

(His imidazole), +0.12 V (Met thioether), and -0.33 V (Cys thiolate), one can estimate the  $E^\circ$  of a tetragonal  $[\text{CuN}_2\text{S}_2]^+$  complex of this composition (Table VII). Reduction potentials of various azurins and plastocyanins (Table VII) lie in the range +0.23-0.38 V. The contribution of the marked departure from tetragonal geometry in most of these proteins' copper centers would thus appear to be about +0.25 V, which deduction involves the assumption that the axial -SCH<sub>3</sub> donor exerts its usual  $\Delta E_L$  in that situation. Nonetheless, this contribution attributable to the geometric factor is similar to some of the values proposed previously from a ligand field computational model<sup>95</sup> and from model compound studies.<sup>68</sup> The combined redox and ESR<sup>96,97</sup> data suggest that fungal laccase

and rusticyanin may have similarly unusual S-containing donor atom sets, though with slightly different geometries. At the opposite  $E^\circ$  extreme, stellacyanin lacks methionine,<sup>98</sup> and cystine disulfide sulfur has been suggested as a donor in its stead.<sup>95</sup> The redox and ESR<sup>99</sup> data seem equally consistent with the presence of an N or O donor.

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**Supplementary Material Available:** Further synthetic details (Appendix), ORTEP stereoview of the  $[\text{Cu}(\text{L}-2)(\text{OH}_2)](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$  unit cell (Figure 8), susceptibility data for  $\text{Cu}(\text{L}-1)\text{Cl}$  (Figure 9), RPE polarograms for  $\text{Cu}(\text{L}-1)(\text{bpy})\text{ClO}_4$  and  $\text{Cu}(\text{L}-2)(\text{bpy})(\text{ClO}_4)_2$  (Figure 10), analytical data for ligands and precursors (Table VIII), analytical data for complexes (Table IX), and positional and thermal parameters (Table X), bond lengths and distances (Table XI), bond angles (Table XII), least-squares planes (Table XIII), and observed and calculated structure factors (Table XIV) for  $[\text{Cu}(\text{L}-2)(\text{OH}_2)](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$  (30 pages).

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## Notes

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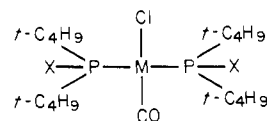
### Evidence for a Strong Similarity in Conformational and Phosphorus-31 NMR Parameters between Two Series of *trans* - $[(t\text{-C}_4\text{H}_9)_2\text{PX}]_2\text{M}(\text{CO})\text{Cl}$ Complexes [M = Rh(I), Ir(I); X = H, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, *n*-C<sub>4</sub>H<sub>9</sub>, C<sub>6</sub>H<sub>5</sub>]

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A variety of square-planar Rh(I) and Ir(I) complexes are important catalysts.<sup>2</sup> It is now apparent that catalysis in general and asymmetric induction in particular depend on the unique stereodynamics of a given achiral or chiral complex.<sup>3</sup> In spite of this, there is a paucity of information concerning the dynamics of rotation about metal-ligand bonds and substituent effects on rotamer preferences.<sup>4,5</sup> We report here a remarkable similarity in the conformational preferences and

<sup>31</sup>P NMR parameters between two series of Rh(I) and Ir(I) complexes (1-10).



- |   |   |
|---|---|
| 1: M = Rh(I), X = H                                       | 6: M = Ir(I), X = H                                       |
| 2: M = Rh(I), X = CH <sub>3</sub>                         | 7: M = Ir(I), X = CH <sub>3</sub>                         |
| 3: M = Rh(I), X = C <sub>2</sub> H <sub>5</sub>           | 8: M = Ir(I), X = C <sub>2</sub> H <sub>5</sub>           |
| 4: M = Rh(I), X = <i>n</i> -C <sub>4</sub> H <sub>9</sub> | 9: M = Ir(I), X = <i>n</i> -C <sub>4</sub> H <sub>9</sub> |
| 5: M = Rh(I), X = C <sub>6</sub> H <sub>5</sub>           | 10: M = Ir(I), X = C <sub>6</sub> H <sub>5</sub>          |

The <sup>31</sup>P{<sup>1</sup>H} NMR spectra (101.2 MHz) of 1-4 (0.05 M in toluene-*d*<sub>8</sub>) below 200 K are consistent with slow rotation about the rhodium-phosphorus bonds on the <sup>31</sup>P NMR time scale and reveal the presence of *three* subspectra. A complete set of spectra for all 10 complexes is available as supplemental Figure 1S. The three subspectra for each of the rhodium complexes 1-4 (Figure 1S) include the B<sub>2</sub> portion of a B<sub>2</sub>X spectrum (X = <sup>103</sup>Rh; *I* = 1/2), the AC portion of an ACX spectrum, and a minor D<sub>2</sub>X spectrum (e.g., see the spectrum of 4 in Figure 1).<sup>6</sup> For the Ir(I) complexes 6-9, each spectrum at slow exchange shows a B<sub>2</sub> singlet, an AC spectrum, and a minor D<sub>2</sub> singlet (e.g., see the spectrum of 9 in Figure 1).

Tolman's cone angles for chlorine and carbon monoxide are 102 and 95°, respectively.<sup>7</sup> Chlorine possesses slightly more

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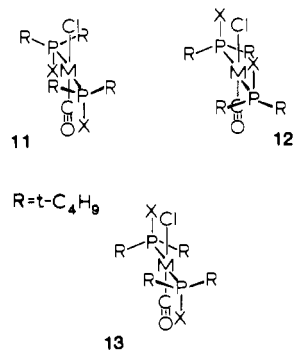
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Table I.  $^{31}\text{P}$  NMR Parameters and Rotamer Populations

compd	spin syst obsd at slow exchange <sup>a</sup>	$^{31}\text{P}$ NMR chem shifts, <sup>b</sup> ppm	$^1J_{\text{RhP}}$ , Hz	$^2J_{\text{PP}}$ , Hz	rel populations
1	B <sub>2</sub> X	80.5	114.6		0.782 (220 K)
	D <sub>2</sub> X	40.8	118.1		0.010
	ACX	85.1	116.2	320.7	0.208
2	B <sub>2</sub> X	47.1	119.3		0.599 (205 K)
	D <sub>2</sub> X	29.8	121.0		0.070
	ACX	48.4	118.2	323.0	0.331
3	B <sub>2</sub> X	31.6	123.1		0.343 (210 K)
	D <sub>2</sub> X	59.2	120.1		0.167
	ACX	47.2	121.1	311.5	0.490
4	B <sub>2</sub> X	48.6	123.0		0.342 (210 K)
	D <sub>2</sub> X	57.6	120.2		0.192
	ACX	45.4	122.1	313.5	0.466
5	E <sub>2</sub> X	58.3	118.2		0.141 (160 K)
	F <sub>2</sub> X	46.4	123.0		0.178
	ACX	53.4	125.0	306.4	0.185
6	B <sub>2</sub>	54.4	124.9		0.496
	D <sub>2</sub>	67.5	122.0		0.178
	AC	54.3	124.8	306.6	0.100
7	B <sub>2</sub>	74.2	124.8		0.550 (220 K)
	D <sub>2</sub>	34.2	120.1		0.074
	AC	80.3	121.1	319.2	0.376
8	B <sub>2</sub>	37.2	123.1		0.305 (210 K)
	D <sub>2</sub>	33.7	119.3		0.179
	AC	18.5	121.0	310.6	0.516
9	B <sub>2</sub>	50.7	120.2		0.364 (210 K)
	D <sub>2</sub>	40.0	122.1		0.168
	AC	52.7	123.0	310.1	0.468
10	B <sub>2</sub>	48.9	118.2		0.197 (160 K)
	D <sub>2</sub>	37.6	120.1		0.151
	AC	50.4	121.1	311.0	0.153
10	E <sub>2</sub>	37.8	123.0		0.499
	F <sub>2</sub>	44.7	124.8		
	AD	44.6	121.0	311.0	
10	BC	61.6	122.0		
		45.0	124.8	310.9	
		60.3	123.0	310.9	

<sup>a</sup> X =  $^{103}\text{Rh}$  ( $I = 1/2$ ). <sup>b</sup> Reference 85%  $\text{H}_3\text{PO}_4$  (see ref 8).

steric bulk in this context than carbon monoxide. Thus, we assign the large B<sub>2</sub> signal to the syn conformer **11** in which



both X groups eclipse or nearly eclipse carbon monoxide and the *tert*-butyl groups are staggered about the chlorine. The minor D<sub>2</sub> signal is assigned to the syn form **12** with both X groups proximate to the more bulky chlorine. The AC signals are assigned to the anti form **13**. Rotamer populations and  $^{31}\text{P}\{^1\text{H}\}$  NMR parameters are compiled in Table I.

The slow-exchange spectra of **5** and **10** (X = C<sub>6</sub>H<sub>5</sub>), respectively, are more complex than those of **1-4** and **6-9**. The

$^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **10** at 160 K (Figure 1, bottom right; 0.015 M in 60% CF<sub>2</sub>ClH/30% CFCl<sub>2</sub>H/10% CDCl<sub>3</sub>, v/v) consists of two closely spaced E<sub>2</sub> and F<sub>2</sub> singlets (see arrows in Figure 1), AD and BC spectra. Four conformations are observed. The spectrum of **5** at 160 K (Figure 1, bottom left; 0.04 M in 50% CF<sub>2</sub>ClH/30%CFCl<sub>2</sub>H/20% CD<sub>2</sub>Cl<sub>2</sub>, v/v) is complex and consists of closely spaced E<sub>2</sub>X and F<sub>2</sub>X doublets (X =  $^{103}\text{Rh}$ ), an ACX spectrum, and a BDX spectrum (Table I). Assignment of subspectra to specific rotamers is problematical in **5** and **10** and will be addressed briefly later.

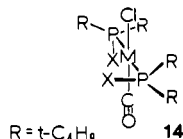
The slow-exchange spectra of pairs of complexes for which X is the same but the metals are different (e.g., **4** and **9**, **5** and **10**; Figure 1) reveal a remarkable correspondence. We have presented in the left-most vertical column of Figure 1S the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of rhodium complexes **1-5**. The chemical shifts and coupling constants for **1-5** compiled in Table I were obtained from complete  $^{31}\text{P}\{^1\text{H}\}$  NMR line-shape simulations at slow exchange.<sup>6</sup> These simulations required, of course, the inclusion of  $^{103}\text{Rh}-^{31}\text{P}$  spin-spin coupling constants (Table I). For an easier visual comparison of the spectra of the rhodium complexes to those of the iridium complexes, we recomputed the theoretical spectral fits for **1-5** without  $^{103}\text{Rh}-^{31}\text{P}$  spin-spin coupling. These spectra are presented in the middle column of Figures 1 and 1S. In the far-right

columns of the figures are the spectra of the iridium complexes (9 and 10 in Figure 1, 6–10 in Figure 1S). Even for the apparently more complicated cases of 5 and 10 (i.e., X = C<sub>6</sub>H<sub>5</sub>), the spectrum of 5 computed without <sup>103</sup>Rh–<sup>31</sup>P spin-spin coupling (Figure 1, bottom center) shows a strong similarity to the spectrum of 10. The arrows in the computed spectrum of 5 and in the experimental spectrum of 10 indicate the presence of the closely spaced E<sub>2</sub> and F<sub>2</sub> signals.

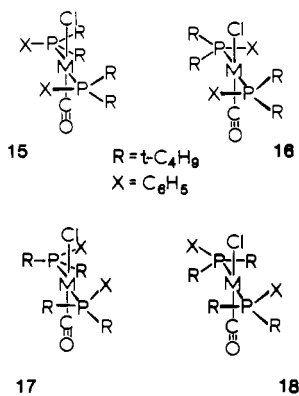
In addition, a careful consideration of Table I and Figure 1S reveals a progressive increase in the population of the minor syn rotamer (12) and the anti rotamers (13), proceeding from X = H to X = CH<sub>3</sub> to X = C<sub>2</sub>H<sub>5</sub> (Table I). Proceeding from X = C<sub>2</sub>H<sub>5</sub> to X = *n*-C<sub>4</sub>H<sub>9</sub>, the effect levels off. It appears that, as the steric bulk of X increases, there is, up to a point, a progressive leveling of rotamer energies. When X = C<sub>6</sub>H<sub>5</sub>, more conformations are observed.

However, perusal of Table I and Figure 1S will indicate that, if X is the same substituent, conformational preference is essentially independent of the metal and is determined by the ligands bonded to the metal. There is also a strong correspondence between the chemical shift values of specific rotamers in the two series of metal complexes (Table I).

In our previous <sup>31</sup>P{<sup>1</sup>H} DNMR study of 5 at 36.43 MHz, the very closely spaced E<sub>2</sub>X and F<sub>2</sub>X doublets merged to give one doublet.<sup>4</sup> We assigned the ACX spectrum to 13 (X = C<sub>6</sub>H<sub>5</sub>), the BDY spectrum to the "skewed" 14, and the ap-

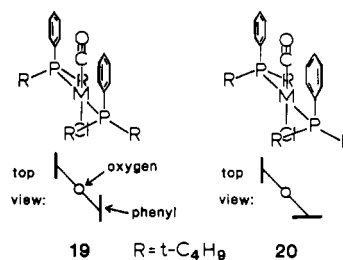


parent doublet resulting from the merged E<sub>2</sub>X and F<sub>2</sub>X doublets to 11. Observation of E<sub>2</sub> and F<sub>2</sub> signals for 5 and 10 at 101.2 MHz reveals a more complex situation. The very small chemical shift separation ( $\Delta\delta_{EF} = 0.1$  ppm) suggests phosphorus atoms that are in nearly corresponding environments, i.e., phosphines oriented similarly with respect to the Cl–M–CO moiety. These E<sub>2</sub> and F<sub>2</sub> signals could arise from a variety of conformational combinations: (1) conformers such as 15 (X = C<sub>6</sub>H<sub>5</sub>; C<sub>s</sub> symmetry if one ignores the orientation



of phenyl groups) and 16 (C<sub>2</sub> symmetry); (2) conformers such as 17 and 18 with the quaternary carbon of two *t*-C<sub>4</sub>H<sub>9</sub> groups oriented in a plane perpendicular to the plane of coordination; (3) syn and anti conformers such as 11 and 13 showing the interesting possibility of a DNMR visible twist about the phenyl–phosphorus bonds. Indeed, chirality and diastereoisomerism induced by rotation about metal–phosphorus bonds and by concomitant twisting about the phenyl–phosphorus bonds in metal complexes of phenylphosphines have been addressed by others.<sup>5b</sup> Chirality induced by phenyl–phosphorus twisting in the free, uncomplexed triarylphosphines has been studied experimentally<sup>9ab</sup> and by using molecular-mechanics

calculations.<sup>9c</sup> With reference to complexes 5 and 10, the two phenyl groups in 11 could be oriented as illustrated in the chiral conformer 19 (C<sub>2</sub> symmetry) or as in the achiral 20 (C<sub>s</sub> sym-



metry). Conformers 19 and 20 are diastereomers and, in principle, NMR distinguishable. For 19 and 20, the nearly corresponding orientations of the phenyl groups with respect to the Cl–M–CO axis would be consistent with the small  $\Delta\delta_{EF}$  values for 5 and 10. A similar rationale may be applied to the anti conformer 13. The small  $\Delta\delta_{AB}$  and  $\Delta\delta_{CD}$  values for 5 could result from diastereomers with different relative orientations of the two anti phenyl groups. This rationale requires the presence of two general types of conformer: (1) one type with the two phenyl groups essentially syn to carbon monoxide (or chlorine?); (2) the other type with one phenyl syn to carbon monoxide and the other phenyl syn to chlorine. This is indeed more consistent with the rotamer assignments for complexes 1–4 and 6–9 (vide supra). However, more research is necessary to obtain a clearer picture of the stereodynamics of 5 and 10.

One trend is unequivocal. Conformational preferences in complexes 1–10 depend to a very small extent on the metal and essentially exclusively on the structure of the phosphine ligand.

### Experimental Section

The 101.2-MHz <sup>31</sup>P{<sup>1</sup>H} FT NMR spectra were recorded on a Bruker WM250 multinuclear NMR spectrometer equipped with a broad-band probe and BVT-1000 variable-temperature controller. Temperatures are accurate to  $\pm 3$  K. All solvents used for NMR samples were thoroughly degassed.

Theoretical spectra were calculated by using a DEC 20/60 computer and were plotted with a HP-7221A flatbed graphics plotter.<sup>6</sup>

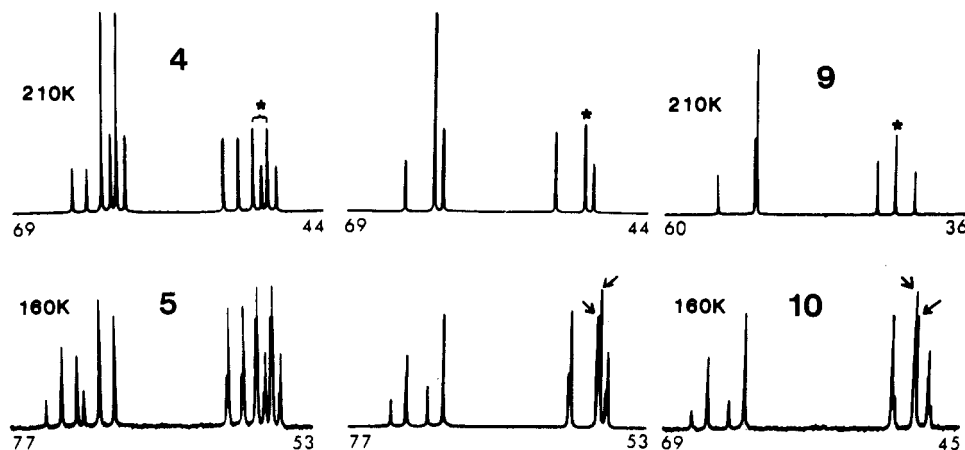
All reactions were performed under N<sub>2</sub> except as noted below. All solvents used for synthesis were thoroughly degassed. Diethyl ether was freshly distilled from sodium/dibenzophenone ketal prior to use.

**trans-Rh(Cl)(CO)[P(*t*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>H]<sub>2</sub> (1)** was prepared according to a previously reported procedure.<sup>5b</sup> Di-*tert*-butylphosphine was added to a solution of bis( $\mu$ -chloro)tetracarbonyldirrhodium (0.0005 mol; Strem Chemicals, Inc.) in 10 mL of methanol. The orange solution of the rhodium(I) dimer turned bright yellow immediately, and a gas (CO) was evolved. The solution was stirred for 1 h. The yellow crystals that formed were washed with methanol and recrystallized three times from toluene/methanol. Anal. Calcd for C<sub>17</sub>H<sub>38</sub>ClO<sub>2</sub>Rh: C, 44.5; H, 8.35; Cl, 7.7; P, 13.5. Found: C, 44.4; H, 8.34; Cl, 7.4; P, 12.5.

**trans-Rh(Cl)(CO)[P(*t*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>CH<sub>3</sub>]<sub>2</sub> (2)** was prepared in the same manner as 1 above using di-*tert*-butylmethylphosphine.<sup>10</sup> Anal. Calcd for C<sub>19</sub>H<sub>42</sub>ClO<sub>2</sub>Rh: C, 46.9; H, 8.70; Cl, 7.3. Found: C, 46.8; H, 8.43; Cl, 6.9.

**trans-Rh(Cl)(CO)[P(*t*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>C<sub>2</sub>H<sub>5</sub>]<sub>2</sub> (3)** was prepared by using a previously reported procedure.<sup>10</sup> Di-*tert*-butylethylphosphine was prepared first by using a modified procedure of Crofts and Parker.<sup>11</sup> Lithium wire (1% sodium amalgam; 0.2 mol) was added to 50 mL of diethyl ether and stirred vigorously. Freshly distilled ethyl bromide (0.08 mol) in 20 mL of ether was added dropwise over the lithium

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**Figure 1.**  $^{31}\text{P}\{^1\text{H}\}$  pulsed Fourier transform NMR spectra (101.25 MHz) of complexes **4**, **5**, **9**, and **10** (see text) under conditions of slow rotation about the metal-phosphorus bonds on the NMR time scale. The middle spectra are theoretically computed with  $^{103}\text{Rh}$ - $^{31}\text{P}$  spin-spin coupling removed and correspond to the spectra of the Rh(I) complexes immediately to the left. An asterisk identifies the least populous subspectrum for complexes **4** and **9**. For an explanation of the arrows (lower spectra) see text. Each spectrum is calibrated at lower left and lower right in ppm.

wire within a 10-min period. An ice bath controlled the reaction. The mixture was stirred for 5 min more at room temperature at which point most of the lithium wire was consumed. Over a 5-min period, di-*tert*-butylchlorophosphine (0.03 mol; Strem Chemicals, Inc.) was added dropwise to the mixture. After refluxing for 1.5 h, the reaction was quenched slowly with water. The ether layer was extracted and dried over  $\text{Na}_2\text{SO}_4$ , and the ether was removed by distillation. The crude phosphine was vacuum distilled to yield a clear colorless liquid in 70% yield (bp 353-356 K (15.5 mm)). Spectral data on the free phosphine:  $^{13}\text{C}\{^1\text{H}\}$  NMR (vinyl chloride, 260 K, 62.9 MHz,  $\text{Me}_4\text{Si}$  reference)  $\delta$  31.5 (quaternary, d,  $^1J_{\text{PC}} = 22.2$  Hz), 29.8 (*tert*-butyl methyls, d,  $^2J_{\text{PC}} = 13.0$  Hz), 15.3 (methyl of ethyl, d,  $^1J_{\text{PC}} = 27.8$  Hz), 14.2 ( $\text{CH}_2$ , d,  $^2J_{\text{PC}} = 20.4$  Hz);  $^{31}\text{P}\{^1\text{H}\}$  NMR (vinyl chloride, 260 K, 101.2 MHz, 85%  $\text{H}_3\text{PO}_4$  reference)  $\delta$  33.7 (s);  $^1\text{H}$  NMR (vinyl chloride, 260 K, 250.1 MHz,  $\text{Me}_4\text{Si}$  reference)  $\delta$  1.33 ( $\text{CH}_2$ , m,  $^3J_{\text{HH}} = 7.8$  Hz,  $^2J_{\text{PH}} = 4.5$  Hz), 1.14 (methyl of ethyl, m,  $^3J_{\text{HH}} = 7.8$  Hz,  $^3J_{\text{PH}} = 16.5$  Hz), 1.08 (*tert*-butyl, d,  $^3J_{\text{PH}} = 10.0$  Hz).

Then, the rhodium complex (**3**) was prepared as described for **1** above by using di-*tert*-butylethylphosphine. Anal. Calcd for  $\text{C}_{21}\text{H}_{46}\text{ClO}_2\text{Rh}$ : C, 49.0; H, 9.00; Cl, 6.9; P, 12.0. Found: C, 48.9; H, 9.18; Cl, 6.9; P, 12.0.

*trans*-Rh(Cl)(CO)[P(*t*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub> (**4**) was prepared in the same manner as **1** above using di-*tert*-butyl-*n*-butylphosphine.<sup>12</sup> Anal. Calcd for  $\text{C}_{23}\text{H}_{54}\text{ClO}_2\text{Rh}$ : C, 52.6; H, 9.53; Cl, 6.2; P, 10.8. Found: C, 52.7; H, 9.50; Cl, 6.3; P, 10.9.

*trans*-Rh(Cl)(CO)[P(*t*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>2</sub> (**5**) was prepared in the same manner described for **1** using di-*tert*-butylphenylphosphine (Strem Chemicals, Inc.).<sup>13</sup> Anal. Calcd for  $\text{C}_{29}\text{H}_{46}\text{ClO}_2\text{Rh}$ : C, 57.0; H, 7.59; Cl, 5.8; P, 10.1. Found: C, 56.8; H, 7.62; Cl, 6.3; P, 11.2.

*trans*-Ir(Cl)(CO)[P(*t*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>H]<sub>2</sub> (**6**)<sup>5b</sup> was prepared by using a modified version of a previously reported procedure.<sup>14</sup>  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$  (0.0005 mol; Strem Chemicals, Inc.) was added to 10 mL of 2-methoxyethanol. A stream of carbon monoxide gas was bubbled continuously through the resulting purple solution. The reaction mixture was allowed to reflux for 1 h at which point di-*tert*-butylphosphine was added by syringe to the stirring, hot, clear yellow solution. A gas (CO) was immediately evolved from the reaction. As the reaction mixture slowly cooled, yellow crystals of the iridium(I) complex formed slowly. The iridium(I) complex was recrystallized from toluene/methanol. Anal. Calcd for  $\text{C}_{17}\text{H}_{38}\text{ClO}_2\text{Ir}$ : C, 37.4; H, 6.99; Cl, 6.5; P, 11.3. Found: C, 37.8; H, 6.91; Cl, 6.5; P, 11.8.

*trans*-Ir(Cl)(CO)[P(*t*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>CH<sub>3</sub>]<sub>2</sub> (**7**) was prepared in the same manner as **6** above using di-*tert*-butylmethylphosphine.<sup>15</sup> Anal. Calcd for  $\text{C}_{19}\text{H}_{42}\text{ClO}_2\text{Ir}$ : C, 39.6; H, 7.35; Cl, 6.2; P, 10.8. Found: C, 39.6; H, 7.35; Cl, 7.9; P, 12.3.

*trans*-Ir(Cl)(CO)[P(*t*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>C<sub>2</sub>H<sub>5</sub>]<sub>2</sub> (**8**) was prepared in the same manner as **6** above using di-*tert*-butylethylphosphine.<sup>15</sup> Anal. Calcd

for  $\text{C}_{21}\text{H}_{46}\text{ClO}_2\text{Ir}$ : C, 41.7; H, 7.67; Cl, 5.9; P, 10.2. Found: C, 41.7; H, 7.63; Cl, 5.9; P, 10.0.

*trans*-Ir(Cl)(CO)[P(*t*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub> (**9**) was prepared in the same manner as **6** above using di-*tert*-butyl-*n*-butylphosphine.<sup>15</sup> Anal. Calcd for  $\text{C}_{25}\text{H}_{54}\text{ClO}_2\text{Ir}$ : C, 45.5; H, 8.25; Cl, 5.4; P, 9.4. Found: C, 45.3; H, 8.29; Cl, 5.4; P, 9.7.

*trans*-Ir(Cl)(CO)[P(*t*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>2</sub> (**10**) was prepared in the same manner as **6** above by using di-*tert*-butylphenylphosphine. Spectral data on **10**:  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 310 K, 62.9 MHz,  $\text{Me}_4\text{Si}$  reference)  $\delta$  171.5 (CO, t,  $^2J_{\text{PC}} = 11.0$  Hz), 37.6 (quaternary, t,  $J_{\text{PC}} = 10.1$  Hz), 31.1 (*tert*-butyl methyls, s), aromatic carbons at 136.1 (t,  $J_{\text{PC}} = 6.6$  Hz), 133.9 (t,  $J_{\text{PC}} = 18.5$  Hz), 129.4 (s), 126.6 (t,  $J_{\text{PC}} = 4.1$  Hz);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 310 K, 101.2 MHz, 85%  $\text{H}_3\text{PO}_4$  reference)  $\delta$  51.5 (s);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K, 250.1 MHz,  $\text{Me}_4\text{Si}$  reference)  $\delta$  1.57 (*tert*-butyl, t,  $J_{\text{PH}} = 6.7$  Hz), aromatics at 8.09 (m, 4 H), 7.33 (m, 6 H). Anal. Calcd for  $\text{C}_{29}\text{H}_{46}\text{ClO}_2\text{Ir}$ : C, 49.7; H, 6.62; Cl, 5.1; P, 8.8. Found: C, 49.6; H, 6.51; Cl, 5.0; P, 8.8.

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**Supplementary Material Available:**  $^{31}\text{P}\{^1\text{H}\}$  pulsed Fourier transform NMR spectra of complexes **1**-**10** (Figure 1S) (2 pages). Ordering information is given on any current masthead page.

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### Control of Spin State in (Porphinato)iron(III) Complexes. Effect of the Porphyrin Ligand

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Changes in spin state of the iron atom of the heme play a major role in the biological activity of the hemoproteins. For example, the change from the high- to the low-spin state accompanying the coordination of dioxygen to deoxyhemoglobin is an essential component of cooperative oxygen binding.<sup>1</sup> The

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