# Spin-State Tuning at Pseudo-tetrahedral d<sup>6</sup> lons: Spin Crossover in [BP<sub>3</sub>]Fe<sup>II</sup>—X Complexes

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**Supporting Information** 



**ABSTRACT:** Low-coordinate transition-metal complexes that undergo spin crossover remain rare. We report here a series of four-coordinate, pseudo-tetrahedral  $P_3Fe^{II}$ -X complexes supported by tris(phosphine)borate  $P_3$  ([PhBP<sub>3</sub><sup>R</sup>]<sup>-</sup>) and phosphiniminato X-type ligands ( $-N=PR'_3$ ) that, in combination, tune the spin-crossover behavior of the system. Most of the reported iron complexes undergo spin crossover at temperatures near or above room temperature in solution and in the solid state. The change in spin state coincides with a significant change in the degree of  $\pi$ -bonding between Fe and the bound N atom of the phosphiniminato ligand. Spin crossover is accompanied by striking changes in the ultraviolet–visible (UV-vis) absorption spectra, which allows for quantitative modeling of the thermodynamic parameters of the spin equilibria. These spin equilibria have also been studied by numerous techniques including paramagnetic nuclear magnetic resonance (NMR), infrared, and Mössbauer spectroscopies; X-ray crystallography; and solid-state superconducting quantum interference device (SQUID) magnetometry. These studies allow qualitative correlations to be made between the steric and electronic properties of the ligand substituents and the enthalpy and entropy changes associated with the spin equilibria.

## INTRODUCTION

Spin-crossover phenomena in molecular systems are of interest, in part due to their potential applications in magnetic sensing and information storage.<sup>1</sup> Spin-crossover complexes can act as a type of molecular switch, where properties such as color and magnetism undergo large changes when appropriate stimuli—for instance heat, pressure, light—are applied. Such responsive behavior is desirable for materials applications, especially when the complexes exhibit abrupt spin transitions and/or bistability.<sup>2–5</sup> Spin-crossover molecules which exhibit gradual and nonhysteretic spin equilibria have also shown potential for applications in sensing.<sup>6</sup> More generally, spin crossover has been implicated as an important factor in chemical processes that occur at and are facilitated by transition-metal centers such as those in metalloenzymes.<sup>7</sup>

Direct and predictable structure-function correlations between magnetic properties and molecular structure that would allow for the rational design and synthesis of spincrossover systems have yet to be fully realized. For this reason, chemists continue to pursue a more thorough understanding of the factors that govern the existence and properties of a spin-crossover transition both in solution and in the solid state.<sup>8</sup> One advantage of studying molecular systems is that, since the spin state of a transition-metal complex is dependent on the balance between the ligand field stabilization energy and spin pairing energy of the valence d-electrons, spin crossover can serve as a sensitive reporter of the energetic landscape of the spin states and valence orbital manifold of a metal complex. Subtle changes in the primary coordination environment of a molecular system affect these properties and thus the energetics of the available spin manifold. Therefore, a molecular system that exhibits well-defined and tunable spin crossover can provide a great deal of information about the impact of small changes to the coordination environment of a metal ion on its electronic structure.

To date, the vast majority of known spin-crossover complexes are 6-coordinate, octahedral  $d^6$  iron(II) complexes, typically with coordination spheres composed primarily of N, O, and C donors, because of the often favorable balance of ligand field strength and spin-pairing energy in these complexes.<sup>9,10</sup>

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Low-coordinate spin-crossover complexes are more rare. For example, earlier work in our own laboratory on pseudotetrahedral cobalt(II) complexes established the possibility of spin crossover in pseudo-tetrahedral d<sup>7</sup> ions. This work capitalized on the electronic structure engendered by strong-field tripodal "PhBP<sub>3</sub>" ligands to facilitate spin-state tuning.<sup>11–13</sup> Five-coordinate spin-crossover complexes of iron have been known since the 1970s,<sup>14</sup> but the first pseudo-tetrahedral spincrossover complex of iron(II) was reported only in 2011,<sup>15</sup> with several other four-coordinate examples having been characterized since then.<sup>16,17</sup> Most of these pseudo-tetrahedral iron(II) spin-crossover complexes, and those that will be described herein, feature electronic structure frameworks related to those that had been established for the [PhBP<sub>3</sub>]Co<sup>II</sup>–X systems.<sup>11–13</sup>

In 2004, our laboratory reported the partial N atom transfer of a terminal iron(IV) nitride,  $[PhBP_3^{iPr}]Fe(N)$ , to triphenylphosphine and triethylphosphine to afford iron(II) phosphiniminato complexes of the type  $[PhBP_3^{iPr}]Fe-N=PR_3$  (Scheme 1A).<sup>18</sup>





<sup>*a*</sup>Cy = cyclohexyl; *m*-ter = *meta*-terphenyl.

During the course of more recent N atom transfer studies, we noted that several complexes of the general type  $[PhBP_3^R]Fe-N = PR'_3$  are involved in spin equilibria at room temperature. These pseudo-tetrahedral d<sup>6</sup> complexes benefit from the electronic properties of the phosphiniminato ligand<sup>15,16</sup> to exhibit spin transitions between diamagnetic S = 0 states and high-spin S = 2 states. Modifications to the ligand substituents, both on the trisphosphine borate chelate and on the phosphiniminato moiety, allow for multifaceted tuning of the spin states and crossover temperatures. They can range from complexes that are high-spin at all temperatures to those with a spin-crossover critical temperature  $(T_{1/2})$  as high as 405 K. We introduce a versatile synthetic protocol for installing the

phosphiniminato ligand that allows the spin-crossover system to be easily and rationally tuned across a wide range of temperatures, including near and above room temperature. This ease of tunability may be of interest for future applications.

## RESULTS

**Synthesis of [PhBP**<sup>8</sup>]**Fe(N==PR**') **Complexes.** Transitionmetal complexes of phosphiniminato  $(-N=PR_3)$  ligands are common, especially for early transition metals such as titanium and other Group 4–6 metals, and are most typically synthesized either by reaction of an electrophilic metal nitride with a phosphine, or via metathesis between Me<sub>3</sub>SiN=PR<sub>3</sub> and an M–Cl species via loss of Me<sub>3</sub>SiCl.<sup>19</sup> With one exception<sup>21</sup> the structurally characterized examples of phosphiniminato ligands on Group 8 or 9 transition metals have generally been synthesized by reaction of terminal nitride complexes with phosphines (Scheme 1A).<sup>15,16,18,20</sup> We sought a more general synthetic pathway that would be applicable to systems where nitride species are not readily accessible.

We have determined that salt metathesis between previously reported [PhBP<sub>3</sub><sup>R</sup>]FeCl precursors<sup>22</sup> and LiN=PR<sub>3</sub><sup>7</sup> reagents affords the desired phosphiniminato complexes in good yields (Scheme 1B). The lithiated phosphiniminatos are generated in situ, first by double deprotonation of the phosphiniminium chlorides, [H2NPR3]Cl, with n-butyllithium, followed by addition to the iron(II) chloride precursors at low temperature in THF. This route was facilitated by the recent report of a synthesis of [H<sub>2</sub>NPPh<sub>3</sub>]Cl by the sequential treatment of triphenylphosphine with hexachloroethane and ammonia gas; we have found that this synthetic route can be generalized to other phosphines, including trialkylphosphines, under anhydrous conditions.<sup>23</sup> The [PhBP<sub>3</sub><sup>iPr</sup>]Fe-N=PPh<sub>3</sub> (7) and [PhBP<sub>3</sub><sup>iPr</sup>]Fe- $N=PEt_3$  (9) complexes synthesized by this method show identical solution spectroscopic properties to those previously generated by reaction of the thermally unstable terminal nitride  $[PhBP_3^{iPr}]Fe \equiv N$  with PPh<sub>3</sub> or PEt<sub>3</sub> (Scheme 1A).<sup>18</sup>

Structural Characterization. Complexes 1, 2, 4, 5, and 7–9 have been structurally characterized by X-ray crystallography (Figure 1). Metrical parameters of interest are tabulated in Table 1. The Fe–P distances are strongly correlated with the spin state, lengthening by ~0.3 Å between the low-spin and high-spin forms, and the complexes can hence be readily divided into two categories (high spin or low spin), based on their structural parameters (pictorially represented in Figure 2). Indeed, the change in Fe-P distance in response to the spin state makes such assignments using the solid-state metrical parameters facile and unambiguous, as was observed for the previously studied [PhBP<sub>3</sub>]CoX system, where the Co-P distances are likewise highly responsive to spin state.<sup>11-13</sup> Accordingly, low-spin complexes 1, 2, 4, and 5 display shorter Fe-P (avg ~2.15 Å) and Fe-N (~1.75 Å) bond lengths, a longer N-P bond (1.58 Å), and an almost linear Fe-N-P angle. In contrast, the high-spin complexes 7, 8, and 9 feature long Fe-P bonds (avg ~2.45 Å), a longer Fe-N bond (1.85 Å), and a somewhat shorter N-P bond (1.53 Å), along with a moderately bent Fe–N–P bond angle  $(160^{\circ}-165^{\circ})$ . The changes in Fe–N and N–P bond lengths are consistent with a higher degree of Fe–N multiple bonding in the low-spin state, concomitant with a shorter Fe-N bond. The high-spin species, by contrast, feature stronger and shorter N-P double bonds and likely minimal multiple bonding character between the Fe and N atoms.

The changes in metrical parameters observed among complexes 1-9 can be compared to those observed by Smith et al.



Figure 1. Crystal structures of complexes 1, 2, 4, 5, 7, and 9. The structure of complex 8 is shown in the Supporting Information. Thermal ellipsoids represented at 50% probability; solvents and hydrogen atoms are omitted for the sake of clarity.

Table 1. Metrical Parameters	for the	e Solid-State	Structures	of 1, 2,	, 4, 5, and	l 7–9 <sup>4</sup>
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	$1^{b}$	2	4 <sup>b</sup>	5	7	8	9
R, R'	Ph, Ph	Ph, Cy	CH <sub>2</sub> Cy, Cy	<i>m</i> -ter, Ph	<i>i</i> Pr, Ph	<i>i</i> Pr, Cy	iPr, Et
Fe–P (avg, Å)	2.1621(11)	2.1673(5)	2.1682(2)	2.1560(7)	2.4629(13)	2.5085(10)	2.4368(5)
Fe–N (Å)	1.757(3)	1.7382(16)	1.7446(17)	1.7360(18)	1.859(3)	1.842(5)	1.8325(17)
N-P (Å)	1.576(3)	1.5972(16)	1.5815(17)	1.5866(19)	1.534(3)	1.559(6)	1.5192(17)
Fe-N-P (deg)	174.8(2)	174.99(11)	174.28(11)	177.48(14)	159.8(2)	163.0(9)	165.30(14)
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<sup>a</sup>All data was acquired at 100(2) K. <sup>b</sup>Parameters averaged over two independent molecules in the asymmetric unit.



**Figure 2.** (A) Visually exaggerated representation of the changes in metrical parameters between structurally characterized low- and highspin  $[PhBP_3^R]Fe(N=PR'_3)$  complexes, with representative approximate bond lengths. (B) Overlay of the representative core structures of 1 (low spin, blue) and 7 (high spin, red).

for a series of tris(carbene)borate iron phosphiniminato complexes ([PhB(MesIm)<sub>3</sub>]Fe(N=PR<sub>3</sub>)). The tris(carbene) complexes exhibit Fe–C bond lengths of ~1.88 Å in low-spin complexes versus 2.07 Å in the high-spin complexes, a somewhat smaller range than for the Fe–P bonds of the tris(phosphine)borate complexes. The Fe–N bonds in the low-spin carbene complexes are slightly longer (at ~1.77 Å), compared to the lowspin phosphine complexes, and the range of Fe–N bond lengths between high- and low-spin complexes is again slightly smaller for the carbene ligands. The trends displayed in these two series of complexes are qualitatively similar.<sup>15,16</sup>

**Ultraviolet–Visible (UV-vis) Spectroscopy.** Spin crossover in complexes **1–6** and **9** is accompanied by a striking color change from deep blue or purple in the low-spin form, populated at low temperature, to a pale yellow in the high-spin form at higher temperature. Notably, the high-spin states (including 7 and 8, which do not undergo spin crossover at any temperature examined) display completely featureless absorption spectra in the range from  $\sim$ 475 nm to 900 nm, whereas the low-spin states display three clear features in this region (Figure 3). The energies of these absorptions vary in each complex (Table 2) but the spectra show the most intense absorption at  $\sim$ 590 nm with a discernible shoulder at ~550 nm, and a slightly weaker, wellseparated absorption at  $\sim$ 700 nm. In some cases, and most notably in complex 4 (Figure 3), the high-spin state displays a discernible absorbance at  $\sim$ 400 nm that is not present in the lowspin state; this feature does not interfere with analysis of the longer-wavelength regime. These spectral properties make it possible to quantitatively model the respective spin equilibria using the absorbance intensities and fitting the data to a Boltzmann equilibrium, as given in eq 1:  $x_{ls}(T)$  is the low-spin mole fraction as a function of the temperature *T*. Values of  $T_{1/2}$  $\Delta H$ , and  $\Delta S$  can be extracted from the UV-vis data (see Figure 4 and Table 3). Further details can be found in the Supporting Information.

$$x_{\rm ls}(T) = \frac{1}{1 + \exp\left[-\frac{\Delta H^{\circ}}{R}\left(\frac{1}{T} - \frac{1}{T_{1/2}}\right)\right]}$$
(1)

While compounds 7 and 8 ( $[PhBP_3^{iPr}]Fe(NPPh_3)$  and  $[PhBP_3^{iPr}]Fe(NPCy_3)$ , respectively) do not undergo observable spin crossover in the temperature range studied, the less sterically



**Figure 3.** Temperature-dependent UV-vis spectra of complexes 1–4 in toluene. Arrows represent the direction of change when the temperature is lowered. Spectra for complexes 5, 6, and 9 can be found in the Supporting Information.

Table 2. Absorption Maxima for Three Ligand-Field Transitions in the Low-Spin Forms of 1-6 and 9 in Toluene Solution

	1	2	3	4	5	6	9
R, R′	Ph, Ph	Ph, Cy	CH <sub>2</sub> Cy, Ph	CH <sub>2</sub> Cy, Cy	<i>m</i> -ter, Ph	<i>m</i> -ter, Cy	iPr, Et
$\lambda_{\max}$ (188 K, nm)	563	549	552	534	557	547	558
	603	596	590	579	604	598	600
	703	698	705	690	713	707	734
$\varepsilon (\mathrm{M}^{-1} \mathrm{cm}^{-1})^{a}$	1700	1400	1100	560	2700	940	Ь

<sup>*a*</sup>Extinction coefficients are provided for the lowest energy transition ( $\sim$ 700 nm) of each complex at the lowest temperature measured in each case. <sup>*b*</sup> $\varepsilon$  was not calculated for **9** because of highly incomplete spin crossover at accessible temperatures.





hindered triethyl phosphiniminato complex 9 begins to populate a low-spin state at very low temperatures; such solutions

concomitantly acquire a greenish tinge when cooled below approximately -50 °C. Low-temperature UV-vis data confirms

	1	2	3	4	5	6
R, R′	Ph, Ph	Ph, Cy	CH <sub>2</sub> Cy, Ph	CH <sub>2</sub> Cy, Cy	<i>m</i> -ter, Ph	<i>m</i> -ter, Cy
$\Delta H^{\circ}$ (kJ/mol)	$32.9 \pm 0.5$	$39.5 \pm 0.8$	$36.3 \pm 0.5$	$38.4 \pm 1.3$	$30.3 \pm 0.9$	$38.3 \pm 2.5$
$\Delta S^{\circ}$ (J/K/mol)	$99 \pm 1$	$112 \pm 2$	$139 \pm 2$	$132 \pm 5$	$89 \pm 2$	$95 \pm 7$
$T_{1/2}$ (K)	$333 \pm 0.4$	$353 \pm 0.4$	$261 \pm 0.4$	$291 \pm 0.8$	$343 \pm 0.8$	405 ± 5
<sup>a</sup> The errors given represent 95% confidence bounds for the fits.						

Table 4. Thermodynamic Parameters for the Spin Equilibria in Compounds 1–5 Derived from Variable-Temperature NMR Chemical Shift Measurements in  $d_s$ -Toluene<sup>a</sup>

	1	2	3	4	5
R, R'	Ph, Ph	Ph, Cy	CH <sub>2</sub> Cy, Ph	СН <sub>2</sub> Су, Су	<i>m</i> -ter, Ph
$\Delta H^{\circ}$ (kJ/mol)	$31.8 \pm 1.3$	$35.6 \pm 1.3$	$38.2 \pm 1.3$	$39.8 \pm 4.6$	$27.4 \pm 0.5$
$\Delta S^{\circ} (J/(K/mol))$	96 ± 4	99 ± 4	$147 \pm 0.6$	139 ± 17	$79 \pm 1$
$T_{1/2}$ (K)	$331 \pm 0.5$	$361 \pm 1.0$	$259 \pm 0.5$	$286 \pm 1.4$	$349 \pm 1.0$

"Thermodynamic parameters are derived from the average of the fitted parameters from at least two different resonances in the NMR spectra (see text and the Supporting Information for additional details). Uncertainties are derived from the 95% confidence bounds of the fits.

that a species with spectral parameters similar to the other low-spin complexes grows in at very low temperature in toluene solution.<sup>24</sup>  $T_{1/2}$  for this complex is well below that observed for complexes 1–6.

NMR Characterization and Solution Magnetic Susceptibility Measurements. All of the complexes studied display paramagnetically shifted and broadened NMR spectra at room temperature, consistent with at least partial occupation of a paramagnetic state. As the temperature is reduced, for complexes 1-6 and 9, the <sup>1</sup>H NMR chemical shifts approach the expected region for diamagnetic complexes (~0-9 ppm), and, in most cases, broad <sup>31</sup>P NMR peaks become discernible. This behavior is consistent with spin crossover to a diamagnetic state at low temperature. For a paramagnetic complex showing Curie behavior, the chemical shift range is expected to expand as the temperature is reduced, because of the inverse relationship between temperature and magnetization. Deviations from the expected Curie behavior for the chemical shifts can be quantitatively accounted for by the spin equilibrium and modeled to extract the thermodynamic parameters of the Boltzmann equilibrium, as given in eq  $2^{2}$ 

$$\delta = \delta_{\rm ls} + \frac{C}{T\left\{1 + \exp\left[-\frac{\Delta H^{\circ}}{R}\left(\frac{1}{T} - \frac{1}{T_{\rm l/2}}\right)\right]\right\}}$$
(2)

where  $\delta$  is the measured chemical shift,  $\delta_{ls}$  the corresponding shift in the diamagnetic state, and *C* the appropriate Curie's law constant. This method has been used to model the solution-state spin-crossover properties of other spin-crossover complexes in previous work.<sup>16,26</sup> The values extracted from these fits are given in Table 4. A representative example of the temperaturedependent chemical shifts of 3, and the resulting fits to eq 2 are shown in Figure 5; corresponding data for complexes 1, 2, 4, and 5 can be found in the Supporting Information. For complexes 6 and 9, although variable-temperature NMR did show evidence of spin crossover through changes in the chemical shifts and the variation in the solution magnetic moment (see below, Figure 6), the temperature range accessible was inadequate to allow for reliable fitting and extraction of thermodynamic parameters.

The thermodynamic parameters derived from the fits to the chemical shifts, according to eq 2, qualitatively reproduce the



**Figure 5.** (A) Variable-temperature <sup>1</sup>H NMR spectra of 3 in  $d_8$ -toluene (0.044 M) from 188 K (bottom) to 368 K (top), in 5 K increments from 188 to 298 and 10 K increments above 298 K. (B) Change in the NMR chemical shift for several resonances from the <sup>1</sup>H NMR spectra of 3 with temperature from 188 K to 368 K (red circles). Low-temperature data are omitted when the peak becomes too broad to be discerned clearly. Data were fit to a Curie Law/Boltzmann equilibrium expression (eq 2) to model spin crossover (blue lines). Data above 300 K were omitted from the fits (see the Supporting Information).

trends in  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  extracted from the UV-vis data. Quantitatively, the parameters are also in good agreement; the  $\Delta H^{\circ}$  values derived from the two methods agree within 10% in all cases and within 5% in most cases; the  $\Delta S^{\circ}$  values agree within 12% in all cases and within 6% in most. The largest deviation is



Figure 6. Variable-temperature magnetic susceptibility data, measured using the Evans method in  $d_8$ -toluene, for compounds 1, 2, 3, 5, and 9. Susceptibility values have been corrected for diamagnetic contributions using Pascal's constants.

observed for complexes 2 and 5. These complexes also exhibit the highest  $T_{1/2}$  of the compounds shown in Table 4 and thus undergo the most incomplete conversion to the high-spin form under the conditions studied.

The solution paramagnetism of these complexes was further examined by variable-temperature Evans method measurements, which more directly probed the change in the paramagnetic susceptibility and effective magnetic moment with temperature.<sup>27</sup> The variable-temperature Evans method results qualitatively confirm the change in spin state and the corresponding change in susceptibility of complexes 1-6 and 9 with temperature; representative data is shown in Figure 6. While the data could be fit to a Boltzmann-equilibrium expression, the fit parameters suffered from large uncertainties because of the relatively small range of temperatures for which  $\chi T$  could be reliably measured using this method (see the Supporting Information for further details).

**Solid-State (SQUID) Magnetometry.** Spin-crossover molecules frequently show different behavior in the solid state than in solution. Often, the spin-state change in the solid state is no longer well described as a simple thermodynamic equilibrium and, instead, becomes dependent on cooperative interactions in the solid state, formation of domains, crystallinity, and other solid-state effects, which can cause either very abrupt or very gradual and incomplete spin crossover.<sup>28</sup> These factors sometimes lead to thermal hysteresis of the magnetic response, depending on the direction of temperature change. Although neither hysteresis nor a very abrupt spin crossover were observed for any of the complexes studied herein, they did show morecomplex behavior in the solid state than in solution.

The magnetic moments of solid samples of complexes 1–4, 7, and 8 were measured using SQUID magnetometry in the temperature range from 4 K to 400 K (see Figure 7). Compounds 7 and 8 do not appear to undergo a spin transition at any temperature recorded. For compounds 1–4, spin crossover is gradual and incomplete; both the degree and rate of crossover proved to be extremely dependent on sample preparation and particularly on the degree of crystallinity, which is a phenomenon that is frequently observed in the solid-state magnetic behavior of mononuclear spin-crossover complexes and often rationalized on the basis of domain formation and grain-size effects.<sup>28,29</sup> For instance, grinding a microcrystalline sample with a mortar and pestle typically resulted in a more-incomplete spin crossover (Figure 8). In the most striking example of these effects, a yellow, crystalline sample of 3 exhibited no spin crossover, maintaining a



Figure 7. Solid-state magnetic moments of compounds 1-4, 7, and 8 measured by SQUID magnetometry. All samples were neat microcrystalline solids, and the magnetic susceptibility was corrected for the approximate diamagnetic contribution derived from Pascal's constants. Measurements were carried out from low temperature to high temperature, following initial cooling in zero field.



**Figure 8.** Variable-temperature solid-state SQUID magnetometry showing the effect of sample preparation on the measured properties of compounds **3** and **4**. Measurements were carried out from low temperature to high temperature, following initial cooling in zero field.

magnetic moment near 5.4  $\mu_{\rm B}$  at least down to 20 K, despite the fact that, in solution, this species has a  $T_{1/2}$  value of 255 K. However, if the sample is lyophilized from benzene instead of crystallized, it takes on a greenish-blue color and a gradual and incomplete spin crossover is observed (see Figure 8).

Many of the complexes display irreversible changes in their magnetic behavior after heating above 300 K, which is a phenomenon that is attributed to a loss of co-crystallized solvent upon heating under vacuum in the magnetometer; except for compounds 7-9, all of the crystallographically characterized compounds contain co-crystallized solvent, which is not lost upon drying the crystals at room temperature under vacuum (see the Supporting Information for details and illustrative data). However, the change in the behavior of compound 3 upon lyophilization is not due to solvent loss, as neither crystalline nor lyophilized 3 includes co-crystallized solvent molecules (as determined by NMR). Other than the effects attributed to solvent loss upon repeatedly cycling the temperature. The fact that the crystal structures of most of these compounds were refined

with static disorder in both complex and solvent moieties (see Supporting Information for details) complicates the analysis of intermolecular interactions and their impact on the solid-state magnetic properties.

**Solid-State Infrared Spectroscopy.** Phosphiniminato ligands typically show a strong  $\nu$ (N=P) vibration in their infrared spectra near 1200 cm<sup>-1</sup>; this is observed for complexes 3, 7, and 9 (Figure 9). However, no strong vibration in this region is



**Figure 9.** Representative solid-state infrared transmission spectra of complexes 7, 9, 3, 5, and 6, illustrating the presence of an  $\nu$ (N=P) vibrational band at ~1207 cm<sup>-1</sup> in the high-spin complexes (7, 9, 3) that is absent in low-spin complexes 5 and 6. Spectra were recorded at room temperature.

present in the low-spin states of the respective  $[PhBP_3^R]Fe-(NPR'_3)$  complexes, as is evident in the room-temperature solidstate IR spectra of complexes **1**, **2**, and **4**–**6** (see Figure 9 for **5** and **6**). This is consistent with weakening of the N=P bond due to increased  $\pi$ -bonding between N and Fe in the low-spin state (*vide infra*). This data corroborates the important role of the electronic flexibility of the phosphiniminato ligand in facilitating access to both low- and high-spin states across this series of pseudo-tetrahedral iron(II) complexes.

**Mössbauer Spectroscopy.** High- and low-spin states of an iron complex typically show distinct Mössbauer parameters (isomer shift and quadrupole splitting),<sup>30</sup> providing another convenient method of characterization of the iron compounds presented in this study. Mössbauer spectra were hence collected for examples of both predominantly low-spin (1 as a microcrystalline solid and 4 as a glassed solution in 2-MeTHF) and high-spin (microcrystalline 7 and 3) complexes at 80 K, as well as for one example (lyophilized 3) for which both spin forms can be distinguished across a series of temperatures (Figure 10; additional variable-temperature data is in the Supporting Information). The relevant parameters are provided in Table 5. The high-spin species show a higher isomer shift and a larger quadrupole splitting relative to the low-spin species.

## DISCUSSION

A sketch of the d-orbital manifold (Figure 11) for Fe(II) in  $[PhBP_3^R]Fe(NPR'_3)$  in the high-spin and low-spin states provides some context for interpreting the spin-crossover behavior and trends delineated in the Results section. The ligand field splitting



**Figure 10.** Representative 80 K Mössbauer spectra and parameters for high-spin 7 (crystalline, panel (A)) and 3 (crystalline, panel (B)); low-spin 1 (crystalline, panel (C)) and 4 (Me-THF glass, panel (D)); and lyophilized 3, exhibiting a mixture of high- and low-spin populations (panel (E)).<sup>31</sup>

Table 5. Mössbauer Parameters for Complexes 1, 3, 4, and 7

	isomer shift, $\delta$ (mm/s)	quadrupole splitting, $\Delta E_{ m Q}  ({ m mm/s})$	composition (%)
1 (crystalline)	0.008	0.559	
4 (2-MeTHF glass)	-0.025	0.392	
7 (crystalline)	0.617	1.373	
3 (crystalline)	0.820	1.449	
3 (lyophilized)	0.000	0.603	51
	0.607	1.252	49

in these complexes is qualitatively similar to that of an octahedral complex<sup>13</sup> with three low-lying, primarily nonbonding orbitals and an antibonding, doubly degenerate orbital set at higher energy. This analogy is noteworthy, given that the overwhelming majority of spin-crossover compounds are octahedral. This orbital scheme—an approximate 2-over-3 splitting with a low-lying  $d_{z^2}$  orbital—is well-established both theoretically and experimentally for pseudo-tetrahedral Fe and Co complexes with  $[PhBP_3^R]^-$  ligands. It can be attributed, in part, to the mixing of  $d_{z^2}$  with the metal-based  $4p_z$  and 4s orbitals, and also to the 90° P–Fe–P bond angles and, correspondingly, >120° P–Fe–N angles, favored by the ligand chelate; these angles lower the relative energy of the  $a_1$  orbital of primarily  $d_{z^2}$  parentage.<sup>11,32,33</sup>

For the Fe(II) complexes of present interest, the lowest unoccupied molecular orbital (LUMO) in the low-spin state is an approximately degenerate set of orbitals with  $d_{xz}/d_{yz}$  character and  $\pi^*$  symmetry, with respect to the apical ligand. Spin crossover to the S = 2 state involves population of this level with two electrons. Therefore, the thermodynamic parameters ( $\Delta H^\circ$ ) of the spin equilibrium are expected to be strongly dependent on the energy of this level.

The qualitative orbital picture (Figure 11) is supported by DFT calculations<sup>34</sup> carried out using the crystallographically determined structures of complexes 4 and 8 in their low- and high-spin forms, respectively (Figure 12). In 4 the high-lying



Figure 11. (A) Schematic of the d-orbital manifold for the low- and high-spin states of pseudo-tetrahedral  $[PhBP_3^R]Fe(NPR'_3)$  complexes. (B) Limiting representations of the bonding interactions in the low-spin (a) and high-spin (b) states.



**Figure 12.** Valence molecular orbitals calculated for (A) low-spin  $[PhBP_{3}^{CH_{3}Cy}]Fe(NPCy_{3})$  (4) and (B) high-spin  $[PhBP_{3}^{Pr}]Fe(NPCy_{3})$  (8).

 $\pi$ -symmetry d-orbitals are mixed with P–N  $\pi$ -bonding orbitals and are unoccupied. In **8**, the related orbitals in the  $\alpha$  manifold are occupied, consistent with the observed shorter P–N bond due to a higher P–N bond order. The HOMO of low-spin **4** is an  $a_1$  orbital of  $d_{z^2}$  parentage that lies slightly higher in energy than the near-degenerate nonbonding orbitals of  $d_{xy}/d_{x^2-y^2}$  parentage (HOMO-1 and HOMO-2).

Based on the variation of the spin-crossover equilibrium parameters among compounds 1–9, some trends can be gleaned (Figure 13). There is a strong correlation between the magnitude



**Figure 13.** Comparison of  $\Delta H^{\circ}$ ,  $\Delta S^{\circ}$ , and  $T_{1/2}$  for [PhBP<sub>3</sub><sup>R</sup>]Fe(NPR<sub>3</sub>') complexes 1–6. Average values from Tables 3 and 4 are plotted.

of  $\Delta H^{\circ}$  and the identity of the phosphiniminato substituent R' (Ph or Cy); among the  $[PhBP_{3}^{R}]Fe(NPR'_{3})$  complexes that undergo spin-crossover, for a given R (-CH<sub>2</sub>Cy, Ph, or *m*-terphenyl), the complex where R' is the more electron-donating Cy has a larger  $\Delta H^{\circ}$  and undergoes spin-crossover at a higher temperature than the complex with R' = Ph, although, in the case of 3 and 4, the difference in  $\Delta H^{\circ}$  is within our margin of error. This observation can be rationalized; the more electron-donating phosphine (R' = Cy) engenders better  $\pi$ -donation from N to Fe, raising the energy of the  $\pi^*$ -orbitals to favor the low-spin state. Consistent with this idea, the metrical parameters (e.g., N-Fe and N-P bond lengths; Table 1) suggest a stronger bond between Fe and N in the low-spin state, and a compensatory weakening of the multiple bonding between N and P; the presence of two stronger  $\pi$ -bonding interactions is also consistent with the near-linear Fe-N-P angles of the low-spin complexes. This can be represented as a more important contribution from an electronic structure picture involving Fe-N multiple bonding in the lowspin state (Figure 11B, structure a). This electronic structure is reminiscent of the previously characterized anionic Fe(II) imido complex,  $\{[PhBP_3^{Ph}]Fe(NR)\}^{-.33}$ 

The influence of the  $[PhBP_3^R]^-$  substituent R on the spin equilibrium parameters is less straightforward to interpret. It seems evident by comparison of **3** and **4** (R = CH<sub>2</sub>Cy) versus the electronically similar 7 and **8** (R = *i*Pr), that steric factors play a large role. It is difficult to rationalize the difference between these pairs of complexes purely on the basis of electronic considerations; **3** and **4** have  $T_{1/2}$  values of 266 and 290 K, while 7 and **8** are high spin at all temperatures. As observed in these complexes, increased steric crowding is expected to favor the

high-spin state, because of the much longer Fe–P bond lengths, resulting in a less-strained environment around the metal center. The fact that **9** ([PhBP<sub>3</sub><sup>iPr</sup>]Fe(NPEt<sub>3</sub>)) undergoes spin crossover, albeit at a relatively low temperature, further corroborates the role of steric crowding. Steric effects were also previously hypothesized to play a role in the greater propensity of [PhBP<sub>3</sub><sup>iPr</sup>]CoX complexes to occupy high-spin states (versus the corresponding [PhBP<sub>3</sub><sup>Ph</sup>]CoX complexes); the data presented here bolster this hypothesis.<sup>13</sup>

There is a strong trend in the  $\Delta S^{\circ}$  values for the different  $[PhBP_3^R]^-$  ligands. For a given R, the pairs of complexes with R' = Ph or Cy have similar  $\Delta S^{\circ}$  values, and among the three ligands (R = *m*-terphenyl, Ph, or  $-CH_2Cy$ ),  $\Delta S^{\circ}$  is smallest for the more-rigid R = *m*-terphenyl (~90 J/K/mol) and largest for the less rigid R =  $-CH_2Cy$  (~144 J/K/mol). This trend can be qualitatively rationalized; the less sterically crowded environment of the high-spin state allows the more "floppy" substituents ( $-CH_2Cy$ ) to move more freely, thus contributing substantially more to the vibrational entropy of the molecule. In contrast, the entropic contributions of the *m*-terphenyl-substituted ligand do not change as much due to the inherent rigidity of the aryl groups and the steric demands of the bulky terphenyls, which likely constrain the molecular geometry, even in the high-spin state.

Electronic considerations with respect to R likely also contribute to  $\Delta H^{\circ}$ , but the trend is less clear. Among complexes 1, 3, and 5 (with R' = Ph),  $\Delta H^{\circ}$  increases significantly, going from R = *m*-ter < Ph < CH<sub>2</sub>Cy. One likely rationale is that the more strong-field alkyl phosphine donors in the [PhBP<sub>3</sub><sup>R</sup>]<sup>-</sup> ligand help raise the energy of the e<sub>(b)</sub> orbital set, which is  $\sigma^*$  antibonding, with respect to the phosphines. The R' = Cy complexes (2, 4, and 6) do not follow quite the same trend, but the absolute differences between the  $\Delta H^{\circ}$  values for this series are smaller and may be within the error of our measurements.

One aspect of our analysis that should be underscored is that it is only upon distilling the equilibrium parameters into  $\Delta S^{\circ}$  and  $\Delta H^{\circ}$  that the trends imparted by the ligand substituents become clear (Figure 13); although these parameters are correlated—for instance, both are affected by changes in bond lengths—their independent consideration can reveal new information. Studies of spin equilibria often attempt to extract trends by considering only  $T_{1/2}$ , which is a parameter that convolutes both entropic and enthalpic contributions. Such an analysis could, in some cases, lead to misinterpretations or make it difficult to identify robust trends concerning the effect of the primary coordination environment on the spin equilibria. While it is sometimes more challenging to determine reliable values for  $\Delta S^{\circ}$  and  $\Delta H^{\circ}$ , the present results emphasize that it is worthwhile to do so when possible.

Further analysis of the UV-vis spectra of the low-spin forms of complexes 1-6 and 9 can provide additional insight into the respective ligand fields of these molecules. In all cases, the spectra display three bands of appreciable intensity in the visible range: a peak at ~600 nm with a high-energy shoulder at ~550 nm, and a second peak at ~700 nm. The exact positions of these peaks, as derived from spectral decomposition, have been tabulated above in Table 1. The energies and intensities of these bands, as well as the fact that they are present in all complexes at similar energies, regardless of the identities of R and R', corroborates their assignment as primarily ligand field d-d transitions (which are Laporte-allowed in  $C_{3\nu}$  symmetry, with strengthened intensity by d-p mixing induced by strong covalency) rather than charge-transfer transitions to the ligand backbone. Significant mixing, especially with the P–N  $\pi$ -orbitals, also contributes.

Time-dependent density functional theory (TD-DFT) calculations on complex 4 support this model (see Supporting Information for details). The lack of similar bands in the highspin forms of the complexes likely results from the fact that the d-d transitions in the high-spin molecules are shifted farther into the near-infrared because of the smaller ligand field splitting.

Qualitative crystal field considerations in idealized  $C_{3\nu}$ symmetry—which approximates well the local geometry around the iron centers in the low-spin complexes—allow a plausible assignment of these three optical bands (see Figure 14). Considering



**Figure 14.** Proposed assignments of UV-vis transitions in low-spin phosphiniminato complexes: (top) qualitative orbital diagrams and electron configurations of ground state and singlet one-electron excited states; (bottom) absorption spectra of 1 at 188 K with proposed assignments labeled.

only spin-allowed transitions to singlet excited states, the <sup>1</sup>A<sub>1</sub> low-spin ground state  $(e_{(a)})^4(a_1)^2(e_{(b)})^0$  can undergo one-electron excitations to either a  $(e_{(a)})^4(a_1)^1(e_{(b)})^1$  or a  $(e_{(a)})^3(a_1)^2(e_{(b)})^1$ configuration. The former is a <sup>1</sup>E state, while the latter has <sup>1</sup>E, <sup>1</sup>A<sub>1</sub>, and  ${}^{1}A_{2}$  components. In  $C_{3\nu}$  symmetry,  ${}^{1}A_{1} \rightarrow {}^{1}E$  and  ${}^{1}A_{1} \rightarrow {}^{1}A_{1}$ optical transitions are orbital-symmetry allowed, while the  ${}^{1}A_{1} \rightarrow$ <sup>1</sup>A<sub>2</sub> transition is forbidden. Therefore, three ligand-field transitions are expected for this state, consistent with the observed spectra. Assigning these reliably is nontrivial; we tentatively assign the lower-energy, well-separated band at  $\sim$ 700 nm to the  $(e_{(a)})^4(a_1)^2(e_{(b)})^0 \rightarrow (e_{(a)})^4(a_1)^1(e_{(b)})^1$  transition  $({}^1A_1 \rightarrow {}^1E)$ , and the two higher-energy, closely spaced bands to the allowed  $(e_{(a)})^4(a_1)^2(e_{(b)})^0 \rightarrow (e_{(a)})^3(a_1)^2(e_{(b)})^1$  transitions  $({}^1A_1 \rightarrow {}^1E$  and  ${}^{1}A_{1} \rightarrow {}^{1}A_{1}$ ). In the lowered symmetry ( $C_{1}$ ) that more rigorously describes the solid-state structure of these complexes, a qualitatively similar assignment can be proposed; the 700 nm band likely arises from transitions between the valence orbital of  $d_{z2}$  parentage to the unoccupied,  $d_{xz}/d_{yz}$ -derived  $\pi$ -symmetry orbitals, while the higher-energy bands derive from transitions from the near-degenerate  $d_{xy}$  and  $d_{x^2-y^2}$  nonbonding orbitals. Notably,  $d^6$  metallocenes such as ferrocene, which have qualitatively similar valence d-orbital electronic structures, similarly show three symmetry-allowed optical d–d transitions, although the precise assignment of these differs, because of the different point-group symmetry.<sup>35</sup>

Therefore, the energies of the visible transitions can provide some information about the ligand field splitting of the d-orbitals in the low-spin complexes. Again, the clearest trend is in the dependence of the transition energies on the identity of the phosphiniminato substituent. In all cases, for a given R, all three absorptions are lower in energy for R' = Ph than R' = Cy, which is consistent with the conclusions discussed above; the  $e_{(b)} \pi^*$ orbital is raised higher in energy in the case of the more strongly electron-donating and  $\pi$ -bonding alkyl phosphiniminato. Interestingly, for complex 9, the transition energies are substantially lower than for the other alkyl phosphiniminato complexes; this may suggest that, although this complex is able to populate a low-spin state, steric strain still enforces longer bond lengths and, therefore, a weaker ligand field than in complexes 2, 4, and 6.

The correlations and trends discussed above suggest that, in these spin-crossover iron(II) complexes, both the specific properties of the [PhBP<sub>3</sub><sup>R</sup>] ligands, enforcing a pseudo-tetrahedral geometry and a corresponding "pseudo-octahedral" orbital arrangement, and the ability of the phosphiniminato ligand to modulate its  $\pi$ -donation between two possible limiting electronic structures, are important to the spin-equilibrium behavior observed. Tuning the electron-donating ability of the phosphiniminato phosphine is a straightforward way to strongly alter the  $T_{1/2}$  and thermodynamic properties of the complexes, which can be further fine-tuned by modifying the steric and electronic properties of the tris(phosphine)borate ligand. Further modification of such complexes along these two independent axes could give rise to molecules with more desirable properties for magnetic memory applications, such as strongly cooperative or hysteretic spin crossover, or light-induced spin-state trapping (LIESST).<sup>3</sup>

#### EXPERIMENTAL DETAILS

**General Considerations.** All syntheses and measurements, unless otherwise stated, were carried out under an inert atmosphere  $(N_2)$  in a glovebox or using standard Schlenk techniques, and solvents were dried and degassed by thoroughly sparging with  $N_2$  and then passing through an activated alumina column in a solvent purification system supplied by SG Water, LLC. Nonhalogenated solvents were tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran, to confirm effective moisture removal. [PhBP<sub>3</sub><sup>Ph</sup>]FeCl,<sup>22a</sup> [PhBP<sub>3</sub><sup>M-ter</sup>]FeCl,<sup>22b</sup> [PhBP<sub>3</sub><sup>CH<sub>2</sub>Cy</sup>]FeCl,<sup>22c</sup> and [Ph<sub>3</sub>PNH<sub>2</sub>]Cl<sup>23</sup> were prepared according to literature procedures. All other reagents were purchased from commercial vendors and used without further purification unless otherwise stated.

**Physical Methods.** Elemental analyses were performed by Midwest Microlab (Indianapolis, IN). Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., degassed, and dried over active 3 Å molecular sieves prior to use. <sup>1</sup>H and <sup>13</sup>C chemical shifts are reported in ppm, relative to tetramethylsilane, using residual proton and <sup>13</sup>C resonances from solvent as internal standards. <sup>31</sup>P chemical shifts are reported in ppm, relative to 85% aqueous H<sub>3</sub>PO<sub>4</sub>. Solution-phase magnetic measurements were performed by the method of Evans in  $d_8$ -toluene solution.<sup>27</sup> The NMR spectrometer temperature was calibrated using 100% methanol (from 25 °C to -85 °C) or 100% ethylene glycol (from 25 °C to 105 °C). Optical spectroscopy

measurements were taken in toluene solution using a Cary 50 UV-vis spectrophotometer using a 1 cm two-window quartz cell, with a Unisoku CoolSpek cryostat for temperature control. Thin-film infrared (IR) spectra were obtained on a Bruker Alpha spectrometer equipped with a diamond ATR probe. Solid-state magnetic data was obtained using a Quantum Designs SQUID magnetometer running MPMSR2 software (Magnetic Property Measurement System Revision 2) at a field strength of 5000 G. Samples were inserted into the magnetometer in plastic straws sealed under nitrogen with polycarbonate capsules. Loaded samples were centered within the magnetometer using the DC centering scan at 35 K and 500 gauss. The magnetic susceptibility was adjusted for diamagnetic contributions using the constitutive corrections of Pascal's constants as well as a diamagnetic correction due to the holder diamagnetism. Microcrystalline samples for SQUID magnetometry were prepared as detailed in the synthetic methods below and dried in vacuo at room temperature before being loaded into the sample capsules. Mössbauer spectra were recorded on a spectrometer from SEE Co (Edina, MN) operating in the constant acceleration mode in a transmission geometry. Spectra were recorded with the temperature of the sample maintained at 80 K, except as otherwise noted. The sample was kept in a Model SVT-400 dewar (Janis, Wilmington, MA) at zero field. The quoted isomer shifts are relative to the centroid of the spectrum of a metallic foil of  $\alpha$ -Fe at room temperature. Solid samples were prepared by mounting in a cup fitted with a screw cap as a boron nitride pellet. Data analysis was performed using the program WMOSS (www.wmoss.org), and quadrupole doublets were fit to Lorentzian lineshapes.

**Computations.** Single-point DFT energy calculations on 4 (S = 0) and 8 (S = 2) were calculated using the Gaussian 09 software package<sup>37</sup> and the hybrid B3LYP functional. The 6-311G(df) basis set was used for the Fe and P atoms, and the 6-31G(d) basis set was used on the remaining atoms.

**X-ray Crystallography.** XRD studies were carried out at the Beckman Institute Crystallography Facility on a Bruker Kappa Apex II diffractometer or Bruker Photon 100 diffractometer (Mo K $\alpha$  radiation). Structures were solved using SHELXS and refined against  $F^2$  on all data by full-matrix least-squares with SHELXL.<sup>38</sup> The crystals were mounted on a wire loop. All crystals were measured at a temperature of 100 K. Methyl group H atoms not involved in disorder were placed at calculated positions starting from the point of maximum electron density. All other H atoms were placed at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of the H atoms were fixed at 1.2 (1.5 for methyl groups) times the  $U_{eq}$  value of the atoms to which they are bonded. 1,2- and 1,3-rigid bond restraints were applied to all non-hydrogen atoms. Further details for each structure can be found in the Supporting Information.

Tricyclohexylphosphiniminium Chloride. Tricyclohexylphosphine (1.00 g, 3.57 mmol) and hexachloroethane (844 mg, 3.57 mmol) were combined in 80 mL of THF and stirred for 2 h at room temperature, during which time a white precipitate develops. The suspension was then cooled to -20 °C and anhydrous gaseous ammonia was bubbled through the solution. The reaction mixture was allowed to warm to room temperature overnight under NH<sub>3</sub> and then concentrated to dryness. The white residue was taken up in 500 mL of dry dichloromethane, filtered through Celite, and concentrated to dryness. The residue was redissolved in minimal MeOH, then 200 mL of Et<sub>2</sub>O were added and the mixture stored in the freezer  $(-40 \ ^{\circ}C)$  for 2 h. The resulting white crystalline solids were collected on a sintered glass frit and washed with Et<sub>2</sub>O, giving 977 mg of the desired product as a white solid (83%). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 162 MHz, 25 °C): δ 53.4 (s) ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz,  $25 \,^{\circ}\text{C}$ :  $\delta 5.70 \,(\text{br s}, 2\text{H}, \text{NH}_2), 2.33 \,(\text{q}, J = 12 \,\text{Hz}, 3\text{H}), 2.01 \,(\text{d}, J = 12 \,\text{Hz}, 3\text{H})$ 6H), 1.86 (d, J = 12 Hz, 6H), 1.72 (d, J = 12 Hz, 3H), 1.56 (q, J = 12 Hz, 6H), 1.37–1.22 (m, 9H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz, 25 °C)  $\delta$ 32.2 (d, J(P) = 54 Hz), 26.4 (d, J(P) = 13 Hz), 26.0 (d, J(P) = 3 Hz), 25.6(s) ppm. Anal. Calcd for C18H35NPCI: C, 65.14; H, 10.63; N, 4.22. Found: C, 65.38; H, 11.05; N, 4.14.

**Triethylphosphiniminium Chloride.** Triethylphosphine (0.500 g, 4.23 mmol) was dissolved in THF and hexachloroethane (1.00 g, 4.22 mmol) was added dropwise as a solution in THF. White precipitate formed immediately, and the reaction was stirred for 2 h at room temperature and then cooled to -20 °C. Anhydrous gaseous ammonia

was bubbled through the solution, and the reaction mixture was allowed to warm to room temperature and stir overnight under NH<sub>3</sub>. The mixture was then concentrated to dryness and the white residue was extracted with dichloromethane, filtered through Celite, and concentrated to a volume of 3 mL. This concentrated solution was layered with 10 mL of Et<sub>2</sub>O and stored at -40 °C for 2 h. The resulting white crystals were isolated atop a sintered glass frit and washed with Et<sub>2</sub>O. The desired product was obtained as 683 mg of a white solid (95%). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 162 MHz, 25 °C):  $\delta$  59.8 (s) ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 25 °C):  $\delta$  5.65 (br s, 2H, NH<sub>2</sub>), 2.18 (dq, *J* = 8, 15 Hz, 6H), 1.22 (dt, 8, 18 Hz, 9H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz, 25 °C)  $\delta$  15.9 (d, *J*(P) = 61 Hz), 5.4 (d, *J*(P) = 5 Hz) ppm. Anal. Calcd for C<sub>6</sub>H<sub>17</sub>ClNP: C, 42.48; H, 10.10; N, 8.26. Found: C, 42.41; H, 9.94; N, 8.08.

[PhBP<sup>Ph</sup><sub>3</sub>]Fe(NPPh<sub>3</sub>)·THF (1·THF). [H<sub>2</sub>NPPh<sub>3</sub>][Cl] (88.9 mg, 0.283 mmol) was suspended in THF (5 mL) and cooled to -78 °C with stirring. *n*-Butyllithium (354  $\mu$ L, 1.6 M in hexane, 0.566 mmol) was added to the solution, which was stirred at low temperature for 30 min, then allowed to warm to room temperature for 30 min, then cooled back to -78 °C. This solution was added dropwise to a separately cooled solution of  $[PhBP_3^{Ph}]FeCl~(200~mg,\,0.257~mmol)$  in THF (5 mL), and the reaction mixture was stirred at low temperature for 30 min before being allowed to warm to room temperature and stirred overnight. The resulting blue solution was concentrated to dryness, extracted with benzene, and filtered through Celite. The filtrate was concentrated to give a blue residue that was recrystallized by taking up in THF (5 mL), layered with pentane (15 mL), and allowing to stand at room temperature overnight. The resulting blue crystals were thoroughly washed with pentane and 1:1 THF/pentane, giving 251 mg of compound 1 as its THF solvate (95%). Crystals suitable for X-ray diffraction (XRD) were grown by vapor diffusion of pentane into a concentrated THF solution at room temperature. <sup>1</sup>H NMR ( $C_6D_6$ , 300 MHz, 25 °C):  $\delta$  42.1 (br), 15.4, 10.4, 10.1, 9.9, 7.3, 6.0, 2.7, 2.5 ppm. Anal. Calcd for C<sub>67</sub>H<sub>64</sub>BFeNP<sub>4</sub>O (1.THF): C, 73.84; H, 5.92; N, 1.29. Found: C, 73.01; H, 5.96; N, 1.06.

[PhBP<sub>3</sub><sup>Ph</sup>]Fe(NPCy<sub>3</sub>) (2). [H<sub>2</sub>NPCy<sub>3</sub>][Cl] (88.3 mg, 0.266 mmol) was suspended in THF (5 mL) and cooled to -78 °C with stirring. *n*-Butyllithium (333  $\mu$ L, 1.6 M in hexane, 0.533 mmol) was added to the solution, which was stirred at low temperature for 30 min, then allowed to warm to room temperature for 30 min, then cooled back to -78 °C. This solution was added dropwise to a separately cooled solution of  $[PhBP_3^{ph}]FeCl$  (196.8 mg, 0.253 mmol) in THF (2 mL), and the reaction mixture was stirred at low temperature for 10 min before being allowed to warm to room temperature for 15 min and then concentrated. The resulting blue solution was concentrated to dryness, extracted with benzene, and filtered through Celite. The filtrate was concentrated to give a blue residue which was recrystallized by taking up in minimal THF, layering with pentane (15 mL), and allowing to stand at -40 °C overnight. The resulting blue crystals were thoroughly washed with pentane, giving 213 mg of the desired product (81%). Crystals suitable for XRD were grown by layering pentane over a concentrated THF solution at -40 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, 25 °C): δ 14.1 (br), 10.5, 8.6, 8.2, 6.7, 5.6, 4.4, 4.2, 3.6, 2.8, 1.9 ppm. Anal. Calcd for C<sub>63</sub>H<sub>74</sub>BFeNP<sub>4</sub>: C, 73.05; H, 7.20; N, 1.35. Found: C, 72.85; H, 7.17; N, 1.24.

[PhBP<sup>CH2Cy</sup><sub>3</sub>]Fe(NPPh<sub>3</sub>) (3). [H<sub>2</sub>NPPh<sub>3</sub>][Cl] (81 mg, 0.258 mmol) was suspended in THF (5 mL) and cooled to -78 °C with stirring. *n*-Butyllithium (321  $\mu$ L, 1.6 M in hexane, 0.616 mmol) was added to the solution, which was stirred at low temperature for 30 min, then allowed to warm to room temperature for 30 min, then cooled back to -78 °C. This solution was added dropwise to a separately cooled solution of  $PhBP_3^{CH_2Cy}FeCl~(199.1$  mg, 0.245 mmol) in THF (2 mL), and the reaction mixture was stirred at low temperature for 10 min, resulting in a dark blue solution, before being allowed to warm to room temperature. The solution, which is dark green at room temperature, was stirred for 1 h and then concentrated to dryness, extracted with benzene, and filtered through Celite. The filtrate was concentrated to dryness, taken up in minimal THF, layered with pentane, and allowed to stand overnight at room temperature. The resulting yellow crystals were thoroughly washed with pentane, giving 172 mg of the desired product (62%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, 25 °C): δ 163.2 (br), 40.6, 40.0, 20.0,

18.1, 8.9, -0.5, -1.4, -3.1, -6.5, -7.8, -13.7, -20.8, -21.8, -29.9, -40.6 ppm.  ${}^{31}P{}^{1}H{}$  NMR (C<sub>6</sub>D<sub>6</sub>, 202 MHz, -75 °C):  $\delta$  77.3 (br s, 3P), 41.7 (br s, 1P) ppm. Anal. Calcd for C<sub>69</sub>H<sub>104</sub>BFeNP<sub>4</sub>: C, 72.82; H, 9.21; N, 1.23. Found: C, 72.62; H, 9.27; N, 1.22.

[PhBP<sub>3</sub><sup>CH<sub>2</sub>Cy</sup>]Fe(NPCy<sub>3</sub>) (4). [H<sub>2</sub>NPCy<sub>3</sub>][Cl] (86 mg, 0.259 mmol) was suspended in THF (5 mL) and cooled to -78 °C with stirring. *n*-Butyllithium (323  $\mu$ L, 1.6 M in hexane, 0.518 mmol) was added to the solution, which was stirred at low temperature for 30 min, then allowed to warm to room temperature for 30 min, then cooled back to -78 °C. This solution was added dropwise to a separately cooled solution of  $\lceil PhBP_3^{CH_2Cy}\rceil FeCl$  (200 mg, 0.246 mmol) in THF (2 mL), and the reaction mixture was stirred at low temperature for 10 min, resulting in a dark blue solution, before being allowed to warm to room temperature. The solution was stirred for an additional 15 min and then concentrated to dryness, extracted with pentane, and filtered through Celite, and concentrated to dryness. The blue residue was taken up in pentane and recrystallized by slow evaporation of the pentane solution. The resulting blue crystals were washed with cold pentane and dried, giving 179 mg of the desired product (63%). Crystals suitable for XRD were grown by slow evaporation of a concentrated pentane solution into HMDSO. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, 25 °C): δ 44.1, 29.2, 22.8, 21.3, 15.8, 14.5, 11.5, 7.5, 5.1, 3.2, -0.7, -1.2, -2.2, -3.0, -4.3, -5.2, 7.6, -8.4, -14.3, -15.8, -19.0, -24.0 ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 202 MHz, -75 °C): δ 82.2 (br s, 3P), 62.2 (br s, 1P) ppm. Anal. Calcd for C<sub>69</sub>H<sub>122</sub>BFeNP<sub>4</sub>: C, 71.67; H, 10.64; N, 1.21. Found: C, 71.30; H, 10.25; N, 0.91.

[PhBP<sub>3</sub><sup>m-ter</sup>]Fe(NPPh<sub>3</sub>) (5). [H<sub>2</sub>NPPh<sub>3</sub>][Cl] (40.2 mg, 0.128 mmol) was suspended in THF (5 mL) and cooled to -78 °C with stirring. *n*-Butyllithium (160  $\mu$ L, 1.6 M in hexane, 0.256 mmol) was added to the solution, which was stirred at low temperature for 30 min, then allowed to warm to room temperature for 30 min, then cooled back to -78 °C. This solution was added dropwise to a separately cooled solution of PhBP<sub>3</sub><sup>m-ter</sup>FeCl (206.1 mg, 0.122 mmol) in THF (2 mL), and the reaction mixture was stirred at low temperature for 10 min before being allowed to warm to room temperature for 2 h and then concentrated. The resulting blue solution was concentrated to dryness, extracted with benzene, and filtered through Celite. The filtrate was concentrated to 2 mL, layered with 15 mL of pentane and allowed to stand at room temperature overnight. The resulting blue crystals were thoroughly washed with pentane, giving 132 mg of the desired product (56%). Crystals suitable for XRD were grown by vapor diffusion of pentane into a concentrated benzene solution. <sup>1</sup>H NMR ( $C_6D_{61}$  300 MHz, 25 °C):  $\delta$ 39.4 (br), 14.7, 14.6, 10.0, 9.9, 9.2, 7.0, 6.9, 6.7, 5.9, 3.3, -1.3 ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 152 MHz, -75 °C): δ 100.2 (br s, 3P), 50.0 (br s, 1P) ppm. Anal. Calcd for C<sub>135</sub>H<sub>104</sub>BFeNP<sub>4</sub>: C, 83.98; H, 5.43; N, 0.73. Found: C, 83.33; H, 5.57; N, 0.54.

[PhBP<sub>3</sub><sup>*m*-ter</sup>]Fe(NPCy<sub>3</sub>) (6). [H<sub>2</sub>NPPh<sub>3</sub>][Cl] (41.2 mg, 0.124 mmol) was suspended in THF (5 mL) and cooled to -78 °C with stirring. *n*-Butyllithium (155  $\mu$ L, 1.6 M in hexane, 0.248 mmol) was added to the solution, which was stirred at low temperature for 30 min, then allowed to warm to room temperature for 30 min, then cooled back to -78 °C. This solution was added dropwise to a separately cooled solution of PhBP<sub>3</sub><sup>*m*-ter</sup>FeCl (200 mg, 0.118 mmol) in THF (2 mL), and the reaction mixture was stirred at low temperature for 10 min before being allowed to warm to room temperature for 2 h and then concentrated. The resulting blue solution was concentrated to dryness, extracted with benzene, and filtered through Celite. The filtrate was concentrated to 2 mL, layered with 15 mL of pentane and allowed to stand at room temperature overnight. The resulting blue crystals were thoroughly washed with pentane, giving 170 mg of the desired product (87%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, 25 °C): δ 9.0, 7.7, 7.5, 7.08, 7.05, 6.99, 3.2, 2.4, 1.7, 1.3, 0.7, 0.5 ppm. <sup>31</sup>P{<sup>1</sup>H} NMR ( $C_6D_{62}$  202 MHz, -75 °C):  $\delta$ 100.5 (br s, 3P), 66.7 (br s, 1P) ppm. We have had difficulty obtaining elemental analysis data on this compound, likely due to its high air sensitivity. The best results that we have obtained are as follows: Anal. Calcd for C<sub>135</sub>H<sub>122</sub>BFeNP<sub>4</sub>: C, 83.19; H, 6.31; N, 0.72. Found: C, 81.94; H, 7.07; N, 0.96.

**[PhBP**<sub>3</sub><sup>**P**</sup>]**Fe(NPPh**<sub>3</sub>) **(7).** [H<sub>2</sub>NPPh<sub>3</sub>][Cl] (56.4 mg, 0.180 mmol) was suspended in THF (5 mL) and cooled to -78 °C with stirring. *n*-Butyllithium (224  $\mu$ L, 1.6 M in hexane, 0.360 mmol) was added to the solution, which was stirred at low temperature for 30 min, then allowed

to warm to room temperature for 30 min, then cooled back to -78 °C. This solution was added dropwise to a separately cooled solution of [PhBP<sub>3</sub><sup>iPr</sup>]FeCl (99.0 mg, 0.173 mmol) in THF (2 mL), and the reaction mixture was stirred at low temperature for 10 min before being allowed to warm to room temperature for 2 h and then concentrated. The resulting yellow solution was concentrated to dryness, extracted with benzene, and filtered through Celite, and concentrated to dryness again. The yellow-orange residue was taken up in minimal ether, layered with pentane, and stored at -40 °C overnight, resulting in the formation of yellow crystals. The isolated material displayed the same spectroscopic characteristics as previously reported for this compound.<sup>18</sup> Crystals suitable for XRD were grown by layering pentane over a concentrated ether solution at -40 °C. <sup>1</sup>H NMR ( $C_6 D_6$ , 300 MHz, 25 °C):  $\delta$  198.2, 53.0, 49.3, 23.6, 21.2, 8.3, 2.0, 1.8, -5.8, -27.2, -48.6 ppm. Anal. Calcd for C45H68BFeNP4: C, 66.43; H, 8.42; N, 1.72. Found: C, 65.96; H, 8.41; N, 2.45.

 $[PhBP_{3}^{iPr}]Fe(NPCy_{3})$  (8).  $[H_{2}NPCy_{3}][Cl]$  (62.9 mg, 0.190 mmol) was suspended in THF (5 mL) and cooled to -78 °C with stirring. *n*-Butyllithium (237  $\mu$ L, 1.6 M in hexane, 0.380 mmol) was added to the solution, which was stirred at low temperature for 30 min, then allowed to warm to room temperature for 30 min, then cooled back to -78 °C. This solution was added dropwise to a separately cooled solution of [PhBP<sub>3</sub><sup>iPr</sup>]FeCl (104.5 mg, 0.181 mmol) in THF (2 mL), and the reaction mixture was stirred at low temperature for 10 min before being allowed to warm to room temperature for 2 h and then concentrated. The resulting yellow solution was concentrated to dryness, extracted with benzene, and filtered through Celite, and concentrated to dryness again. The yellow-orange residue was taken up in minimal ether, layered with pentane, and stored at -40 °C overnight, resulting in the formation of yellow crystals which were collected, washed with cold pentane, and dried to give 69 mg of the desired compound (46%). Crystals suitable for XRD were grown by slow evaporation of a pentane solution. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, 25 °C): δ 194.2, 84.7, 50.3, 42.5, 23.7, 21.4, 20.1, 13.9, 7.7, 6.0, -7.7, -26.2, -49.3 ppm. Anal. Calcd for C45H86BFeNP4: C, 64.98; H, 10.42; N, 1.68. Found: C, 64.79; H, 10.42; N, 1.61.

[PhBP<sub>3</sub><sup>*i*Pr</sup>]Fe(NPEt<sub>3</sub>) (9). [H<sub>2</sub>NPEt<sub>3</sub>][Cl] (63.9 mg, 0.377 mmol) was suspended in THF (5 mL) and cooled to -78 °C with stirring. *n*-Butyllithium (468  $\mu$ L, 1.6 M in hexane, 0.754 mmol) was added to the solution, which was stirred at low temperature for 30 min, then allowed to warm to room temperature for 30 min, then cooled back to -78 °C. This solution was added dropwise to a separately cooled solution of [PhBP<sub>3</sub><sup>iPr</sup>]FeCl (200 mg, 0.346 mmol) in THF (2 mL), and the reaction mixture was stirred at low temperature for 10 min before being allowed to warm to room temperature for 2 h and then concentrated. The resulting yellow solution was concentrated to dryness, extracted with benzene, and filtered through Celite, and concentrated to dryness again. The yellow-orange residue was taken up in minimal ether, layered with pentane, and stored at -40 °C overnight, resulting in the formation of yellow crystals. The isolated material displayed the same spectroscopic characteristics as previously reported for this compound.<sup>18</sup> Crystals suitable for XRD were grown by slow evaporation of a pentane solution. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz, 25 °C): δ 197.0, 84.8, 48.7, 47.7, 23.0, 21.0, -6.6, -23.8, -48.7 ppm. Anal. Calcd for C<sub>33</sub>H<sub>68</sub>BFeNP<sub>4</sub>: C, 59.21; H, 10.24; N, 2.09. Found: C, 59.27; H, 10.27; N, 2.42.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b00066.

Additional spectral data for novel compounds, crystallographic details, and further details concerning the analysis of variable-temperature UV-vis and NMR data (PDF) Crystallographic data for compounds 1, 2, 4, 5 and 7–9. (CIF) AUTHOR INFORMATION

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#### **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

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