

eters, bond distances, bond angles, and torsion angles (12 pages). Ordering information is given on any current masthead page.

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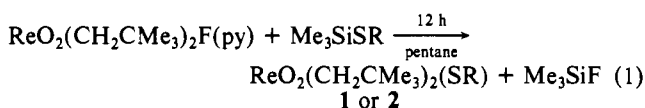
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### Alkoxide and Thiolate Rhenium(VII) Oxo-Alkyl Complexes and $\text{Re}_2\text{O}_5(\text{CH}_2\text{CMe}_3)_4$ , a Compound with a $[\text{O}_2\text{Re}-\text{O}-\text{ReO}_2]^{4+}$ Core

We recently reported synthetic routes to the Re(VII) dioxo compounds  $\text{ReO}_2(\text{CH}_2\text{CMe}_3)_2\text{X}(\text{py})$  ( $\text{X} = \text{Br}, \text{Cl}, \text{F}$ ).<sup>1</sup> Rhenium(VII) compounds supported by only two oxo groups are rare, presumably because a convenient general synthesis has not been available.<sup>2</sup> The synthesis of the halide complexes gave us the opportunity to prepare a range of compounds via simple substitution reactions. Herein, we report the synthesis of the alkoxide and thiolate Re(VII) dioxo compounds  $\text{ReO}_2(\text{CH}_2\text{CMe}_3)_2(\text{ER})$  and describe the synthesis and structure of  $\text{Re}_2\text{O}_5(\text{CH}_2\text{CMe}_3)_4$ , the first example of a rhenium oxo compound containing a  $[\text{O}_2\text{Re}-\text{O}-\text{ReO}_2]^{4+}$  core.

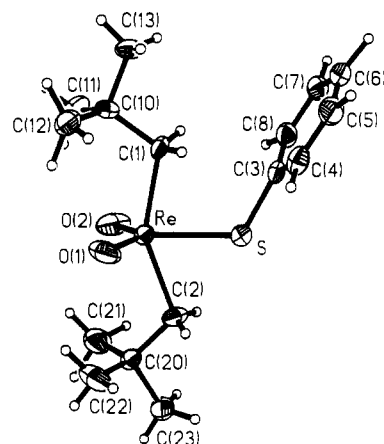
Reactions of  $\text{ReO}_2(\text{CH}_2\text{CMe}_3)_2\text{F}(\text{py})$  with  $\text{Me}_3\text{SiSR}$  reagents give  $\text{ReO}_2(\text{CH}_2\text{CMe}_3)_2(\text{SR})$  ( $\text{R} = \text{Me}$  (1), Ph (2)) (eq 1). IR



$\text{R} = \text{Me}$  (1) (65%), Ph (2) (47%)

spectra recorded for 1 and 2 show the two-band pattern characteristic of a *cis*- $\text{MO}_2$  moiety [e.g.,  $\nu(\text{ReO}_2) = 985, 949 \text{ cm}^{-1}$  for 1].<sup>3</sup> Room-temperature  $^1\text{H}$  NMR spectra for 1 and 2 each reveal singlets corresponding to two equivalent neopentyl ligands, but at low temperatures singlets arising from two different neopentyl groups are observed for both compounds. This, together with the IR data, indicates that the molecules have trigonal-bipyramidal (tbp) geometries in which rapidly exchanging neopentyl ligands occupy axial and equatorial positions or both neopentyl ligands occupy axial positions and rotation about the Re-S bond is slow at low temperatures. The latter structure for 2 is found in the solid state from an X-ray crystallographic study (Figure 1).<sup>4</sup>

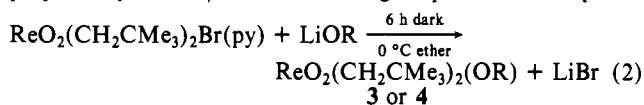
- (1) Cai, S.; Hoffman, D. M.; Wierda, D. A. *Organometallics* **1988**, *7*, 2069.  
(2) Other Re(VII) dioxo compounds: Aynsley, E. E.; Peacock, R. D.; Robinson, P. L. *J. Chem. Soc.* **1950**, 1622. Peacock, R. D. *J. Chem. Soc.* **1955**, 602; Mertis, K.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 1488. Beattie, I. R.; Crocombe, R. A.; Ogden, J. S. *J. Chem. Soc., Dalton Trans.* **1977**, 1481. Cai, S.; Hoffman, D. M.; Lappas, D.; Woo, H.-G.; Huffman, J. C. *Organometallics* **1987**, *6*, 2273. Cai, S.; Hoffman, D. M.; Wierda, D. A. *J. Chem. Soc., Chem. Commun.* **1988**, 313.  
(3) Griffith, W. P.; Wickins, T. D. *J. Chem. Soc. A* **1968**, 400.



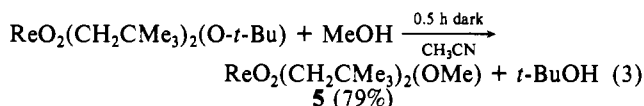
**Figure 1.** ORTEP plot of  $\text{ReO}_2(\text{CH}_2\text{CMe}_3)_2(\text{SPh})$  (2) showing the atom numbering scheme (50% probability ellipsoids). Selected distances ( $\text{\AA}$ ) and angles (deg): Re-S, 2.395 (2); Re-O(1), 1.692 (7); Re-O(2), 1.694 (6); Re-C(1), 2.160 (7); Re-C(2), 2.188 (8); S-C(3), 1.774 (7); S-Re-O(1), 121.2 (2); S-Re-O(2), 120.8 (2); O(1)-Re-O(2), 117.7 (3); S-Re-C(1), 79.6 (2); S-Re-C(2), 69.8 (2); C(1)-Re-C(2), 149.5(3); Re-S-C(3), 118.3 (3).

The most unusual structural feature of 2 is the large O(1)-Re-O(2) angle [117.7 (3) $^\circ$ ]; O=M=O angles in  $d^0$  compounds usually fall in the range 100-110 $^\circ$  [e.g.,  $\angle\text{O}=\text{Mo}=\text{O} = 110.5$  (3) $^\circ$  in *tbp*  $\text{MoO}_2(\text{L}-\text{NS}_2)$ ].<sup>5</sup> There is no obvious electronic reason for an open angle in 2. There are, however, four intramolecular contacts between the neopentyl methyl groups [C(11), C(12), C(21) and C(22)] and the oxo ligands, which average 0.3  $\text{\AA}$  less than the van der Waals contact distance of 3.4  $\text{\AA}$ ,<sup>6</sup> that may explain the large angle.

The alkoxide complexes  $\text{ReO}_2(\text{CH}_2\text{CMe}_3)_2(\text{OR})$  ( $\text{R} = \text{CH}_2\text{CMe}_3$  (3), *t*-Bu (4)) are prepared by the salt metathesis reactions shown in eq 2, and  $\text{ReO}_2(\text{CH}_2\text{CMe}_3)_2(\text{OMe})$  (5) is prepared by alcohol/alkoxide exchange, eq 3. Each compound



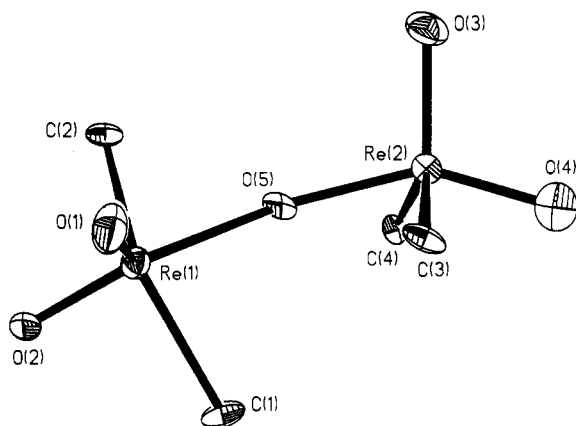
$\text{R} = \text{CH}_2\text{CMe}_3$  (3) (69%), *t*-Bu (4) (82%)



shows IR bands arising from the  $\text{ReO}_2$  group [e.g., 955, 923  $\text{cm}^{-1}$  ( $\text{Re}^{18}\text{O}_2$ ; 898, 878  $\text{cm}^{-1}$ ) for 4] that are lower in energy than those observed for five-coordinate 1 and  $\text{ReO}_2(\text{CH}_2\text{CMe}_3)_2\text{Br}$  (1001, 961  $\text{cm}^{-1}$ ).<sup>1</sup> This is consistent with the alkoxide ligand being a stronger  $\pi$ -donor to the Re(VII) center than a halide or thiolate and therefore competing more effectively with the oxo ligands for multiple bonding.

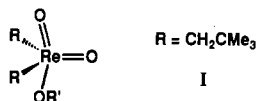
Efforts to obtain a high-quality X-ray structure of an alkoxide

- (4) Crystal data for  $\text{C}_{16}\text{H}_{27}\text{O}_2\text{SRe}$  at -40 (1)  $^\circ\text{C}$ : dark orange blocks from a cold (-20  $^\circ\text{C}$ )  $\text{CH}_3\text{CN}$  solution,  $0.24 \times 0.36 \times 0.40 \text{ mm}$ , triclinic, space group  $P\bar{1}$ ,  $a = 9.196$  (2)  $\text{\AA}$ ,  $b = 10.067$  (2)  $\text{\AA}$ ,  $c = 11.122$  (2)  $\text{\AA}$ ,  $\alpha = 102.22$  (1) $^\circ$ ,  $\beta = 103.24$  (1) $^\circ$ ,  $\gamma = 105.25$  (1) $^\circ$ ,  $d_{\text{calcd}} = 1.69 \text{ g cm}^{-3}$ ,  $Z = 2$ ,  $\mu = 67.61 \text{ cm}^{-1}$ . X-ray diffraction data were collected on a Nicolet R3m/V diffractometer using a graphite-monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) in the  $\theta$ - $2\theta$  scan mode. Lorentz and polarization corrections and an empirical absorption correction (PSCOR) were applied to the data. A total of 3858 reflections were collected in the range  $4^\circ < 2\theta < 50^\circ$  ( $\pm h, \pm k, l$ ); 3259 were unique reflections ( $R_{\text{int}} = 0.0289$ ), and 2853 with  $F_o > 6\sigma(F_o)$  were used in the structure solution. An extinction correction was applied in the final cycles of refinement.  $R(F) = 0.0346$ ;  $R_w(F) = 0.0358$ . Structure factors from: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.  
(5) (a) Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 917. See also: Hawkins, J. M.; Dewan, J. C.; Sharpless, K. B. *Inorg. Chem.* **1986**, *25*, 1501.  
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**Figure 2.** ORTEP plot of the  $\text{Re}_2(\mu\text{-O})\text{O}_4\text{C}_4$  core of  $\text{Re}_2(\mu\text{-O})\text{O}_4(\text{CH}_2\text{CMe}_3)_4$  (**6**) showing the atom-numbering scheme (50% probability ellipsoids). The geometries at Re(1) and Re(2) are similar. Selected distances (Å) and angles (deg): Re(1)–O(1), 1.691 (10); Re(1)–O(2), 1.701 (13); Re(1)–O(5), 1.940 (11); Re(2)–O(5), 1.896 (11); O(1)–Re(1)–O(2), 108.5 (5); O(1)–Re(1)–O(5), 100.2 (5); O(2)–Re(1)–O(5), 151.3 (4); O(1)–Re(1)–C(1), 112.8 (5); O(2)–Re(1)–C(1), 88.1 (6); O(5)–Re(1)–C(1), 80.4 (5); O(1)–Re(1)–C(2), 111.5 (5); O(2)–Re(1)–C(2), 89.4 (5); O(5)–Re(1)–C(2), 80.1 (5); C(1)–Re(1)–C(2), 134.0 (5); Re(1)–O(5)–Re(2), 166.3 (5).

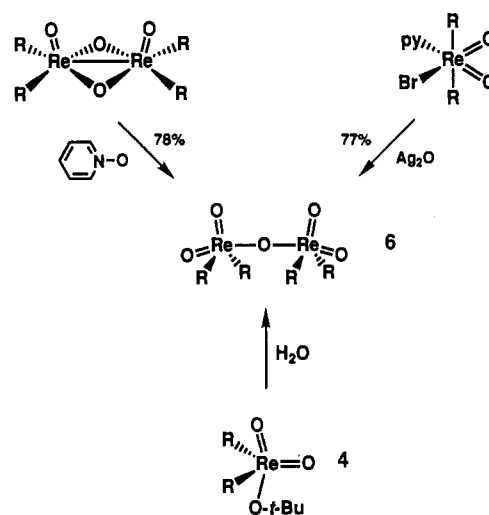
derivative for comparison with **2** have been thwarted by disorder problems. In both of the cases attempted (**4** and **5**), however, it is clear that the gross solid-state structure is **I**, which is similar



to the solid-state structure of  $\text{Re}_2\text{O}_5(\text{CH}_2\text{CMe}_3)_4$  discussed below. In solution, the alkoxides are fluxional, but the low-temperature limiting  $^1\text{H}$  NMR spectrum of **4** can be obtained and it is in accord with **I**.<sup>7</sup> It is not clear why the alkoxide and thiolate compounds differ in structure, but presumably it is due to the greater steric congestion in the inner coordination sphere of the alkoxide derivatives (viz., the Re–OR bond distances will be at least 0.5 Å shorter than the Re–SR distances).<sup>8</sup> It should be noted, however, that the energy difference between the alkoxide and thiolate structures is not large; if it is assumed that the fluxionality of the alkoxide derivatives involves passing through a geometry similar to **2**, then on the basis of the variable-temperature NMR data for **4**, the energy difference between the alkoxide and thiolate geometries can be at most 10 kcal/mol.<sup>9</sup>

The alkoxide compounds are surprisingly light-sensitive (fluorescent light), all decomposing in the solid state to give  $[\text{Re}(\mu\text{-O})\text{O}(\text{CH}_2\text{CMe}_3)_2]_2$  as the only identifiable product.<sup>10</sup> This dimer can be interpreted as arising from the coupling of two  $d^1$   $\text{ReO}_2(\text{CH}_2\text{CMe}_3)_2$  fragments, and its appearance is suggestive of homolytic Re–OR bond cleavage. In contrast to the solid-state decompositions, complex mixtures of organometallic products are obtained when solutions of the alkoxides are exposed to light. In the mixtures,  $[\text{Re}(\mu\text{-O})\text{O}(\text{CH}_2\text{CMe}_3)_2]_2$ ,<sup>10</sup>  $\text{ReO}_2[=\text{C}(\text{H})\text{CMe}_3](\text{CH}_2\text{CMe}_3)$ ,<sup>11</sup> and  $\text{ReO}_3(\text{CH}_2\text{CMe}_3)$ , an analogue of  $\text{ReO}_3\text{Me}$ ,<sup>12</sup> have been identified. There is also a new type of

Scheme I



organometallic compound,  $\text{Re}_2\text{O}_5(\text{CH}_2\text{CMe}_3)_4$  (**6**), which has been characterized by spectroscopic studies and X-ray crystallography (Figure 2).<sup>13,14</sup>

The coordination geometry about the rhenium centers in **6** can loosely be described as trigonal bipyramidal. At each rhenium, a terminal oxo group and the bridging oxo ligand occupy the axial sites [e.g.,  $\angle\text{O}(2)\text{-Re}(1)\text{-O}(5) = 151.3 (4)^\circ$ ], and one terminal oxo and two neopentyl ligands occupy the equatorial sites [e.g.,  $\angle\text{C}(1)\text{-Re}(1)\text{-C}(2)$  and the average  $\angle\text{O}(1)\text{-Re}(1)\text{-C}$  are  $134.0 (5)$  and  $112.2 (5)^\circ$ , respectively]. The Re–O(5) bridge distances (average 1.92 Å) are consistent with some multiple bond character and can be compared to the Re–( $\mu\text{-O}$ ) distance of 1.856 (5) Å in  $[\text{ReO}(\text{CH}_2\text{SiMe}_3)_3](\mu\text{-O})$ ,<sup>15</sup> a diamagnetic compound in which there must be Re–( $\mu\text{-O}$ )  $\pi$  bonding in order to couple the  $d^1$  centers.

The large-scale synthesis of **6** by alkoxide decomposition is impractical, and alternative syntheses have been developed (Scheme I). Most convenient are the reactions of  $[\text{Re}(\mu\text{-O})\text{O}(\text{CH}_2\text{CMe}_3)_2]_2$  with pyridine *N*-oxide and  $\text{ReO}_2(\text{CH}_2\text{CMe}_3)_2\text{Br}(\text{py})$  with  $\text{Ag}_2\text{O}$ .<sup>16</sup> Compound **6** can also be

- (13) Anal. Calcd. for  $\text{C}_{20}\text{H}_{44}\text{O}_5\text{Re}_2$ : C, 32.60; H, 6.02. Found: C, 32.91; H, 5.80.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  3.27 (s, 8,  $\text{CH}_2\text{CMe}_3$ ), 1.14 (s, 36,  $\text{CH}_2\text{CMe}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  86.19 ( $\text{CH}_2\text{CMe}_3$ ), 35.37 ( $\text{CH}_2\text{CMe}_3$ ), 32.42 ( $\text{CH}_2\text{CMe}_3$ ). IR ( $\text{CS}_2$ , NaCl,  $\text{cm}^{-1}$ ):  $\nu(\text{ReO}_2)$  977 s, 944 s [ $\nu(\text{Re}^{18}\text{O}_2)$  925, 896];  $\nu(\text{asym Re-O-Re})$  692 [ $\nu(\text{Re}^{18}\text{O-Re})$  675].
- (14) Crystal data for  $\text{C}_{20}\text{H}_{44}\text{O}_5\text{Re}_2$  at  $-83 (1)^\circ\text{C}$ : red blocks from a cold ( $-20^\circ\text{C}$ )  $\text{CH}_3\text{CN}$  solution,  $0.27 \times 0.32 \times 0.40$  mm, monoclinic, space group  $P2_1/c$ ,  $a = 12.378 (3)$  Å,  $b = 19.087 (4)$  Å,  $c = 11.717 (3)$  Å,  $\beta = 108.86 (2)^\circ$ ,  $d_{\text{calcd}} = 1.87$  g  $\text{cm}^{-3}$ ,  $Z = 4$ ,  $\mu = 93.83$   $\text{cm}^{-1}$ . X-ray diffraction data were collected on a Nicolet R3m/V diffractometer using graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å) in the  $\theta$ - $2\theta$  scan mode. Lorentz and polarization corrections and an empirical absorption correction (DIFABS) were applied to the data. A total of 4168 reflections were collected in the range  $4^\circ < 2\theta < 45^\circ$  ( $h, k, \pm l$  + Friedel pairs); 3203 were unique reflections ( $R_{\text{int}} = 0.0398$ ), and 2227 with  $F_o > 6\sigma(F_o)$  were used in the structure solution. An extinction correction was applied in the final cycles of refinement.  $R(F) = 0.0392$ ;  $R_w(F) = 0.0366$ .
- (15) Stavropoulos, P.; Edwards, P. G.; Wilkinson, G.; Motevalli, M.; Malik, K. M. A.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 2167.
- (16) Preparation of **6**. Method A. A mixture of  $\text{ReO}_2(\text{CH}_2\text{CMe}_3)_2\text{Br}(\text{py})$  (0.202 g, 0.39 mmol) and an excess of  $\text{Ag}_2\text{O}$  (0.090 g, 0.39 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL) was stirred in the dark for 45 min. The  $\text{CH}_2\text{Cl}_2$  was then removed in vacuo, and the residue was extracted with pentane (2  $\times$  15 mL). The red pentane extracts were combined and filtered, and the pentane was then removed in vacuo. The residue was redissolved in a minimum amount of  $\text{CH}_3\text{CN}$  and cooled to  $-20^\circ\text{C}$  (24 h). This gave red crystals, which were isolated by decanting the solution and then drying in vacuo (yield 0.110 g, 77%). Method B. A mixture of  $[\text{Re}(\mu\text{-O})\text{O}(\text{CH}_2\text{CMe}_3)_2]_2$  (0.150 g, 0.21 mmol) and pyridine *N*-oxide (0.020 g, 0.21 mmol) was dissolved in toluene (20 mL). The resulting yellow solution was stirred in the dark for 30 min, turning deep red in the process. The toluene was then removed in vacuo, and the residue was dissolved in a minimum amount of  $\text{CH}_3\text{CN}$ . Cooling of the red solution to  $-20^\circ\text{C}$  gave red crystals, which were isolated and dried as in method A (yield 0.120 g, 78%).

- (7)  $^1\text{H}$  NMR ( $-70^\circ\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ , 300 MHz) for **4**:  $\delta$  3.37 and 2.69 (d of an AB q, 4,  $J_{\text{HH}} = 11.9$  Hz,  $\text{CH}_2\text{CMe}_3$ ), 0.99 (s, 18,  $\text{CH}_2\text{CMe}_3$ ), 1.34 (s, 9,  $\text{OCMe}_3$ ).  $^1\text{H}$  NMR at  $23^\circ\text{C}$ :  $\delta$  3.02 (s, 4,  $\text{CH}_2\text{CMe}_3$ ), 1.12 (s, 18,  $\text{CH}_2\text{CMe}_3$ ), 1.43 (s, 9,  $\text{OCMe}_3$ ).
- (8) Edwards, P. G.; Wilkinson, G.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 2467.
- (9)  $\Delta G^\ddagger \approx 10.3$  kcal/mol. Bovey, F. A. *Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Academic Press: New York, 1988; pp 291–321.
- (10) Cai, S.; Hoffman, D. M.; Woo, H.-G.; Huffman, J. C.; Wierda, D. A. *Inorg. Chem.* **1987**, *26*, 3693. Huggins, J. M.; Whitt, D. R.; Lebioda, L. *J. Organomet. Chem.* **1986**, *312*, C15.
- (11) Cai, S.; Hoffman, D. M.; Wierda, D. A. *J. Chem. Soc., Chem. Commun.* **1988**, 1489.
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prepared by hydrolysis of  $\text{ReO}_2(\text{CH}_2\text{CMe}_3)_2(\text{O}-t\text{-Bu})$ , a reaction that presumably involves  $\text{ReO}_2(\text{CH}_2\text{CMe}_3)_2(\text{OH})$  as an intermediate.<sup>17</sup> All of these preparations must be carried out in the absence of light, because **6**, like its alkoxide congeners, is light-sensitive.

In conclusion, we have synthesized alkoxide and thiolate Re(VII) dioxo complexes of the type  $\text{ReO}_2(\text{CH}_2\text{CMe}_3)_2(\text{ER})$ . The alkoxides are decomposed by light in a process which may involve homolytic Re-OR bond cleavage.  $\text{Re}_2\text{O}_5(\text{CH}_2\text{CMe}_3)_4$ , a product of alkoxide decomposition, has been structurally characterized and found to have a  $[\text{O}_2\text{Re}-\text{O}-\text{ReO}_2]^{4+}$  core. We know of no other rhenium compounds with a  $d^0-d^0$   $[\text{O}_2\text{M}-\text{O}-\text{MO}_2]$  core,<sup>18</sup>

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 (18) Cotton, F. A.; Morehouse, S. M.; Wood, J. S. *Inorg. Chem.* **1964**, *3*, 1603. See also, Marabella, C. P.; Enemark, J. H.; Miller, K. F.; Bruce, A. E.; Pariyadath, N.; Corbin, J. L.; Stiefel, E. I. *Inorg. Chem.* **1983**, *22*, 3456. Barnhart, K. M.; Enemark, J. H. *Acta Crystallogr., Sect. C* **1984**, *40*, 1362. Wiegardt, K.; Backes-Dahmann, G.; Herrmann, W.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 899. Matsumoto, K.; Marutani, Y.; Ooi, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2671. Gebreyes, K.; Shaikh, S. N.; Zubieta, J. *Acta Crystallogr., Sect. C* **1985**, *41*, 871.

nor of any other organometallic examples.

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**Supplementary Material Available:** Details of the X-ray structure determinations and tables of crystal data, atomic coordinates, thermal parameters, bond lengths, and bond angles for **2** and **6** (21 pages). Ordering information is given on any current masthead page.

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## Articles

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### Electron-Transfer Reactions in Mixed Solvents. An Electrochemical Probe of Unsymmetrical Selective Solvation

Robert L. Blackburn and Joseph T. Hupp\*

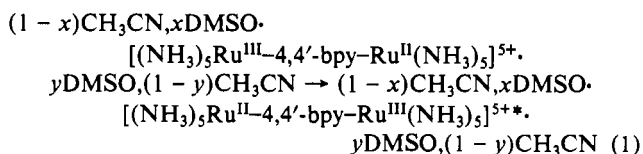
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One of the unique aspects of electron-transfer reactions in mixed solvents is the possibility for unsymmetrical selective solvation of reactants versus products. We have developed a versatile electrochemical method, based on reaction-entropy measurements, to detect its occurrence. The method is illustrated by results for five related redox systems:  $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ ,  $\text{Ru}(\text{NH}_3)_5(\text{py})^{3+/2+}$ ,  $\text{Ru}(\text{NH}_3)_4(\text{bpy})^{3+/2+}$ ,  $\text{Ru}(\text{NH}_3)_2(\text{bpy})_2^{3+/2+}$ , and  $\text{Ru}(\text{bpy})_3^{3+/2+}$  (bpy = 2,2'-bipyridine; py = pyridine), in mixtures of acetonitrile and dimethyl sulfoxide as solvent. The key finding is that a sharp increase (and a more gradual decrease) in reaction entropy occurs over the range of solvent composition where unsymmetrical selective solvation is significant. The dependence of the reaction entropy for  $\text{Ru}(\text{NH}_3)_5(\text{py})^{3+/2+}$  on mixed-solvent composition can be described fairly well by a simple statistical model. There are difficulties, however, in understanding the magnitudes of the observed entropy effects.

#### Introduction

One of the unique aspects of electron-transfer (ET) reactions in mixed solvents is the possibility for unsymmetrical selective solvation of reactants versus products.<sup>1,2</sup> The occurrence of this effect is important because it may lead to substantial increase in the Franck-Condon barrier to electron transfer and presumably, therefore, to significant rate effects.<sup>1,2</sup> Indeed, in an earlier study of intramolecular ET in the dimer  $[(\text{NH}_3)_5\text{Ru}-4,4'\text{-bpy}-\text{Ru}(\text{NH}_3)_5]^{5+}$  (4,4'-bpy = 4,4'-bipyridine) in mixtures of  $\text{CH}_3\text{CN}$  and dimethyl sulfoxide (DMSO) as solvent, we found that differential solvation could increase the barrier to optical electron transfer by as much as  $1100\text{ cm}^{-1}$ .<sup>1</sup> The effect was also noted by Curtis and co-workers in their study<sup>2</sup> of a related system,  $[(\text{bpy})_2\text{ClRu}-\text{pz}-\text{Ru}(\text{NH}_3)_4(\text{py})]^{4+}$  (bpy = 2,2'-bipyridine; py = pyridine; pz = pyrazine). In addition, there is growing evidence that unsymmetrical selective solvation (ground versus excited state) can play an important role in single-chromophore photophysical and photochemical events.<sup>3,4</sup>

Given the known or suspected significance of unsymmetrical selective solvation in mixed-solvent reactions, the invention of methods to identify its occurrence would clearly be desirable. We have, in fact, developed two such methods.<sup>1,5</sup> The first is based upon a measurement of metal-to-metal charge transfer energies ( $E_{\text{op}}^{\text{MMCT}}$ ) in symmetrical mixed-valence systems, as a function of mixed-solvent composition. For example:



In eq 1, redox-state-dependent secondary coordination ( $x \neq y$ , where  $x$ ,  $y$ ,  $1-x$ , and  $1-y$  signify fractional occupancies of the second sphere) can lead to an extra difference between final and initial state energies, and this difference ( $\Delta E$ ) appears as an additional contribution to  $E_{\text{op}}^{\text{MMCT}}$ . This method is clearly limited to mixed-valence systems. Furthermore, it is only semiquantitative, since additional solvent-dependent factors are known to affect  $E_{\text{op}}^{\text{MMCT}}$ .<sup>1b,6</sup>

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 (3) Fung, E. Y.; Chua, A.; Curtis, J. C. Private communication.  
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- (5) Besides these two methods, a hybrid method has been described in ref 2.