

Registry No.  $\text{Cl}_2\text{CSCL}$ , 594-42-3;  $\text{Br}_2\text{CSBr}$ , 993-30-6;  $\text{Cl}_2\text{BrCSCL}$ , 51174-92-6;  $\text{Cl}_2\text{HCSCl}$ , 42172-24-7;  $\text{Cl}_2\text{HCSCHCl}_2$ , 51174-93-7;  $\text{HCl-CS}$  trimer, 51174-94-8;  $\text{HBrCS}$  trimer, 51174-95-9;  $\text{CS}$ , 2944-05-0.

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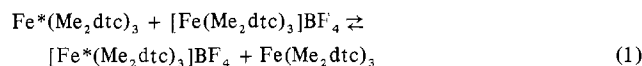
### Rate of Electron Transfer between Tris(dithiocarbamate) Complexes of Iron(III) and Iron(IV) by Proton Magnetic Resonance<sup>1</sup>

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The rate of the electron-transfer reaction, eq 1, between



tris(*N,N*-dimethyldithiocarbamate)iron(III),  $\text{Fe}(\text{Me}_2\text{dtc})_3$ , and tris(*N,N*-dimethyldithiocarbamate)iron(IV) tetrafluoroborate,  $[\text{Fe}(\text{Me}_2\text{dtc})_3]\text{BF}_4$ , has been measured by pmr line-broadening techniques in  $\text{CD}_2\text{Cl}_2$  solution. Reaction 1 is ideally suited for a pmr kinetic investigation of electron transfer because the *N*- $\text{CH}_3$  resonances of the iron(III) and -(IV) species are well separated (before mixing) with a chemical shift difference of 111 ppm at  $-91^\circ$ . This large separation, which permits the measurement of rates of very fast reactions (second-order rate constants of  $ca. 10^8 \text{ l. mol}^{-1} \text{ sec}^{-1}$ ) results from the difference in paramagnetism of the iron(III) and iron(IV) complexes.<sup>2,3</sup>

A mixture of  $\text{Fe}(\text{Me}_2\text{dtc})_3$  and  $[\text{Fe}(\text{Me}_2\text{dtc})_3]\text{BF}_4$  in  $\text{CD}_2\text{-Cl}_2$  solution shows one *N*- $\text{CH}_3$  resonance at  $30^\circ$  which is a weighted average of the iron(III) and -(IV) *N*- $\text{CH}_3$  positions. As the temperature is lowered, the averaged *N*- $\text{CH}_3$  resonance broadens more rapidly than predicted from spectra of the unmixed complexes<sup>4</sup> and at  $ca. -91^\circ$  broadens almost to the base line (see Figure 1). Over this temperature range the *N*-methyl resonances in the unmixed complexes remain sharp with line widths at half-height at  $-91^\circ$  of 46 and 35 Hz for iron(III) and -(IV), respectively,<sup>2</sup> while a value of 1700 Hz is found for the mixture. The averaging and kinetic broadening result from electron exchange as shown in reaction 1. The observation of exchange broadening due to electron transfer in a mixture of these complexes has not previously been reported.<sup>1</sup> This is the first report of electron transfer between dithiocarbamate complexes and indeed between any complexes of iron(III) and -(IV).

Kinetic parameters for electron transfer were determined by a total line shape analysis of the exchange-broadened *N*- $\text{CH}_3$  resonance. The Binsch CLATUX computer program, which employs the modified Bloch equations and allows unequal nonexchanging line widths, was used.<sup>5</sup> The best fit line shapes are shown with dashed lines above the experi-

Table I. Pmr Data<sup>a</sup> and Rate Constants for Electron Transfer between  $\text{Fe}(\text{Me}_2\text{dtc})_3$  and  $[\text{Fe}(\text{Me}_2\text{dtc})_3]\text{BF}_4$

Temp, °C (±1°)	$10^{-8}k_2,^b \text{ l. mol}^{-1} \text{ sec}^{-1}$	$\Delta\nu,^c \text{ ppm}$	$H_{1/2},^d \text{ Hz}$	
			Fe(III)	Fe(IV)
-32	$2.5 \pm 0.2$	35.94	46	13.5
-38	$2.4 \pm 0.2$	40.26	46	14.5
-45	$2.1 \pm 0.1$	45.61	46	16.0
-50	$1.6 \pm 0.1$	49.63	46	17.0
-56	$1.3 \pm 0.1$	54.68	46	18.8
-62	$1.1 \pm 0.1$	60.04	46	20.5
-69	$1.0 \pm 0.1$	66.69	46	23.0
-73	$0.83 \pm 0.1$	70.69	46	25.0
-81	$0.68 \pm 0.1$	79.20	46	28.0

<sup>a</sup> *N*- $\text{CH}_3$  resonance recorded at 100 MHz using  $\text{CD}_2\text{Cl}_2$  solvent. Complex concentrations for Fe(III) and Fe(IV) are  $2.45 \times 10^{-3}$  and  $1.63 \times 10^{-3} \text{ M}$ , respectively, at  $25^\circ$ . Density corrections were applied for the other temperatures. <sup>b</sup> Errors in  $k_2$  are estimated using errors in concentration ( $\sim 10\%$ ) and the visual line shape fit which includes the errors in  $\Delta\nu$  and  $H_{1/2}$ . <sup>c</sup> Chemical shift separations between Fe(III) and Fe(IV). Error is estimated to be  $\pm 0.1$  ppm. <sup>d</sup> Line width at half-height. Error is estimated to be  $\pm 0.5$  Hz.

mental spectra in Figure 1 at several temperatures. The rate constants,  $k$ , shown in this figure are pseudo first order and represent the quantity  $k_2[\text{III}]$  in

$$\text{rate} = k_2[\text{III}][\text{IV}]$$

where III and IV are the iron(III) and -(IV) complexes, respectively. Therefore the reciprocal of  $k$  equals the lifetime of the iron(IV) complex. A concentration study at  $-57^\circ$  shows that the reaction is second order overall with  $k_2 = (1.5 \pm 0.4) \times 10^8 \text{ l. mol}^{-1} \text{ sec}^{-1}$  in good agreement with the variable-temperature data ( $k_2(-57^\circ) = (1.4 \pm 0.1) \times 10^8$  calculated from a least-squares fit, Figure 2). The data used in the line shape fit and the second-order rate constants,  $k_2$ , are listed in Table I. Figure 2 shows the Eyring plot of  $\ln k_2/T$  vs.  $1/T$  for the variable-temperature rate data. The chemical shift difference between the Fe(III) and Fe(IV) species,  $\Delta\nu$ , and the line widths at half-height,  $H_{1/2}$ , for the nonexchanging complexes are directly observed at each temperature and are listed in Table I. No extrapolation is required. Activation parameters were determined from the Eyring plot by a linear least-squares fit. The enthalpy and entropy of activation are  $\Delta H^\ddagger = 2.1 \pm 0.4 \text{ kcal/mol}$  and  $\Delta S^\ddagger = -11 \pm 4 \text{ eu}$ . Errors were estimated by drawing the maximum and minimum sloped lines within the error bars on the Eyring plot. The error bars come from errors listed in Table I.

The temperature dependence of the chemical shift separation needs some mention. As can be seen in Table I,  $\Delta\nu$  greatly increases with decreasing temperature. This phenomenon is unusual and results because the *N*- $\text{CH}_3$  resonance position of the Fe(III) complex shows non-Curie temperature dependence due to the presence of an  $S = 1/2 \rightleftharpoons S = 5/2$  spin state equilibrium (*vide infra*).<sup>2</sup> The Fe(IV) complex is low spin,  $S = 1$ , and is magnetically well behaved.<sup>2</sup>

Numerous electron-transfer reactions have been studied,<sup>6</sup> however, only a few by nmr line-broadening techniques.<sup>7-9</sup>

(6) See for example the following references: (a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, Chapter 6; (b) R. G. Linck, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci.: Inorg. Chem., Ser. One*, 9, 303 (1972); (c) W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer," Ronald Press, New York, N. Y., 1966; (d) H. Taube, "Electron Transfer Reactions of Complex Ions in Solution," Academic Press, New York, N. Y., 1970.

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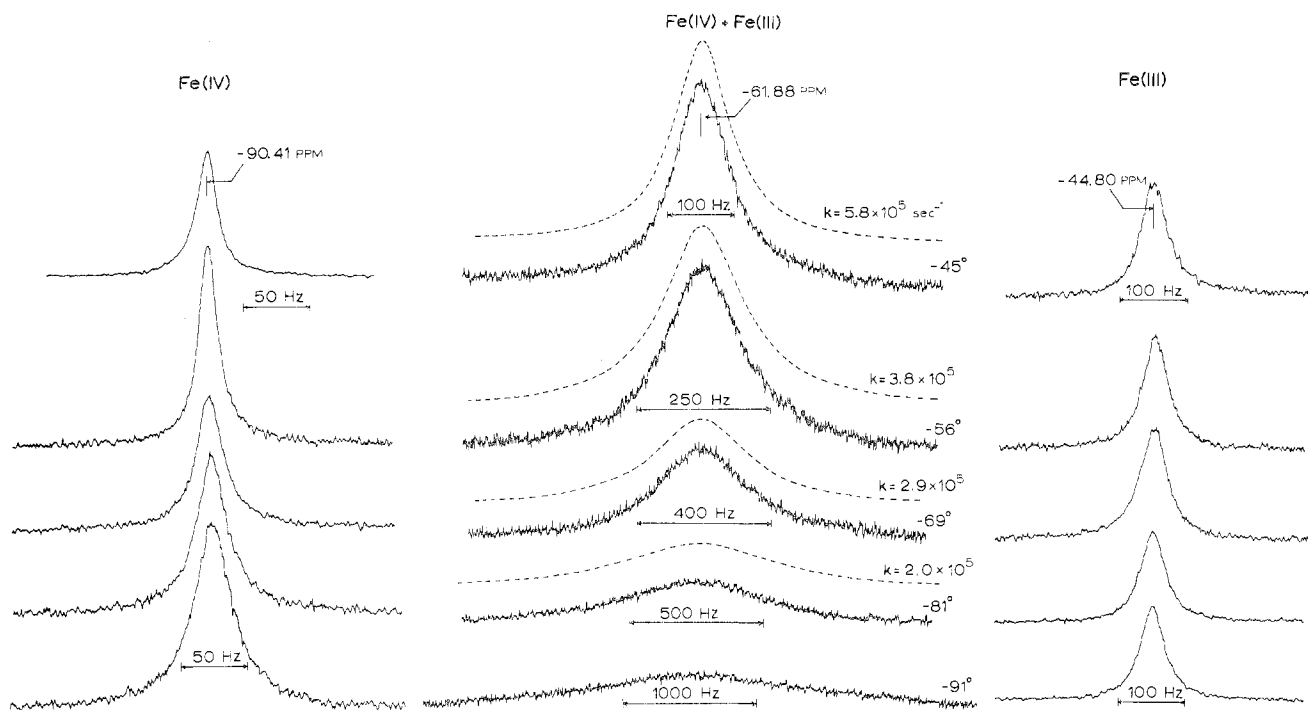
(1) Some of this work was presented at the 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 26-31, 1973.

(2) M. C. Palazzotto, D. J. Duffy, B. L. Edgar, L. Que, Jr., and L. H. Pignolet, *J. Amer. Chem. Soc.*, 95, 4537 (1973).

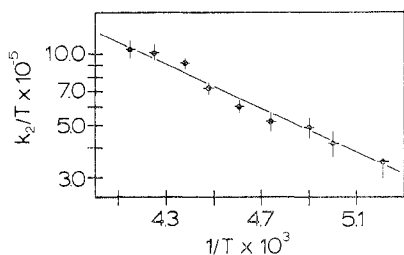
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(4) In the absence of exchange broadening (*i.e.*, in the fast-exchange limit) the averaged line width is simply a weighted average of the nonexchanging resonance widths.

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**Figure 1.** Observed  $N\text{-CH}_3$  resonances for  $\text{Fe}(\text{Me}_2\text{dtc})_3$ ,  $[\text{Fe}(\text{Me}_2\text{dtc})_3]\text{BF}_4$ , and a mixture of the two  $2.45 \times 10^{-3}$  and  $1.63 \times 10^{-3} M$ , respectively, in  $\text{CD}_2\text{Cl}_2$  solution. Pmr traces were recorded at 100 MHz by Fourier transform techniques (200–500 transients). The dashed lines are the best fit computer-calculated line shapes for the mixture and  $k$  is the pseudo-first-order rate constant and equals  $[\text{Fe}(\text{Me}_2\text{dtc})_3]k_2$  (see text). The  $-91^\circ$  spectrum was not fit due to the severe exchange broadening.



**Figure 2.** Eyring plot for the second-order electron-transfer reaction between  $\text{Fe}(\text{Me}_2\text{dtc})_3$  and  $[\text{Fe}(\text{Me}_2\text{dtc})_3]\text{BF}_4$ . Details are given in the text, Table I, and Figure 1.

Most of the reactions which have been examined take place in aqueous media.<sup>6</sup> In the present study a noncoordinating solvent is used and an outer-sphere mechanism is postulated because ligand exchange occurs only at very slow rates with  $\Delta H^\ddagger \gg 15$  kcal/mol.<sup>2,10</sup> Also, breaking of one of the dithiocarbamate Fe-S bonds to form five-coordinate species does not occur on the time scale of electron transfer.<sup>2</sup> Indeed, if this process occurs at all,  $\Delta H^\ddagger$  must be greater than 13 kcal/mol, the barrier for geometric isomerization.<sup>10</sup> The second-order kinetics and negative  $\Delta S^\ddagger$  are consistent with simple electron-transfer reactions.<sup>8,9</sup> The low value for  $\Delta H^\ddagger$  is also consistent with simple outer-sphere electron transfer.<sup>7,11</sup>

A possible complication with the Fe(III)-Fe(IV) system is the presence of an  $S = 1/2 \rightleftharpoons S = 5/2$  spin state equilibrium in the Fe(III) complex.<sup>12</sup> The dimethyl complex has a temperature-dependent magnetic moment in the temperature

range of the line-broadening experiment and hence the populations of the two spin states vary. This could result in a non-linear Eyring plot if the rate of electron transfer depends significantly on the Fe(III) spin state. The fact that a linear plot is obtained between  $-32$  and  $-81^\circ$  could be fortuitous due to the small temperature interval.<sup>13-16</sup> This possibility is under current study because it is possible to measure electron-transfer rates with different N substituents which significantly alter the position of the spin state equilibrium.<sup>12-17</sup> We have preliminary results with the tetramethylene N-substituted complexes where the Fe(III) is entirely in the  $S = 5/2$  spin state which show that the rate of electron transfer is at least an order of magnitude slower in this case. It is expected that the  $\text{Fe}(\text{IV}) \rightarrow \text{Fe}(\text{III})$  ( $S = 5/2$ ) exchange should be slower due to a higher Franck-Condon barrier; however, it is difficult to assess the importance of steric effects without more experiments.

The transfer of the electron from iron(III) to iron(IV) is probably accompanied by exchange of the  $\text{BF}_4^-$  counterion. Molecular weight data using  $\text{CHCl}_3$  solvent at  $37^\circ$  show that the iron(IV) complex is monomeric and not dissociated at the concentration of the variable-temperature experiment;

(13) The rate of interconversion between the high-spin and low-spin states is presumably very fast with a first-order rate constant  $> 10^7 \text{ sec}^{-1}$ . Evidence for this derives from Mossbauer results for  $\text{Fe}(\text{dtc})_3$  complexes where an average isomer shift is found.<sup>14,15</sup> A recent calculation by Beattie<sup>16</sup> suggested that such reactions have rates with  $k \approx 10^7 \text{ sec}^{-1}$ . The fact that this rate may be faster than the electron-transfer reactions could lead to a linear Eyring plot because during the lifetime of an iron(III) oxidation state many spin state changes may have occurred and the electron transfer could proceed from either the high- or low-spin state.

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however, slight dissociation (<10%) was found for the most dilute samples used in the concentration study. It is assumed that these results are valid for  $\text{CH}_2\text{Cl}_2$  solvent. The diffusion-limited second-order rate constant has been calculated using  $8 \pm 2 \text{ \AA}$  as the distance of closest approach and is  $(3.2 \pm 0.7) \times 10^{10} \text{ l. mol}^{-1} \text{ sec}^{-1}$  at  $25^\circ$ .<sup>18</sup> The observed second-order rate constant is  $(7.6 \pm 3.0) \times 10^8 \text{ l. mol}^{-1} \text{ sec}^{-1}$  at  $25^\circ$ . These values suggest that electron transfer is not diffusion controlled especially when the tetramethylene derivative is considered in which case  $k_2$  is at least another order of magnitude smaller. Studies under current investigation involve rate measurements for various counterions, solvents, and N substituents.

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**Registry No.**  $\text{Fe}(\text{Me}_2\text{dte})_3$ , 14484-64-1;  $[\text{Fe}(\text{Me}_2\text{dte})_3]\text{BF}_4$ , 35270-32-7.

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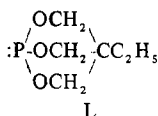
### Gold(I) Complexes of 4-Ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane

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Gold(I) complexes of phosphorus donor ligands have long been of interest because the phosphorus donor stabilizes the univalent oxidation state, and such complexes are generally resistant to disproportionation to gold metal and Au(III) compounds.<sup>2</sup> In connection with studies of the electronic structure and reactivity of two-coordinate complexes, we have prepared several Au(I) complexes of the caged phosphite ligand<sup>3</sup> 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (ETPB), L. This ligand is of interest because its  $\sigma$ -donor and



$\pi$ -acceptor abilities are similar to those of cyanide,<sup>4</sup> which forms an exceptionally stable two-coordinate complex of Au(I). In addition, L is virtually transparent in the uv spectral region and allows the observation of electronic absorptions of the complex unmasked by strong ligand absorptions.

(1) Abstracted in part from the M.S. thesis of G. P. F., Northern Illinois University, June 1974.

(2) See for example B. F. G. Johnson and R. Davis, "Comprehensive Inorganic Chemistry," A. F. Trotman-Dickenson, Ed., Pergamon Press, Oxford, 1973, Chapter 29.

(3) For a review of this and related ligands see J. G. Verkade and K. J. Coskran, "Organic Phosphorus Compounds," Vol. 2, G. M. Kosolapoff and T. Maier, Eds., Wiley-Interscience, New York, N. Y., 1972, p 1; J. G. Verkade, *Coord. Chem. Rev.*, 9, 1 (1972).

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A complex of Au(I) with a similar ligand, MTPB, with a 4-methyl substituent, was reported by Verkade and Piper<sup>5</sup> as a dinuclear complex  $[\text{Au}_2\text{Cl}]_2$ . However, we were unable to prepare complexes of this stoichiometry. Instead in this note we report five complexes of ETPB, all of which are monomeric:  $[\text{AuL}(\text{CH}_3\text{CN})]\text{ClO}_4$ ,  $[\text{AuL}_2]\text{ClO}_4$ ,  $[\text{AuL}_4]\text{ClO}_4$ ,  $\text{AuLCl}$ , and  $\text{AuLBr}$ . The successive formation of the three cationic complexes was studied in acetonitrile, and their stabilities are discussed.

### Experimental Section

**Preparation of Compounds.** The gold compounds were prepared from either  $[\text{Au}(\text{CH}_3\text{CN})_2]\text{ClO}_4$ <sup>6</sup> or  $[(n\text{-C}_4\text{H}_9)_3\text{N}][\text{AuX}_4]$  (X = Cl, Br).<sup>7</sup> The ETPB ligand was obtained from Strem Chemicals, Inc., Danvers, Mass., and purified by distillation (mp  $55\text{--}57^\circ$ ; lit.<sup>8</sup> mp  $56^\circ$ ). *Anal.* Calcd for  $\text{C}_6\text{H}_{11}\text{O}_3\text{P}$ : C, 44.45; H, 6.84. Found: C, 44.2; H, 6.85. Acetonitrile was Spectro Grade and all other chemicals were of reagent grade. For the perchlorate salts, gold was determined spectrophotometrically as  $\text{Au}(\text{CN})_2^-$ . An excess of cyanide ( $\text{CN}^-$ : Au > 5) was added to a known quantity of the salt dissolved in acetonitrile. The absorbance was measured at 41.9 kK and compared to that of a standard,  $[(n\text{-C}_4\text{H}_9)_3\text{N}][\text{Au}(\text{CN})_2]$ ,<sup>9</sup> using an absorptivity of  $3888 \text{ M}^{-1} \text{ cm}^{-1}$ . The precision of duplicate determinations was within 0.2%; the accuracy was within 1% of theory.

**Halo(4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)gold(I),  $\text{Au}(\text{C}_6\text{H}_{11}\text{O}_3\text{P})\text{X}$ .** A concentrated acetonitrile solution containing a 3–4 fold excess of ETPB was added slowly to a concentrated acetonitrile solution of  $[(n\text{-C}_4\text{H}_9)_3\text{N}][\text{AuX}_4]$  (X = Cl, Br). Colorless solutions resulted and these were evaporated to a small volume and cooled in a Dry Ice-acetone slush bath. Colorless crystals were collected and washed with water. The solids were recrystallized from ethanol, washed with anhydrous ether, and dried *in vacuo* at room temperature overnight. Yield: AuLCl, 74%; AuLBr, 70%. *Anal.* Calcd for  $\text{Au}(\text{C}_6\text{H}_{11}\text{O}_3\text{P})\text{Cl}$ : Au, 49.9; C, 18.26; H, 2.81; P, 7.85; Cl, 8.99. Found: Au, 49.2; C, 18.3; H, 2.82; P, 7.79; Cl, 8.90. Calcd for  $\text{Au}(\text{C}_6\text{H}_{11}\text{O}_3\text{P})\text{Br}$ : Au, 44.9; C, 16.42; H, 2.53; P, 7.06; Br, 18.20. Found: Au, 44.2; C, 16.4; H, 2.57; P, 6.92; Br, 17.7.

**(Acetonitrile)(4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)gold(I) Perchlorate,  $[\text{Au}(\text{C}_6\text{H}_{11}\text{O}_3\text{P})(\text{CH}_3\text{CN})]\text{ClO}_4$ .** A stoichiometric amount of ETPB in a concentrated acetonitrile solution was added slowly to  $\text{Au}(\text{CH}_3\text{CN})_2^+$  in acetonitrile solution. The addition of the ligand and subsequent isolation was performed in a dry nitrogen atmosphere. The resulting solution was evaporated to a small volume, cooled in a Dry Ice-acetone slush bath, and excess anhydrous ether was added. A gummy colorless precipitate remained after the ether-acetonitrile solution was decanted. The precipitate was washed with two additional portions of ether and dried *in vacuo* at room temperature for 2.5 hr. The white salt darkened on standing at room temperature and was analyzed immediately. It could be stored for a few days at  $-16^\circ$  without apparent decomposition, however; yield 40%. *Anal.* Calcd for  $[\text{Au}(\text{C}_6\text{H}_{11}\text{O}_3\text{P})(\text{CH}_3\text{CN})]\text{ClO}_4$ : Au, 39.4; C, 19.23; H, 2.83; N, 2.80. Found: Au, 40.1; C, 19.0; H, 2.93; N, 2.62.

**Bis(4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)gold(I) Perchlorate,  $[\text{Au}(\text{C}_6\text{H}_{11}\text{O}_3\text{P})_2]\text{ClO}_4$ .** A 2:1 stoichiometric amount of ETPB in a concentrated acetonitrile solution was added slowly under nitrogen to a solution of  $\text{Au}(\text{CH}_3\text{CN})_2^+$  in acetonitrile. The resulting solution was evaporated to a small volume and cooled in a Dry Ice-acetone slush bath. Anhydrous ether was added whereupon a pale yellow crystalline precipitate was formed. The precipitate was collected, washed with ether, and dried *in vacuo* at room temperature overnight; yield 60%. *Anal.* Calcd for  $[\text{Au}(\text{C}_6\text{H}_{11}\text{O}_3\text{P})_2]\text{ClO}_4$ : Au, 31.7; C, 23.22; H, 3.57; P, 9.98. Found: Au, 31.1; C, 23.6; H, 3.78; P, 10.20.

**Tetrakis(4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)gold(I) Perchlorate,  $[\text{Au}(\text{C}_6\text{H}_{11}\text{O}_3\text{P})_4]\text{ClO}_4$ .** A 10% excess of ETPB in a concentrated acetonitrile solution was added slowly under dry nitrogen to  $\text{Au}(\text{CH}_3\text{CN})_2^+$  in acetonitrile. Colorless crystals were formed on evaporating the resulting solution to a small volume and cooling in a Dry Ice-acetone slush bath. These crystals were collected, washed with anhydrous ether, and dried *in vacuo* at room tempera-

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