# **ORGANOMETALLICS**

# Contrasting Protonation Behavior of Diphosphido vs Dithiolato Diiron(I) Carbonyl Complexes

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### **Supporting Information**



**ABSTRACT:** This paper reports on the protonation of phosphine-substituted diiron diphosphido carbonyls, analogues of diiron dithiolato centers at the active sites of hydrogenase enzymes. Reaction of the diphosphines  $(CH_2)_n(PPHH)_2$  (n = 2 (edpH<sub>2</sub>) and n = 3 (pdpH<sub>2</sub>)) with Fe<sub>3</sub>(CO)<sub>12</sub> gave excellent yields of Fe<sub>2</sub>(edp)(CO)<sub>6</sub> (1) and Fe<sub>2</sub>(pdp)(CO)<sub>6</sub> (2). Substitution of Fe<sub>2</sub>(edp)(CO)<sub>6</sub> with PMe<sub>3</sub> afforded Fe<sub>2</sub>(edp)(CO)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub> (3;  $\nu_{CO}$  1855 and 1836 cm<sup>-1</sup>). Crystallographic analysis showed that 3 adopts an idealized C<sub>2</sub> symmetry, with pairs of phosphine ligands occupying apical–basal sites on each Fe center. Relative to that in the dithiolato complex, the Fe–Fe bond (2.7786(8) Å) is elongated by 0.15 Å. Treatment of 3 with H(OEt<sub>2</sub>)<sub>2</sub>BAr<sup>F</sup><sub>4</sub> (Ar<sup>F</sup> = C<sub>6</sub>H<sub>3</sub>-3,5-(CF<sub>3</sub>)<sub>2</sub>) gave exclusively the C<sub>2</sub>-symmetric  $\mu$ -hydride complex [HFe<sub>2</sub>(edp)(CO)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub>]<sup>+</sup>. This result contrasts with the behavior of the analogous ethanedi*thiolate* Fe<sub>2</sub>(edt)(CO)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub> (edt = 1,2-C<sub>2</sub>H<sub>4</sub>S<sub>2</sub>), protonation of which gives both the bridging *and terminal* hydride complexes. This difference points to the participation of the sulfur centers in the formation of terminal hydrides. The absence of terminal hydride intermediates was also revealed in the protonation of the diphosphine ligands, which convert to the isomer where the diphosphine is dibasal. In contrast, protonation of the dithiolato complex Fe<sub>2</sub>(pdt)(CO)<sub>4</sub>(dppv) gave terminal hydrides, which isomerize to  $\mu$ -hydrides. In a competition experiment, **4** was shown to protonate faster than Fe<sub>2</sub>(pdt)(CO)<sub>4</sub>(dppv).

#### INTRODUCTION

The active site of the [FeFe]-hydrogenases is a well-known bioorganometallic reaction center. Many publications describe the behavior of this structurally unusual center because of its novelty and the importance of the reactions that it catalyzes.<sup>1</sup> Most modeling efforts focus on substituted derivatives of  $Fe_2(pdt)(CO)_{6^{\prime}}$  especially those containing phosphine ligands.<sup>2</sup> Some studies have examined the effect of replacing the dithiolate ligand with diamides,<sup>3</sup> diselenoates,<sup>4</sup> ditelluroates,<sup>5</sup> diphosphides,<sup>6,7</sup> and diarsenides.<sup>8,9</sup> Studies on such species should guide the design of bioinspired catalysts for hydrogen production. Of these classes of diiron complexes, the diphosphido complexes are particularly intriguing to us because of the thermal robustness of the  $Fe_2(PR_2)_2$  core. Qualitatively,

this robustness is associated with the strength of the C–P and M–P bonds. The similar stereodynamic properties of bis-(thiolato)- vs bis(arsenido)- vs bis(phosphido)-bridged diiron hexacarbonyl complexes have been established.<sup>8</sup>

This paper focuses on the protonation of diiron diphosphido complexes as analogues of the biologically more relevant diiron dithiolato complexes. The chemistry of diiron diphosphido carbonyls is extensive<sup>10–14</sup> and includes unsaturated derivatives  $Fe_2(PR_2)_2(CO)_{5-x}(PR_3)_x^{10,13,14}$  that are not observed in diiron dithiolato complexes. Since the acidities of typical secondary phosphines  $R_2PH$  are lower than those of typical thiols,<sup>15</sup> the

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diiron phosphides are expected to display enhanced basicity leading to highly stabilized hydrides. Indeed, complexes of the type  $Fe_2(PPh_2)_2(CO)_4L_2$  were described as "markedly more basic" than the dithiolato complex  $Fe_2(SPh)_2(CO)_4L_2$ .<sup>16</sup> Since the publication of the active site structure of the [FeFe]hydrogenases,<sup>17</sup> two reports have appeared on the related diiron diphosphido carbonyls. In the complex  $Fe_2[(PhPCH_2)_2NCH_2CH_2OMe](CO)_{67}^{7}$  the organic backbone features a basic amine, as seen in the azadithiolate cofactor of the enzyme.<sup>18</sup> This amine protonates in the expected way,<sup>19,20</sup> but protonation of the Fe center was not observed. It is known from FT-IR measurements that N-protonation of related complexes diminishes the basicity of the diiron(I) core;<sup>2,19</sup> it is consequently not surprising that this ammonium diphosphido complex would not readily tautomerize to the hydride. In a study of hydrogen evolution by diiron diphosphido complexes, the protonation and subsequent catalytic hydrogen evolution have been described for the Fe(0) complex  $[Fe_2(PPh_2)_2(CO)_6]^{2-.6,21}$ 

In this work we prepared complexes of the type  $Fe_2[(PhP)_2(CH_2)_n](CO)_6$ , analogues of the archetypal  $Fe_2(edt)(CO)_6$  and  $Fe_2(pdt)(CO)_6$  (edt = 1,2- $C_2H_4S_2$ , pdt = 1,3- $C_3H_6S_2$ ). We converted these diphosphido hexacarbonyls to a series of substituted derivatives, which were expected to be analogous to the better known diiron dithiolato complexes.<sup>2</sup> It is known that protonation of complexes of the type  $Fe_2(SR)_2(CO)_{4-x}(PR_3)_{2+x}$  can afford either terminal or bridging hydrido derivatives.<sup>22,23</sup> In this work we investigated if similar reactivity patterns apply to the corresponding diphosphido complexes (Scheme 1, X = PPh).

Scheme 1. Known (X = S) and Predicted (X = PPh) Regiochemistry of Protonation of Diiron(I) Complexes



We expected that the diiron(I) diphosphido complexes would protonate to give terminal hydrides that would be more kinetically stable than the hydrides of diiron dithiolato complexes. As we show below, these predictions proved to be incorrect, and the explanation for this surprising difference provides insights into the behavior of the diiron dithiolato carbonyl complexes.

#### RESULTS

**Preparation of Fe<sub>2</sub>(edp)(CO)<sub>6</sub> and Fe<sub>2</sub>(pdp)(CO)<sub>6</sub> and Their Protonation.** Heating the diphosphines  $(CH_2)_n(PPhH)_2$  (n = 2, 3) with Fe<sub>3</sub>(CO)<sub>12</sub> in toluene at 100 °C was found to afford the diiron hexacarbonyl derivatives in high yields (eq 1). Chromatography on silica gel afforded clean products in good yields of both the ethylene and trimethylene derivatives Fe<sub>2</sub>(edp)(CO)<sub>6</sub> (1) and Fe<sub>2</sub>(pdp)(CO)<sub>6</sub> (2), respectively. Both compounds are known,<sup>9,11</sup> but the new route is more efficient.

$$(CH_2)_n (PPhH)_2 + Fe_3 (CO)_{12}$$
  
 $\rightarrow Fe_2 [(PhP)_2 (CH_2)_n] (CO)_6 + Fe (CO)_5 + CO + H_2$   
 $1 (n = 2)$   
 $2 (n = 3)$  (1)

Relative to the dithiolato complexes, **1** and **2** are noticeably more electron-rich. This difference is indicated by the positions of the CO bands in the IR spectra. For **2**,  $\nu_{CO}$  spans the range 2052–1983 cm<sup>-1</sup>, whereas for Fe<sub>2</sub>(pdt)(CO)<sub>6</sub> these bands are found in the range 2077–1950 cm<sup>-1</sup> (for medium and strong bands).<sup>24</sup> Cyclic voltammetry experiments show that **1** and **2** reduce at -2.25 V ( $i_{pa}/i_{pc} = 0.11$ ) and -2.15 V ( $i_{pa}/i_{pc} = 0.95$ ), respectively. For comparison, Fe<sub>2</sub>(edt)(CO)<sub>6</sub> and Fe<sub>2</sub>(pdt)-(CO)<sub>6</sub> are reduced near -1.7 V.<sup>25</sup>

Treatment of dichloromethane solutions of the diiron diphosphido hexacarbonyl complexes with  $H(OEt_2)_2BAr_4^F$ afforded the corresponding diferrous hydrides. According to  ${}^{31}P{}^{1}H$  NMR analysis, treatment of Fe<sub>2</sub>(edp)(CO)<sub>6</sub> with 1.2 equiv of the acid at room temperature resulted in ~92% protonation (Figure S1, Supporting Information). The observation of coexisting diferrous hydride and its parent Fe<sup>I</sup>Fe<sup>I</sup> complex is consistent with slow intermetallic proton exchange, as is typical for related compounds.<sup>20</sup> The <sup>1</sup>H NMR spectrum confirmed the presence of the hydride with a triplet at  $\delta$  -17.2 ( $J_{\rm PH}$  = 38 Hz). Under the same conditions,  $Fe_2(edt)(CO)_6$  does not react noticeably with H- $(OEt_2)_2BAr^{F_4}$ .<sup>26</sup> Qualitative tests suggest that 2 is more basic than 1 since, as a  $CD_2Cl_2$  solution, it quantitatively converted to the hydride on treatment with 1 equiv of  $H(OEt_2)_2BAr_4^F$ . The  $^1H$  and  $^{31}P\{^1H\}$  NMR spectra of the hydrido complex are consistent with a symmetrical species:  $\delta - 15.91 (J_{PH} = 39 \text{ Hz})$ and  $\delta$  125.2, respectively.

Fe<sub>2</sub>(edp)(CO)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub> and Its Protonation. The substitution of CO ligands in 1 and 2 with phosphines has been examined. Treatment of 1 with excess PMe<sub>3</sub> followed by UV irradiation afforded the tetrasubstituted complex Fe<sub>2</sub>(edp)- $(CO)_2(PMe_3)_4$  (3). The reaction conditions are comparable to those employed for the conversion of the ethanedithiolate  $Fe_2(edt)(CO)_6$  into  $Fe_2(edt)(CO)_2(PMe_3)_4$ <sup>22</sup> Complex 3 was isolated as a fine red powder and exhibited good solubility in toluene, dichloromethane, and pentane. The new complex was characterized by IR and NMR spectroscopy. The IR spectrum of 3 shows  $\nu_{\rm CO}$  bands at 1855 and 1836 cm<sup>-1</sup>, whereas for 1, these bands are in the range 2052-1966 cm<sup>-1</sup>. At room temperature, the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (Figure S5, Supporting Information) features multiplets at  $\delta$  136.2 and 17.0, as well as a triplet at  $\delta$  15.8 with 1:1:1 integration, confirming that 3 exists in solution with a bis(apical-basal) disposition of the phosphine ligands.

The structure of **3** was confirmed by single-crystal X-ray diffraction (Figure 1). The molecule has an idealized  $C_{2h}$  symmetry with a bis(apical-basal) disposition of the phosphines. The phenyl substituents project away from the Fe<sub>2</sub> core.

With a distance of 2.7786(8) Å, the Fe–Fe bond is much longer than 2.631(1) Å for Fe<sub>2</sub>[(PhPCH<sub>2</sub>)NCH<sub>2</sub>CH<sub>2</sub>OMe]-(CO)<sub>6</sub>.<sup>7</sup>). Even derivatives with bulky phosphide groups are shorter, as in Fe<sub>2</sub>(PPh<sub>2</sub>)(PBu<sup>t</sup><sub>2</sub>)(CO)<sub>6</sub> with an Fe–Fe distance of 2.707(1) Å.<sup>14</sup> Apparently the Fe–Fe bond elongates to



Figure 1. Structure of 3 with thermal ellipsoids set at the 50% probability level. Hydrogen atoms have been omitted for clarity. Key bond distances (Å) and angles (deg): Fe1–Fe2, 2.7786(8); Fe1–P1, 2.204(1); Fe1–P2, 2.191(1); Fe1–C7, 1.757(4); P4–Fe1–Fe2–P3, 95.89; P1–Fe1–Fe2–P6, 100.07.

accommodate the steric bulk of the four phosphine ligands. The Fe–P distances are in the normal range, however.<sup>27</sup>

Protonation of 3 at -80 °C afforded a bridging hydride with the same bis(apical-basal) configuration of the phosphines as the starting material. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the product features three multiplets consistent with a single isomer (Figure S7, Supporting Information). The <sup>1</sup>H NMR signal for the hydride ligand appears as a triplet of triplets of triplets at  $\delta$ -21.72 (Figure 2). This spectrum can be simulated with *J*(H,P)



**Figure 2.** <sup>1</sup>H NMR spectrum of a  $CD_2Cl_2$  solution of  $[(\mu-H)Fe_2(edp)(CO)_2(PMe_3)_4]^+$  in the hydride region at -80 °C (the spectrum remains constant to room temperature).

= 38.3, 26.3, and 4.1 Hz. Previous work, e.g. on  $[\mu H - Fe_2(pdt)(CO)_4(PMe_3)_2]^+$ ,<sup>28</sup> shows that  $J(H,P)_{trans}$  is typically 5 Hz, whereas  $J(H,P)_{cis}$  is around 28 Hz.

Fe<sub>2</sub>(pdp)(CO)<sub>4</sub>(dppv) (4) and Fe<sub>2</sub>(pdp)(CO)<sub>4</sub>(dppbz) (5) and Their Protonation. The new compounds Fe<sub>2</sub>(pdp)-(CO)<sub>4</sub>(dppv) (4; dppv = *cis*-1,2-C<sub>2</sub>H<sub>2</sub>(PPh<sub>2</sub>)<sub>2</sub>) and Fe<sub>2</sub>(pdp)-(CO)<sub>4</sub>(dppbz) (5; dppbz = 1,2-C<sub>6</sub>H<sub>5</sub>(PPh<sub>2</sub>)<sub>2</sub>) were prepared by photosubstitution of **2** by the diphosphine. These reactions proceeded more slowly than the synthesis of the related ethaneand propanedithiolates  $Fe_2(xdt)(CO)_4(chel)$ .<sup>29</sup> Both compounds were obtained as red-orange powders after purification by chromatography on silica gel. For **4**, the room-temperature  ${}^{31}P{}^{1}H{}$  NMR spectrum shows multiplets near  $\delta$  106.2 and 93.6 (Figure S9, Supporting Information). For **5**, the  ${}^{31}P{}^{1}H{}$  NMR spectrum features multiplets at  $\delta$  103.8 for the diphosphido bridge and at  $\delta$  89.3 (Figure 3). The  ${}^{31}P{}$  NMR



Figure 3.  ${}^{31}P{}^{1}H$  NMR spectra of a  $CD_2Cl_2$  solution of Fe<sub>2</sub>(pdp)-(CO)<sub>4</sub>(dppbz) (5) at various temperatures (from the top: +20, -30, -60, and -90 °C).

signals for 1 and 2 are  $\delta$  131.6 and 166.4. Thus, in these mixed phosphide—phosphine complexes, the low-field signals are assigned to the diphosphido ligands. As can be seen by the multiplicity of the signals at low temperatures, the diphosphine must span apical—basal sites in 4 and 5. Variable-temperature NMR studies demonstrate that the chelating diphosphine oscillates rapidly between equivalent positions, as is seen for Fe<sub>2</sub>(pdt)(CO)<sub>4</sub>(dppv) and related complexes (eq 2, Figure 3).<sup>29,30</sup>



The complex  $Fe_2(pdt)(CO)_4(dppv)$  exists as a 90:10 mixture of apical–basal and dibasal isomers, respectively. This ratio does not perceptibly change from room temperature to -90 °C.<sup>31</sup> Thus, it appears that the dibasal isomer is less stabilized in the diiron diphosphido complexes. Variable-temperature NMR results show that cessation of the dynamics of the Fe(CO)-(diphos) center coincides with the temperature range where the signals for the phosphido ligands split.

Protonations of **4** and **5** with 1 equiv of  $H(OEt_2)_2BAr^F_4$  were conducted at low temperatures and monitored by NMR spectroscopy. For the protonation of a  $CD_2Cl_2$  solution of **4**, the <sup>1</sup>H NMR spectrum of the initially observed hydride (T = -90 °C) complex shows a triplet of doublets at  $\delta - 15.4$  ( $J_{PH} = 49.5$ , 25.0 Hz; Figure S10, Supporting Information). The corresponding <sup>31</sup>P NMR spectrum shows three sets of complex multiplets, consistent with an apical-basal disposition of the dppv ligand. Above -30 °C, this kinetic product converts to a more stable isomer wherein the diphosphine is dibasal, this species showing a triplet of triplets at  $\delta - 15.96$  ( $J_{PH} = 40.5$ , 22.0 Hz). The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of this second isomer features equally intense resonances at  $\delta$  129.05 and 89.03 for the diphosphido bridge and the dppv, respectively. The protonation of Fe<sub>2</sub>(pdt)(CO)<sub>4</sub>(dppv) followed a very similar pattern (Scheme 2; see below). The protonation of 5 proceeded in a very similar way (Figure 4).

#### Scheme 2



We briefly examined the edp analogues of **4** and **5**, and the results were similar. As seen for  $Fe_2(edt)(CO)_4(dppv)$ ,<sup>29</sup> only the apical-basal isomer was observed. When they were protonated at room temperature, both the edp-dppv and edp-dppbz compounds afforded the corresponding  $\mu$ -hydrido complexes, again with apical-basal diphosphine ligands. These kinetic isomers were found to convert to the more stable isomer with a dibasal configuration of the diphosphine within 1 h at room temperature.

Protonation of Fe<sub>2</sub>(pdt)(CO)<sub>4</sub>(dppv). Prior to comparing the protonation of diiron diphosphido and diiron dithiolato complexes, we re-examined the protonation of the Fdithiolate  $Fe_2(pdt)(CO)_4(dppv)$  (6) to address a discrepancy in the literature.<sup>31</sup> When a mixture of Fe<sub>2</sub>(pdt)(CO)<sub>4</sub>(dppv) and  $H(OEt_2)_2BAr_4^F$  in  $CD_2Cl_2$  is allowed to thaw and then immediately checked by NMR spectroscopy, we observe rapid formation of the terminal hydrido complex. In this kinetic isomer, the dppv is dibasal on the unprotonated Fe center. We had previously misassigned this kinetic hydride as the apicalbasal isomer.<sup>31</sup> When this experiment was examined in the presence of an integration standard, we found that substantial amounts of the starting Fe<sup>I</sup>Fe<sup>I</sup> species had not dissolved. The insolubility of such diiron complexes plagues related experiments conducted at very low temperatures, even when the diiron(I) complex is fully dissolved prior to cooling the sample. As described previously,<sup>31</sup> the terminal hydrides [HFe<sub>2</sub>(pdt)- $(CO)_4(dppv)$ <sup>+</sup> isomerize near -40 °C to the unsymmetrical and then symmetrical bridging hydrides, wherein the dppv is apical-basal and then dibasal.

**Protonation of Fe\_2(pdt)(CO)\_4(dppv) vs Fe\_2(pdp)-**(CO)<sub>4</sub>(dppv). At -90 °C, the protonation of 4 is slow, requiring several minutes. In contrast, protonation of the related dithiolato complex 6 is rapid and quantitative under these conditions.<sup>28</sup> Surprisingly, when a mixture of  $Fe_2(pdt)$ -(CO)<sub>4</sub>(dppv) and 4 was treated with  $H(OEt_2)_2BAr^F_4$ , the only hydride product obtained (immediately upon mixing at -90 °C) was the hydride derivative of the diiron diphosphido complex. It thus appears that 6 catalyzes the protonation of 4. These surprising results are summarized in eqs 3–5.

**Computational Experiments.** To better understand the absence of terminal hydride derivatives of the phosphido complexes, we carried out DFT calculations to compare structural and electronic properties of diiron complexes with bridging diphosphido vs dithiolato ligands. Recall that protonation of  $Fe_2(pdt)(CO)_4(dppv)$  with strong acids gives the terminal hydride [*term*-HFe\_2(pdt)(CO)\_4(dppv)]<sup>+</sup>, which converts near -40 °C to two isomeric  $\mu$ -hydride derivatives. Even more striking, the terminal hydride [*term*-HFe\_2(edt)-



**Figure 4.** <sup>1</sup>H NMR spectra for various stages in the protonation of a  $CD_2Cl_2$  solution of  $Fe_2(pdp)(CO)_4(dppbz)$  with 1 equiv of  $H(OEt_2)_2BAr^F_4$  (from the bottom: T = -90, -60, -30, and +20 °C).

 $(CO)_2(PMe_3)_4]^+$  is stable for several minutes at room temperature,<sup>22</sup> but we detected none of the analogous [*term*-HFe\_2(edp)(CO)\_2(PMe\_3)\_4]^+.

slow: 
$$Fe_2(pdp)(CO)_4(dppv) + H^+$$
  
 $\rightarrow [HFe_2(pdp)(CO)_4(dppv)]^+$ 
(3)

fast: 
$$\operatorname{Fe}_{2}(\operatorname{pdt})(\operatorname{CO})_{4}(\operatorname{dppv}) + \operatorname{H}^{+}$$
  
 $\rightarrow [\operatorname{HFe}_{2}(\operatorname{pdt})(\operatorname{CO})_{4}(\operatorname{dppv})]^{+}$ 
(4)

$$\begin{aligned} \text{fast: } & \text{Fe}_2(\text{pdp})(\text{CO})_4(\text{dppv}) + \text{Fe}_2(\text{pdt})(\text{CO})_4(\text{dppv}) \\ & + \text{H}^+ \rightarrow [\text{HFe}_2(\text{pdp})(\text{CO})_4(\text{dppv})]^+ \\ & + \text{Fe}_2(\text{pdt})(\text{CO})_4(\text{dppv}) \end{aligned} \tag{5}$$

The comparison of energy differences between unrotated and rotated forms of  $Fe_2(edp)(CO)_4(dppv)$  and  $Fe_2(edt)$ - $(CO)_4(dppv)$  (Scheme 3) showed that in both cases unrotated forms have lower energies. More importantly, the energy gaps between rotated and unrotated forms (which always correspond to transition states of FeL<sub>3</sub> rotation) are almost the same in  $Fe_2(edp)(CO)_4(dppv)$  and  $Fe_2(edt)(CO)_4(dppv)$ . Therefore, the absence of terminal hydride derivatives of  $Fe_2(edp)$ - $(CO)_4(dppv)$  cannot be ascribed to hindered formation of rotated forms. Notably, the comparison of rotated forms reveals that structures characterized by dibasal dppv are more destabilized relative to basal–apical species in the edp complex.

To qualitatively evaluate the relative basicity of iron atoms in rotated and unrotated complexes containing edt or edp ligands, we have computed atomic partial charges (according to the NBO—natural bond orbital—partition scheme of the electron density) for  $Fe_2(edt)(CO)_6$ ,  $Fe_2(edp)(CO)_6$ ,  $Fe_2(edt)$ - $(CO)_4(dppv)$ , and  $Fe_2(edp)(CO)_4(dppv)$ . We found that iron centers in the edp complexes are more electron-rich than in edt species (Scheme S1, Supporting Information). Moreover, the partial charge of the five-coordinated iron atoms is always slightly less negative in the rotated forms. Analyses of NBO charges have been complemented by the computation of proton affinities for  $Fe_2(pdt)(CO)_4(dppv)$  and  $Fe_2(pdp)$ -

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 $(CO)_4(dppv)$  complexes (the two different terminal-axial coordination modes and the diiron bridging coordination have been tested; see Table S1 in the Supporting Information). As expected, the Fe–Fe bond in the pdp complex has a higher affinity for protons. The corresponding proton affinity for the pdt complex is lower by about 3 kcal/mol.

# CONCLUSIONS

These studies were enabled by the preparation of phosphinesubstituted diiron diphosphido complexes, only a few of which were known prior to this work.<sup>13,14,32</sup> The new complexes are highly basic, readily affording the corresponding  $\mu$ -hydrido derivatives. To our surprise and in contrast with extensive results on related diiron dithiolato complexes,<sup>2</sup> protonation experiments never revealed detectable amounts of the terminal hydrido complexes. This finding is consistent with our recent hypothesis that  $\mu$ -thiolate ligands function as proton relays leading to terminal hydrides.<sup>28</sup> In the absence of such sites, attack at the Fe–Fe bond is favored.

The behavior of  $Fe_2(pdp)(CO)_4(dppv)$  illustrates the complexity of the protonation chemistry. The protonation of this species appears to be *catalyzed* by  $Fe_2(pdt)(CO)_4(dppv)$ . A proposed structure for the bimolecular intermediate is depicted in eq 6.



A similar pathway was invoked in the bimolecular pathway for the protonation of  $Fe_2(pdt)(CO)_2(PMe_4)_4$  and  $Fe_2(edt)-(CO)_2(PMe_4)_4$ .<sup>28</sup> S-protonation would be expected to diminish the basicity of the associated Fe centers toward further protonation. The susceptibility of terminal thiolato ligands to protonation is long established.<sup>33</sup> Typical  $\mu$ -thiolato ligands are much less basic, although the apparent S-protonation of diiron dithiolato carbonyls by strong acids has been observed by IR<sup>34</sup> and NMR spectroscopy.<sup>28</sup>

The presence of phosphorus at the bridging sites provides an opportunity to probe the new details of the stereodynamics of this family of diiron complexes. Thus, we show that cessation of the turnstile dynamics of the Fe(CO)(dppv) center in Fe<sub>2</sub>(pdp)(CO)<sub>4</sub>(dppv) correlates with the splitting of the <sup>31</sup>P NMR signals for the phosphide groups. Overall, the barriers for the stereodynamic behavior for the Fe<sup>I</sup>Fe<sup>I</sup> diphosphido and dithiolato complexes are similar, which suggests that their dynamic behavior does not involve breaking of Fe–( $\mu$ -X) bonds (X = SR, PR<sub>2</sub>).<sup>9</sup> Likewise, the similar rates of isomerization of the  $\mu$ -hydrides [HFe<sub>2</sub>(pdx)(CO)<sub>4</sub>(dppv)]<sup>+</sup> for the pdt and pdp derivatives suggests that the breaking of Fe–S and Fe–P(phosphido) bonds is not involved in the isomerization of these  $\mu$ -hydrido complexes, consistent with the proposed twist mechanism.<sup>35</sup>

## EXPERIMENTAL SECTION

#### Methods have been recently reported.<sup>28</sup>

HPhP( $CH_2$ )<sub>2</sub>PPhH (edpH<sub>2</sub>). In this reaction, lithium is used to cleave phenyl-phosphorus bonds, but without care, we also observed scission of P-CH<sub>2</sub> bonds. Good selectivity for cleavage of the phenyl-

Scheme 3. Structures and Energy Differences (kcal/mol) between Rotated and Unrotated Forms in  $Fe_2(edt)(CO)_4(dppv)$  and  $Fe_2(edp)(CO)_4(dppv)^a$ 



<sup>a</sup>All rotated isomers correspond to the transition states.

P bonds was observed when the reaction was maintained at 0  $^\circ$ C. A round-bottomed flask equipped with a dropping funnel was loaded with a glass-coated stir bar and 1.2 g (0.17 mmol) of lithium wire cut into small (~5 mm) pieces, followed by 30 mL of freshly distilled THF. The lithium suspension was cooled to 0 °C. The addition funnel was charged with a solution of 6.5 g (0.016 mmol) of 1,2bis(diphenylphosphino)ethane in 75 mL of THF. The dppe solution was added to a cold suspension of lithium over the course of 3 h. The reaction mixture was stirred for 20 h, being careful to maintain the temperature at 0 °C. The course of the reaction was monitored by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. The reaction was judged complete when the signal for dppe at  $\delta$  –15.2 had vanished. A solution of 15 mL of water in 35 mL of THF was slowly added through the dropping funnel over the course of 1 h, carefully maintaining the mixture at 0 °C. After the mixture was stirred for an additional 10 min, the solvent was removed under vacuum. The sticky residue was washed with 50 mL of water to remove LiOH. The product was extracted into  $4 \times 50$  mL of Et<sub>2</sub>O. The ether was transferred by cannula into a flask containing 3.5 g of MgSO<sub>4</sub>. After the MgSO<sub>4</sub> suspension was vigorously stirred, the ether solution was transferred into a new flask, and solvent was removed under vacuum. The product was distilled at 5 mTorr (135-140 °C). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  -46.08, -46.66 (~1:1 mixture of diastereoisomers).<sup>3</sup>

**HPhP(CH<sub>2</sub>)<sub>3</sub>PPhH (pdpH<sub>2</sub>).** This compound was prepared by following the same procedure described above for edpH<sub>2</sub>. The following amounts were used: 2 g (28 mmol) of lithium and 5 g (28 mmol) of 1,3-bis(diphenylphosphino)propane. The mixture was stirred overnight at 0 °C, and the reaction was judged to be complete when the signal of the starting material had vanished in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum. Workup was similar to that for edpH<sub>2</sub>, except that it was not necessary to distill the product since <sup>31</sup>P{<sup>1</sup>H} NMR analysis showed that the product was >98% pure. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  -55.88, -56.01 (~1:1 mixture of diastereoisomers).<sup>36</sup>

**Fe<sub>2</sub>(edp)(CO)<sub>6</sub> (1).** A 300 mL round-bottom flask was charged with 2.939 g (5.835 mmol) of Fe<sub>3</sub>(CO)<sub>12</sub> and 75 mL of dry toluene. The reaction solution was then treated with a solution of 1.437 g (5.835 mmol) of edpH<sub>2</sub> in 10 mL of toluene. The reaction mixture was stirred at an oil bath temperature of 100 °C for 3 h. Volatiles were removed under vacuum, and the yellow residue was extracted into ~100 mL of hexane. Removal of the solvent afforded the product in analytical purity. Yield: 2.46 g (81%). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 166.4 (s). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.42–7.45 (m, C<sub>6</sub>H<sub>5</sub>, 10H), 216 (d, PCH<sub>2</sub>, 4H). IR (CDCl<sub>3</sub>):  $\nu_{CO}$  2052 (m), 2013 (m), 1990 (m), 1966 (s) cm<sup>-1</sup>. Anal. Calcd (found) for C<sub>20</sub>H<sub>14</sub>Fe<sub>2</sub>O<sub>6</sub>P<sub>2</sub>: C, 45.85 (45.94); H, 2.69 (2.82).

**Fe<sub>2</sub>(pdp)(CO)<sub>6</sub> (2).** Compound **2** was prepared by following the procedure for **1** with pdpH<sub>2</sub> in place of edpH<sub>2</sub>. The following amounts were used: 2.042 g (4.05 mmol) of Fe<sub>3</sub>(CO)<sub>12</sub> and 1.055 g (4.05 mmol) of pdpH<sub>2</sub>. After the reaction mixture was stirred for 3 h, solvent was removed under vacuum. The residue was extracted into 10 mL of CH<sub>2</sub>Cl<sub>2</sub>. This extract was subjected to chromatography on a 2.5 × 30 cm column of silica gel with 3/7 CH<sub>2</sub>Cl<sub>2</sub>/hexanes as eluent. The first yellow band was collected. Solvent was removed under vacuum to afford the product. Yield: 2.05 g (94%). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ

131.6 (s). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.83–7.40 (m, C<sub>6</sub>H<sub>5</sub>, 10H), 2.00 (m, PCH<sub>2</sub>, 4H), 2.09 (m, PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>P, 2H). IR:  $\nu$ <sub>CO</sub> 2052 (m), 2013 (m), 1990 (m), 1966 (s) cm<sup>-1</sup>. Anal. Calcd (found) for C<sub>21</sub>H<sub>16</sub>Fe<sub>2</sub>O<sub>6</sub>P<sub>2</sub>: C, 46.88 (47.01); H, 3.00 (3.22).

**Fe<sub>2</sub>(edp)(CO)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub> (3).** In a 100 mL Schlenk tube containing a solution of 300 mg (0.57 mmol) of 1 in 50 mL of toluene was added 0.5 mL (4.8 mmol) of PMe<sub>3</sub>. After 10 min of stirring, being careful to vent the evolved CO, the reaction flask was irradiated at 450 nm for 20 h. Volatiles were removed under vacuum, after which the red solid residue was extracted into 60 mL of pentane. Evaporation of the pentane extracts afforded a red fine powder. Yield: 326 mg (80%). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 136.4 (m, diphosphido bridge), 17.05 (m, broad), 15.82 (m, broad). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 1.96 (broad s, PCH<sub>2</sub>, 4H), 1.96 (m, PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>P, 2H), 1.33 (d, PMe<sub>3</sub>, 36H). IR (toluene):  $ν_{CO}$  1855 (m), 1836 (m) cm<sup>-1</sup>. Anal. Calcd (found) for C<sub>28</sub>H<sub>30</sub>Fe<sub>2</sub>O<sub>2</sub>P<sub>6</sub>: C, 46.95 (47.10); H, 7.04 (7.18).

**Fe<sub>2</sub>(pdp)(CO)<sub>4</sub>(dppv) (4).** In a 100 mL Schlenk tube charged with a solution of 0.300 g (0.56 mmol) of Fe<sub>2</sub>(pdp)(CO)<sub>6</sub> in 50 mL of dry toluene was added a solution of 0.221 g (0.56 mmol) of dppv in 25 mL of toluene. The reaction mixture was then irradiated with an LED lamp ( $\lambda$  450 nm). After 24 h, the solvent was removed under vacuum. The product was obtained in analytical purity after chromatography on silica, with a 1/1 toluene/pentane mixture as eluent. The first yellow band was found to be the starting diiron hexacarbonyl compound, and the second yellow band was an unidentified product. The third (redorange) band contained the product. Yield: 0.217 g (44%). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 106.2 (PhPCH<sub>2</sub>, s), 93.6 (dppv, s). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.83–7.40 (m, C<sub>6</sub>H<sub>5</sub>, 10H), 2.00 (m, PCH<sub>2</sub>, 4H) 2.09 (m, PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>P, 2H). IR:  $\nu_{CO}$  2001 (m), 1938 (m), 1922 (m) cm<sup>-1</sup>. Anal. Calcd (found) for C<sub>45</sub>H<sub>38</sub>Fe<sub>2</sub>O<sub>4</sub>P<sub>4</sub>: C, 61.53 (61.86); H, 4.46 (4.63).

Fe2(pdp)(CO)4(dppbz) (5). In a 100 mL Schlenk tube flask charged with 0.300 g (0.56 mmol) of Fe<sub>2</sub>(pdp)(CO)<sub>6</sub> was added 50 mL of toluene followed by a solution of 0.248 g (0.56 mmol) of dppbz in 25 mL of toluene. The reaction mixture was then irradiated at 450 nm for 24 h. The reaction was judged complete when the  ${}^{31}P{}^{1}H$ NMR resonance of the free diphosphine at  $\delta$  -12 vanished. Volatiles were removed under vacuum to give a red-orange solid material. Compound 5 was obtained in analytical purity after chromatography on silica, with a 1/1 CH<sub>2</sub>Cl<sub>2</sub>/hexanes mixture as eluent. The first yellow band was found to be the starting diiron hexacarbonyl compound, and the second red-orange band turned out to be the product. Solvent was removed under vacuum to afford an fine orange powder. Yield: 0.281 g (54%).  ${}^{31}P{}^{1}H$  NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  103.8 (diphosphido bridge, s), 89.3 (dppbz, s). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.83– 7.40 (m, C<sub>6</sub>H<sub>5</sub>, 10H), 2.00 (m, PCH<sub>2</sub>, 4H), 2.09 (m, PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>P, 2H). IR:  $\nu_{CO}$  2000 (m), 1937 (m), 1921 (m) cm<sup>-1</sup>. Anal. Calcd (found) for C<sub>49</sub>H<sub>40</sub>Fe<sub>2</sub>O<sub>4</sub>P<sub>4</sub>: C, 63.39 (63.56); H, 4.34 (4.72)

**Computational Details.** Density functional theory (DFT) calculations were carried with the TURBOMOLE suite of programs.<sup>37</sup> A high-quality level of theory (BP86/TZVP<sup>38</sup>) was employed to treat explicitly (no effective core potential was used; inner shell electrons were explicitly treated) the full electronic structure of all atoms of the diiron species investigated. Such a DFT scheme has been shown to be suitable for investigating hydrogenase models.<sup>35,39</sup>

All stationary points on the potential energy surface were determined by means of energy gradient techniques, and a full vibrational analysis was carried out to further characterize the nature of each point. Transition state structures were searched by means of a procedure based on a quasi-Newton–Josephson algorithm.<sup>40</sup> As a preliminary step, the geometry optimization of a putative transition state structure was carried out by freezing the molecular degrees of freedom corresponding to the reaction coordinate (RC). After the vibrational analysis of the constrained minimum energy structures was performed, the negative eigenmode associated to the RC was followed to locate the true transition state structure, which corresponds to the maximum energy point along the trajectory that joins two adjacent minima (i.e., reactants, products, and reaction intermediates).

An implicit treatment of solvent effects (COSMO;<sup>41</sup>  $\varepsilon$  = 9.1, dichloromethane) was used to evaluate possible polarization

phenomena. However, it was verified that solvent-corrected energies do not vary significantly compared to those computed under vacuum. In light of available experimental data and considering the chemical nature of the ligands, only low-spin forms of FeFe complexes were considered for DFT calculations. The resolution of the identity procedure<sup>42</sup> was used for approximating expensive four-center integrals (describing the classical electron–electron repulsive contribution to the total energy) through a combination of two three-center integrals. This procedure was made possible by expanding the density  $\rho$  in terms of an atom-centered and very large basis, the auxiliary basis set.

# ASSOCIATED CONTENT

#### Supporting Information

<sup>1</sup>H NMR, <sup>31</sup>P NMR, and IR spectra and cyclic voltammograms for new complexes and schematic structures, partial atomic charges, and relative energies for  $Fe_2(edt)(CO)_6$ ,  $Fe_2(edp)-(CO)_6$ ,  $Fe_2(edt)(CO)_4(dppv)$ , and  $Fe_2(edp)(CO)_4(dppv)$ , a table giving computed proton affinities for  $Fe_2(pdt)-(CO)_4(dppv)$  and  $Fe_2(pdp)(CO)_4(dppv)$ , and a CIF file giving X-ray crystallographic data for 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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