

# Synthesis, Characterization, and Reactivity of the Heterometallic Dinuclear $\mu$ -PH<sub>2</sub> and $\mu$ -PPhH Complexes FeMn(CO)<sub>8</sub>( $\mu$ -PH<sub>2</sub>) and FeMn(CO)<sub>8</sub>( $\mu$ -PPhH)<sup>‡</sup>

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Deprotonation of Fe(CO)<sub>4</sub>PRH<sub>2</sub> and treatment with Mn(CO)<sub>5</sub>Br afforded the dinuclear complexes FeMn(CO)<sub>8</sub>( $\mu$ -PRH) (1a, R = H; 1b, R = Ph), which contain the relatively rare  $\mu$ -PH<sub>2</sub> and  $\mu$ -PPhH functionalities. The heterometallic nature of these complexes was confirmed by mass spectrometry, and the molecular structures of **1a** and **1b** were determined by X-ray diffraction experiments. Deprotonation of **1b** and subsequent addition of Mn(CO)<sub>5</sub>Br or AuPPh<sub>3</sub>Cl yielded the trinuclear complexes  $\text{FeMn}(\text{CO})_8[\mu-\text{PPh}(\text{Mn}(\text{CO})_5)]$  (3a) and  $\text{FeMn}(\text{CO})_8[\mu-\text{PPh}(\text{AuPPh}_3)]$  (3b), both of which were characterized structurally and spectroscopically. Deprotonation of **1a** at room temperature resulted in rapid coupling of the deprotonated product [2a]<sup>-</sup> with neutral 1a to form  $M^{+}[FeMn(CO)_{8}(\mu_{3}-PH)Mn(CO)_{4}(\mu-PH_{2})Fe(CO)_{4}]^{-}(M^{+}[4]^{-})(M^{+}=Li^{+}, Na^{+}, K^{+})$ , the formation of which was observed using *in situ* infrared spectroscopy.  $M^{+}[4]^{-}$  was found to decompose upon solvent removal, and the structure of  $[4]^-$  was elucidated by examination of spectroscopic data. The <sup>1</sup>H NMR spectrum of [4]<sup>-</sup> was characterized by first-order [ABMX] and [AMX] spin systems, and ESI-MS data confirmed that  $[4]^{-}$  was formed by direct coupling of  $[2a]^{-}$  with 1a without concomitant fragmentation or loss of CO ligands. Deprotonation of **1a** at lower temperatures slowed the coupling process, allowing for the metalation of the monomeric anion [2a]<sup>-</sup> by treatment with AuPPh<sub>3</sub>Cl, the product of which was found to decompose gradually in solution and rapidly upon concentration.

## Introduction

Organometallic complexes containing transition metals and main group elements may be used as precursors to advanced materials such as nanoparticles or thin films.<sup>1</sup> We have been exploring the use of iron carbonylphosphorus compounds for the production of binary  $Fe_xP$ (x = 1-3) phase nanomaterials.<sup>1</sup> The known complex  $FeMn(CO)_8(\mu-PPh_2)^2$  was explored as a single-source precursor to the mixed-metal phase FeMnP, but proved ineffective, leading only to the formation of  $Fe_xO_y$  phases. In order to overcome these difficulties, the syntheses of previously unknown  $\mu$ -PH<sub>2</sub> and  $\mu$ -PRH analogues were explored to determine if these might prove to be more effective precursors by having lower barriers to decomposition. The conversion of these complexes to solid phase materials will be reported elsewhere. This paper reports the results of the synthetic molecular studies of the  $\mu$ -PH<sub>2</sub> and  $\mu$ -PRH single-source precursor complexes.

Extensive research has been conducted on transition metal complexes exhibiting one or more bridging phosphido

functionalities, and the bridging phosphide has been observed to prevent fragmentation of the complex during reactions with organic substrates.<sup>3–6</sup> However, the majority of these studies have focused on homometallic dinuclear complexes containing the  $\mu$ -PR<sub>2</sub> (R = aryl, alkyl) group, with relatively few references describing the structures and chemistry of dinuclear complexes containing  $\mu$ -PRH and  $\mu$ -PH<sub>2</sub> groups.<sup>7–11</sup> Fewer still are references to *heterometallic* dinuclear complexes exhibiting the  $\mu$ -PRH or  $\mu$ -PH<sub>2</sub> functionalities.<sup>12,13</sup> In addition to serving as precursors to advanced materials, complexes of this type are of

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Scheme 1. Synthesis and Reactivity of FeMn(CO)<sub>8</sub>(µ-PH<sub>2</sub>) (1a) and FeMn(CO)<sub>8</sub>(µ-PPhH) (1b)



interest because the presence of a P–H bond can be a useful synthetic scaffold for additional derivatization and tuning of the complex. Additionally, the inherent electronic differences between homometallic and heterometallic species may affect catalytic cycles or reactive pathways.<sup>14–21</sup>

Here we report the synthesis and structural characterizations of two new heterobimetallic carbonyl complexes containing the  $\mu$ -PRH and  $\mu$ -PH<sub>2</sub> functionalities: FeMn(CO)<sub>8</sub>( $\mu$ -PH<sub>2</sub>) (1a) and FeMn(CO)<sub>8</sub>( $\mu$ -PPhH) (1b) (Scheme 1). Derivatization of 1b was achieved to give FeMn(CO)<sub>8</sub>[ $\mu$ -PPh(Mn(CO)<sub>5</sub>)] (3a) and FeMn(CO)<sub>8</sub>[ $\mu$ -PPh(AuPPh<sub>3</sub>)] (3b). Deprotonation of 1a at room temperature, on the other hand, led to rapid coupling of the deprotonated product [2a]<sup>-</sup> and neutral 1a to form M<sup>+</sup>[FeMn-(CO)<sub>8</sub>( $\mu$ -PH)Mn(CO)<sub>4</sub>( $\mu$ -PH<sub>2</sub>)Fe(CO)<sub>4</sub>]<sup>-</sup> (M<sup>+</sup>[4]<sup>-</sup>) (M<sup>+</sup> = Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>).

### **Results and Discussion**

Complexes **1a** and **1b** were both prepared by employing the strategy described by Yasufuku and Yamazaki to prepare the structurally analogous FeMn(CO)<sub>8</sub>( $\mu$ -PPh<sub>2</sub>) complex.<sup>2</sup> The preparations of **1a** and **1b** are achieved through the intermediacy of the highly air-, light-, and moisture-sensitive complexes Fe(CO)<sub>4</sub>PH<sub>3</sub> and Fe(CO)<sub>4</sub>PPhH<sub>2</sub>. Freshly prepared samples of the former were treated with diethylamine and Mn(CO)<sub>5</sub>Br in THF to yield **1a** via a bridge-assisted displacement reaction, the metal centers being brought sufficiently close together for a metal–metal bond to form. Similarly, **1b** was prepared from Fe(CO)<sub>4</sub>PPhH<sub>2</sub> and Mn(CO)<sub>5</sub>Br, with *n*-butyl-lithium being used as the base. The preparation of **1b** appears to be more prone to redox side-reactions than **1a**, as Mn<sub>2</sub>(CO)<sub>10</sub>

was isolated jointly with the desired product. Although  $Fe(CO)_4PH_3$  and  $Fe(CO)_4PPhH_2$  are both extremely sensitive to air and moisture, complexes **1a** and **1b** can be handled in the air for short periods of time with no discernible decomposition. Complexes **1a** and **1b** obey the EAN rule, and all metal centers can be assigned 18 electrons.

The <sup>1</sup>H NMR spectra of **1a** and **1b** in C<sub>6</sub>D<sub>6</sub> show doublets centered at 3.00 and 5.28 ppm, respectively. The large coupling constants, 364 Hz for **1a** and 357 Hz for **1b**, are consistent with direct phosphorus—hydrogen coupling over a single bond.<sup>22</sup> The <sup>31</sup>P NMR spectrum of **1a** contains a single phosphorus resonance centered at 2.91 ppm and appears as a triplet in the proton-coupled experiment. The proton-coupled <sup>31</sup>P NMR spectrum of **1b** shows a doublet at 100 ppm, the downfield shift being attributed to deshielding of the phosphorus nucleus by the replacement of a hydrogen atom by a more electronegative carbon atom.<sup>22–24</sup> The structures of **1a** and **1b** were confirmed by single-crystal X-ray diffraction studies (*vide infra*).

The possibility of derivatizing 1b by reaction at the phosphorus atom was investigated. Complexes 3a and 3b were prepared by addition of Mn(CO)5Br and AuPPh3Cl, respectively, to a solution of [2b]<sup>-</sup>, which was prepared by treating 1b with one equivalent of *n*-butyllithium at -76 °C. The reaction of  $[2b]^{-}$  with AuPPh<sub>3</sub>Cl appeared to proceed rapidly and cleanly when monitored by IR spectroscopy, and 3b was isolated with a relatively good yield of 73%. By contrast, 3a was isolated with a significantly lower yield of 17%. This difference in isolated yields may be accounted for in several ways. First, the pseudotetrahedral phosphorus atom of 2b is already sterically crowded due to the presence of the phenyl ring and the carbonyl ligands of the attached metal centers (see Figure 8), and the reaction with the sterically encumbered Mn(CO)<sub>5</sub>Br fragment would be expected to be less favorable than the reaction with AuPPh<sub>3</sub>Cl, which is more accessible. Additionally, the reaction of 2b with Mn(CO)5Br

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Figure 1. FTIR spectra of 1a before (A) and after (B) deprotonation to form  $[4]^-$  in THF. The peaks marked with an asterisk (\*) were used as reference peaks for *in situ* IR studies.

is prone to redox side-reactions, as evidenced by the formation of  $Mn_2(CO)_{10}$ . Finally, **3b** was observed to exhibit thermal instability and decomposed slowly in solution and in the solid state. Davies and co-workers have reported similar instability during the preparation of  $Cp_2Mo_2(CO)_4$ -( $\mu$ -H)[ $\mu$ -PH(Mn(CO)<sub>5</sub>)].<sup>10</sup>

The <sup>31</sup>P NMR spectrum of **3a** displays a singlet at 144 ppm that exhibits considerable broadening due to coupling to two quadrupolar Mn nuclei (I = 5/2). The <sup>31</sup>P NMR spectrum of **3b** contains a doublet centered at 43.0 ppm (PPh<sub>3</sub>) and another doublet centered at 151 ppm ( $\mu$ -PPh(AuPPh<sub>3</sub>)), the large <sup>2</sup>J<sub>PP</sub> value of ~280 Hz indicating a nearly linear P-Au-P bond angle, as confirmed by the X-ray structure (*vide infra*). The downfield shifting of the phosphorus resonances of **3a** and **3b** reflects the deshielding of the phosphorus nuclei by addition of metals with larger Pauling electronegativities. The molecular structures of **3a** and **3b** (Figures 8 and 9) derived from X-ray diffraction experiments are consistent with the spectroscopic data.

Similar attempts at metalation using **1a** were made using a variety of reaction conditions. Deprotonation of **1a** using potassium *tert*-butoxide or sodium hydride at room temperature or 0 °C gave rise to a product  $M^+[4]^- (M^+ = K^+ \text{ or Na}^+)$  that decomposed upon removal of solvent. The infrared spectrum of this product (Figure 1) in solution appeared more complex than the shift toward lower wavenumbers that one would expect from simple deprotonation of **1a**. Furthermore, the complete consumption of **1a** was observed even when substoichiometric amounts of base were used.

In order to study this result in more detail, a careful titration of **1a** with potassium *tert*-butoxide was performed, and the reaction was monitored using *in situ* infrared spectroscopy. The strong IR peak at 2039 cm<sup>-1</sup> of **1a** and the peak at 1920 cm<sup>-1</sup> of the unknown product [**4**]<sup>-</sup> were selected as representative peaks to monitor the concentrations of each species in solution. Figure 2 contains a plot depicting the change in the absorbance values of the representative peaks as a function of the amount of base added. According to this plot, the representative peak for **1a** at 2039 cm<sup>-1</sup> had a maximum absorbance when no base had been added, and the absorbance decreased linearly with incremental base addition, reaching a minimum when 0.50 molar equiv of base had



Figure 2. Change in the absorbance of representative peaks of 1a and  $[4]^-$  as a function of the amount of base added.



**Figure 3.** Experimental (A) and simulated (B) <sup>1</sup>H NMR (500 MHz) spectrum of [4]<sup>-</sup> in THF- $d_8$ . The peaks indicated by (\*) and (\*\*) arise from residual THF and *tert*-butanol, respectively. The large <sup>1</sup>J<sub>HP</sub> coupling constants are indicated, while the <sup>3</sup>J<sub>HP</sub> and <sup>2</sup>J<sub>HH</sub> coupling constants have been omitted for clarity.

been added. Conversely, the representative peak for  $[4]^-$  at 1920 cm<sup>-1</sup> displayed minimum absorbance before base addition and increased linearly with base addition, attaining a maximum absorbance at 0.50 equivalents of base. In both cases, the absorbance reached one-half of the maximum absorbance after 0.25 molar equiv of base had been added. On the basis of these data and the reaction stoichiometry, we began to suspect that deprotonated **1a** underwent a coupling reaction with its neutral parent compound.

<sup>31</sup>P and <sup>1</sup>H NMR data support the hypothesis of a baseinduced coupling reaction. The proton-coupled <sup>31</sup>P NMR spectrum obtained after treating 1a with 0.50 equivalents of potassium tert-butoxide in THF-d<sub>8</sub> showed complete consumption of 1a and two new phosphorus resonances at -74.0 and 97.6 ppm. Unfortunately, coupling constants and multiplicities could not be determined from these peaks due to their considerable width, each peak having a full width of ~600 Hz at one-half of the maximum intensity due to coupling to quadrupolar manganese nuclei. The <sup>1</sup>H NMR spectrum, however, provides much more insight into the structure of [4]<sup>-</sup>. This spectrum, shown in Figure 3, is characterized by a first-order [ABMX] spin system and a first-order [AMX] spin system. The [ABMX] system is manifested as a pair of doublets of doublets (ddd) centered at 3.14 and 3.04 ppm arising from two geminal diastereotopic protons HA and  $H_B (^2 J_{HH} = 6.25 \text{ Hz})$ . The geminal protons  $H_A$  and  $H_B$  appear to reside on a single common phosphorus atom, as evidenced by



Figure 4. Proposed structure of complex  $M^+[4]^-$  ( $M^+ = Li^+$ ,  $Na^+$ ,  $K^+$ ).

large  ${}^{1}J_{\text{HP}}$  coupling constants of 295 and 292 Hz for H<sub>A</sub> and H<sub>B</sub>, respectively. The coupling of H<sub>A</sub> and H<sub>B</sub> to a second phosphorus nucleus completes the observed ddd pattern, the coupling constants being consistent with coupling over three bonds ( ${}^{3}J_{\text{H}_{A}\text{P}} = 12.4 \text{ Hz}$ ,  ${}^{3}J_{\text{H}_{B}\text{P}} = 13.8 \text{ Hz}$ ). The [AMX] spin system observed in Figure 3 appears as a doublet of doublets and arises as a result of a single proton H<sub>C</sub> coupling to two phosphorus atoms with coupling constants  ${}^{1}J_{\text{HP}} = 243 \text{ Hz} \text{ and } {}^{3}J_{\text{HP}} = 19.6 \text{ Hz}$ , indicating that H<sub>C</sub> is directly bound to one phosphorus atom but is additionally arranged so that it can couple to a second phosphorus atom over three bonds.

On the basis of the NMR and in situ IR data, we have assigned  $M^{+}[4]^{-}$  ( $M^{+} = Li^{+}$ ,  $Na^{+}$ ,  $K^{+}$ ) the structure shown in Figure 4. Negative-ion electrospray mass spectrometry of  $M^{+}[4]^{-}$  displays a base peak with m/z = 734.63, which is twice the mass of **1a** less a proton, supporting the hypothesis that 1a undergoes base-induced coupling without loss of any CO ligands. Thus, it is likely that the condensation reaction results in the breaking of a Fe-Mn bond in order to satisfy the EAN rule at all metal sites. The absence of peaks in the region 1900 to 1700 cm<sup>-1</sup> in the IR spectrum also indicates that isomers containing bridging carbonyls are not present in [4]<sup>-</sup>. We have rationalized the connectivity of [4]<sup>-</sup> based on the EAN rule, the terminal Fe(CO)<sub>4</sub> fragment being satisfied by a two-electron dative bond from phosphorus, and manganese assuming the common LMn(CO)<sub>4</sub>X motif, where  $L = [FeMn(CO)_8(\mu-PH)]^-$  and  $X = [Fe(CO)_4PH_2]^-$ . Lindner and Funk proposed a similar, albeit charge-neutral, bonding arrangement upon treating  $FeMn(CO)_8(\mu-PPh_2)$  with trimethylphosphine.<sup>25</sup> The alternative possibility in which addition occurs at the iron atom of 1a to produce a terminal  $Mn(CO)_4$  group is less likely, as the EAN rule would not be satisfied for at least one of the metal centers. Five-coordinate  $Mn(CO)_4L$  species are rare, and in order for the metal center to achieve an 18-electron count, it would need to be the location of a negative charge. This does not fit the chemistry of the system, as the negative charge should reside on the phosphorus atom of the  $[FeMn(CO)_8(\mu-PH)]^-$  fragment to produce an anionic twoelectron donor that adds to the metal center of an adjacent molecule of **1a**. Additionally, one would expect a  $Mn(CO)_4L^{-1}$ complex to readily undergo protonation to produce an octahedral HMn(CO)<sub>4</sub>L species. No reaction, however, is observed when  $[4]^-$  is treated with acid.

In an effort to achieve deprotonation while avoiding coupling, a solution of 1a in THF was cooled to -40 °C and treated with *n*-butyllithium, and the reaction was monitored by *in situ* IR spectroscopy. Under these conditions, complete consumption



Figure 5. FTIR spectra of (A)  $FeMn(CO)_8[\mu-PPh(AuPPh_3)]$ (3b) and (B) product of reaction of [2a]<sup>-</sup> with AuPPh\_3Cl in THF.

of 1a was not observed until 1.0 molar equiv of n-butyllithium had been added, suggesting that the previously observed coupling was inhibited at lower temperatures, favoring complete deprotonation to form the ion [2a]<sup>-</sup>. The IR spectrum of the product displayed similar peak patterns and intensities to **1a**, but was shifted to lower wavenumbers by approximately 40-50 units, as one would predict from the formation of an anion by simple deprotonation and as is observed during the formation of [2b]<sup>-</sup> (see Supporting Information). Continued monitoring of the characteristic peaks of  $[2a]^-$  at -40 °C revealed that the intensities of the peaks diminished linearly over time, becoming unobservable after 30 min and giving rise to a product characterized by a broad distribution of peaks in the range  $1980-1830 \text{ cm}^{-1}$  (see Supporting Information). Although the latter material was not isolated, it was observed that brief exposure to the atmosphere lead to rapid conversion to [4]<sup>-</sup>, suggesting the possibility that [2a]<sup>-</sup> may first condense to form a dianionic dimer that is readily protonated upon contact with ambient moisture.

In an attempt to trap [2a]<sup>-</sup>, AuPPh<sub>3</sub>Cl was added to a solution of 1a immediately after deprotonation with *n*-butyllithium at -40 °C. IR spectroscopy indicated rapid consumption ( < 10 s) of [2a]<sup>-</sup>. The product formed from this reaction was observed to decompose gradually in solution and rapidly decomposed as the solvent was removed. Although the product of this reaction could not be isolated for complete analysis, the infrared spectrum in THF is markedly similar to that of FeMn-(CO)<sub>8</sub>[ $\mu$ -PPh(AuPPh<sub>3</sub>)] (3b), indicating that the desired product FeMn(CO)<sub>8</sub>[ $\mu$ -PH(AuPPh<sub>3</sub>)] was likely formed (Figure 5). The instability of [4]<sup>-</sup> and FeMn(CO)<sub>8</sub>[ $\mu$ -PH(AuPPh<sub>3</sub>)] toward concentration and solvent removal may be a result of the high reactivity of the P–H bond of the triply bridging phosphide.

**Structural Analysis.** X-ray quality single crystals of **1a** and **1b** were grown by slow sublimation at 30 °C and approximately  $10^{-7}$  Torr, and their molecular structures were determined (Figure 6). Selected bond angles and distances for **1a**, **1b**, and the analogous diphenyl complex FeMn(CO)<sub>8</sub>- $(\mu$ -PPh<sub>2</sub>) are given in Table 1. In all three cases, the bridging phosphorus atom adopts a distorted tetrahedral geometry with acute M–P–M bond angles of 78.887(30)° for **1a**, 78.599(69)° for **1b**, and 77.8(2)° for FeMn(CO)<sub>8</sub>( $\mu$ -PPh<sub>2</sub>). The M–M bond lengths of **1a** (2.8374(8) Å) and **1b** (2.8361(16) Å) are very similar, differing from the M–M bond length of FeMn(CO)<sub>8</sub>( $\mu$ -PPh<sub>2</sub>) by only 0.02 Å.

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Figure 6. Molecular structure of 1a (left) and 1b (right). The thermal ellipsoids are shown at the 30% probability level with the exception of the hydrogen atoms, which were refined isotropically. Optimal refinement was achieved by treating the occupancies of the metal centers as a statistical mixture.

Table 1. Selected Bond Lengths and Angles for Complexes 1a, 1b, and FeMn(CO)<sub>8</sub>( $\mu$ -PPh<sub>2</sub>) (1c)

	1a	1b	1c <sup>28</sup>			
	Lengths (Å)					
Fe/Mn1-Fe/Mn2 Fe/Mn1-P1 Fe/Mn2-P1 P1-H P1-C	2.8374(8) 2.2328(9) 2.2334(10) 1.23(4), 1.35(3)	2.8361(16) 2.2521(21) 2.2255(22) 1.15(5) 1.8199(61)	2.8182(8) 2.2498(1) 2.2457(11) 1.8250(34), 1.8297(34)			
Angles (deg)						
Fe/Mn1-P1-Fe/Mn2 R <sub>1</sub> -P1-R <sub>2</sub> (R = H or C)	78.887(30) 101(2)	78.599(69) 102(2)	77.641(64) 100(2)			

Structural comparisons between 1a and 1b and isoelectronic homometallic dinuclear complexes containing iron and manganese can also be made. The Fe-Fe bond length in Cp<sub>2</sub>Fe<sub>2</sub>- $(CO)_2(\mu-H)(\mu-PHMes)$  is 2.6969(6) Å, considerably shorter than the M-M bonds of 1a and 1b.<sup>26</sup> Conversely, the Mn-Mn distance (2.937(5) Å) in Mn<sub>2</sub>(CO)<sub>8</sub>( $\mu$ -PPh<sub>2</sub>)( $\mu$ -H) is longer than the M-M distance observed in 1a and 1b.<sup>27</sup> Interestingly, the M-M distance in 1a and 1b very nearly matches the arithmetic mean of the M-M distances in Cp<sub>2</sub>Fe<sub>2</sub>(CO)<sub>2</sub>- $(\mu$ -H) $(\mu$ -PHMes) and Mn<sub>2</sub>(CO)<sub>8</sub> $(\mu$ -PPh<sub>2</sub>) $(\mu$ -H). The major differences between 1a and 1b are the torsion angles between complementary carbonyl ligands on opposite metal centers, shown in Figure 7. The twisting observed in 1b likely results from the minimization of steric interactions between the phenyl ring and equatorial CO ligands. The twisting observed in **1b** is absent in  $FeMn(CO)_8(\mu-PPh_2)$ , presumably because the steric interactions between phenyl rings and equatorial CO ligands are equally distributed on both faces of the molecule.

The molecular structures of 3a and 3b are presented in Figures 8 and 9. The steric congestion around the triply bridging phosphorus atom and the six-coordinate manganese atom in 3a is readily apparent and may contribute to the low yields obtained for 3a, as mentioned earlier. The M-M bond of 3a remains intact after deprotonation and metalation of 1b

and is only slightly shorter than the M-M bond lengths in 1a and 1b.

The triply bridging phosphorus atom of **3b** is less sterically crowded than the phosphorus atom of **3a** due to the longer P-Au-P distance separating the bulky triphenylphosphine group from the rest of the molecule. Similar to **3a**, the M-M bond of **3b** also remains intact upon metalation and is also slightly shorter than the M-M bonds observed in **1a** and **1b**. The P-Au-P bond angle (173.7(3)°) is slightly less than the ideal angle of 180°. A similar deviation from the ideal 180° P-Au-P bond angle was observed in the isoelectronic homometallic complex Mn<sub>2</sub>(CO)<sub>8</sub>[ $\mu$ -P(Cy)(AuPCy<sub>3</sub>)]( $\mu$ -H), which was reported to have a P-Au-P angle of 171.12(5)°.<sup>29</sup>

### Conclusions

Complexes 1a and 1b represent rare examples of dinuclear heterometallic complexes containing a  $\mu$ -PH<sub>2</sub> or  $\mu$ -PRH functionality. Although structurally similar, these two complexes differ greatly in their reactivities. 1b can be deprotonated and metalated to yield the isolable complexes 3a and 3b, which contain a triply bridging phosphorus atom. By contrast, deprotonation of **1a** at room temperature leads to rapid and complete coupling with the parent complex to form complex  $M^{+}[4]^{-}(M^{+} = Li^{+}, Na^{+}, K^{+})$ , which decomposes upon concentration. At lower temperatures, coupling of 1a and [2a]<sup>-</sup> is arrested and metalation of [2a]<sup>-</sup> can be achieved via addition of AuPPh<sub>3</sub>Cl. However, the product of this metalation decomposes slowly in solution and rapidly decomposes as the solvent is removed. Further investigation will be necessary to determine how the reactivity of 1a can be exploited in the preparation of higher nuclearity complexes.

#### **Experimental Section**

General Considerations. All manipulations were carried out under an argon atmosphere using standard Schlenk techniques in order to exclude moisture and oxygen. Argon was prepurified

<sup>(26)</sup> Sugiura, J.; Kakizawa, T.; Hashimoto, H.; Tobita, H.; Ogino, H. Organometallics 2005, 24, 1099.

<sup>(27)</sup> Doedens, R. J.; Robinson, W. T.; Ibers, J. A. J. Am. Chem. Soc. **1967**, *89*, 4323.

<sup>(28)</sup> Vahrenkamp, H. Z. Naturforsch., B: Anorg. Chem., Org. Chem. **1975**, 30B, 814. The CIF file previously deposited with the Cambridge Crystallographic Data Center (CCDC) does not include atomic coordinates. Therefore, the bond lengths and angles reported in Table 1 are the results of data collected and refined in our laboratory. A complete CIF file for this complex can be found in the Supporting Information and has also been deposited with the CCDC.

<sup>(29)</sup> Flörke, U.; Haupt, H. J. Acta Crystallogr., Sect. C: Cryst. Struct. Commun. 1995, 51, 573.



**Figure 7.** Projections of **1a** (left), **1b** (center), and FeMn(CO)<sub>8</sub>( $\mu$ -PPh<sub>2</sub>)<sup>28</sup> (right) down the metal-metal bond showing the differences in torsion angles between complementary carbonyl ligands. Oxygen atoms have been omitted for clarity. Only the ipso carbons of the phenyl rings have been shown.



**Figure 8.** Molecular structure of **3a** with thermal ellipsoids at the 30% probability level. For clarity, only the ispo carbon (C141) of the phenyl ring is shown. Selected bond distances (Å) and angles (deg): Fe/Mn1A–Fe/Mn1B 2.7954(9), Fe/Mn1A–P1 2.3067(10), Fe/Mn1B–P1 2.2891(11), P1–Mn3A 2.4774(11); Fe/Mn1A–P1–Fe/Mn1B 74.9(6).



Figure 9. Molecular structure of 3b with ellipsoids shown at 30% probability. Selected bond distances (Å) and angles (deg): Fe/Mn1–Fe/Mn2 2.7894(7), Fe/Mn1–P1 2.2969(9), Fe/Mn2–P1 2.2785(9), Au1–P1 2.3126(8), Au1–P2 2.3009(8); Fe/Mn1–P1–Fe/Mn2 75.1(6), P1–Au1–P2 173.7(3).

by passing through columns of BTS catalyst and molecular sieves. All solvents were dried and distilled prior to use according to standard procedures.<sup>30</sup> P(SiMe<sub>3</sub>)<sub>3</sub>, Mn(CO)<sub>5</sub>Br, and Fe(CO)<sub>4</sub>PPhH<sub>2</sub> were prepared according to literature procedures.<sup>23,31,32</sup> Fe(CO)<sub>4</sub>PH<sub>3</sub> was prepared using a modified literature procedure.<sup>24</sup> AuPPh<sub>3</sub>Cl and Fe(CO)<sub>5</sub> were purchased from Strem and used without further purification. Potassium

(30) Perrin, D. D.; Armarego, W. L. Purification of Laboratory Chemicals; Pergamon Press: New York, 1993.

*tert*-butoxide was purchased from Sigma-Aldrich and was sublimed prior to use. General infrared (FTIR) spectra were obtained using a Thermo-Nicolet 670 FT-IR with a 0.1 mm  $CaF_2$  cell. *In situ* FTIR data were collected on a Mettler Toledo 45m ReactIR system using an immersion probe with a silicon sampling tip coupled to a silver halide fiber. <sup>1</sup>H and <sup>31</sup>P NMR data were recorded on Bruker spectrometers operating at 400 MHz (162 MHz for <sup>31</sup>P) or 500 MHz (202 MHz for <sup>31</sup>P).

Modified Synthesis of Fe(CO)<sub>4</sub>PH<sub>3</sub>. P(SiMe<sub>3</sub>)<sub>3</sub> (2.50 mL, 8.61 mmol) and Fe(CO)<sub>5</sub> (1.30 mL, 9.89 mmol) were added to a standard Schlenk flask and dissolved in 100 mL of THF. The flask was then irradiated with a 450 W mercury-vapor UV lamp for 4 h. After irradiation, THF and unreacted Fe(CO)<sub>5</sub> were removed under reduced pressure, and the remaining residues were redissolved in diethyl ether and cooled to 0 °C. Methanol (2.10 mL, 51.9 mmol) was added dropwise, and the reaction mixture was stirred at 0 °C for 20 min in the dark. Diethyl ether and unreacted methanol were removed in vacuo at 0 °C, leaving behind a brown solid residue. The Schlenk flask was then fitted with a jacketed condenser and a stopcock, and the assembly was placed in a horizontal position and connected to a vacuum line  $(10^{-7} \text{ Torr})$ . The jacketed condenser was filled with liquid nitrogen, and pure Fe(CO)<sub>4</sub>PH<sub>3</sub> was sublimed from the Schlenk flask into the cooled condenser. The sublimation apparatus was refilled with argon, and the pale yellow Fe(CO)<sub>4</sub>PH<sub>3</sub> was transferred to a tared Schlenk flask under a vigorous flow of argon (1.11 g, 64% yield based on phosphorus). Spectral analysis of the solid was consistent with data reported elsewhere.24

 $FeMn(CO)_8(\mu-PH_2)$  (1a). Freshly prepared  $Fe(CO)_4PH_3$ (498 mg, 2.47 mmol) was added to a Schlenk flask and dissolved in 50 mL of THF. The solution was cooled to 0 °C, and one equivalent (255 µL, 2.47 mmol) of diethylamine was added. The solution was stirred at 0 °C for five minutes, followed by the addition of 679 mg (2.47 mmol) of Mn(CO)<sub>5</sub>Br. The reaction was covered with a dark cloth and stirred at 0 °C for four hours. The solvent was removed under reduced pressure, and the residue was chromatographed on silica using hexane as the eluent. The hexane was removed under reduced pressure, leaving red-orange crystals that could be further purified by sublimation (467 mg, 51% yield). Single crystals for X-ray diffraction studies were obtained by slow sublimation in a Schlenk tube at 30 °C and 10<sup>-7</sup> Torr. IR (hexanes,  $cm^{-1}$ ):  $\nu_{CO}$  2096 (w), 2042 (s), 2026 (w), 2017 (vs), 2007 (m), 1992 (w), 1971 (w), 1963 (m), 1942 (vw). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  3.00 (d, <sup>1</sup>J<sub>HP</sub> = 364 Hz, 2H). <sup>31</sup>P NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>, H<sub>3</sub>PO<sub>4</sub> standard):  $\delta$  2.91 (t, <sup>1</sup>J<sub>PH</sub> = 365 Hz). MS(EI): *m*/*z* 367.8 (M<sup>+</sup>), 339.8 (M<sup>+</sup> - CO), 311.8 (M<sup>+</sup> - 2CO), 283.8 (M<sup>+</sup> - 3CO), 255.8  $(M^+ - 4CO), 227.8 (M^+ - 5CO), 199.8 (M^+ - 6CO), 171.8 (M^+ - 6CO))$ 7CO), 143.8 (M<sup>+</sup> - 8CO). Anal. Calcd for FeMnC<sub>8</sub>O<sub>8</sub>PH<sub>2</sub>: C, 26.12; H, 0.55. Found: C, 25.79; H, 0.74.

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Table 2. X-ray Collection and Refinement Parameters for Complexes 1a, 1b, 3a, and 3b

	<b>1</b> a	1b	3a	3b
formula	C <sub>8</sub> H <sub>2</sub> FeMnO <sub>8</sub> P	C <sub>14</sub> H <sub>6</sub> FeMnO <sub>8</sub> P	C <sub>19</sub> H <sub>5</sub> FeMn <sub>2</sub> O <sub>13</sub> P	C <sub>32</sub> H <sub>20</sub> AuFeMnO <sub>8</sub> P <sub>2</sub>
fw	367.86	443.95	637.93	902.18
cryst syst	triclinic	monoclinic	triclinic	orthorhombic
space group	$P\overline{1}$	$P2_1/c$	$P\overline{1}$	Pbcn
a (Å)	7.8647(8)	10.242(4)	12.325(2)	18.4784(14)
b(Å)	9.2226(10)	14.193(6)	14.204(3)	12.6296(9)
c(Å)	9.3681(10)	11.935(5)	14.926(3)	28.196(2)
α (deg)	90.966(2)	90.00	107.600(3)	90.00
$\beta$ (deg)	91.141(2)	97.927(8)	106.384(3)	90.00
$\gamma$ (deg)	110.032(2)	90.00	95.561(4)	90.00
$V(Å^3)$	638.06(12)	1718.4(13)	2341.8(8)	6580.3(8)
Z	2	4	4	8
$D_{\text{calc}} (g \cdot \text{cm}^{-3})$	1.915	1.716	1.809	1.821
$\lambda$ (Mo K $\alpha$ ) (Å)	0.71073	0.71073	0.71073	0.71073
<i>T</i> (K)	223(2)	293(2)	213(2)	213(2)
$\theta_{\rm max}$ (deg)	28.33	28.370	28.420	28.29
abs coeff $(mm^{-1})$	2.280	1.710	1.808	5.407
rflns (coll)	5030	20 831	23 216	76 896
rflns (unique)	2066	4226	9627	8102
params	181	230	649	407
F(000)	360	880	1256	3488
$R_1 \left[ I > 2\sigma(I) \right]$	0.0276	0.0775	0.0310	0.0249
$wR_2[I > 2\sigma(I)]$	0.0591	0.1328	0.0532	0.0551
GOF (on $F^2$ )	0.795	1.122	0.453	1.111

FeMn(CO)<sub>8</sub>(µ-PPhH) (1b). Fe(CO)<sub>4</sub>PPhH<sub>2</sub> (285 mg, 1.02 mmol) was added to a Schlenk flask and dissolved in 30 mL of THF. The solution was cooled to -76 °C, and one equivalent (1.02 mmol) of *n*-butyllithium was added dropwise, followed by the addition of Mn(CO)<sub>5</sub>Br (282 mg, 1.02 mmol). The solution was then transferred to a 0 °C bath and stirred for four hours. The solvent was removed in vacuo, and the oily residue was extracted with hexanes. The hexanes extract was concentrated and chromatographed on a silica column using hexanes as eluent. **1b** eluted jointly with  $Mn_2(CO)_{10}$ , which formed as a byproduct of the reaction. The collected fractions were concentrated and cooled to -40 °C for several days, whereupon red crystals of 1b and yellow crystals of Mn<sub>2</sub>(CO)<sub>10</sub> formed and were separated manually using a hand lens and were further purified by sublimation (93 mg, 21% yield). Single crystals suitable for X-ray diffraction studies were prepared by slow sublimation in a Schlenk tube at 30 °C and  $10^{-7}$  Torr. IR (hexanes, cm<sup>-1</sup>):  $\nu_{CO}$ 2092 (w), 2075 (vw), 2039 (s), 2024 (m), 2015 (vs), 2002 (m), 1988 (w), 1967 (m), 1957 (m). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.37 (m, 2H); 6.89 (m, 2H); 5.28 (d,  ${}^{1}J_{\text{HP}} = 357$  Hz, 1H).  ${}^{31}P$  NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>, H<sub>3</sub>PO<sub>4</sub> standard):  $\delta$  100 (d, <sup>1</sup>J<sub>PH</sub> = 357 Hz). MS(EI): m/z 443.8 (M<sup>+</sup>), 415.9 (M<sup>+</sup> – CO), 387.8 (M<sup>+</sup> – 2CO), 359.8  $(M^+ - 3CO), 331.8 (M^+ - 4CO), 303.9 (M^+ - 5CO), 275.9 (M^+ - 5CO), 275.9 (M^+ - 5CO))$ 6CO), 247.9 ( $M^+$  – 7CO), 219.9 ( $M^+$  – 8CO). Anal. Calcd for FeMnC<sub>14</sub>O<sub>8</sub>PH<sub>6</sub>: C, 37.88; H, 1.36. Found: C, 37.32; H, 1.32.

FeMn(CO)<sub>8</sub>[µ-PPh(Mn(CO)<sub>5</sub>)] (3a). A solution of 1b (132 mg, 0.297 mmol) in 30 mL of THF was cooled to -78 °C and treated with one equivalent (0.297 mmol) of *n*-butyllithium, whereupon the color of the solution changed from bright red-orange to dark red. Mn(CO)<sub>5</sub>Br (82.0 mg, 0.297 mmol) was then added, and the solution was removed from the cold bath and allowed to warm to room temperature. As the solution warmed, the color gradually became a lighter shade of red. The solution was stirred at room temperature for two hours, after which the solvent was removed under reduced pressure, leaving behind a viscous, oily residue. The residue was extracted with a 3:1 hexanes/toluene solution and filtered through diatomaceous earth. The filtrate was chromatographed on silica using 3:1 hexanes/toluene as eluent. The collected fractions that were not contaminated with  $Mn_2(CO)_{10}$  were dried *in vacuo*, redissolved in minimal pentane, and cooled to -40 °C for several days, whereupon red crystals of 3a formed (32.2 mg, 17% yield). 3a exhibits considerable thermal instability in solution and in the solid state, resulting in larger-than-expected deviations in the observed C and H

elemental analyses. IR (hexanes, cm<sup>-1</sup>):  $\nu_{CO}$  2117 (w), 2078 (m), 2061 (vw), 2036 (vs), 2015 (m), 1998 (m), 1992 (m), 1979 (w), 1955 (w), 1942 (w). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.70 (m, 1H); 7.45 (m, 1H); 6.83 (m, 3H). <sup>31</sup>P NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>, H<sub>3</sub>PO<sub>4</sub> standard):  $\delta$  144 (s, br). MS(EI): *m/z* 637.8 (M<sup>+</sup>), 609.8 (M<sup>+</sup> - CO), 553.8 (M<sup>+</sup> - 3CO), 525.8 (M<sup>+</sup> - 4CO), 497.8 (M<sup>+</sup> - 5CO), 469.8 (M<sup>+</sup> - 6CO), 441.8 (M<sup>+</sup> - 7CO), 413.8 (M<sup>+</sup> - 8CO), 385.8 (M<sup>+</sup> - 9CO), 357.8 (M<sup>+</sup> - 10CO), 329.8 (M<sup>+</sup> - 11CO), 301.8 (M<sup>+</sup> - 12CO), 273.8 (M<sup>+</sup> - 13CO), 218.9 (M<sup>+</sup> - 13CO, - Mn). Anal. Calcd for FeMn<sub>2</sub>C<sub>19</sub>O<sub>13</sub>PH<sub>5</sub>: C, 35.77; H, 0.79. Found: C, 35.07; H, 0.92.

FeMn(CO)<sub>8</sub>[µ-PPh(AuPPh<sub>3</sub>)] (3b). A solution of 1b (118 mg, 0.266 mmol) in 30 mL of THF was cooled to -78 °C and treated with *n*-butyllithium (0.266 mmol), causing the bright red-orange solution to darken. AuPPh<sub>3</sub>Cl (132 mg, 0.266 mmol) was then added, and the reaction mixture was removed from the cold bath and allowed to warm to room temperature. As the reaction mixture warmed, the dark coloration dissipated and the solution took on a bright orange-yellow color. The reaction mixture was stirred at room temperature for two hours, after which the solvent was removed in vacuo. The resulting residue was extracted with hexanes, passed through a short pad of silica gel, and dried under reduced pressure. The slightly oily residue was then dissolved in minimal CH<sub>2</sub>Cl<sub>2</sub>, layered with two volumes of hexanes, and placed in a -40 °C freezer. Red-orange crystals of **3b** formed after several days (176 mg, 73% yield). **3b** displays slight thermal instability in solution and in the solid state, resulting in larger-than-expected deviations in the observed C and H elemental analyses. The agreement between observed and calculated values for the elemental analyses improved when the shipping and holding times of the samples were reduced. IR (hexanes, cm<sup>-1</sup>):  $\nu_{CO}$  2076 (m), 2047 (w), 2022 (vs), 2008 (s), 1995 (s), 1980 (s), 1969 (m), 1947 (m), 1935 (m). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.97 (m, 2H); 7.23 (m, 6H), 6.99-6.86 (m, (400 MH2, C<sub>6</sub>D<sub>6</sub>): 0 7.97 (m, 211), 7.25 (m, 611), 0.99 0.80 (m, 12H). <sup>31</sup>P NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>, H<sub>3</sub>PO<sub>4</sub> standard):  $\delta$  151 (d, <sup>2</sup>J<sub>PP</sub> = 281 Hz); 43 (d, <sup>2</sup>J<sub>PP</sub> = 281 Hz). Anal. Calcd for FeMn-C<sub>32</sub>O<sub>8</sub>P<sub>2</sub>H<sub>20</sub>Au: C, 42.60; H, 2.23. Found: C, 41.93; H, 2.25. MS(EI) data for **3b** showed no evidence of the  $M^+$  ion or any readily identifiable fragments, leading us to conclude that the complex decomposed completely upon heating.

Deprotonation of 1a Using the Mettler Toledo 45m ReactIR System. A solution of 1a (85.0 mg, 0.230 mmol) in 50 mL of THF was titrated with successive 23.0  $\mu$ mol portions of potassium *tert*-butoxide until the presence of 1a could no longer be detected by *in situ* IR spectroscopy, which occurred after 0.115 mmol of KO'Bu had been added. After the addition of 0.115 mmol of KO'Bu, <sup>1</sup>H and <sup>31</sup>P NMR showed only peaks corresponding to [4]<sup>-</sup> and *tert*-butanol. Attempts to isolate K<sup>+</sup>[4]<sup>-</sup> for elemental and structural analysis resulted in decomposition, as evidenced by the formation of an insoluble brown solid upon concentration. IR (THF, cm<sup>-1</sup>):  $\nu_{CO}$  2080 (w), 2054 (m), 2043 (w), 2026 (m, sh), 2018 (vs), 1997 (s), 1942 (s), 1920 (s), 1868 (w). <sup>1</sup>H NMR (500 MHz, THF-*d*<sub>8</sub>):  $\delta$  3.32 (d, <sup>1</sup>*J*<sub>HP</sub> = 243 Hz, <sup>3</sup>*J*<sub>HP</sub> = 19.6 Hz, 1H); 3.14 (ddd, <sup>1</sup>*J*<sub>HP</sub> = 295 Hz, <sup>3</sup>*J*<sub>HP</sub> = 12.4 Hz, <sup>2</sup>*J*<sub>HH</sub> = 6.25 Hz, 1H); 3.04 (ddd, <sup>1</sup>*J*<sub>HP</sub> = 292 Hz, <sup>3</sup>*J*<sub>HP</sub> = 13.8 Hz, <sup>2</sup>*J*<sub>HH</sub> = 6.25 Hz, 1H). <sup>31</sup>P NMR (202 MHz, THF-*d*<sub>8</sub>, H<sub>3</sub>PO<sub>4</sub> standard):  $\delta$  98.0 (s, br); -74.0 (s, br). HRMS (ESI-TOF; negative-ion mode): calcd for [C<sub>16</sub>O<sub>16</sub>H<sub>3</sub>P<sub>2</sub>Mn<sub>2</sub>Fe<sub>2</sub>]<sup>-</sup> *m*/*z* 734.6356, found 734.6336 (M<sup>-</sup>).

Crystal Structure Determinations of 1a, 1b, 3a, and 3b. Diffraction data were collected on a Bruker SMART 1000 CCD diffractometer equipped with a Mo-target X-ray tube in a hemisphere with exposure times of 10-50 s. The collected

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(34) Sheldrick, G. M. *SADABS*, v. 5.1; University of Göttingen: Göttingen, 1997.

(35) Sheldrick, G. M. *SHELXTL*; University of Göttingen: Göttingen, 2001.

(36) Sheldrick, G. Acta Crystallogr., Sect. A: Found. Crystallogr. 2008, 64, 112.

(37) Brandenburg, K. *Diamond*, v. 3.2e; Crystal Impact GbR: Bonn, Germany, 2010.

frames were integrated with the Bruker SAINTPLUS software package and corrected for absorption effects using empirical methods (SADABS).<sup>33,34</sup> Structures were solved using direct methods and refined by full-matrix least-squares on  $F^2$  using the SHELXTL software package.<sup>35,36</sup> Optimum refinements were achieved by treating the iron and manganese sites as a statistical mixture of the two metal atoms. The hydrogen atoms bound to phosphorus in **1a** and **1b** were refined isotropically, and all other protons were assigned idealized locations. Anisotropic displacement parameters were assigned to all non-hydrogen atoms. All thermal ellipsoid plots were generated using the Diamond software package.<sup>37</sup> A summary of X-ray data collection and refinement parameters for complexes **1a**, **1b**, **3a**, and **3b** is given in Table 2. Crystallographic data in CIF format can be found in the Supporting Information.

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**Supporting Information Available:** Additional data from *in situ* IR spectroscopy studies, tables of X-ray data collection and refinement parameters, and crystallographic data in CIF format are available free of charge via the Internet at http:// pubs.acs.org.