Monomerization of a Rhenium(V) Dimer by Ligation

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Received April 6, 1999

Stoichiometric and catalytic oxygen atom transfer reactions involving Re(V) and Re(VII) oxides and their derivatives have received great attention in recent years.[1−3] Our recent work has focused on elucidating the mechanisms of these reactions, in particular those involving methyltrioxorhenium(VII), MTO, and its reduced forms.[4−6] A yellow dimeric dithiolato(oxo)rhenium(V) compound, designated **D** in Chart 1, has been prepared from MTO and the dithiolate, **1**. The synthesis and characterization of **D** have been reported.[7] We have found that reactions between **D** and prospective ligands (L) cause its monomerization. With the resulting family of compounds designated as **M**−L, the net reaction is represented by eq 1. The structural formulas of the participants are given in **Chart 1**. Examples of ligand-induced monomerization reactions are rare, although ones somewhat similar to reaction 1 are known for the dimer $[Rh(CO)_2Cl]_2$[8] and for certain proteins[9] as well.

$$\mathbf{D} + 2L \rightarrow 2\mathbf{M}{-}L \qquad (1)$$

To learn about the mechanism of reaction 1, experiments along several lines were carried out in toluene and benzene, with L = PPh_3 and Me_2SO; each ligand elucidates a separate facet of the mechanism. We have characterized the products and, in the case of dmso, have isolated the intermediate and characterized it by X-ray crystallography. These results are presented herein.

In the reaction between **D** and PPh_3 in toluene, a few hours is needed to complete the formation of the green complex **M**−PPh_3 (λ_{max} 606 nm, ϵ 190 L mol^{-1} cm^{-1}, $\delta = 2.97$ ppm for ReCH_3), whose crystal structure we reported earlier.[7] The reaction rate is first-order with respect to [**D**]. The pseudo-first-order rate-constant k_{obs} varies nonlinearly with [PPh_3], as shown in Figure 1. The rate law is made up of two terms with first-order and second-order dependences on [PPh_3]:

$$\frac{d[M - PPh_3]}{dt} = 2\{k_a[PPh_3] + k_b[PPh_3]^2\}\cdot[\mathbf{D}] \qquad (2)$$

These values at 25.0 °C in toluene were found by least-squares fitting: $k_a = (8.2 \pm 0.2) \times 10^{-3}$ L mol^{-1} s^{-1} and $k_b = (5.2 \pm 0.2) \times 10^{-2}$ L^2 mol^{-2} s^{-1}.

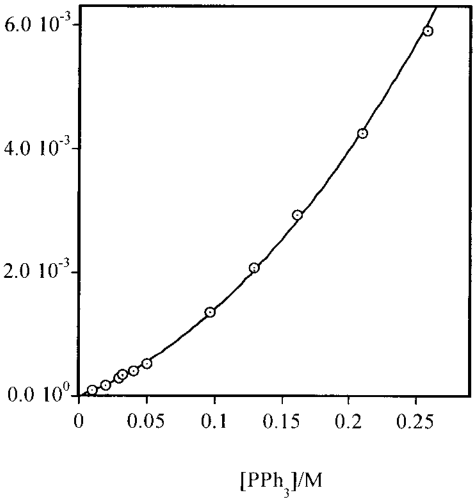
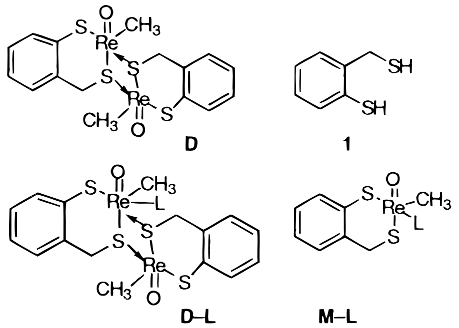


Figure 1. Dependence of the pseudo-first-order rate constant k_{obs} on the concentration of triphenylphosphine in toluene at 25.0 °C. The solid line represents the least-squares fit based parallel paths with first-order and second-order dependences on phosphine concentration, as expressed by eq 2.

Chart 1



One possible reaction scheme features a **D** ⇌ 2**M** interconversion, followed by the step **M** + PPh_3 → **M**−PPh_3. Such a mechanism has been observed for the dimeric Re(V) oxo compound, $(Cp^*ReO)_2(\mu\text{-}O)_2$, not strictly with a ligand, but with an epoxide.[10] That mechanism cannot apply in this instance, however, because the rate law would not have the correct form. The scheme presented in eqs 3−5 does agree with kinetics. It features a dimeric intermediate, **D**−PPh_3, that is asymmetric with respect to its binding of PPh_3.

The equilibrium constants for direct coordination of PPh_3 to **D** are known to be small, since only **D** and **M**−PPh_3 were detected during the time course. The rate law then agrees with eq 2, with $k_a = k_3K_1$ and $k_b = k_4K_1K_2$. These composite constants cannot be resolved further from the available information.

We next turned to the case of L = Me_2SO. The reaction between **D** and dmso is exceptionally rapid. The yellow color of **D** turned pink immediately upon addition of dmso. Stopped-flow

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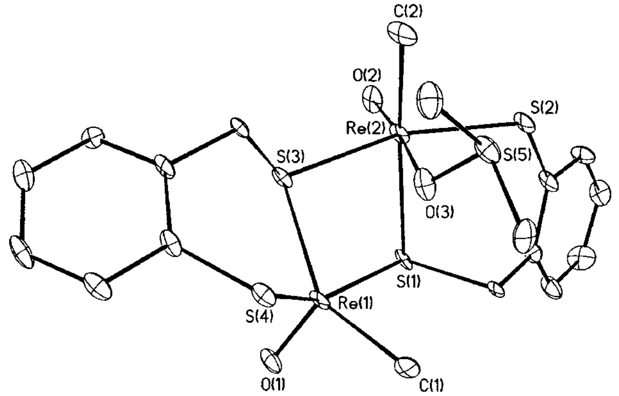
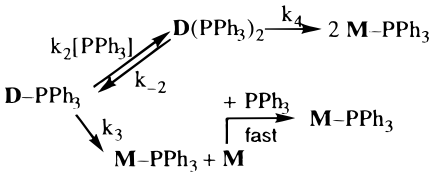


Figure 2. Perspective view of the asymmetric dinuclear dmso complex, **D**−L with thermal ellipsoids of 30% probability level. Selected bond lengths (pm) and angles (deg): Re(2)−O(2), 169.4; Re(2)−C(2), 215.0; Re(2)−S(2), 233.0; Re(2)−O(3), 238.6; Re(2)−S(1), 238.8; Re(2)−S(3), 241.8; O(2)−Re(2)−O(3), 171.9; C(2)−Re(2)−O(3), 78.1; S(2)−Re(2)−O(3), 83.4; O(3)−Re(2)−S(1), 75.2; O(3)−Re(2)−S(3), 73.8.

$$\mathbf{D} + PPh_3 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathbf{D} - PPh_3 \qquad (3)$$



(4)

(5)

determinations at the lowest allowable concentrations and temperature (1.0 mM **D** and 8.0 mM dmso in benzene at 280 K) gave evidence only for a completed reaction.[11] From that we set $k_1 > 3 \times 10^5$ L mol^{-1} s^{-1}. Spectrophotometric and NMR determinations (details in the Supporting Information) gave evidence of the equilibrium written in eq 3, with $K_1 = 120 \pm 6$ L mol^{-1} (298 K, benzene). From the temperature-dependent values of K_1 (283−333 K), $\Delta H_1° = -35.6 \pm 0.8$ kJ mol^{-1} and $\Delta S_1° = -80 \pm 3$ J mol^{-1} K^{-1} were determined.

We were able to crystallize the 1:1 adduct of **D** and dmso, **D**−dmso. Its molecular structure is shown in Figure 2.[12,13] The two Re atoms are different, one being six-coordinate, the other five. A similar asymmetric dmso complex has been reported for a dimeric Re(III) complex.[14] The geometry around Re(1) in the new compound is best described as distorted square pyramidal with atoms S(1), S(3), S(4), and C(1) in the basal plane and atom O(1) in the apex. Atoms S(1), S(3), S(4), and C(1) are planar within 6 pm while vector Re(1)−O(1) forms an 84.4° angle with this plane. The coordination sphere around Re(2) is severely distorted octahedral due to the coordination of one dmso molecule trans to O(2). The displacement of Re(2) from the plane defined by atoms C(2), S(1), S(2), and S(3) is 49 pm, and the sum of the angles around Re(2) defined by these atoms is 349.6°. These values can be contrasted with the corresponding parameters for the square pyramidal Re(1) which comprised 64 pm and 342.1°, respectively. For the bound dmso, the Re(2)−O(3) distance is 238.6pm and the Re(1)−O(3) distance is 287.4 pm.

The NMR signals of **D** and **D**−dmso could not be resolved even at −50 °C. The proximity of the second rhenium to the oxygen atom of dmso in **D**−dmso raises the possibility of a fast internal exchange of dmso between the two rhenium centers. However, this cannot be claimed unequivocally because the equilibration time in reaction 3 is also very brief.

Much weaker and also very fast coordination of a second dmso yields **D**(dmso)$_2$. The changes in the UV−vis and NMR spectra were too small to characterize this species reliably. Kinetic studies of the subsequent monomerization reaction gave $K_2 \cong 0.6$ L mol^{-1} and (for the reaction analogous to eq 4 with dmso in place of PPh$_3$), $k_4 \cong 7 \times 10^{-5}$ s^{-1} (293 K, benzene) with k_3 for dmso being too small to give a measurable contribution to the rate. **M**−dmso was not detected, however, since subsequent fast redox reactions, including the breaking of the S−O bond, ensued. These events are unrelated to the present subject and will be reported separately.

In summary, we have shown that the monomerization of **D** by ligands goes through an initial 1:1 adduct, which was characterized by X-ray crystallography in the case of dmso. The kinetic role of the analogous adduct is clear in the reaction with PPh$_3$, but that adduct is not formed in significant concentrations. We are currently investigating the mechanism of monomerization with other neutral and anionic ligands.

Acknowledgment. This research was supported by a grant from the National Science Foundation (CHE-9625349). Some experiments were conducted with the use of the facilities of the Ames Laboratory. Helpful suggestions made by Professor Albert Haim are acknowledged.

Supporting Information Available: Experimental descriptions and figures showing UV−vis changes, NMR chemical shift changes, temperature dependence accompanying the equilibrium between **D** and dmso, and repetitive scans made during the reaction between **D** and PPh$_3$ as well as one X-ray crystallogrphic data file for the asymmetric dmso complex **D**−L, in CIF format. These materials are available free of charge from the Internet at http://pubs.acs.org.

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(11) Under these conditions the complex formation reaction is not shifted to give the stoichiometric amount of **D**−L, but is still accompanied by an easily detected absorbance change, ∼0.2 absorbance units at 390 nm.

(12) X-ray crystal data for $C_{25}H_{43}O_5Re_2S_7$: monoclinic, $P2_1/n$, $a = 14.1515(12)$ Å, $b = 10.8017(9)$ Å, $c = 22.9054(19)$ Å, $\beta = 101.503(2)°$, $V = 3431.0(5)$ Å^3, $Z = 4$, $T = 193(2)$K, $D_{calc} = 1.975$ Mg/m^3, $R(F) = 6.21\%$ for 4862 independently observed ($I \geq 2\sigma(I)$) reflections ($4° \leq 2\theta \leq 53°$).

(13) The software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI). Absorption corrections were carried out using the program DIFABS (Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158).

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