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Addition of Alkynes and Alkenes to ReS_4^-: Reactivity Akin to OsO_4

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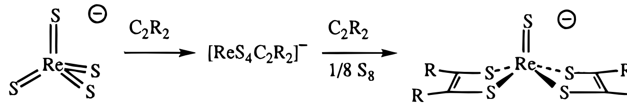
The tetrathiometallates, anions of the formula MS_4^{n-}, represent one of the most fundamentally important classes of soluble metal sulfides.[1] In the course of our studies on thiometallates, we noticed that the complex $(MeC_5H_4)Ru(dppe)SReS_3$ is reactive toward alkenes.[2] This is not very surprising since unsaturated organic compounds are known to add to a variety of organometallic sulfido compounds[3] as well as the cluster $Mo_3S_4(H_2O)_9^{4+}$.[4] A series of control experiments demonstrated however that ReS_4^- itself is highly reactive toward a wide range of unsaturated organic substrates—this is significant since simple thiometallates were not thought to be reactive toward unactivated alkynes and alkenes.[5] Additionally, the new transformations define routes from simple precursors to oxo(or sulfido)−dithiolene complexes that resemble the active sites of several Mo- and W-containing enzymes, the structures of which have recently been determined.[6]

Our primary finding is that most alkynes and alkenes react with ReS_4^-.[7] These reactions are signaled by a color change from violet, characteristic of ReS_4^-, to the brown color of the adducts. Alkynes that tested successfully are Ph_2C_2, Me_2C_2, $(Me_3Si)_2C_2$, PhC_2H, C_2H_2, and $C_2(CO_2Me)_2$.[8] Kinetic studies show that the reaction of Ph_2C_2 with ReS_4^- is first order in each reactant ($k = 0.085 \pm 0.002$ s^{-1} mol^{-1} at 23 °C). The temperature dependence of the reaction rate reveals a large negative $\Delta S^{\ddagger}$ of -109.4 J mol^{-1}, as expected for an associative process.

A modified sulfidation process, allowing for isolation of single products in high yields, involves the use of elemental sulfur as a supplemental oxidant (eq 1). Under these conditions, sulfur does not react with the ReS_4^-; in fact, sulfur does not appreciably dissolve in the reaction solvent (MeCN) until after the addition of the unsaturated substrate. Thus, the added sulfur intercepts an intermediate. In situ ^1H NMR studies of the ReS_4^- + C_2Me_2 + $^1/_8S_8$ reaction show that it proceeds within minutes at 19 °C to sequentially afford two adducts prior to the formation of **1**. The intermediates have the stoichiometry $ReS_xC_2Me_2^-$, the ReS_x^- being assayed by the intensity of the counterion signal. The rate of the consumption of ReS_4^- is independent of sulfur. In a typical synthesis, $NR_4[ReS_4]$ was treated with 3 equiv of alkyne and $^1/_8$ equiv of S_8 in acetonitrile. After the reaction mixtures were filtered through a bed of alumina, the products were crystallized by the addition of a nonpolar solvent. By this method, we obtained analytically pure salts of the bis(dithiolene) complexes $ReS(S_2C_2R_2)_2^-$ derived from diphenylacetylene (**1a**), 2-butyne (**1b**), and bis(trimethylsilyl)acetylene (**1c**).[9] These compounds were isolated in 30−50% yields as their tetraalkylammonium salts and were identified through spectroscopic studies and, for R = Ph and Me, by single-crystal X-ray analyses.[10] The crystallographic studies confirm the expected square pyramidal arrangement of sulfur atoms surrounding the Re^V center.



(**1**)

(1)

The use of sulfur as a supplemental oxidant also applies to reactions involving olefins, although the reaction takes a different course. In the presence of excess sulfur, ReS_4^- and C_2H_4 (1 atm) react at room temperature in ~1 h to give $NEt_4[ReS(S_4)(S_2C_2H_4)]$ (**2**) in ~90% isolated yield.[10] This formally Re^V complex consists of tetrasulfido, ethanedithiolato, and terminal sulfido ligands arranged in a square pyramidal structure[11] (Figure 1). As seen for **1**, there is one very short Re=S bond (2.05 Å) and four longer Re−S bonds (~2.3 Å).

The existence of the S_4^{2-} ligand in **2** indicates that elemental sulfur serves multiple roles in the addition process. In order to avoid this complication, we modified the reaction conditions based on an analogy to OsO_4-catalyzed oxidations,[12] which utilize amine oxides as supplemental oxidants (Scheme 1).[13] Both Me_3NO and *N*-methylmorpholine *N*-oxide (NMO) have been employed for this purpose. The reaction of $NEt_4[ReS_4]$, C_2H_4 (1 atm, room temperature, 1 h), and NMO afforded $NEt_4[ReO(S_2C_2H_4)_2]$ (**3a**) in 51% yield as orange crystals.[10] This species is spectroscopically identical to the compound inde-

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(7) *n*-Bu_4NReS_4 can be purchased from Strem Chemicals or prepared (Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 4635). For a recent discussion of some reactions of ReS_4^-, see: Murray, H. H.; Wei, L.; Sherman, S. E.; Greaney, M. A.; Eriksen, K. A.; Carstensen, B.; Halbert, T. R.; Stiefel, E. I. *Inorg. Chem.* **1995**, *34*, 841.

(8) We have found that solutions of ReS_4^- react with a wide range of substrates including H_2, $H_2 + S_8$ (to give H_2S), and PhCN. These results will be discussed in future publications.

(9) All new compounds gave satisfactory elemental analyses, showed molecular anions in their mass spectra, and displayed IR and ^1H and ^{13}C NMR spectra consistent with the proposed formulations. These data were provided to the referees and is available upon request.

(10) See Supporting Information.

(11) Crystal data for $C_{10}H_{24}NReS_7$: $P2/c$, $a = 16.5613(3)$ Å, $b = 13.3247(1)$ Å, $c = 26.5712(4)$ Å, $\beta = 100.078(1)°$, $V = 5773.11(14)$ Å^3, $Z = 4$, $D_{calcd} = 1.964$ g cm^{-3}. The structure was solved by direct methods, and all nonhydrogen atoms were refined anisotropically. For 13 768 unique reflections (λ (Mo Kα) = 0.710 73 Å, [$I > 2\sigma(I)$]) collected at $T = 198(2)$ K for $2.50 < 2\theta < 57.56$, the final R value is 0.0500 (wR_2 = 0.0942). There are three independent molecules in the asymmetric unit, and in one the S_4^{2-} and the $C_2H_4S_2^{2-}$ were disordered but this disorder was successfully modeled.

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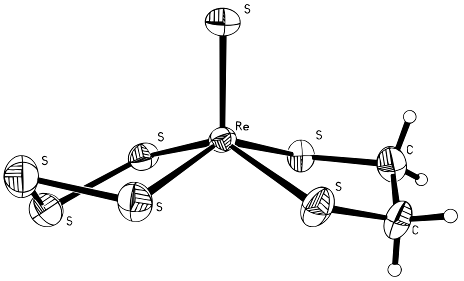
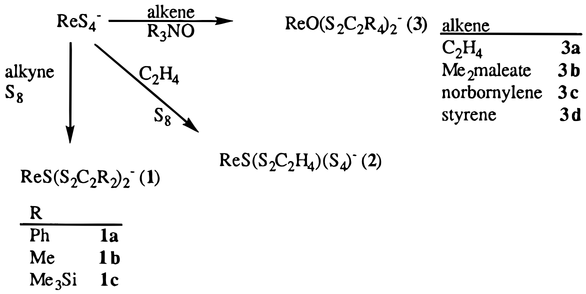


Figure 1. Structure of the anion in $Et_4N[ReS(S_4)(S_2C_2H_4)]$ with thermal ellipsoids drawn at the 50% probability level.

Scheme 1



pendently synthesized from $ReCl_3O(PPh_3)_2$ and ethanedithiol.[14] When in the presence of 1 equiv of NMO, norbornylene (21 °C, 30 h, 92% yield) and dimethyl maleate (22 °C, 10 h, 82% yield) react readily, while styrene required more forceful conditions (65 °C, 18 h, 35% yield).[10] Compounds **3b**−**d** exist as mixtures of isomers. Further work is planned to clarify the stereochemical details of these additions.

The olefin addition reaction using NMO enjoys some generality. In terms of potential synthetic applications, the NMO method utilizes Re more efficiently, since two substrates add per Re. These experiments suggest that ReS_4^- could be employed for the conversion of alkenes to 1,2-dithiols. Preliminary measurements indicate that alkynes also react with ReS_4^-/NMO to give adducts whose stoichiometry is 1:1.

The reactivity of ReS_4^- toward unsaturated substrates contrasts with the relative inertness of ReO_4^- (which we reconfirmed). We suggest that the higher reactivity of ReS_4^- vs ReO_4^- is related to the π-donor properties of S vs O as reflected by the redox couples for $ReO_4^{-/2-}$ (−2.1 V vs Ag/AgCl) and for $ReS_4^{-/2-}$ (−1.15 V).[15] Finally, there are obvious similarities between ReS_4^- and the widely used OsO_4.[12] The present results suggest that the thiometallates and their many analogs[1] merit attention for their potential reactivity toward simple organic compounds.

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Supporting Information Available: Details of syntheses, kinetics measurements, and crystal structure analyses (36 pages) See any current masthead page for ordering and Internet access instructions.

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