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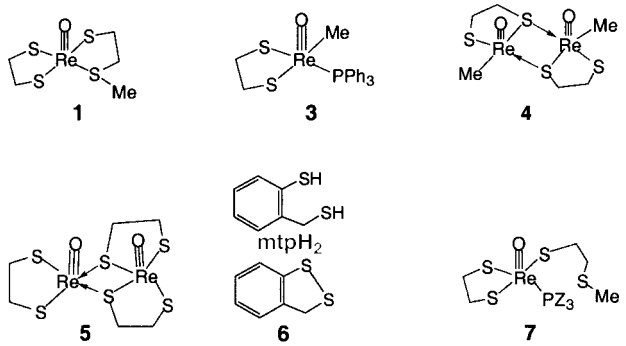
Methyl Transfer from Rhenium to Coordinated Thiolate Groups**

Xiaopeng Shan, Arkady Ellern, and James H. Espenson*

A prominent reaction of vitamin B_{12} is the conversion of D,L-homocystein, $HS(CH_2)_2CHNH_2CO_2H$, to L-methionine, $MeS(CH_2)_2CHNH_2CO_2H$, with methylcobalamin and methylcobinamide.[1–4] Methyl bis(dimethylglyoximato)cobalt(III) and related complexes also convert thiols to thioethers [Eq. (1)]:[5]

$$Co^{III}-CH_3 + RSH \rightarrow [Co^{I}]^- + RSCH_3 + H^+ \quad (1)$$

There are, however, a lack of precedents in the literature for similar conversions that do not involve organocobalt complexes. In this work, new reactions of rhenium complexes have been examined, and sound evidence for the analogous conversion has now been obtained.



$MeReO_3$ (MTO, **2**)[6] reacts with the readily-oxidized 2-(mercaptomethyl)thiophenol ($mtpH_2$), to yield a disulfide [Eq. (2)]:

$$2\,MeReO_3 + 4\,mtpH_2 \rightarrow \{MeReO(mtp)\}_2\,(\mathbf{4}) + 2\,(\mathbf{6}) + 4\,H_2O \quad (2)$$

With 1,2-ethanedithiol ($edtH_2$), however, a quite different result was obtained. As Re^{VII} was reduced to Re^{V}, one $edtH_2$ molecule was transformed to $HS(CH_2)_2SMe$, which remains coordinated to the rhenium(V) center through both sulfur atoms in a κ^2 fashion [Eq. (3)]:

$$MeReO_3 + 2\,edtH_2 \rightarrow \mathbf{1} + 2\,H_2O \quad (3)$$

Details of the synthesis and characterization of the dark-red complex **1** are given in the Experimental Section. A similar reaction starting with [MeReO(edt)(PPh_3)] (**3**)[7] gave the same product in lower yield. Crystals of **1** suitable for X-ray diffraction could not be obtained. We have formulated the composition of **1** to be [ReO(κ^2-edt)(κ^2-edtMe)] based on elemental analysis and spectroscopic data. An alternative formulation as an organorhenium(VII) compound, [MeReO(edt)$_2$], could not be ruled out by these data. However, the evidence is in favor of structure **1** as the CH_3 resonance appears at $\delta = 1.90$ ppm, which is further downfield than would be expected for a methyl group coordinated to a Re^{VII} center. Indeed, the proposed mechanism suggests that [MeReO(edt)$_2$] lies on the pathway to **1**.

Chemical methods were therefore used to obtain information about the molecular structure of **1**, particularly with respect to whether the Me–Re interaction present in the starting material is retained. The reaction of **1** with H_2O_2 in wet acetonitrile gave ReO_4^- ions, which are easily recognized from the characteristic UV spectrum. The same product was obtained from **5**, another compound that lacks a Me–Re bond. In contrast, several compounds that do contain a Me–Re bond (**2**, **3**, and **4**) cleanly reacted with H_2O_2 to form

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[**] This work was supported by the US National Science Foundation, Grant No. CH-9982004. We are grateful to Professor G. M. Miller for a discussion concerning crystallography and to Professor D. J. Darensbourg for the gift of 1,3,5-triaza-phosphaadamantane.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

  0044-8249/02/11420-3961 $ 20.00+.50/0

$[MeReO(\kappa^2\text{-}O_2)_2(OH_2)]$, with a characteristic absorption maximum at 360 nm ($\varepsilon = 1200$). Thus, these results suggest that no Me–Re bond exists in **1**.[8]

The reaction of compound **1** with phosphanes (PZ_3, in general) yields a new series of compounds, $[ReO(\kappa^2\text{-edt})(\kappa^1\text{-edtMe})(PZ_3)]$ (**7**) in which the thioether arm has been displaced. One such compound, where $PZ_3 = 1,3,5$-triazaphosphaadamantane (PTA),[9] has been characterized crystallographically; the molecular structure is displayed in Figure 1. Phosphanes are generally much stronger Lewis bases than

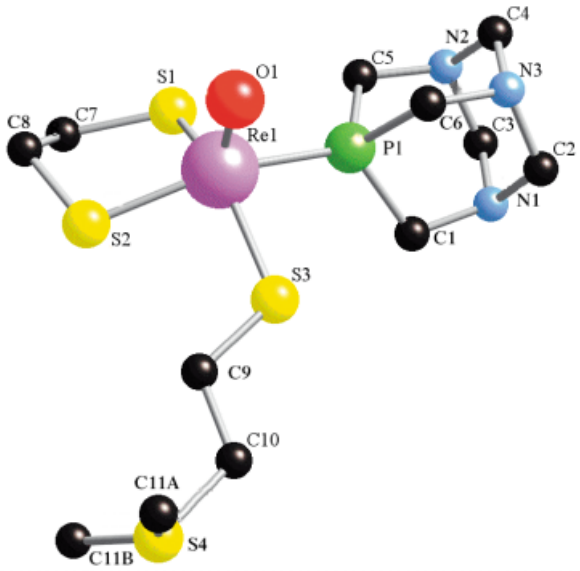


Figure 1. The molecular structure of $[ReO(\kappa^2\text{-edt})(\kappa^1\text{-edtMe})(PTA)]$. The methyl group at S_4 was disordered; the structure was refined at 50% occupancy of the two sites. Selected bond lengths [pm] and angles [°] are: Re-O 170.0(5), Re-S3 230.54(17), Re-P 242.25(18), S4-C10 181.0(9), S4-C11A 175.6(17), S4-C11B 184.0(4); O-Re-S3 110.68(19), O-Re-P 97.3(2), S2-Re-P 153.94(6), S1-Re-S3 133.58(7), C10-S4-C11A 102.7(7), C10-S4-C11B 104.3(17), C11A-S4-C11B 133.1(14). The structure was drawn with the CrystalMaker program.[13]

thioethers and will, to a great extent, displace RSR′ groups. In keeping with this fact, the equilibrium constant for PPh_3 [K_4, Eq. (4)] is 6×10^5 (C_6H_6, 25 °C),[10] whereas the equilibrium constant for Equation (5) (K_5) is 8.0 under the same conditions. The large difference in these values arises from the chelate effect, and illustrates its very substantial importance in this case.

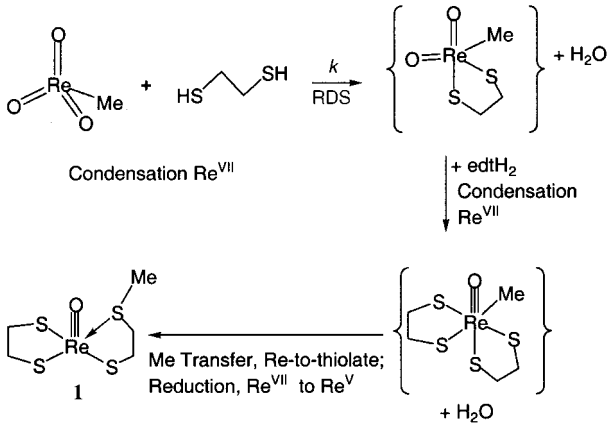
$$MeReO(edt)(Me_2S) + PPh_3 = MeReO(edt)PPh_3 + Me_2S \; K_4 \quad (4)$$

$$\mathbf{1} + PPh_3 = ReO(\kappa^2 - edt)(\kappa^1 - edtMe)(PPh_3) \; K_5 \quad (5)$$

The formation of **1**, as shown in reaction (3), follows the net 1:2 stoichiometry given. It is a sequential process that obeys the rate law [Eq. (6)]:

$$d[\mathbf{1}]/dt = k\,[\mathbf{2}]\,[edtH_2] \quad (6)$$

with $k = 7.3 \times 10^{-2}$ L mol^{-1} s^{-1} (Me_2SO, 25 °C). Clearly the first condensation step is rate determining, as the methylation step occurs more rapidly and is not manifest in the kinetics. The sequential mechanism proposed is given in Scheme 1. The



Scheme 1. Proposed mechanism for the formation of **1** (RDS = rate-determining step).

final step appears to involve nucleophilic attack of the coordinated thiolate sulfur atom on the methyl group of the intermediate. Precedents for this mechanism, aside from those found in organocobalt systems, are rare. While the transfer of a phenyl group to the oxo group of an intermediate species ($[TpRe(O)_2Ph]^+$, Tp = hydrotris(1-pyrazolyl)borate) represents a distantly related example,[11] a more relevant case is the thermal decomposition of $[MeReO(\kappa^2\text{-}O_2)_2(OH_2)]$, which yields MeOOH and $[HReO_4]$.[12]

In summary, a novel transformation of the [MeRe(edt)] complex to give a [Re(thiolate–methylthioether)] complex (**1**) has been discovered and established. This transformation is without precedent, aside from the homocystein-to-methionine transformation found for vitamin B_{12} and its mimics. Furthermore, the thioether group can be replaced by a phosphane; the derivative with PTA was characterized crystallographically. All of these reactions proceed to equilibrium, but owing to the chelate effect, the equilibrium constants are smaller by a factor of 10^5 than the analogous values of K for the displacement of a nonchelated RSR′ group.

Experimental Section

1: Dimethylsulfoxide (0.2 mmol) was added to **2** (0.5 mmol) in toluene (5 mL). 1,2-Ethanedithiol (0.5 mmol) was added to this mixture, whereupon the solution turned red. After 4 h, hexanes (10 mL) were layered on top of the solution, which yielded a deep-red solid (87% yield) which was purified by recrystallization from dichloromethane/hexanes. Elemental analysis (%) calcd for $C_5H_{11}ORES_4$: C 14.95, H 2.76, S 31.94; found: C 15.16, H 2.82, S 32.09; ^{1}H NMR (400 MHz, [D$_6$]benzene, 25 °C): $\delta = 3.55$ (m, 1H; CH_2), 3.36 (m, 1H; CH), 2.70 (m, 1H; CH_2), 2.51 (m, 2H; CH_2), 2.11 (m, 1H; CH_2), 1.92 (m, 1H; CH_2), 1.90 (s, 3H; CH_3), 0.84 ppm (m, 1H; CH_2); ^{13}C NMR (100 MHz, [D$_6$]benzene, 25 °C): $\delta = 45.6$, 45.0, 43.5, 36.2, 22.3 ppm; UV/Vis (C_6H_6): λ_{max} (ε) = 510 (160), 389 nm (3400).

$[ReO(\kappa^2\text{-edt})(\kappa^1\text{-edtMe})(PTA)]$: A 1:1 reaction between **1** and PTA in toluene gave dark, shiny single crystals after recrystallization from toluene/hexanes. Elemental analysis (%) calcd for $C_{11}H_{23}ON_3PReS_4$: C 23.65, H 4.15, N 7.52, S 22.96, P 5.54; found: C 23.57, H 4.12, N 7.55, S 23.25, P 5.61; ^{1}H NMR (400 MHz, [D$_6$]benzene, 25 °C): $\delta = 4.34$ (m, 1H; CH_2), 4.21 (m, 7H; CH_2), 3.86 (m, 6H; CH_2); 3.43 (m, 1H; CH_2), 3.34 (m, 1H; CH_2), 3.20 (m, 1H; CH_2), 2.97 (m, 1H; CH_2), 2.41 (m, 2H; CH_2), 1.98 ppm (s, 3H; CH_3); ^{13}C NMR (100 MHz, [D$_6$]benzene, 25 °C): $\delta = 72.5$ (d, J(C,P) = 7 Hz), 51.9 (d, J(C,P) = 16 Hz), 43.6 (d, J(C,P) = 8 Hz), 42.0(s), 37.2(s), 35.5 (d, J(C,P) = 9 Hz), 15.3 ppm (s); ^{31}P NMR (162 MHz, [D$_6$]benzene, 25 °C): $\delta = -74.0$ ppm; UV/Vis (C_6H_6): λ_{max} (ε) = 386 (1900), 318 (1600; sh),

  0044-8249/02/11420-3962 $ 20.00+.50/0 *Angew. Chem.* **2002**, *114*, Nr. 20

262 nm (3800). CCDC-190226 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 Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Received: June 13, 2002
Revised: August 1, 2002 [Z19200]

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[8] Each compound was treated with 30% hydrogen peroxide to give a final concentration of 38 mM H_2O_2 in acetonitrile. The final spectra from these procedures confirming the two indicated Re^{VII} products are given in the Supporting Information.
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Naked-Eye Detection of Phosphate Ions in Water at Physiological pH: A Remarkably Selective and Easy-To-Assemble Colorimetric Phosphate-Sensing Probe**

Min Su Han and Dong H. Kim*

Phosphate anions are one of most important constituents of living systems. Together with heterocyclic bases and sugars, phosphates make up the genes, the hereditary elements of living systems. In addition, phosphate ions and their derivatives play pivotal roles in signal transduction and energy storage in biological systems.[1] Numerous sensors for anions, including phosphate ions, have been devised, but most of them use organic solvents as the detection medium because these sensors rely on hydrogen-bonding and electrostatic interactions for the recognition of analytes.[2] These interactions are, however, attenuated drastically in a highly polar medium such as water, because of the competing solvation effect.[3] The detection of anions such as phosphate in water is, hence, a challenging task.[4] We report herein a colorimetric sensor that can detect phosphate anions in an aqueous solution of neutral pH values. The sensor is easy to assemble and shows a high sensitivity and excellent selectivity for phosphate ions over other anions.

In assembling the sensor, we took advantage of metal–ligand interactions. Such interactions are so highly favorable that they occur even in polar media. Furthermore, the metal ion can present some geometrical preferences, thus imparting selective binding tendencies towards anions of a given shape.[5] 2,6-Bis(bis(2-pyridylmethyl)aminomethyl)-4-methylphenol (H-bpmp) was reported to form a crystalline dinuclear complex with Co^{II},[6] and Seo et al. reported that the phenylphosphonate anion binds to the dinuclear complex of Co^{III} with H-bpmp by bridging the two metal ions.[7] These reports led us to explore the metal complex of H-bpmp as a receptor for phosphate ions. The dinuclear Zn^{II} complex of H-bpmp was readily obtained by dissolving H-bpmp and zinc perchlorate in water; the complex is colorless and has a good water solubility, which are features desirable for using the complex as a receptor for a water-soluble chemosensor. We chose pyrocatechol violet, a catechol-type pH-sensitive dye, as the chromogenic indicator for the sensor. Catechols are known to coordinate to the two metal ions in a phenoxo-bridged binuclear metal complex.[8] Furthermore, it is known that the yellow color of pyrocatechol violet at neutral pH may change to blue when it binds to a metal ion.[9] Therefore, the displacement of the receptor-bound pyrocatechol violet by a phosphate anion would be communicated visually as well as spectrophotometrically. The competition approach[10] used for assembling the present sensor is schematically illustrated in Figure 1.

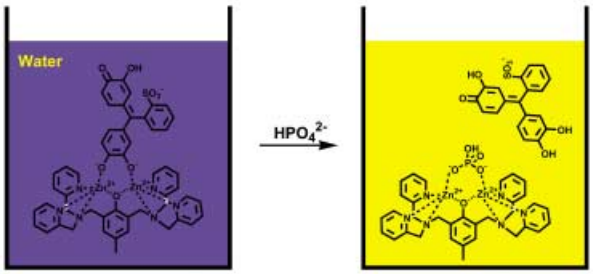

Figure 1. A schematic representation of the phosphate anion sensor.

The sensing ensemble was prepared by simply mixing H-bpmp,[11] zinc perchlorate, and pyrocatechol violet[12] in a 1:2:1 molar ratio in an aqueous solution of 10 mM HEPES buffer pH 7.0 (HEPES = 2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid). Figure 2a shows the UV/Vis spectra obtained when the solution of $[Zn_2(H\text{-bpmp})]^{3+}$ was titrated into the aqueous buffer (pH 7.0) solution of the indicator (50 μM). The color change from yellow ($\lambda_{max} = 444$ nm) to blue ($\lambda_{max} = 624$ nm) observed upon the addition of $[Zn_2(H\text{-bpmp})]^{3+}$ is ascribed to the binding of pyrocatechol violet to the Zn^{II} ions

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[**] This work was supported by the Korea Science and Engineering Foundation, and M.S.H. is a recipient of a BK21 fellowship from the Ministry of Education and Human Resources, Republic of Korea.

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