

The structural parameters, therefore, suggest to describe the molecule as containing a semiquinone and a quinone coordinated to the nickel ion, and charge compensation considerations require that the adduct is formulated as Ni<sup>I</sup>(TCSQ)(TCQ). Whether this ionic description is correct or it simply indicates that one unpaired electron is more delocalized on the metal and the other more on one dioxolene is largely a semantic problem at this stage. The alternative formulation as Ni<sup>II</sup>(TCCat)(TCQ) could be accepted only if the bond length criterion within the dioxolene ligands were shown to be false. In favor of the Ni(I) formulation are also the Ni–O distances of the chelate ring which are significantly longer than those observed for nickel(II)– or cobalt(II)–semiquinone pseudooctahedral derivatives (205–206 pm).<sup>14–16</sup>

The effective magnetic moment of the complex is 2.97  $\mu_B$ , practically independent of temperature in the range 300–20 K. This value is consistent with a nickel(I)–semiquinone strongly ferromagnetically coupled, as observed in analogous copper(II) and nickel(II) complexes.<sup>16,17</sup> The observed value of the effective magnetic moment is low for a nickel(II) complex, while it agrees well with a system in which a nickel(I) is coupled with a radical.<sup>18</sup> By comparison the effective magnetic moment of the parent NiL(TCCat) corresponds to  $g = 2.27$ .

The two dioxolene moieties interact with each other as shown by the very short distances and the small angle between the planes<sup>19</sup> which are stacked in a pseudo eclipsed configuration. A similar geometry was previously observed in a bis-semiquinone molybdenum complex.<sup>20</sup> The intense absorption band occurring at 12 700  $\text{cm}^{-1}$  is tentatively attributed to the transition between the HOMO of the semiquinone and the LUMO of the quinone. A MLCT character of this transition is also possible.

This compound sheds light on the mechanism of electron transfer in dioxolene molecules in the presence of metal ions. Indeed, although in the present case the two quinoid molecules have the ideal geometry for direct electron transfer, it is in fact the metal ion which acts as electron sink. We suggest that this is presumably due to the stabilization of the adduct determined by  $\pi$  back donation from the low valent metal to the quinone. Similar explanations were provided for justifying the stability of ruthenium(II) quinone complexes.<sup>21</sup>

It is tempting to speculate that the redox process in principle might proceed further with the transfer of the electron from nickel(I) to the quinone either via the  $t_{2g}$  orbitals or via the semiquinone ligand.

**Acknowledgment.** The Italian Ministry of Public Education and the CNR are gratefully acknowledged for the financial support.

**Supplementary Material Available:** Tables of positional parameters and isotropic thermal factors, bond distances and angles, anisotropic thermal factors, and positional parameters of hydrogen atoms (8 pages); listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

(14) Lynch, M. W.; Buchanan, R. M.; Pierpont, C. G.; Hendrickson, D. N. *Inorg. Chem.* **1981**, *20*, 1038.

(15) Buchanan, R. M.; Fitzgerald, B. J.; Pierpont, C. G. *Inorg. Chem.* **1979**, *18*, 3439.

(16) Benelli, C.; Dei, A.; Gatteschi, D.; Pardi, L. *Inorg. Chem.*, **1988**, in press.

(17) Kahn, O.; Prins, R.; Reedijk, J.; Thompson, J. S. *Inorg. Chem.* **1987**, *26*, 3557.

(18) Gatteschi, D.; Bencini, A. *Magneto-Structural Correlations in Exchange Coupled Systems*; Willett, R. D., Gatteschi, D., Kahn, O., Eds.; Reidel: Dordrecht, **1983**; p 241.

(19) Interatomic contact distances less than 350 pm involving the quinoid molecules: C1...C7, 293 (2); C2...C7, 277 (1); C2...C8, 300 (2); C3...C7, 339 (2); C3...C8, 321 (2); C3...C9, 327 (2); C3...C10, 347 (3); C4...C10, 340 (3); C4...C11, 336 (2); C5...C11, 340 (3); C5...C12, 346 (2); C6...C12, 321 (2); O1...O3, 275 (2); O2...O4, 288 (2). The angle between the least-square planes through the atoms O1–O2–C1–C2–C3–C4–C5–C1 and O3–O4–C7–C8–C9–C10–C11–C12 is 12.7°.

(20) Pierpont, C. G.; Buchanan, R. M. *J. Am. Chem. Soc.* **1975**, *97*, 6450.

(21) Pell, S. D.; Salmonsén, R. B.; Abelleira, A.; Clarke, M. *Inorg. Chem.* **1984**, *23*, 385.

## Modeling the Dinuclear Sites of Iron Biomolecules: Synthesis and Properties of Fe<sub>2</sub>O(OAc)<sub>2</sub>Cl<sub>2</sub>(bipy)<sub>2</sub> and Its Use as an Alkane Activation Catalyst

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The study of synthetic models containing the [Fe<sub>2</sub>( $\mu$ -O)( $\mu$ -O<sub>2</sub>CR)<sub>2</sub>]<sup>2+</sup> core established in the oxygen carrier protein hemerythrin (Hr)<sup>2</sup> has received additional impetus and importance with the realization that such units may also be present in other dinuclear iron biomolecules. These include the purple acid phosphatases (PAP),<sup>3</sup> ribonucleotide reductases (RR),<sup>4</sup> and methane monooxygenases (MMO).<sup>5</sup> By using a variety of tridentate N-based ligands (L), synthetic materials of formulation [Fe<sub>2</sub>O(O<sub>2</sub>CR)<sub>2</sub>L<sub>2</sub>] have been prepared,<sup>6</sup> establishing the accessibility and stability of this unit outside a polypeptide environment. The tridentate ligands, however, block all terminal binding sites, precluding investigation of native substrate or substrate-analogue binding.<sup>7</sup> Use of bidentate ligands to overcome this problem has led to dimerization of the [Fe<sub>2</sub>O(O<sub>2</sub>CR)<sub>2</sub>]<sup>2+</sup> unit to yield [Fe<sub>4</sub>O<sub>2</sub>(O<sub>2</sub>CR)<sub>4</sub>]<sup>4+</sup>-containing products.<sup>8</sup> However, we herein report a procedure employing 2,2'-bipyridine (bipy) that successfully allows access to a [Fe<sub>2</sub>O(O<sub>2</sub>CR)<sub>2</sub>]<sup>2+</sup> product and describe the structure, properties, and alkane activation reactivity of Fe<sub>2</sub>O(OAc)<sub>2</sub>Cl<sub>2</sub>(bipy)<sub>2</sub> (1), possessing Cl<sup>-</sup> ligands bound to the now available sixth coordination sites.

To a stirred solution of [Fe<sub>4</sub>O<sub>2</sub>(OAc)<sub>7</sub>(bipy)<sub>2</sub>](ClO<sub>4</sub>) (2) (0.60 g, 0.5 mmol)<sup>9</sup> in MeCN was added bipy (0.69 g, 5.0 mmol) and NEt<sub>4</sub>Cl·H<sub>2</sub>O (1.48 g, 8.1 mmol). The dark green-brown solution

(1) Alfred P. Sloan Research Fellow, 1987–1989. Camille and Henry Dreyfus Teacher-Scholar, 1987–1992.

(2) (a) Stenkamp, R. E.; Sieker, L. C.; Jensen, L. H.; McCallum, J. D.; Sanders-Loehr, J. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 713. (b) Wilkins, P. C.; Wilkins, R. G. *Coord. Chem. Rev.* **1987**, *79*, 195.

(3) Averill, B. A.; Davis, J. C.; Burman, S.; Zirino, T.; Sanders-Loehr, J.; Loehr, T. M.; Sage, J. T.; Debrunner, P. G. *J. Am. Chem. Soc.* **1987**, *109*, 3760, and references therein.

(4) (a) Lammers, M.; Follman, H. *Struct. Bonding (Berlin)* **1983**, *54*, 27. (b) Bunker, G.; Petersson, L.; Sjöberg, B.-M.; Sahlin, M.; Chance, M.; Chance, B.; Ehrenberg, A. *Biochemistry* **1987**, *26*, 4708. (c) Scarrow, R. C.; Maroney, M. J.; Palmer, S. M.; Que, L.; Roe, A. L.; Salowe, S. P.; Stubbe, J. *J. Am. Chem. Soc.* **1987**, *109*, 7857. (d) Sjöberg, B. M.; Sanders-Loehr, J.; Loehr, T. M. *Biochemistry* **1987**, *26*, 4242.

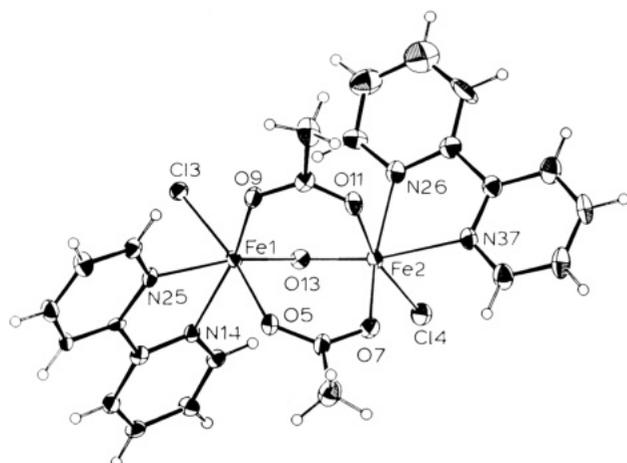
(5) (a) Prince, R. C.; George, G. N.; Savas, J. C.; Cramer, S. P., Patel, R. N. *Biochim. Biophys. Acta* **1988**, *952*, 220. (b) Ericson, A.; Hedman, B.; Hodgson, K. O.; Green, J.; Dalton, H.; Bentsen, J. G.; Beer, R. H.; Lippard, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 2330. (c) Dalton, H. *Adv. Appl. Microbiol.* **1980**, *26*, 71. (d) Woodland, M. P.; Dalton, H. *J. Biol. Chem.* **1984**, *259*, 53.

(6) (a) Wieghardt, K.; Pohl, K.; Gebert, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 727. (b) Armstrong, W. H.; Spool, A.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 3653. (c) Toftlund, H.; Murray, K. S.; Zwack, P. R.; Taylor, L. F.; Anderson, O. P. *J. Chem. Soc., Chem. Commun.* **1986**, 191. (d) Gomez-Romero, P.; Casan-Pastor, N.; Ben-Hussein, A.; Jameson, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 1988.

(7) Wieghardt, K.; Pohl, K.; Ventur, D. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 392.

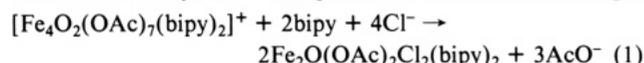
(8) (a) Armstrong, W. H.; Roth, M. E.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 6318. (b) Gorun, S. M.; Lippard, S. J. *Inorg. Chem.* **1988**, *27*, 149.

(9) Vincent, J. B.; Huffman, J. C.; Christou, G., unpublished results. The structure of this complex is the same as its Mn analogue: Vincent, J. B.; Christmas, C.; Huffman, J. C.; Christou, G.; Chang, H.-R.; Hendrickson, D. N. *J. Chem. Soc., Chem. Commun.* **1987**, 236.

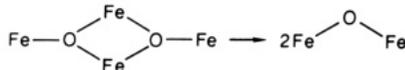


**Figure 1.** ORTEP representation of the structure of complex **1** at the 50% probability level (hydrogen atoms are arbitrary size). Selected bond lengths (Å) and angles (deg) are as follows: Fe1–Fe2, 3.151 (1); Fe1–O13, 1.783 (4); Fe2–O13, 1.787 (4); Fe1–Cl13, 2.389 (2); Fe2–Cl14, 2.360 (2); Fe1–O5, 2.144 (4); Fe1–O9, 2.009 (4); Fe2–O7, 2.011 (4); Fe2–O11, 2.156 (4); Fe1–N14, 2.146 (5); Fe1–N25, 2.204 (5); Fe2–N26, 2.155 (5); Fe2–N37, 2.212 (5); Fe1–O13–Fe2, 123.9 (2); Cl13–Fe1–Fe2–Cl14, 82.3 (2).

was left undisturbed for 18 h to produce dark green crystals of **1**·MeCN in 66% yield.<sup>10</sup> The procedure is summarized in eq 1.



The formation of **1** can be considered as a cleavage of the  $[\text{Fe}_4(\mu_3\text{-O})_2]$  core into two  $\text{Fe}_2(\mu\text{-O})$  units, viz



The structure<sup>11</sup> of complex **1** is shown in Figure 1. Clearly evident is the  $[\text{Fe}_2(\mu\text{-O})(\mu\text{-O}_2\text{CR})_2]^{2+}$  core present in methemerythrin (met-Hr) and the other model complexes, but terminal ligation at each Fe is now provided by a  $\text{Cl}^-$  and a bidentate bipy group. Structural parameters (Figure 1 caption) are similar to those found in complexes with tridentate L ligands and establishes that the latter are not essential for stabilizing the  $[\text{Fe}_2\text{O}(\text{O}_2\text{CR})_2]^{2+}$  unit outside a protein environment. Complex **1** represents the first model of a substrate-analogue-bound form of Hr, namely meth-chlorohemerythrin (met-Cl-Hr).<sup>12,13a</sup>

Variable-temperature solid-state magnetic susceptibility studies were performed on a powdered sample of **1** in the range 5.0–300.5 K. The effective magnetic moment decreases gradually from 2.48  $\mu_B$  per  $\text{Fe}_2$  at 300.5 K<sup>13b</sup> to 0.58  $\mu_B$  at 5.0 K. The data were fit to the expression for an isotropic exchange interaction ( $\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$ ) for two  $\text{Fe}^{\text{III}}$  ions ( $S_1 = S_2 = 5/2$ ) to give the fitting parameters  $J = -132 \text{ cm}^{-1}$ ,  $g = 1.90$ ,  $\text{TIP} = 800 \times 10^{-6} \text{ cgs}$ , and  $\text{PAR} = 1.0\%$ .<sup>14</sup> The magnitude of the antiferromagnetic interaction is extremely similar to that found for methemerythrin from *P. gouldii* ( $J = -134 \text{ cm}^{-1}$ )<sup>15</sup> and slightly greater than those

(10) Anal. Calcd for  $\text{C}_{26}\text{H}_{25}\text{N}_5\text{O}_5\text{Cl}_2\text{Fe}_2$ : C, 46.60; H, 3.76; N, 10.45; Cl, 10.58; Fe, 16.66. Found: C, 46.4; H, 3.7; N, 10.6; Cl, 10.75; Fe, 16.9.

(11) The data were collected at  $\sim -150^\circ\text{C}$ , and the structure was solved by direct methods (MULTAN) and Fourier techniques and refined by full-matrix least squares. Crystal data: triclinic,  $P\bar{1}$ ,  $T = -155^\circ\text{C}$ ,  $a = 21.531$  (13) Å,  $b = 8.859$  (4) Å,  $c = 8.415$  (3) Å,  $\alpha = 97.44$  (2)°,  $\beta = 100.47$  (3)°,  $\gamma = 92.16$  (3)°,  $Z = 2$ ,  $V = 1562.01$  Å<sup>3</sup>, unique data = 4098, observed data = 3406,  $F > 2.33\sigma(F)$ ,  $R = 5.34$ ,  $R_w = 5.40$ .

(12) (a) Garbett, K.; Darnall, D. W.; Klotz, I. M.; Williams, R. J. P. *Arch. Biochem. Biophys.* **1969**, *103*, 419. (b) Keresztes-Nagy, S.; Klotz, I. M. *Biochemistry* **1965**, *4*, 919.

(13) (a) Complex **1** in  $\text{CH}_2\text{Cl}_2$ :  $\lambda_{\text{max}}$ , nm ( $\epsilon_M$ ,  $\text{L}\cdot\text{mol}^{-1}\text{cm}^{-1}$ ) 464 (br sh, 387), 329 (6060). Met-Cl-Hr 656 (90), 490 (br sh, 375), 380 (3000). (b) A similar value in solution (Evans method in  $\text{CD}_3\text{CN}$ ) supports retention of the dinuclear structure on dissolution.

(14) PAR is the paramagnetic impurity as a percentage by weight and assumed to be a mononuclear  $\text{Fe}^{\text{III}}$  ( $S = 5/2$ ) species.

(15) Dawson, J. W.; Gray, H. B.; Hoenig, H. E.; Rossman, G. R.; Schredder, J. M.; Wang, R.-H. *Biochemistry* **1972**, *11*, 461.

**Table I.** Hydroxylation of  $\text{C}_2$ ,  $\text{C}_3$ , and Cyclo- $\text{C}_6$  Hydrocarbons with Complex **1** Using  $\text{Bu}^t\text{OOH}$  as the Monooxygen Transfer Reagent<sup>a</sup>

| hydrocarbon | product <sup>b</sup> (%) | % $\text{Bu}^t\text{OOH}$ consumed | turnover no. <sup>c</sup> |
|-------------|--------------------------|------------------------------------|---------------------------|
| ethane      | ethanol (<1)             | 95                                 | 1.2 <sup>d</sup>          |
| propane     | isopropyl alcohol (8.8)  | 82                                 | 13 <sup>e</sup>           |
|             | <i>n</i> -propanol (1.5) |                                    |                           |
| cyclohexane | cyclohexanol (32)        | 90                                 | 72 <sup>d</sup>           |
|             | cyclohexanone (22)       |                                    |                           |

<sup>a</sup> Reactions with ethane and propane were carried out in a Parr Kinetic Apparatus at pressures of 250 and 90 psi, respectively, at ambient temperature in MeCN with a catalyst concentration of  $7 \times 10^{-4} \text{ M}$ . The  $\text{Bu}^t\text{OOH}$ :catalyst ratio was 150:1. The cyclohexane reactions were run in Schlenk flasks at ambient temperature with a substrate:  $\text{Bu}^t\text{OOH}$ :catalyst ratio of 1100:150:1 and a catalyst concentration of  $7 \times 10^{-4} \text{ M}$ . <sup>b</sup> Yields based on  $\text{Bu}^t\text{OOH}$  consumed (iodometric titration). <sup>c</sup> Oxidizing equivalents/mmol catalyst. <sup>d</sup> 3 days. <sup>e</sup> 2 days.

for  $[\text{Fe}_2\text{O}(\text{O}_2\text{CR})_2\text{L}_2]$  complexes ( $J = -117$  to  $-121 \text{ cm}^{-1}$ ).<sup>6b,d,16</sup>

The <sup>57</sup>Fe Mossbauer spectrum of **1** at 120 K shows one quadrupole-split doublet with parameters characteristic of high-spin  $\text{Fe}^{\text{III}}$ : isomer shift  $\delta = 0.366$ (1) mm/s versus Fe metal at room temperature and quadrupole splitting  $\Delta E_Q = 1.795$ (2) mm/s. The corresponding values of  $\delta$  ( $\Delta E_Q$ ) for met-Cl-Hr are 0.59 (2.12) and 0.50 (2.04) at 4.2 and 77 K, respectively.<sup>17</sup> Complex **1** displays only very broad, irreversible reduction peaks in the 0 to  $-0.5 \text{ V}$  range (versus SCE) when studied by cyclic voltammetry in MeCN.<sup>18</sup>

Since the  $[\text{Fe}_2(\mu\text{-O})(\mu\text{-O}_2\text{CR})_2]^{2+}$  unit may also be present in methane monooxygenase (MMO), biomimetic catalysis studies were conducted with complex **1** to investigate its ability to model functionally the MMO enzyme in the hydroxylation of  $\text{C}_2$ ,  $\text{C}_3$ , and cyclo- $\text{C}_6$  hydrocarbons. Table I shows the results employing  $\text{Bu}^t\text{OOH}$  as the monooxygen transfer reagent in MeCN at room temperature. Catalytic activity was observed in all cases, and, not surprisingly, the reactivity sequence follows the ease of C–H bond dissociation, i.e.,  $\text{C}_6 > \text{C}_3 > \text{C}_2$ . Since MMO utilizes molecular  $\text{O}_2$  as the monooxygen donor,<sup>5</sup> we have also evaluated the activity of complex **1** in MeCN with  $\text{O}_2$  as the monooxygen transfer reagent in the presence of zinc powder and glacial acetic acid as electron and proton donors, respectively.<sup>19</sup> Initial experiments with cyclohexane have yielded cyclohexanone, and no cyclohexanol, with a turnover number of 2.5.<sup>20</sup> The activity of **1** is thus greater with  $\text{Bu}^t\text{OOH}$  than with  $\text{Zn}/\text{HOAc}/\text{O}_2$ , a result suggesting that formation of the active Fe-oxo species is more favorable in the former system or that the two systems generate different Fe-oxo intermediates.<sup>21</sup>

In summary, the synthetic analogue approach to Hr and other oxo-bridged  $\text{Fe}_2$  biomolecules has now been extended to the

(16) Hartman, J. R.; Rardin, R. L.; Chaudhuri, P.; Pohl, K.; Wieghardt, K.; Nuber, P.; Weiss, J.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 7387.

(17) Garbett, K.; Johnson, C. E.; Klotz, I. M.; Okamura, M. Y.; Williams, R. J. P. *Arch. Biochem. Biophys.* **1971**, *142*, 574.

(18) An irreversible oxidation is observed at  $\sim +1.2 \text{ V}$ , and this is very similar to that observed for  $\text{NET}_4\text{Cl}$ . We suspect this to indicate a solvent-for- $\text{Cl}^-$  exchange equilibrium to be occurring in **1** in MeCN.

(19) The reactions were run in Schlenk flasks at ambient temperature with a substrate:HOAc:Zn:catalyst ratio of 397:199:191:1 under one atmosphere of pressure and a catalyst concentration of  $7 \times 10^{-4} \text{ M}$ .

(20) While our work was nearing completion, the use of  $\text{Fe}_2\text{O}(\text{OAc})_2(\text{HB}(\text{pz})_3)_2$  to oxidize cyclohexane and adamantane in a  $\text{O}_2/\text{Zn}/\text{HOAc}$  system was reported: Kitajima, N.; Fukui, H.; Morooka, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 485. With cyclohexane, yields were similar to those from complex **1**, but both cyclohexanone and cyclohexanol were detected in comparable quantities.

(21) Similar investigations are in progress with other available Fe complexes.  $[\text{Fe}_2\text{O}_2(\text{OAc})_7(\text{bipy})_2](\text{ClO}_4)$ , for example, displays far greater catalytic activity in the  $\text{Bu}^t\text{OOH}$  system: with cyclohexane we obtained 119 turnovers in a 5-h period (64% cyclohexanol, 33% cyclohexanone); with propane, we obtained five turnovers in 18 h (2.7% isopropyl alcohol, 0.6% *n*-propanol); and with ethane, we obtained <1 turnover in 16 h (0.6% ethanol). Thus, it appears that the  $\text{Fe}_4$  complex facilitates formation of an active oxidant species since it is much faster in the C–H activation reaction than complex **1**.

(22) Christmas, C.; Vincent, J. B.; Huffman, J. C.; Christou, G., unpublished results.

preparation of a substrate-analogue-bound form and its properties described. Ligand exchange reactions with  $\text{NaN}_3$  are being investigated to prepare the  $\text{N}_3^-$  analogue of **1** as a model of met- $\text{N}_3$ -Hr. While met-Cl-Hr and met- $\text{N}_3$ -Hr possess  $\text{Cl}^-$  and  $\text{N}_3^-$  at only one Fe center, other Fe biomolecules may well possess anion binding sites on both metals. For example, RR may contain a terminally coordinated  $\text{OH}^-$  at each Fe,<sup>4d</sup> and attempts are therefore in progress to replace the  $\text{Cl}^-$  ligands of **1** with  $\text{OH}^-$  and also with  $\text{PhO}^-$ , the latter to model PAP which is believed to possess Fe-OPh (tyrosine) linkages.<sup>3</sup> Also under investigation is the introduction at a  $\text{Cl}^-$  site of a peroxide or hydroperoxide ( $\text{HO}_2^-$ ) group to yield a model of oxy-Hr and allow current thinking on the mode of  $\text{O}_2$  binding to be assessed.

**Note Added in Proof.** We have now prepared and structurally characterized the  $\text{PhCO}_2^-/\text{N}_3^-$  analogue of complex **1**, viz  $\text{Fe}_2\text{O}(\text{O}_2\text{CPh})_2(\text{N}_3)_2(\text{bipy})_2$ , corresponding to met- $\text{N}_3$ -Hr.<sup>22</sup>

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**Supplementary Material Available:** Tables of atomic coordinates, thermal parameters, and bond distances and angles (8 pages). Ordering information is given on any current masthead page.

## A Novel Type of Selectivity in Anionotropic Rearrangements

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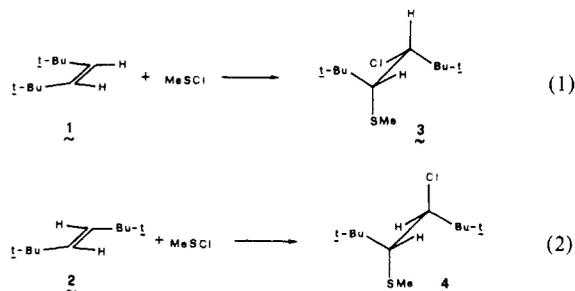
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Anionotropic rearrangements (i.e., those where the migrating group moves with its electron pair)<sup>1</sup> prefer that geometric situation which maximizes orbital overlap in the transition state. When the rearrangement occurs under  $\text{SN}_1$  type conditions, the maximum overlap is obtained in the two configurations with zero dihedral angle between the vacant p-orbital and the migrating bond.<sup>2,3</sup> In  $\text{SN}_2$  type rearrangements the maximum overlap between the migrating bond and the bond associated with the leaving group occurs for antiperiplanar or synperiplanar geometries. The differences in configurational stability dictate a preference for the antiperiplanar rearrangement.<sup>2</sup> In this communication we wish to report about a novel restriction imposed to an  $\text{SN}_2$  type anionotropic rearrangement by the particular molecular asymmetry.

During our investigations<sup>4</sup> on the mechanistic details of the addition of sulfenyl halides to olefins and acetylenes, we have been concerned with the identification and isolation of thiiranium and thirenium ions,<sup>5</sup> with their structure-stability relationships, their

reactivity toward nucleophiles,<sup>6</sup> and the alternative reaction paths, which are possible in long living ions (when the reactions with nucleophiles are suppressed).

Our search for stable ions led us to reconsider a rather old report<sup>7</sup> on the reaction of arenesulfonyl chlorides on (*Z*)-di-*tert*-butylethylene (**1**) (which gives a stable adduct) and on the *E* isomer **2** (with formation of an adduct which rearranges and eliminates  $\text{HCl}$ ). In our hands the addition of methanesulfonyl chloride to **1** in  $\text{CD}_2\text{Cl}_2$  gives instantaneously and quantitatively the stable adduct **3** (as monitored by NMR spectroscopy), while the adduct **4** from **2** is formed in about 1 h at room temperature and converts within 24 h into a series of decomposition products, which were not further investigated.



At first sight, the different stability of adducts **3** and **4** may be attributed to their conformational preference, as dictated by the steric repulsion of the two *tert*-butyl groups.<sup>8</sup> In conformer **4** the methylthio and chloride groups are antiperiplanar, thus favoring the formation of a thiiranium ion which may be supposed to mediate the rearrangement process. As a matter of fact, in a solvent such as sulfur dioxide, with strong solvolytic power toward saturated and unsaturated  $\beta$ -chlorosulfides,<sup>9</sup> the adduct **3** is indefinitely stable, while the adduct **4** converts instantaneously to thiiranium chloride **7**, which then undergoes the slow rearrangement described below. This is however only an incomplete rationale for this process.

The hexachloroantimonate salts of thiiranium ions **6**<sup>8</sup> and **7** can be easily prepared through the action of methylbis(methylthio)sulfonium hexachloroantimonate (**5**) on **1** and **2**.<sup>5b</sup> Their behavior demonstrates that the intermediacy of thiiranium ion is a necessary but not a sufficient condition for the occurrence of the rearrangement process. In fact at room temperature in  $\text{CH}_2\text{Cl}_2$  thiiranium ion **6** is indefinitely stable, while thiiranium ion **7** converts quantitatively in about 5 days to thietanium ion **8**.<sup>10</sup> The hexachloroantimonates of ions **6**, **7**, and **8** can be isolated and fully characterized.<sup>11</sup> The addition of chloride ion (from *N*-methylpyridinium chloride) to a solution of salt **8** in  $\text{CH}_2\text{Cl}_2$  yields quantitatively the rearranged product **9**.

At this stage of the investigation the other necessary condition can be tentatively proposed: only that antiperiplanar methide group can migrate, which belongs to the *tert*-butyl moiety syn to the *S*-methyl group. This condition is substantiated by the analysis of the rearrangement kinetics of the thiiranium ions **10** and **11**

(5) (a) Pettitt, D. J.; Helmkamp, G. H. *J. Org. Chem.* **1963**, *28*, 2932. (b) Capozzi, G.; De Lucchi, O.; Lucchini, V.; Modena, G. *Tetrahedron Lett.* **1975**, 2603. (c) Capozzi, G.; Lucchini, V.; Modena, G.; Scrimin, P. *Tetrahedron Lett.* **1977**, 911. (d) Bolster, J.; Kellogg, R. M.; Meijer, E. W.; Wynberg, H. *Tetrahedron Lett.* **1979**, 285. (e) Gybin, A. S.; Smit, W. A.; Krimer, M. Z.; Zefirov, N. S.; Novgorodtseva, L. A.; Sodovaya, N. K. *Tetrahedron* **1980**, *36*, 1361. (f) Gybin, A. S.; Smit, W. A.; Bogdanov, V. S.; Krimer, M. Z.; Kalyan, J. B. *Tetrahedron Lett.* **1980**, *21*, 383. (g) Lucchini, V.; Modena, G.; Valle, G.; Capozzi, G. *J. Org. Chem.* **1981**, *46*, 4720.

(6) Schmid, G. H.; Strukelj, M.; Dalipi, S.; Ryan, M. D. *J. Org. Chem.* **1987**, *52*, 2403.

(7) Dean, C. L.; Garratt, D. G.; Tidwell, T. T.; Schmid, G. H. *J. Am. Chem. Soc.* **1974**, *96*, 4958.

(8) Reynolds, P.; Zonnebelt, S.; Bakker, S.; Kellogg, R. M. *J. Am. Chem. Soc.* **1974**, *96*, 3146.

(9) Lucchini, V.; Modena, G.; Zaupa, T.; Capozzi, G. *J. Org. Chem.* **1982**, *47*, 590.

(10) For other observations of thietanium ions: (a) Trost, B. M.; Schinski, W. L.; Mantz, I. B. *J. Am. Chem. Soc.* **1969**, *91*, 4320. (b) Trost, B. M.; Schinski, W. L.; Chen, F.; Mantz, I. B. *J. Am. Chem. Soc.* **1971**, *93*, 676.

(11) The stereochemistry of hexachloroantimonate salts of **6**, **7**, **8**, **10**, **11**, **12**, and **13** was ascertained through NOE analysis in the differential mode.

(1) March, J. *Advanced Organic Chemistry*; John Wiley and Sons: New York, 1985; Chapter 18.

(2) Delongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon Press: Oxford, 1983; Chapters 5 and 6.

(3) (a) Brouwer, D. M. Hogeveen, H. *Recl. Trav. Chim. Pays Bas* **1970**, *89*, 211. (b) Schleyer, P. v. R.; Lam, L. K. M.; Raber, D. J.; Fry, J. L.; McKervey, M. A.; Alford, J. R.; Cuddy, B. D.; Keizer, V. G.; Geluk, H. W.; Schlattmann, J. L. M. A. *J. Am. Chem. Soc.* **1970**, *92*, 5246.

(4) Capozzi, G.; Lucchini, V.; Modena, G. *Rev. Chem. Intermediates* **1979**, *4*, 347.