

**Table I.** Dependence of Cluster Type Formation<sup>a</sup> on Phosphine Cone Angle  $\theta$ 

phosphine	cluster type <sup>b</sup>			$\theta$ , deg
	4:5:4	3:3:3	3:3:4	
PMe <sub>2</sub> Ph	+		+	122
PEt <sub>3</sub>	+		+	132
PMePh <sub>2</sub>	+		+	136
PPh <sub>3</sub>	(+)	(+)	+	145
PEt <sub>2</sub> <sup>i</sup> Bu	+	+	+	148
PPh <sub>2</sub> <sup>i</sup> Pr		+	+	150
PPh <sup>i</sup> Pr <sub>2</sub>		+		152
P <sup>i</sup> Pr <sub>3</sub>		+		154
PPhCy <sub>2</sub>		+		160
PBz <sub>3</sub>	+	+		161
PCy <sub>3</sub>		+		170

<sup>a</sup>These clusters have also been prepared by a variety of other methods.<sup>9b,19,20</sup> <sup>b</sup>3:3:3 = [Pt<sub>3</sub>( $\mu_2$ -CO)<sub>3</sub>(PR<sub>3</sub>)<sub>3</sub>]; 4:5:4 = [Pt<sub>4</sub>( $\mu_2$ -CO)<sub>5</sub>(PR<sub>3</sub>)<sub>4</sub>]; 3:3:4 = [Pt<sub>3</sub>( $\mu_2$ -CO)<sub>3</sub>(PR<sub>3</sub>)<sub>4</sub>]. The clusters marked with + were isolated, characterized, and obtained analytically pure. Those marked (+) were only detected in solution by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. The same technique showed no evidence for the formation of any of the other possible clusters.

and that compounds **1a-d** and **2a-c** can easily be obtained in good yields simply by adding 1 equiv of tertiary phosphine to a suspension of either [PtCl<sub>2</sub>(MeCN)<sub>2</sub>] (**3**) or [PtCl<sub>2</sub>(COD)] (**4**) in acetonitrile, under 1 atm of carbon monoxide, and treating the resulting mixture with sodium borohydride. Since [PtCl<sub>2</sub>(MeCN)<sub>2</sub>] is simply and quantitatively obtained by refluxing PtCl<sub>2</sub> in acetonitrile, this procedure represents a direct "one-pot" synthetic method with yields ranging from 60 to 90%, depending on the phosphine employed.

The bulky phosphines P<sup>i</sup>Pr<sub>3</sub>, PCy<sub>3</sub>, PPh<sup>i</sup>Pr<sub>2</sub>, and PPhCy<sub>2</sub> form preferentially complexes of type **1**, while the less bulky phosphines PEt<sub>3</sub> and PPhMe<sub>2</sub> yield only clusters of the type **2**.

Problems were encountered when phosphines containing more than one aryl group, e.g., PMePh<sub>2</sub> or PPh<sub>3</sub>, were employed. In these cases <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy of the methylene chloride extracts showed the presence of mixtures of clusters of the types [Pt<sub>3</sub>( $\mu_2$ -CO)<sub>3</sub>L<sub>3</sub>] (**1**; 3:3:3), [Pt<sub>4</sub>( $\mu_2$ -CO)<sub>5</sub>L<sub>4</sub>] (**2**; 4:5:4), and [Pt<sub>3</sub>( $\mu_2$ -CO)<sub>3</sub>L<sub>4</sub>] (**5**; 3:3:4). Furthermore, it proved to be extremely difficult to prepare clusters of the type [Pt<sub>3</sub>( $\mu_2$ -CO)<sub>3</sub>L<sub>4</sub>] (**5**) by this route.

The preferential formation of clusters of type **1**, **2**, or **5** depends largely (1) on the Pt:PR<sub>3</sub> ratio and (2) on the bulk of the phosphine. Using the method described above as well as other synthetic routes,<sup>9,10</sup> it has been possible to establish the dependence of the cluster type formed on the phosphine cone angle,  $\theta$ .<sup>18</sup> The results are summarized in Table I. When the Pt:P ratio is 1, only complexes of the types **1** and **2** are formed. As can be seen there, phosphines with  $\theta$  of 136° or below form only clusters of type **2**, while phosphines of cone angle of 152° and above form only compounds of type **1**, with the exception of PBz<sub>3</sub>, which has been assigned a  $\theta$  value of 161°. However, this anomaly may be explained by taking into account the great flexibility of these substituents, which, in part, can be folded up to give a ligand with  $\theta$  of ca. 148°. It is also observed that for phosphines with  $\theta$  between 145 and 150° both types of compounds coexist in solution.

Analogous studies carried out on solutions containing Pt:P ratios of 1:2, or larger, showed that clusters of type **5** were formed if the phosphine cone angle does not exceed 150°. Also, in these cases, clusters of different type can coexist in solution. However, as they are in equilibrium, in general one can only isolate the least soluble compound.

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### Synthesis and Characterization of Rhenium Complexes with 4-Ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (P(OCH<sub>2</sub>)<sub>3</sub>CeT)

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#### Introduction

The chemistry of rhenium phosphite complexes is relatively unexplored as compared to that of the phosphine analogues. Only a few reports on rhenium phosphites have appeared in the literature.<sup>1</sup> In particular, little work has been done on rhenium phosphite polyhydride complexes. This is surprising because a wide range of the corresponding phosphine complexes are known. Such complexes can have unusual structures and reactivity patterns.<sup>2</sup> For example, protonation of ReH<sub>3</sub>(CO)(PMe<sub>2</sub>Ph)<sub>3</sub> gives an equilibrium mixture of a classical eight-coordinate tetrahydride [ReH<sub>4</sub>(CO)(PMe<sub>2</sub>Ph)<sub>3</sub>]<sup>+</sup> and its nonclassical seven-coordinate dihydrogen dihydride tautomer [ReH<sub>2</sub>( $\eta^2$ -H<sub>2</sub>)(CO)(PMe<sub>2</sub>Ph)<sub>3</sub>]<sup>+</sup>,<sup>3</sup> and ReH<sub>7</sub>(PPh<sub>3</sub>)<sub>2</sub> is an efficient catalyst for C-H bond activation.<sup>4</sup>

As ligands, phosphites are generally more electron-withdrawing and sterically less bulky than phosphines.<sup>5</sup> Replacement of phosphines in a polyhydride complex by phosphites may have interesting effects on both structure and reactivity as a result of different electronic and steric properties. For example, the electron-withdrawing character of phosphite ligands may favor nonclassical structures with one or more  $\eta^2$ -H<sub>2</sub> ligands by reducing the M(d<sub>xy</sub>) to H<sub>2</sub>( $\sigma^*$ ) back-donation.

Very few phosphite-supported polyhydrides are known, probably because phosphite ligands do not usually tolerate strongly reducing hydridometalates such as LiAlH<sub>4</sub> and NaBH<sub>4</sub>, which are often used in the preparation of polyhydrides from their halide precursors. For example, an attempted preparation of ReH<sub>5</sub>[P(OMe)<sub>3</sub>]<sub>3</sub> by treatment of ReCl<sub>3</sub>[P(OMe)<sub>3</sub>]<sub>3</sub> with various hydridometalates led to an intractable product.<sup>1b</sup>

In a brief communication, Caulton et al. reported the first examples of high-oxidation-state rhenium phosphite polyhydrides, ReH<sub>5</sub>[P(OEt)<sub>3</sub>]<sub>3</sub> and ReH<sub>7</sub>[P(OEt)<sub>3</sub>]<sub>2</sub>.<sup>18</sup> We looked at the coordination chemistry of rhenium with the cyclic phosphite 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (P(OCH<sub>2</sub>)<sub>3</sub>CeT, ETPB) in the hope that the special cage structure of the ligand might make it more resistant to hydridometalates in the preparation of polyhydrides. In this paper we describe the synthesis and characterization of several new rhenium complexes with ETPB, including two rare rhenium phosphite polyhydrides.

#### Results

The synthetic routes to the rhenium ETPB complexes, starting from ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>, are summarized in Scheme I. The new complexes were identified by microanalysis and spectroscopic studies, including T<sub>1</sub> data. These are presented in the Experimental Section and in Table I.

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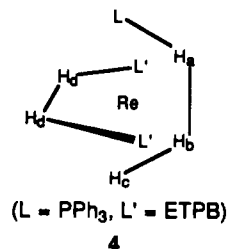
## Discussion

**Synthesis and Characterization.** Reaction of  $\text{ReOCl}_3(\text{PPh}_3)_2$  with an excess of ETPB at room temperature in  $\text{CH}_2\text{Cl}_2$  leads to reduction of Re(V) to Re(III), with the formation of a mixed phosphine-phosphite complex, *mer-cis*- $\text{ReCl}_3(\text{ETPB})_2(\text{PPh}_3)$  (**1**). Like other paramagnetic complexes of the general form  $\text{ReCl}_3\text{L}_3$  (L = phosphine or phosphite), which contain a  $d^4$  Re(III) center in an octahedral environment,<sup>16,6</sup> compound **1** gives sharp Knight-shifted resonances in the  $^1\text{H}$  NMR spectrum. The *mer-cis*-octahedral configuration is confirmed by the chemical inequivalence of the two ETPB ligands. The ETPB ligands are mutually *cis*, probably as a result of their strong  $\pi$ -acceptor character disfavoring a *trans* configuration.

Replacement of the remaining  $\text{PPh}_3$  in **1** by ETPB occurs in refluxing toluene to give *mer*- $\text{ReCl}_3(\text{ETPB})_3$  (**2**). Compound **2** also exhibits a Knight-shifted  $^1\text{H}$  NMR spectrum with narrow resonances. The *mer*-octahedral structure of **2** is based on the observation of two sets of chemically inequivalent ETPB ligands in a ratio of 1:2.

The seven-coordinate 18-electron complex  $\text{ReCl}_3(\text{CO})(\text{ETPB})_3$  (**3**) is synthesized by passing of CO through a suspension of **2** in refluxing THF or by similar carbonylation of **1** in the presence of ETPB. It is noteworthy that stable neutral carbonyl complexes are rarely found for any metal in the formal oxidation state III, which is especially true for early transition metals. The IR spectrum of **3** in Nujol mull shows a strong  $\nu(\text{CO})$  band at  $1952\text{ cm}^{-1}$ . This frequency is significantly higher than that for  $\text{ReCl}_3(\text{CO})(\text{PMe}_2\text{Ph})_3$  ( $\nu(\text{CO}) = 1862\text{ cm}^{-1}$ ),<sup>6d</sup> which is consistent with there being less back-donation into the CO ligand in **3** due to the higher  $\pi$ -acceptor character of ETPB as compared to  $\text{PMe}_2\text{Ph}$ . The  $^1\text{H}$ ,  $^{31}\text{P}\{^1\text{H}\}$ , and  $^{13}\text{C}$  NMR spectra of **3** in  $\text{CD}_2\text{Cl}_2$  show that the three ETPB ligands are equivalent, indicating rapid fluxionality, as is commonly observed for seven-coordinate complexes.<sup>7</sup> The  $^{13}\text{C}$  NMR spectrum displays a quartet resonance ( $\delta\ 220.0$ ,  $^2J_{\text{PC}} = 51.3\text{ Hz}$ ) for the CO ligand.

Treatment of **1** with  $\text{NaBH}_4$  in refluxing EtOH gives  $\text{ReH}_5(\text{ETPB})_2(\text{PPh}_3)$  (**4**). The IR spectrum (Nujol mull) of **4** shows characteristic  $\nu(\text{Re-H})$  bands at 1988, 1946, and  $1891\text{ cm}^{-1}$ . No bands which can be assigned to the vibrations of an  $\text{Re}(\eta^2\text{-H}_2)$  unit are observed. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **4** in  $\text{CD}_2\text{Cl}_2$  at 298 K shows an AB<sub>2</sub> pattern ( $^2J_{\text{PP}} = 56.0\text{ Hz}$ ), consistent with the presence of one  $\text{PPh}_3$  and two equivalent ETPB ligands. The  $^1\text{H}$  NMR spectrum at 298 K shows a quartet ( $\delta\ -6.93$ ,  $^2J_{\text{PH}} = 16.4\text{ Hz}$ ) in the hydride region; the five hydride ligands apparently become equivalent through rapid fluxionality, as is commonly observed for rhenium polyhydrides.<sup>8</sup> The hydride resonance becomes a broad feature on cooling to 213 K, which collapses at 183 K into a triplet ( $\delta\ -6.35$ ,  $^2J_{\text{PH}} = 32.7\text{ Hz}$ , 1 H) and a pseudoquartet ( $\delta\ -7.08$ ,  $^2J_{\text{PH}} = 18.0\text{ Hz}$ , 1 H) partially overlapping with a broad bump ( $\delta\ -7.40$ , 3 H). The low-temperature hydride pattern is consistent with a classical eight-coordinate dodecahedral structure of the sort found for  $\text{ReH}_5(\text{PPh}_3)_3$ <sup>9</sup> and  $\text{ReH}_5(\text{PMePh}_2)_3$ <sup>10</sup> by X-ray and neutron diffraction studies. According to Orgel's rule,<sup>11</sup> the better  $\pi$ -acceptor ligands, ETPB and  $\text{PPh}_3$ , occupy the B positions to maximize the  $\pi$ -back-bonding with the filled metal  $d_{x^2-y^2}$  orbital:



The structure predicts that four hydride resonances in a 1:1:1:2 ratio should be present at low temperature. We observed three resonances in a 1:1:3 ratio probably because two of the resonances overlap.

$\text{ReH}_5(\text{ETPB})_3$  (**5**) is prepared by treatment of **2** with  $\text{NaBH}_4$  in refluxing EtOH. The IR spectrum (Nujol mull) of **5** shows  $\nu(\text{Re-H})$  bands at 1960, 1927, and  $1885\text{ cm}^{-1}$ . The selectively hydride-coupled  $^{31}\text{P}$  NMR spectrum of **5** in  $\text{CD}_2\text{Cl}_2$  at 298 K shows a binomial sextet ( $^2J_{\text{PH}} = 15.6\text{ Hz}$ ), confirming the presence of five hydride ligands. The  $^1\text{H}$  NMR spectrum at 298 K shows a quartet hydride resonance ( $\delta\ -7.94$ ,  $^2J_{\text{PH}} = 16.3\text{ Hz}$ ) which becomes a broad feature upon cooling to 183 K, suggesting the onset of decoalescence. It is not clear whether the more fluxional character of **5** compared to **4** is a result of steric or electronic effects.

$^1\text{H}$  NMR  $T_1$  Studies on  $\text{ReH}_5(\text{ETPB})_2(\text{PPh}_3)$  (**4**) and  $\text{ReH}_5(\text{ETPB})_3$  (**5**).  $^1\text{H}$  NMR spin-lattice relaxation times ( $T_1$ ) have been found useful in the structural assignment of hydride complexes as to whether they contain one or more  $\eta^2\text{-H}_2$  ligands.<sup>2a-c,12</sup> The variable-temperature  $T_1$  data of the hydride resonances of **4** and **5** are given in Table I. The minimum  $T_1$  values observed for **4** and **5** are 77 and 84 ms, respectively. These values are lower than usually found for classical polyhydrides, but they are well within the range previously found for classical rhenium polyhydrides with high coordination number.<sup>9,13-18</sup> Bakhmutov et al. and we have recently shown that Re-H dipole-dipole relaxation can make a significant contribution to the  $T_1$  relaxation of rhenium hydride complexes.<sup>19</sup> The  $T_1$  data of **4** and **5** are therefore consistent with classical structures containing no  $\eta^2\text{-H}_2$  ligands. The minimum  $T_1$  value of **4** is slightly lower than that of **5**, probably as a result of steric effects. The greater steric bulk of  $\text{PPh}_3$  compared to ETPB may force the hydride ligands in **4** to be closer together, which leads to a lower  $T_1(\text{min})$  value due to shorter nonbonding H...H contacts.

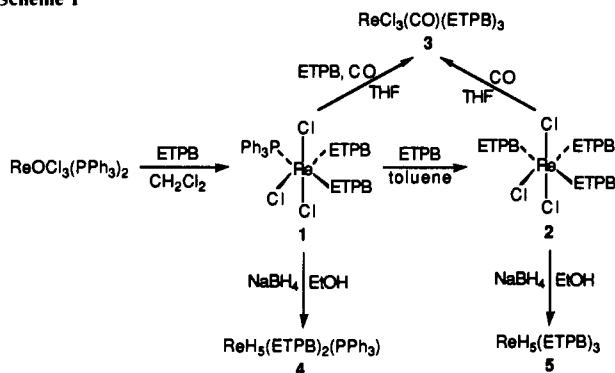
## Conclusion

We have synthesized and characterized a number of Re(III) and Re(V) complexes with a cyclic phosphite, ETPB. The ETPB ligand is unusual in resisting attack by  $\text{NaBH}_4$  and so allowing the synthesis of two rare high-oxidation-state rhenium phosphite polyhydride complexes, **4** and **5**, from the halide precursors **1** and

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Scheme 1



**Table I.** Variable-Temperature  $^1\text{H}$  NMR  $T_1$  Measurements on the Hydride Resonances of  $\text{ReH}_5(\text{ETPB})_2(\text{PPh}_3)$  (4) and  $\text{ReH}_5(\text{ETPB})_3$  (5) in  $\text{CD}_2\text{Cl}_2$  at 250 MHz

4		5	
temp, K	$T_1$ , ms	temp, K	$T_1$ , ms
213	87	180	140
217	81	190	100
223	78	194	92
228	77	200	84
233	78	207	86
243	86	210	94
250	93	215	96
256	102	220	105
263	113	227	122

2. This method might also be used to prepare other transition-metal polyhydride complexes supported by ETPB. The variable-temperature  $^1\text{H}$  NMR spectra and  $T_1$  data for 4 and 5 are consistent with classical structures containing no  $\eta^2\text{-H}_2$  ligands.

### Experimental Section

**General Procedures.** All manipulations were performed under a dry  $\text{N}_2$  atmosphere by standard Schlenk-tube techniques. Diethyl ether, hexane, toluene, and tetrahydrofuran were distilled from  $\text{Na}/\text{Ph}_2\text{CO}$ ; dichloromethane was distilled from  $\text{CaH}_2$ . All solvents were stored under  $\text{N}_2$  over 4-Å molecular sieves.  $\text{ReOCl}_3(\text{PPh}_3)_2$  was prepared according to the literature method.<sup>64</sup>

$^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR spectra were recorded on a Bruker WM 250 or WM 500 spectrometer;  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts were measured with the residual solvent resonance as reference;  $^{31}\text{P}$  chemical shifts were measured with external 85%  $\text{H}_3\text{PO}_4$  as reference. IR spectra were recorded on a Nicolet 5-SX FT-IR spectrometer.  $^1\text{H}$  NMR  $T_1$  measurements were carried out by the inversion-recovery method using a standard  $180^\circ\text{-}\tau\text{-}90^\circ$  pulse sequence.

**mer-cis-Trichlorobis(4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)(triphenylphosphine)rhenium(III) (1).** A mixture of  $\text{ReOCl}_3(\text{PPh}_3)_2$  (2.80 g, 3.36 mmol) and ETPB (1.63 g, 10.08 mmol) was stirred in  $\text{CH}_2\text{Cl}_2$  (40 mL) at room temperature for 24 h. The resulting orange solution was filtered through Celite to remove a small amount of an insoluble white solid, and the filtrate was concentrated to 5 mL in vacuo. Addition of  $\text{Et}_2\text{O}$  (60 mL) resulted in the precipitation of a yellow solid, which was filtered off, washed with  $\text{Et}_2\text{O}$  ( $4 \times 10$  mL), and dried in vacuo. Yield: 2.48 g, 84%. Anal. Calcd for  $\text{C}_{30}\text{H}_{37}\text{Cl}_3\text{O}_6\text{P}_3\text{Re}$ : C, 40.99; H, 4.24. Found: C, 41.16; H, 4.29.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 298 K):  $\delta$  14.50 (d,  $J = 7.3$  Hz, 6 H, ortho H of Ph), 11.38 (s, 6 H,  $\text{OCH}_2$ ), 10.63 (s, 6 H,  $\text{OCH}_2$ ), 8.78 (t,  $J = 7.3$  Hz, 6 H, meta H of Ph), 8.12 (t,  $J = 7.3$  Hz, 3 H, para H of Ph), 4.19 (q,  $J = 7.8$  Hz, 2 H,  $\text{CH}_2\text{CH}_3$ ), 3.78 (q,  $J = 7.8$  Hz, 2 H,  $\text{CH}_2\text{CH}_3$ ), 3.08 (t,  $J = 7.8$  Hz, 3 H,  $\text{CH}_2\text{CH}_3$ ), 2.73 (t,  $J = 7.8$  Hz, 3 H,  $\text{CH}_2\text{CH}_3$ ).

**mer-Trichlorotris(4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)rhenium(III) (2).** *mer-cis*- $\text{ReCl}_3(\text{ETPB})_2(\text{PPh}_3)$  (1) (2.00 g, 2.27 mmol) was suspended in a solution of ETPB (0.405 g, 2.50 mmol) in toluene (75 mL), and the mixture was refluxed for 2.5 h. The solvent was removed and the residue extracted with  $\text{CH}_2\text{Cl}_2$  ( $4 \times 10$  mL). A small amount of insoluble impurity was filtered off, and the filtrate was concentrated to ca. 5 mL. Addition of  $\text{Et}_2\text{O}$  (60 mL) resulted in the precipitation of a greenish yellow solid, which was filtered off, washed with  $\text{Et}_2\text{O}$  ( $4 \times 10$  mL), and dried in vacuo. Yield: 1.40 g, 78%. Anal. Calcd for  $\text{C}_{18}\text{H}_{33}\text{Cl}_3\text{O}_6\text{P}_3\text{Re}$ : C, 27.76; H, 4.27. Found: C, 28.01; H, 4.34.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 298 K):  $\delta$  11.27 (s, 12 H,  $\text{OCH}_2$ ), 10.62 (s, 6 H,  $\text{OCH}_2$ ), 4.31 (q,  $J = 7.5$  Hz, 4 H,  $\text{CH}_2\text{CH}_3$ ), 3.70 (q,  $J = 7.5$  Hz,

2 H,  $\text{CH}_2\text{CH}_3$ ), 3.11 (t,  $J = 7.5$  Hz, 6 H,  $\text{CH}_2\text{CH}_3$ ), 2.71 (t,  $J = 7.5$  Hz, 3 H,  $\text{CH}_2\text{CH}_3$ ).

**mer-Trichlorocarbonyltris(4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)rhenium(III) (3).** **Method 1.** A stream of CO was bubbled for 1 h through a boiling suspension of *mer*- $\text{ReCl}_3(\text{ETPB})_3$  (2) (0.40 g, 0.51 mmol) in THF (40 mL). The solvent volume was reduced to ca. 3 mL in vacuo and  $\text{Et}_2\text{O}$  (40 mL) added. The resulting cream-colored solid was filtered off, washed with  $\text{Et}_2\text{O}$  ( $4 \times 10$  mL), and dried in vacuo. Yield: 0.34 g, 81%. Anal. Calcd for  $\text{C}_{19}\text{H}_{33}\text{Cl}_3\text{O}_{10}\text{P}_3\text{Re}$ : C, 28.28; H, 4.12. Found: C, 28.43; H, 4.17. IR (Nujol):  $\nu_{\text{CO}}$  1952  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 298 K):  $\delta$  4.40 (br s, 18 H,  $\text{OCH}_2$ ), 1.26 (q,  $J = 7.6$  Hz, 6 H,  $\text{CH}_2\text{CH}_3$ ), 0.83 (t,  $J = 7.6$  Hz, 9 H,  $\text{CH}_2\text{CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 298 K):  $\delta$  81.4. Off-resonance  $^1\text{H}$ -decoupled  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 298 K):  $\delta$  220.0 (q,  $^2J_{\text{PC}} = 51.3$  Hz, 1 C, CO), 76.1 (t, 9 C,  $\text{OCH}_2$ ), 35.2 (c, 3 C,  $\text{OCH}_2\text{C}$ ), 22.8 (t, 3 C,  $\text{CH}_2\text{CH}_3$ ), 6.4 (q, 3 C,  $\text{CH}_2\text{CH}_3$ ).

**Method 2.** A stream of CO was bubbled for 1.5 h through a boiling suspension of *mer-cis*- $\text{ReCl}_3(\text{ETPB})_2(\text{PPh}_3)$  (1) (0.40 g, 0.46 mmol) and ETPB (0.089 g, 0.55 mmol) in THF (40 mL). The solvent was evaporated to ca. 3 mL and  $\text{Et}_2\text{O}$  (40 mL) added. The resulting cream-colored solid was filtered off, washed with  $\text{Et}_2\text{O}$  ( $4 \times 10$  mL), and dried in vacuo. Yield: 0.31 g, 85%.

**Pentahydrido bis(4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)(triphenylphosphine)rhenium(V) (4).** A suspension of *mer-cis*- $\text{ReCl}_3(\text{ETPB})_2(\text{PPh}_3)$  (1) (0.40 g, 0.46 mmol) and  $\text{NaBH}_4$  (0.35 g, 9.2 mmol) in EtOH (25 mL) was heated at reflux for 20 min. After removal of the solvent in vacuo, the residue was extracted with  $\text{CH}_2\text{Cl}_2$  ( $4 \times 10$  mL), and the extract was filtered through Celite. The yellow filtrate was concentrated to ca. 2 mL in vacuo. Addition of hexane (40 mL) resulted in the precipitation of an off-white solid, which was filtered off, washed with hexane ( $4 \times 10$  mL), and dried in vacuo. Yield: 0.23 g, 65%. Anal. Calcd for  $\text{C}_{30}\text{H}_{42}\text{O}_6\text{P}_2\text{Re}$ : C, 46.32; H, 5.44. Found: C, 46.18; H, 5.39. IR (Nujol):  $\nu_{\text{Re-H}}$  1988, 1946, 1891  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 298 K):  $\delta$  7.3-7.6 (c, 15 H, Ph), 3.99 (virtual t,  $^3J_{\text{PH}} = 4.4$  Hz, 12 H,  $\text{OCH}_2$ ), 1.07 (q,  $J = 7.5$  Hz, 4 H,  $\text{CH}_2\text{CH}_3$ ), 0.73 (t,  $J = 7.5$  Hz, 6 H,  $\text{CH}_2\text{CH}_3$ ), -6.93 (q,  $^2J_{\text{PH}} = 16.4$  Hz, 5 H, Re-H).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 298 K):  $\delta$  116.7 (d,  $^2J_{\text{PP}} = 56.0$  Hz, 2 P, ETPB), 31.0 (t,  $^2J_{\text{PP}} = 56.0$  Hz, 1 P,  $\text{PPh}_3$ ). Off-resonance  $^1\text{H}$ -decoupled  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 298 K):  $\delta$  139.8 (d,  $^1J_{\text{PC}} = 48.1$  Hz, 3 C, C1 of  $\text{PPh}_3$ ), 134.3 (dd,  $^2J_{\text{PC}} = 11.1$  Hz, 6 C, C2 of  $\text{PPh}_3$ ), 129.4 (s, 3 C, C4 of  $\text{PPh}_3$ ), 127.6 (d,  $^3J_{\text{PC}} = 11.1$  Hz, 6 C, C3 of  $\text{PPh}_3$ ), 74.1 (t, 6 C,  $\text{OCH}_2$ ), 34.2 (c, 2 C,  $\text{OCH}_2\text{C}$ ), 24.2 (t, 2 C,  $\text{CH}_2\text{CH}_3$ ), 7.1 (q, 2 C,  $\text{CH}_2\text{CH}_3$ ).

**Pentahydridotris(4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)rhenium(V) (5).** A suspension of *mer*- $\text{ReCl}_3(\text{ETPB})_3$  (1) (0.40 g, 0.51 mmol) and  $\text{NaBH}_4$  (0.39 g, 10.3 mmol) in EtOH (25 mL) was heated at reflux for 20 min. After removal of the solvent in vacuo, the residue was extracted with benzene ( $4 \times 15$  mL), and the extract was filtered through Celite. The pale yellow filtrate was concentrated to ca. 1 mL in vacuo. Addition of  $\text{Et}_2\text{O}$  (40 mL) resulted in the precipitation of a white solid, which was filtered off, washed with  $\text{Et}_2\text{O}$  ( $4 \times 10$  mL), and dried in vacuo. Yield: 0.12 g, 35%. Anal. Calcd for  $\text{C}_{18}\text{H}_{38}\text{O}_6\text{P}_3\text{Re}$ : C, 31.91; H, 5.65. Found: C, 32.04; H, 5.72. IR (Nujol):  $\nu_{\text{Re-H}}$  1960, 1927, 1885  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 298 K): 4.13 (s, 18 H,  $\text{OCH}_2$ ), 1.14 (q,  $J = 7.6$  Hz, 6 H,  $\text{CH}_2\text{CH}_3$ ), 0.77 (t,  $J = 7.6$  Hz, 9 H,  $\text{CH}_2\text{CH}_3$ ), -7.94 (q,  $^2J_{\text{PH}} = 16.3$  Hz, 5 H, Re-H). Selectively hydride-coupled  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 298 K):  $\delta$  116.3 (sextet,  $^2J_{\text{PH}} = 15.6$  Hz). Off-resonance  $^1\text{H}$ -decoupled  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 298 K): 74.3 (t, 9 C,  $\text{OCH}_2$ ), 34.2 (virtual q,  $^3J_{\text{PC}} = 11.1$  Hz, 3 C,  $\text{OCH}_2\text{C}$ ), 24.2 (t, 3 C,  $\text{CH}_2\text{CH}_3$ ), 7.1 (q, 3 C,  $\text{CH}_2\text{CH}_3$ ).

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### Structural and Spectroscopic Properties of the $[\text{FeCl}_2(\text{Cat})]_2^{2-}$ Anion

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Much of the bioinorganic chemistry of catechols has concerned complexes of iron. Tris(catecholato)iron(III) complexes are