C–S Bond Cleavage

Phosphine-Promoted Conversion of Oxo(dithiolato)rhenium(V) into Thio(thiolatoalkyl)rhenium(V) Compounds**

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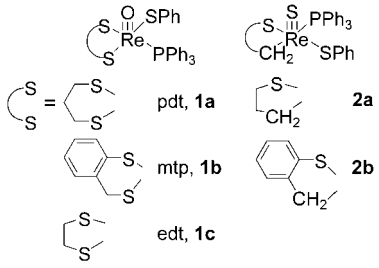
The cleavage of C–S bond is the most important step for removing sulfur from petroleum feedstocks.[1] The common strategies include thermal decomposition,[2] photolysis,[3] reduction and/or protonation[4] of sulfur-containing metal complexes. We have now found that reaction under mild conditions between oxo(dithiolato)rhenium(v) complexes and triphenylphosphine cleaves a C–S bond, giving a thio(thiolatoalkyl)rhenium(v) product. This reaction, to our knowledge, is unprecedented.

Treatment of **1a** or **1b** with triphenylphosphine leads to **2a** or **2b**, as in Equation (1). The reaction follows second-



order kinetics; $k_{1a} = 3.61(2) \times 10^{-3}$ and $k_{1b} = 2.61(5) \times 10^{-4}\,L\,mol^{-1}\,s^{-1}$ (benzene, 25.0 °C). In the reaction in Equation (1) the Re≡O bond is cleaved and P=O and Re≡S bonds are formed at the expense of a CH_2-S-Re bond, and a new Re–C bond is formed; consequently, the six-membered chelate ring becomes a five-membered one.

$$\mathbf{1a}(\mathbf{1b}) + PPh_3 \rightarrow \mathbf{2a}(\mathbf{2b}) + Ph_3PO \qquad (1)$$

On the other hand **1c** does not undergo this reaction, thus avoiding formation of a four-membered chelate ring. Additionally, but incidental to the new chemistry, all three versions of **1** exchange PAr_3 for PPh_3, as do their methyl analogues [MeReO(dithiolato)PPh_3].[5]

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Both **2a** and **2b** were characterized spectroscopically and analytically (Experimental Section). The methylene resonance signals shift downfield: $\delta = 4.95$ and 3.30 ppm for **1b** as compared to $\delta = 5.89$ and 3.61 ppm for **2b**. Further, the ν_{ReO} frequencies change from the typical values for oxorhenium(v) complexes,[6] 947 cm^{-1} (**1b**) to ν_{ReS} 500 (**2a**) and 510 cm^{-1} (**2b**).[7] The ^{31}P NMR spectrum in C_6D_6 showed the slow disappearance of the resonance signal of **1b** at $\delta = 19.0$ ppm and the growth of new signals for **2b** at $\delta = 34.8$ ppm and for Ph_3PO at $\delta = 26.0$ ppm. Compounds **2a** and **2b** were also characterized by X-ray crystallography.[8] Their molecular structures are based on a square pyramid with an apical thio ligand (Figure 1). The rhenium–element bond lengths are

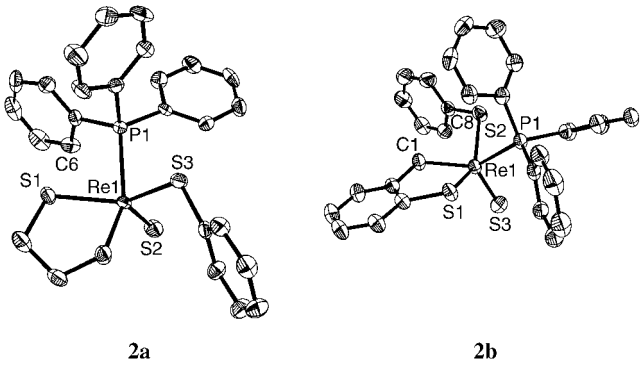
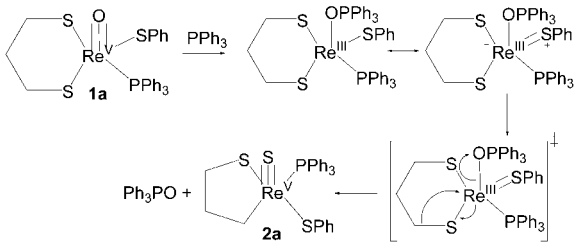


Figure 1. Molecular structures of **2a** and **2b** (thermal ellipsoids set at 50 % probability). Selected bond lengths [pm]: **2a**, Re-S(2) 208.08(15), Re-S(1) 228.49(15), Re-S(3) 228.98(15), Re-C 214.0(6), Re-P 241.56(14); **2b**, Re-S(3) 208.83(9), Re-S(2) 229.50(9), Re-S(1) 229.12(8), Re-C 215.6(3) Re-P 242.02(8).

comparable to those found in related rhenium(v) complexes,[7,9] save for reported Re≡O bonds of 168(3) pm, compared to the Re≡S bonds of 208 pm in **2a**, **2b**. Note that in **1b** the phosphorus atom and the phenolic sulfur are in *trans* positions whereas in the product **2b** they lie *cis* to one another (see below).

On the basis of the data obtained, we suggest the mechanism shown in Scheme 1. The first step comprises nucleophilic attack on the oxo group of **1a**, a process which is reasonable given the formal charges, $Re^{-}\equiv O^{+}$; moreover, attack of phosphine at a terminal oxo group has precedent.[10] The resulting intermediate is assisted to the product by the $Re^{-}=S^{+}Ph$ resonance form. The intervention of this resonance form may be the ultimate reason for the failure of [MeReO(dithiolato)PPh_3] complexes to undergo parallel



Scheme 1. Proposed mechanism for the conversion of **1a** into **2a**.

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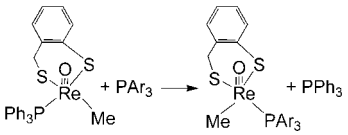
reactions. Reaction of **1a** or **1b** with PAr_3 always leads to PAr_3 products analogous to **2a** or **2b**, because phosphine exchange in **1** occurs more rapidly than the reaction in Equation (1). We have found no precedent for the reaction in Equation (1), although certain features are common to an organic rearrangement.[11]

Finally, there is an issue for **2b** not accounted for by the mechanism shown in Scheme 1, namely that the crystal structure establishes that the PhS group lies *trans* to the phenolic sulfur atom (S1), opposite to its location in **1b**. Isomerization is not an issue for the reaction of **1a**, of course, because it has equivalent sulfur atoms. It has been shown that geometrical isomerization accompanies the bimolecular, associative ligand substitution reactions between [MeReO(mtp)PPh_3] and PAr_3, Equation (2).[5] This precedent constitutes the basis for **2b** not being obtained the same isomer as **1b**; it leaves unanswered the question as to whether **2b**, as isolated, is the more stable geometric isomer.



(2)

Experimental Section

2a: As a mixture of [{PhSReO(pdt)}$_2$] (the precursor of **1a**[12] (165 mg, 0.20 mol) and PPh_3 (484 mg, 1.85 mmol) in toluene (100 mL) was stirred for two days, the solution changed gradually from brown to yellowish. During removal of the solvent a yellowish solid precipitated. This solid was dissolved in the minimum volume of CH_2Cl_2, loaded onto a silica gel column, and eluted with diethyl ether/hexanes. Yield 71 %; ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 7.77$ (b, 6H), 7.56 (dd, $J = 7.2$ Hz, 2H), 7.52–7.43 (m, 9H), 7.30 (t, $J = 7.6$ Hz, 2H), 7.23 (t, $J = 7.6$ Hz, 1H), 5.40 (dd, $J = 13.6$ Hz, 1H), 3.37–3.33 (m, 1H), 3.24–3.18 (m, 1H), 3.02–2.90 (m, 1H), 2.39–2.31 (m, 1H), 1.74–1.66 ppm (m, 1H), ^{31}P NMR (162 MHz, external reference 85 % aq. H_3PO_4, CD_2Cl_2): $\delta = 31.2$ ppm, IR (KBr pellet) 500 cm^{-1}. Elemental analysis (%) calcd for $C_{27}H_{26}S_3PRe{\cdot}0.5\,(C_2H_5)_2O$:C 49.69, H 4.46, S 13.72; found: C 50.17, H 4.05, S 12.98. Crystals of $C_{27}H_{26}S_3PRe{\cdot}0.5\,C_6H_6$ suitable for diffraction were grown from benzene solutions of **2a**.

2b: The analogous procedure was used to prepare the brown compound **2b** in 61 % yield, from **1b**[12] (50 mg, 0.07 mmol) and PPh_3 (92 mg, 0.35 mmol) in toluene (20 mL). Yield 61 %, ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 7.83$ (b, 6H), 7.61–7.56 (m, 3H), 7.52–7.45 (m, 11H), 7.30 (t, 1H), 7.22 (d, 1H), 7.07 (t, 1H), 6.99 (t, 1H), 5.89 (dd, $J_1 = 1.2$ Hz, $J_2 = 17$ Hz, 1H), 3.61 ppm (dd, $J_1 = 9$ Hz , $J_2 = 17$ Hz, 1H), ^{31}P NMR (162 MHz, external reference 85 % aq. H_3PO_4, CD_2Cl_2): $\delta = 34.4$ ppm (34.8 ppm in C_6D_6). IR (KBr pellet), 510 cm^{-1} (m, $\nu_{Re=S}$). Elemental analysis (%) calcd for $C_{31}H_{26}S_3PRe{\cdot}0.5\,C_7H_8$: C 54.73, H 3.99, S 12.69, P 4.09; found: C 55.67, H 3.76, S 11.52, P 3.25. the solvent contained in the powdered sample for analysis was detected by ^{1}H NMR spectrosocpy. The red-brown single crystals of $C_{31}H_{26}S_3PRe$ that were grown from toluene-hexanes solutions of **2b** contained no solvent of crystallization.

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[8] Crystal data for $C_{27}H_{26}PReS_3{\cdot}0.5\,C_6H_6$. **2a**, $M_r = 702.88$, $0.2 \times 0.18 \times 0.08$ mm^3, monoclinic, space group $P2_1/n$, $a = 9.6367(19)$, $b = 13.743(3)$, $c = 20.877(4)$ Å, $\beta = 94.338(4)°$, $V = 2757.0(9)$ Å^3, $\rho_{calcd} = 1.693$ Mg m^{-3}, $Z = 4$, $2\theta_{max} = 56.66°$, 6614 independent reflections, $R_1 = 0.0366$ for 4636 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.0659$, 316 parameters. Crystal data for $C_{31}H_{26}PReS_3$, **2b**, $M_r = 711.87$, $0.25 \times 0.13 \times 0.10$ mm^3, monoclinic, space group $P2_1/n$, $a = 11.6792(19)$, $b = 14.108(2)$, $c = 17.107(3)$ Å, $\beta = 94.460(3)°$, $V = 2810.2(8)$ Å^3, $\rho_{calcd} = 1.683$ Mg m^{-3}, $Z = 4$, $2\theta_{max} = 56.56°$, 6554 independent reflections, $R_1 = 0.0252$ for 5645 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.0603$, 316 parameters. CCDC-241807 (**2a**) and CCDC-235612 (**2b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union

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[12] Compounds **1a**–**c** with a PhS-Re group are new but will not be described herein as they are the exact analogues of the Me–Re counterparts already reported.[6]

