 499 ($\nu_{Re=S}$), 616 (ν_{C-S}), 625 (ν_{C-S}), 833 (ν_{Si-C}), 859 (ν_{Si-C}) cm^{-1}. UV−vis (CH_3CN): 360, 388 nm.

(8) Crystallographic results for $(Ph_4P)_2$**3**. The data crystal was obtained from a MeCN/Et_2O solution: $P\bar{1}$, $a = 11.2285(9)$ Å, $b = 11.3957(9)$ Å, $c = 17.4186(14)$ Å, $\alpha = 79.952(2)°$, $\beta = 75.646(2)°$, $\gamma = 74.310(1)°$, $V = 2065.0(3)$ Å^3, $Z = 1$, $D_{calcd} = 1.451$ 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 Kα) = 0.710 73 Å, $[I > 2\sigma(I)]$) collected at 198(2) K for $2.42 < 2\Theta < 56.58°$, the final R_1 (on F^2) = 0.0477 (wR_2 = 0.0879).

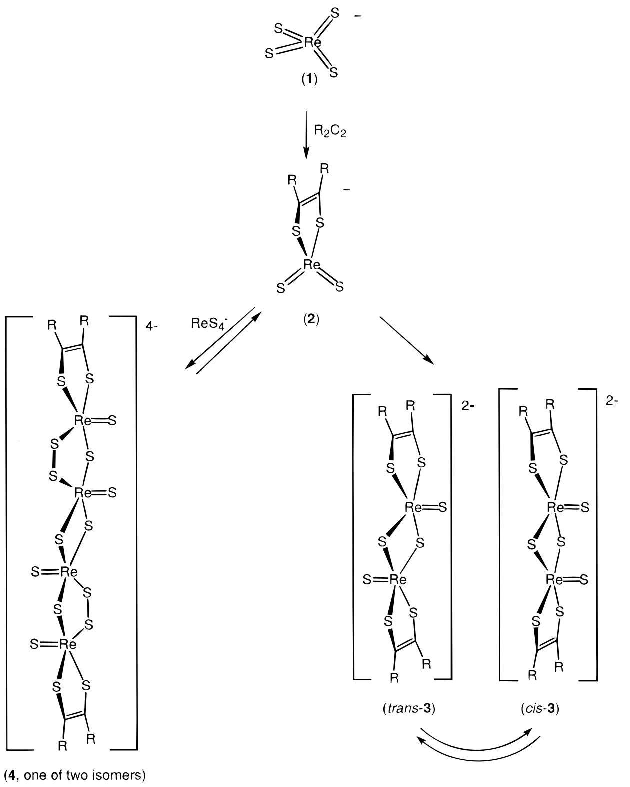
(9) $(\eta^5\text{-}C_5Me_5)_2Re_2O_4$: Herrmann, W. A.; Jung, K. A.; Herdtweck, E. *Chem. Ber.* **1989**, *122*, 2041. $Os_2O_4(O_2C_2Me_4)_2$: Phillips, F. L.; Skapski, A. C. *J. Chem. Soc., Dalton Trans.* **1975**, 2586.

(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} ($(D_3C)_2SO$); $k_{reverse}$ (s^{-1}) = 3.7×10^{-3} (CD_3CN), 1.3×10^{-3} ($(CD_3)_2SO$).

(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.

S0020-1669(98)00596-5 CCC: $15.00

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. 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]

Acknowledgment. This research was funded by the National Science Foundation and the Department of Energy. J.T.G. thanks the School of Chemical Sciences for the Drickamer Fellowship.

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

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(12) Crystallographic results for $(Et_4N)_4$**4**. The data crystal was obtained from a MeCN/Et$_2$O solution: $P2_1/c$, $a = 21.0659(2)$ Å, $b = 11.3603(1)$ Å, $c = 21.3777(2)$ Å, $\beta = 113.89°$, $V = 4677.79(7)$ Å^3, $Z = 4$, $D_{calcd} = 1.616$ g·cm^{-3}. The structure was solved by direct methods. All nonhydrogen atoms were refined anisotropically with the exception of one Et_4N^+ and one MeCN. For 11 156 unique reflections (λ (Mo Kα) = 0.710 73 Å, [$I > 2\sigma(I)$]) collected at 198(2) K for $2.12 < 2\theta < 56.62°$, the final R_1 (on F^2) = 0.0558 ($wR_2 = 0.0912$).

(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 $C_{56}H_{52}P_2Re_2S_8\cdot Et_2O$: C, 48.37 (48.03); H, 4.19 (4.25); Re, 24.99 (24.56); S, 17.22 (17.28). ^1H NMR (500 MHz, CD_3CN): δ 2.32 (Me), 2.68 (Me), 7.6−7.95 (Ph_4P^+).