

# Synthesis and Decarbonylation Reactions of Diiron Cyclopentadienyl Complexes with Bent-Phosphinidene Bridges

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The phosphinidene complexes  $[Fe_2Cp_2(\mu-PR)(\mu-CO)(CO)_2]$  (Cp =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>; R=Cy, Ph, Mes, Mes\*; Mes = 2,4,6-C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>, Mes\* = 2,4,6-C<sub>6</sub>H<sub>2</sub><sup>t</sup>Bu<sub>3</sub>) were readily prepared in high yields through a two-step procedure starting from the corresponding phosphine complexes  $[Fe_2Cp_2(\mu-CO)_2(CO) (PH_2R)$ ]. When R = Cy, Ph, Mes, the first step required the oxidation of the phosphine complex with 1 equiv of [FeCp<sub>2</sub>]BF<sub>4</sub>, this being followed by spontaneous dehydrogenation to yield the cationic phosphide complexes [Fe<sub>2</sub>Cp<sub>2</sub>(µ-PHR)(µ-CO)(CO)<sub>2</sub>]BF<sub>4</sub>, while the formation of the related PMes\*H-bridged complex required a double oxidation of the corresponding neutral precursor in the presence of a deprotonating agent. In all cases the final step involved the deprotonation of the above cations with strong bases such as M(OH) (M = Na, K). Attempts to decarbonylate the above phosphinidene complexes by either thermolysis or photolysis in solution gave results strongly dependent on the nature of R. Thus, the photolysis of the cyclohexylphosphinidene complex gave a mixture of the clusters  $[Fe_4Cp_4(u_3-PCy)_2(u_3-CO)(u-CO)(CO)]$  (Fe-Fe distances 2.6115(7) and 2.5332(8) Å) and [Fe<sub>3</sub>Cp<sub>3</sub>( $\mu_3$ -PCy)( $\mu$ -PCyH)( $\mu$ -CO)<sub>2</sub>], while the thermal decarbonylation of the mesitylphosphinidene complex in refluxing toluene gave the trinuclear derivative [Fe<sub>3</sub>Cp<sub>3</sub>( $\mu$ -PMes)- $(\mu$ -PMesH) $(\mu$ -CO)<sub>2</sub>(CO)], having a trigonal phosphinidene ligand bridging two iron atoms (Fe–P = 2.161(8), 2.165(8) Å). The formation of all these compounds presumably involves the participation of the corresponding intermediate complex  $[Fe_2Cp_2(\mu-PR)(\mu-CO)_2]$ , a species likely to contain a trigonal (four-electron-donor) phosphinidene ligand, not detected. In contrast, the supermesitylphosphinidene complex undergoes a C(Bu)-H oxidative addition to the P atom under mild thermal conditions to give the phosphine derivative  $[Fe_2Cp_2(\mu-CO)_2(CO){PH(CH_2CMe_2)C_6H_2}^{t}Bu_2]]$ , while its photolysis gave a mixture of the above phosphine complex and the phosphide-hydride derivatives *cis*- and *trans*-[Fe<sub>2</sub>Cp<sub>2</sub>( $\mu$ -H){ $\mu$ -P(CH<sub>2</sub>CMe<sub>2</sub>)C<sub>6</sub>H<sub>2</sub><sup>t</sup>Bu<sub>2</sub>}(CO)<sub>2</sub>], the latter resulting from the oxidative addition of a P-H bond to the dimetal center.

#### Introduction

The study of the synthesis and reactivity of phosphinidene (PR) complexes has constituted a very active area of research within the organometallic chemistry in the last three decades.<sup>1</sup> Most of this work has been devoted to the terminal bent-phosphinidene complexes, which are usually compared to carbenes and can be also classified as electrophilic or nucleophilic, depending on the nature of the metal fragments

to which these ligands are bound.<sup>1d,g,h</sup> In a simplified way, the M-P bonding in these complexes can be described as single and double, respectively (**A** and **B** in Chart 1), with a lone pair of electrons on the phosphorus atom in any case, which makes these compounds very reactive toward unsaturated organic molecules and useful in the synthesis of organophosphorus derivatives.<sup>1</sup>

In contrast, the chemistry of binuclear complexes bearing phosphinidene bridges (C–E in Chart 1) has remained comparatively little explored until recently, although the presence of multiple M–P bonding or lone pairs should render these molecules quite reactive toward unsaturated organic compounds or metal fragments. Within the chemistry of binuclear phosphinidene complexes, the number of diiron species described in the literature is comparatively scarce. Moreover, most of the reported compounds of this type were either thermally unstable (as the cyclopentadienyl complex [Fe<sub>2</sub>Cp<sub>2</sub>( $\mu$ -PPh)(CO)<sub>4</sub>])<sup>2</sup> or were transient species

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generated in situ from suitable precursors, such as  $[Fe_2\{\mu-P(N^iPr_2)\}_2(CO)_6]$ ,<sup>3</sup>  $[Fe_2(\mu-P'Bu)(CO)_6]$ ,<sup>4</sup>  $[Fe_3(\mu_2-PPh)(\mu_3-PPh)(CO)_9]^{n-}$  (n = 1, 2),<sup>5</sup> and  $[Fe_2(\mu-PPh)_2(CO)_6]^{2-}$ .<sup>6</sup> All these circumstances impose significant restrictions upon the study of the chemical behavior of the aforementioned complexes. Finally, there are just a couple of previous examples of isolable diiron phosphinidene complexes,  $[Fe_2\{\mu-P(OR)\}_2(CO)_6]^7$  and  $[Fe_2(\mu-PPh)_2(L_2)_2]^8$  both of them having bulky protecting groups ( $R = 4,2,6-C_6H_2Me^tBu_2$ ,  $^7L_2 = HC(CMeNC_6H_3^tPr_2)_2$ )<sup>8</sup> and a trigonal geometry around phosphorus, but no reactivity appears to have been developed around these complexes.

Recently, our group reported a high-yield synthetic procedure for new stable diiron complexes with bridging bent (or pyramidal)-phosphinidene ligands of the formula [Fe<sub>2</sub>Cp<sub>2</sub>(u-PR) $(\mu$ -CO) $(CO)_2$ ] (R = Cy (**3a**), <sup>9</sup> Ph (**3b**), <sup>9</sup> 2,4,6-C<sub>6</sub>H<sub>2</sub><sup>t</sup>Bu<sub>3</sub> or Mes\* (3d)<sup>10</sup>), using a two-step process. First, the phosphine complexes [Fe2Cp2(µ-CO)2(CO)(PRH2)] are transformed into the corresponding phosphide-bridged complexes [Fe<sub>2</sub>Cp<sub>2</sub>- $(\mu$ -PHR) $(\mu$ -CO)(CO)<sub>2</sub>]BF<sub>4</sub> via oxidation with [FeCp<sub>2</sub>]BF<sub>4</sub> coupled to dehydrogenation (R = Cy, Ph) or deprotonation  $(R = Mes^*)$  processes. In the second step, deprotonation of the cationic phosphide complexes with KOH or other strong bases gave the corresponding phosphinidene derivatives. Preliminary studies on the reactivity of the PCy-9,11 and PMes\*-bridged<sup>10</sup> complexes revealed that these highly nucleophilic complexes have a strong potential for the synthesis of novel organophosphorus ligands. This was confirmed by a recent detailed study on the reactions of these complexes toward diazoalkanes,<sup>1</sup> which led to the uncovering of three novel coordination modes for the phosphadiazadiene ligands.

In this paper we report full details, including complementary electrochemical experiments, of the synthetic procedure leading to the phosphinidene complexes **3a,b,d**, which we have further extended to include the new mesitylphosphinidene complex [Fe<sub>2</sub>Cp<sub>2</sub>( $\mu$ -PMes)( $\mu$ -CO)(CO)<sub>2</sub>] (**3c**; Mes = 2,4, 6-C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>). We also report our studies on the decarbonylation reactions of compounds **3a–d**, aimed to explore the

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possibility of generating diiron complexes of the type  $[Fe_2Cp_2-(\mu-PR)(\mu-CO)_2]$  with trigonal-phosphinidene bridges. As will be discussed below, such dicarbonyl derivatives actually might be formed but would in any case be very unstable, and only different triiron or tetrairon derivatives of these putative intermediates can be isolated from the corresponding reaction mixtures, with only one of them displaying a trigonal phosphinidene bridge.

#### **Results and Discussion**

Synthesis and Structural Characterization of Compounds 1. The phosphine complexes 1a-d were synthesized through a two-step procedure. First, a photochemically induced decarbonylation of [Fe<sub>2</sub>Cp<sub>2</sub>(CO)<sub>4</sub>] was carried out in MeCN at 263 K to give the tricarbonyl complex  $[Fe_2Cp_2(\mu-CO)_2-$ (CNMe)(CO)],<sup>13</sup> this having a coordinated acetonitrile molecule that is then easily displaced upon addition of the stoichiometric amount of the appropriate primary phosphine  $PRH_2$  (R = Cy, Ph, Mes, Mes\*) to give the corresponding derivative  $[Fe_2Cp_2(\mu-CO)_2(CO)(PRH_2)]$  (1a-d) in high yield. The IR spectra in solution for these compounds (Table 1) display two bands due to the C–O stretch of the bridging CO ligands, with the expected pattern (weak and strong, in order of decreasing frequencies) for a transoid relative positioning of these ligands,<sup>14</sup> and a third band in the region of the terminal C-O stretches of these groups. The frequency of the latter band suggests a transoid arrangement of the terminal ligands as well, by comparison with analogous diiron complexes described in the literature.<sup>15</sup> As expected, compounds 1a,b display a single resonance in the corresponding  ${}^{31}P{}^{1}H$  NMR spectra ( $\delta$  17.2 and 3.4 ppm, respectively). In contrast, compounds 1c,d exhibited two resonances with different intensities in each case (20:1 for 1c and 5:1 for 1d in  $CD_2Cl_2$  at room temperature), which we attribute to the presence in solution of a small amount of the corresponding cis isomer, in addition to the major (trans) isomer. These two isomers are in a solvent-dependent equilibrium, as denoted by the distinct ratios found in  $C_6D_6$  at room temperature (25:1 for 1c and 13:1 for 1d). This type of equilibrium has been studied in detail previously for analogous complexes such as  $[Fe_2Cp_2(\mu-CO)_2(CO){P(OPh)_3}]^{16}$ or even the tetracarbonyl dimer [Fe<sub>2</sub>Cp<sub>2</sub>(CO)<sub>4</sub>],<sup>17</sup> and therefore does not need to be discussed in detail.

Synthesis and Structural Characterization of Compounds 2. The removal of a hydrogen atom from the coordinated PRH<sub>2</sub> ligand of compounds 1 to give the corresponding

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compd	$\nu(\mathrm{CO})^a$	$\delta_{ m P} \left( J_{ m PP}  ight)^b$	$\delta_{ m H} \left( J_{ m HP}  ight)^c$
$[Fe_2Cp_2(\mu-CO)_2(CO)(PC_VH_2)]$ (1a)	1935 (s), 1770 (w), 1730 (vs)	$17.2^{d}$	3.28 (327) <sup>a</sup>
$[Fe_2Cp_2(\mu-CO)_2(CO)(PPhH_2)]$ (1b)	1939 (s), 1767 (w), 1732 (vs)	$3.4^{d}$	4.47 (342)
$[Fe_2Cp_2(\mu-CO)_2(CO)(PMesH_2)]$ (trans-1c)	1938 (m), 1772 (w), 1734 (vs)	-24.7	3.87 (345)
$[Fe_2Cp_2(\mu-CO)_2(CO)(PMesH_2)]$ ( <i>cis</i> -1c)		-27.9	× /
$[Fe_2Cp_2(\mu-CO)_2(CO)(PMes^*H_2)]$ (trans-1d)	1936 (m), 1772 (w), 1732 (vs)	-21.3	4.44 (343)
$[Fe_2Cp_2(\mu-CO)_2(CO)(PMes^*H_2)]$ ( <i>cis</i> -1d)		-24.7	4.51 (343)
$[Fe_2Cp_2(\mu-PCyH)(\mu-CO)(CO)_2]BF_4$ (2a)	2019 (vs), 1990 (w), 1833 (m)	$223.4^{d}$	8.13 (390)
$[Fe_2Cp_2(\mu-PPhH)(\mu-CO)(CO)_2]BF_4$ (cis, anti-2b)	2021 (vs), 1995 (w), 1834 (m)	189.6	9.10 (413)
$[Fe_2Cp_2(\mu-PPhH)(\mu-CO)(CO)_2]BF_4$ (cis, syn-2b)		184.5	
$[Fe_2Cp_2(\mu-PMesH)(\mu-CO)(CO)_2]BF_4$ (2c)	2026 (vs), 1998 (w), 1830 (m)	156.6	9.00 (397)
$[Fe_2Cp_2(\mu-PMes^*H)(\mu-CO)(CO)_2]BF_4$ (2d)	2028 (vs), 2000 (w), 1825 (m)	$181.7^{e}$	9.88 (385)
$[Fe_2Cp_2(\mu-PCy)(\mu-CO)(CO)_2] (3a)$	1977 (vs), 1940 (w), 1773 (m)	531.6 <sup>g</sup>	
$[Fe_2Cp_2(\mu-PPh)(\mu-CO)(CO)_2]$ (3b)	1988 (vs), 1952 (w), 1783 (m)	498.2	
$[Fe_2Cp_2(\mu-PMes)(\mu-CO)(CO)_2]$ (3c)	1989 (vs), 1951 (w), 1782 (m)	495.1	
$[Fe_2Cp_2(\mu-PMes^*)(\mu-CO)(CO)_2] (3d)$	1991 (vs), 1958 (w), 1769 (m)	593.4	
$[Fe_4Cp_4(\mu_3-PCy)_2(\mu_3-CO)(\mu-CO)(CO)]$ (4)	1896 (vs), 1740 (m), 1611 (m)	$352.2^{d}$	
$[Fe_3Cp_3(\mu_3-PCy)(\mu-PCyH)(\mu-CO)_2]$ (anti-5)	$1772 (vs), 1730 (w)^{h}$	495.8 (305), -16.1 (305)	0.49 (253)
$[Fe_3Cp_3(\mu_3-PCy)(\mu-PCyH)(\mu-CO)_2](syn-5)$	$1767(vs), 1725 (w)^{h}$	501.3 (286), -43.8 (286)	2.33 (304)
$[Fe_3Cp_3(\mu-PMes)(\mu-PMesH)(\mu-CO)_2(CO)]$ (syn-6)	1953 (vs), 1763 (w), 1724 (s)	761.4 (55), 25.5 (55)	6.44 (306)
$[Fe_3Cp_3(\mu-PMes)(\mu-PMesH)(\mu-CO)_2(CO)]$ (anti-6)		746.2 (51), 22.3 (51)	× /
$[Fe_2Cp_2(\mu-CO)_2(CO){PH(CH_2CMe_2)C_6H_2^{t}Bu_2}] (trans-7)$	1934 (m), 1772 (w), 1730 (vs)	36.8 <sup>g</sup>	$4.56(348)^{g}$
$[Fe_2Cp_2(\mu-CO)_2(CO)]PH(CH_2CMe_2)C_6H_2^{t}Bu_2](cis-7)$		37.5 <sup>g</sup>	× /
$[Fe_2Cp_2(\mu-H){\mu-P(CH_2CMe_2)C_6H_2^{t}Bu_2}(CO)_2] (trans-8)$	1926 (w, sh), 1908 (vs)	170.5	
$[Fe_2Cp_2(\mu-H){\mu-P(CH_2CMe_2)C_6H_2^{t}Bu_2}(CO)_2]$ (cis-8)	1939 (vs), 1901 (w)	167.6	

<sup>*a*</sup> Recorded in dichloromethane solution, with C–O stretching bands ( $\nu$ (CO)) in cm<sup>-1</sup>. <sup>*b*</sup> Recorded in CD<sub>2</sub>Cl<sub>2</sub> solutions at 290 K and 121.50 MHz unless otherwise stated;  $\delta$  in ppm relative to external 85% aqueous H<sub>3</sub>PO<sub>4</sub> and *J* in Hz. <sup>*c*</sup><sup>-1</sup>H NMR resonance for the hydrogen atoms bonded to phosphorus, recorded in CD<sub>2</sub>Cl<sub>2</sub> solutions at 290 K and 300 MHz unless otherwise stated;  $\delta$  in ppm relative to internal SiMe<sub>4</sub> and *J* in Hz. <sup>*d*</sup>In CDCl<sub>3</sub> solution. <sup>*e*</sup> Recorded at 162.00 MHz. <sup>*f*</sup> Recorded at 400.13 MHz. <sup>*g*</sup> In C<sub>6</sub>D<sub>6</sub> solution. <sup>*h*</sup> In toluene solution.

Scheme 1. Synthesis of the Phosphinidene Complexes 3



phosphide-bridged cations 2 was found to be strongly dependent on the particular phosphine ligand (Scheme 1). Thus, when R = Cy, Ph, Mes, the process was accomplished by oxidation of the phosphine complexes with 1 equiv of [FeCp<sub>2</sub>]BF<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> at 273 K, this being followed by a spontaneous and fast dehydrogenation leading directly to the corresponding complexes  $[Fe_2Cp_2(\mu-PHR)(\mu-CO) (CO)_2$ ]BF<sub>4</sub> (2a-c). In contrast, when R = Mes<sup>\*</sup>, the formation of the cationic phosphide complex required the addition of 2 equiv of the oxidizing agent and the presence of a weak base (NaHCO<sub>3</sub>). The best and more reproducible yields were obtained when using THF as solvent and a temperature of 243 K, although the formation of 2d can be also accomplished in CH<sub>2</sub>Cl<sub>2</sub>. In any case, it should be noted that the above reactions differ substantially from previous synthetic procedures to prepare related diiron cations, these relying on

Chart 2. Projections of the Possible Isomers of Compounds 2, Viewed along the Axis Joining the Bridging PRH and CO Ligands



decarbonylation or carbonylation reactions of phosphidebridged precursors.<sup>2,18</sup>

The IR spectra of compounds 2a-d display three C-O stretching bands with a similar pattern (Table 1). The low frequency of the band at ca.  $1830 \text{ cm}^{-1}$  is indicative of the presence of a bridging carbonyl, while the relative intensities of the bands at around  $2000 \text{ cm}^{-1}$  denote the presence of two terminal carbonyls almost parallel to each other.14 Compounds 2a,c,d display a single, quite deshielded resonance in the corresponding  ${}^{31}P{}^{1}H$  NMR spectrum, as expected for a complex having a phosphide ligand bridging two metal atoms connected by a metal-metal bond.<sup>19</sup> In contrast, compound 2b exhibits two resonances, also quite deshielded: a very intense one at 189.6 ppm and a weak one at 184.5 ppm, this being indicative of the presence of two isomers in solution. The major isomer is most likely to be the unique isomer present for the other complexes: that is, that with the R group pointing away from the Cp ligands (isomer cis, anti in Chart 2),

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Scheme 2. Reaction Pathway in the Formation of Compounds 2a-c



expectedly more favored on steric grounds. Out of the two other possible isomers for these compounds (Chart 2), we propose the cis,syn structure for the minor isomer of **2b**, due to the similar <sup>31</sup>P chemical shifts displayed by these isomers. It should be noticed that the R group in **2b** (Ph) is that having the smallest steric demands of the whole family of compounds **2**, thus reinforcing the hypothesis that the isomerism in these species is a matter governed by steric effects. We finally note that the above isomerism is reminiscent of that previously found for carbene-bridged diiron and diruthenium complexes of the type [M<sub>2</sub>Cp<sub>2</sub>( $\mu$ -CO)(CO)<sub>2</sub>( $\mu$ -CXY)] (X, Y = H, R, SR).<sup>20</sup>

Proposed Reaction Pathways in the Formation of Compounds 2. The formation of compounds 2a-c (Scheme 2) is obviously initiated by the removal of one electron from the corresponding phosphine complexes 1a-c, and this would give initially the paramagnetic cation A. In order to account for the dominant (cis) positioning of the Cp ligands in the products 2, as opposed to the trans arrangement dominant in the starting complexes 1, we propose that the intermediate A would completely rearrange into the corresponding cis isomer (**B**) possibly via an isomer  $\mathbf{A}'$  with only terminal ligands, as proposed previously for the neutral complexes [Fe2Cp2(µ- $CO_{2}(CO){P(OPh)_{3}}^{16}$  and  $[Fe_{2}Cp_{2}(CO)_{4}]^{17}$  That the cis structure **B** would be more stable than the trans isomer **A** in the paramagnetic cation would not be unusual. For instance, we have shown previously that the oxidation of the phosphide-hydride complexes *trans*- $[Fe_2Cp_2(\mu-H)(\mu-PPh_2) (CO)_2$ ] and trans- $[M_2Cp_2(\mu-H)(\mu-PPh_2)(CO)_4]$  (M = Mo, W) yields the paramagnetic cations  $[M_2Cp_2(\mu-H)(\mu-PR_2) (CO)_x$ ]<sup>+</sup> (x = 2, 4) specifically with a cis geometry.<sup>15f,21</sup> The

Scheme 3. Reaction Pathway in the Formation of Compound 2d



radical intermediate **B** would then undergo a fast dehydrogenation process to give the diamagnetic intermediate C with a terminal phosphide ligand, this finally rearranging into a bridging position to give compounds 2, specifically with a cis positioning of the terminal ligands. We note that a related dehydrogenation process most likely takes place in the reactions of the dinuclear radical species  $[Mo_2Cp_2(\mu-PR_2) (CO)_4$  with secondary phosphines HPR'<sub>2</sub> to give the mixed phosphide derivatives  $[Mo_2Cp_2(\mu-PR_2)(\mu-PR'_2)(CO)_2]^{22}$ Clearly, the key step in the formation of compounds 2 is the homolytic fission of a P-H bond in a radical species, as opposed to more common processes involving the oxidative addition of a P-H bond to multiple metal-metal bonds<sup>23</sup> or to an unsaturated mononuclear center,<sup>24</sup> and thus represents a novel synthetic entry to binuclear complexes having bridging organophosphide ligands.

According to the experimental observations, the formation of compound 2d follows a pathway different from that outlined above (Scheme 3). In the first place we must note that, if only 1 equiv of the ferrocenium salt is added to a solution of 1d in either CH<sub>2</sub>Cl<sub>2</sub> or THF at 243 K, then an NMR-silent purple solution is formed, probably containing the paramagnetic species  $[Fe_2Cp_2(\mu-\kappa^1:\eta^2-PMes^*H_2)(\mu-\kappa^1:\eta^2-PMes^*H_2)]$  $CO)(CO)_2$ ]BF<sub>4</sub> (**D**) instead of the expected diamagnetic phosphide complex. The intermediate **D** is a very air-sensitive species, and it has a lifetime of only a few minutes at temperatures above 243 K, decomposing into a mixture of several uncharacterized products and significant amounts of the tetracarbonyl dimer [Fe<sub>2</sub>Cp<sub>2</sub>(CO)<sub>4</sub>]. Although intermediate D does not react with excess [FeCp<sub>2</sub>]BF<sub>4</sub> itself, when a solution of **D** is stirred with a base such as  $Na_2CO_3$  or NaHCO<sub>3</sub>, it then undergoes a clean disproportionation to give an equimolar mixture of compounds 1d and 2d. At this point, the addition of another 1 equiv of the oxidizing agent under these conditions leads to the complete consumption of

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the phosphine complex 1d and almost quantitative formation of the phosphide derivative 2d. Of course, 2d is therefore more conveniently prepared in a single step by adding 2 equiv of  $[FeCp_2]BF_4$  to a solution of 1d in the presence of excess NaHCO<sub>3</sub>.

From the above data it is clear that intermediate D still retains a coordinated PR\*H2 ligand. In addition, an inspection of the IR spectra of different reaction mixtures in CH<sub>2</sub>Cl<sub>2</sub> suggests that at least two C-O stretching bands at 2010 (vs) and 1852 (m)  $\text{cm}^{-1}$  can be attributed to this intermediate. Actually, these bands are not very different from those of the final phosphide-bridged cation 2d. Hence, we propose for **D** a similar structure, with a bridging carbonyl and two terminal CO ligands arranged in a cis fashion, with the other bridging position being occupied now by a phosphine ligand bound to the second metal center through an agostic-type P-H····Fe interaction. As noted above, intermediate D does not react to a detectable extent with [FeCp<sub>2</sub>]BF<sub>4</sub> unless a base is present. It seems, therefore, that the oxidation of **D** to the corresponding diamagnetic dipositive cation  $[Fe_2Cp_2(\mu-\kappa^1:\eta^2-PMes^*H_2)(\mu-CO)(CO)_2]^{2+}$ (E) would be an unfavorable event unless it is coupled to a deprotonation step of the agostic phosphine, this leading to the phosphide-bridged cation 2d, a matter to be confirmed through the electrochemical studies described below. However, we should stress that a similar deprotonation/protonation relationship linking bridging agostic phosphine ligands to the corresponding bridging phosphide ligands has been recently reported by us for cations of the type  $[Mo_2Cp_2(\mu-\kappa^1:\eta^2 HPR_2(\mu - PR'_2)(CO)_2]^+$ .<sup>25</sup>

Cyclic Voltammetry Studies on Compounds 1a.d. In order to gain further insight into the different reaction pathways leading to compounds 2, cyclic voltammetry (CV) experiments were carried out for compounds 1a (Figure 1) and 1d (Figures 2 and 3) in CH<sub>2</sub>Cl<sub>2</sub>. We note first that the results obtained for compound 1a are fully consistent with the mechanism depicted in Scheme 2. Thus, we observe a nearly reversible wave at ca. -0.2 V (vs the FeCp<sub>2</sub><sup>+/0</sup> couple) when scanning at 200 mV s<sup>-1</sup>. However, when the scan rate is slowed to 50 mV  $s^{-1}$ , then the reduction wave almost disappears, which is consistent with an irreversible chemical transformation (dehydrogenation) taking place at the paramagnetic cation initially formed. Indeed, the second cycle displays a new and reversible wave at -1.23 V, not present in the first cycle (Figure 1), which is attributed to the formation of 2a. This was confirmed by an independent CV study carried out on the phosphide complex.

In contrast, the CV diagram of compound 1d shows a wave at a potential (ca. -0.15 V) slightly higher than that of 1a, as expected, but now this wave remains reversible regardless of the scan rate (Figure 2), while successive scans showed no traces of new waves attributable to the phosphide cation 2d (shown by independent CV experiments to give rise to a reversible wave at -1.14 V). This is in full agreement with our proposal that dehydrogenation does not take place after the initial oxidation of the phosphine complex 1d. A second, now irreversible, oxidation wave at ca. 0.73 V can be observed for 1d when scanning at higher potentials (Figure 3), this clearly indicating that the ferrocenium salt itself would not be able to further oxidize the paramagnetic cation initially formed to give the dipositive cation E, in agreement with our





Figure 1. CV of compound 1a, recorded at 200 mV s<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>, two cycles, from -2.0 to 0 V, starting at -0.6 V and sweeping toward negative potentials.



**Figure 2.** CV of compound **1d**, recorded at 200 mV s<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>, from 0 to -1.1 V, starting at -0.6 V and sweeping toward positive potentials.



**Figure 3.** CV of compound **1d**, recorded at 200 mV s<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>, from 1.15 to -1.0 V, starting at -0.6 V and sweeping toward positive potentials.

experimental data. Only when this process is coupled to a proton transfer reaction due to the presence of a base, as noted above, would the unfavorable thermodynamics to reach compound **2d** be overcome. A similar effect has been previously found in the chemical and electrochemical studies of the hydride derivatives  $[M_2Cp_2(\mu-H)(\mu-PPh_2)(CO)_4]$ (M = Mo, W),<sup>21</sup> where the second oxidation process to give  $[M_2Cp_2(\mu-H)(\mu-PPh_2)(CO)_4]^{2+}$  occurred irreversibly at a



Figure 4. ORTEP diagrams of compound 3b, with H atoms omitted for clarity (left, taken from ref 9), and of compound 3d, with H atoms and the p-<sup>t</sup>Bu group omitted for clarity (right, taken from ref 10).

potential higher than that of the ferrocenium cation (0.1-0.25 V), but only in the presence of a weak base, yielding the monopositive cations  $[M_2Cp_2(\mu-PPh_2)(CO)_4]^+$ . Unfortunately, in the case of **1d**, the return sweep to negative potentials after the second oxidation shows a greatly diminished reduction wave corresponding to the first oxidation process, this being indicative of hampered diffusion of the analyte to the surface of the working electrode, most probably due to adsorption of the decomposition products formed after the second and irreversible oxidation of **1d**, thus precluding the extraction of any further information from this experiment.

Synthesis and Structural Characterization of Compounds 3. The final step in the formation of compounds 3 involves the reversible deprotonation of the corresponding PHR-bridged precursors 2, this being one of the common procedures to generate pyramidal phosphinidene bridges.<sup>2b,26</sup> In our case, this can be conveniently accomplished using solid Na(OH) or K(OH), a process easily reversed by addition of HBF<sub>4</sub>·OEt<sub>2</sub> to the resulting complexes 3.

The solid-state structures of compounds 3b,d (Figure 4 and Table 2) were reported in our preliminary studies.<sup>9,10</sup> In both cases the overall geometries are very similar, with two FeCp-(CO) fragments arranged in a cis fashion and symmetrically bridged by a CO ligand and an arylphosphinidene ligand. The aryl group is positioned anti to the Cp ligands, a conformation presumably more favored on steric grounds and also dominant in the cationic precursors 2, as discussed above. The intermetallic distances in these compounds (ca. 2.58 Å) are consistent with the presence of a metal-metal single bond and are comparable to those measured for related cyclopentadienyl compounds having P and C atoms at the bridging positions, such as the phosphide-bridged complexes [Fe2Cp2{µ-P-(CH=CHPh)Ph  $(\mu-CO)(CO)_2$  OTf<sup>18</sup> and  $[Fe_2Cp(\mu-PMe_2) (\mu$ -CO)(CO)<sub>4</sub>]<sup>27</sup> (ca. 2.62 Å). The most remarkable feature in **3b**,**d** is of course the bridging bent-phosphinidene ligand, with the phosphorus atom in a pyramidal environment as denoted by the C(ipso)-P-Fe<sub>2</sub>(centroid) angles of ca. 120°. The Fe-P distances, ca. 2.26 Å for 3b and ca. 2.31 Å for 3d, are slightly longer than those found for the phosphide derivatives mentioned above (ca. 2.19 Å) and are consistent with single Fe-P bonds, as expected for a two-electron-donor, bent-

Table 2. Selected Bond Lengths (A) and Angles (deg	) for			
Compounds $3b_{d}$				

	<b>3b</b> <sup>9</sup>	$\mathbf{3d}^{10}$	
Fe-Fe	2.5879(4)	2.5763(5)	
Fe-CO <sup>t</sup>	1.756(2)	1.760(3)	
Fe-CO <sup>b</sup>	1.925(2)	1.913(3)	
Fe-P	2.262(1)	2.306(1)	
P-C(aryl)	1.845(2)	1.893(2)	
Fe-Fe-CO <sup>t</sup>	97.7(1)	99.5(1)	
P-Fe-CO <sup>t</sup>	91.5(1)	94.2(1)	
CO <sup>t</sup> -Fe-CO <sup>b</sup>	86.8(1)	86.0(1)	
Fe-P-C(aryl)	113.9(1)	113.4(1)	

<sup>*a*</sup> Values involving the iron atoms are averaged figures for Fe(1) and Fe(2); terminal and bridging CO ligands are identified with t and b superscripts, respectively.

phosphinidene ligand bearing a lone electron pair not involved in the binding to the metal centers. There are, however, some significant differences between both structures, most likely induced by the steric bulk of the supermesityl moiety in 3d: (a) a slight elongation (by ca. 0.05 Å) in both the P–C(aryl) and the already mentioned Fe-P lengths in 3d, (b) a strong deviation of the aryl ring of 3d from planarity, adopting an incipient boat conformation that takes the ortho <sup>t</sup>Bu groups away from the terminal Cp ( $H \cdots H = ca. 2.2 \text{ Å}$ ) and CO  $(H \cdots C/O = ca. 2.6 \text{ Å})$  ligands, and (c) a slight bending of the terminal carbonyls in **3d** away from the aryl group. We notice that similar "boat deformations" of supermesityl groups have been previously described in the literature for other molecules,<sup>28</sup> although that observed in **3d** seems particularly strong according to the tip angles for the ipso and para C atoms of the ring (ca. 22 and 10°, respectively).

The spectroscopic data in solution for compounds 3a-d are fully consistent with the solid-state structures just discussed. We first note that the IR spectra display three C–O stretching bands indicative of the retention in solution of a bridging CO and almost parallel terminal CO ligands, the pattern being similar to that of the parent cationic phosphide complexes **2**, but with the bands shifted to lower frequencies (by ca. 40 cm<sup>-1</sup>), as expected from the increased electron density in the phosphinidene complexes. The PR ligand in these compounds gives rise to a characteristic strongly deshielded resonance in the <sup>31</sup>P{<sup>1</sup>H} NMR spectra ( $\delta$  495–595 ppm, Table 1). For comparison, these shifts are higher than that of the recently reported diruthenium

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compound  $[Ru_2Cp^*_2(\mu$ -PPh)( $\mu$ -CO)(CO)\_2] (457 ppm),<sup>29</sup> a difference expected when comparing Fe and Ru complexes bridged by PR<sub>2</sub> or PR ligands.<sup>19</sup> However, we should stress that the huge difference between the chemical shift of the PMes\* complex (593.5 ppm) and those of the aryl compounds **3b**,**c** (ca. 500 ppm) is totally unexpected and is not observed in the compounds of type **1** and **2** (Table 1). Although obviously this large difference must be somehow related to the great steric demands of the Mes\* substituent in the phosphinidene ligand, currently we cannot offer a satisfactory explanation for this spectroscopic observation.

**Decarbonylation Reactions of Compounds 3a,b.** Decarbonylation reactions were attempted for both complexes either by heating of their toluene solutions or by irradiation with visible–UV light, but the results were quite different. In the case of the phenylphosphinidene complex **3b**, full decomposition takes place in toluene solution at 333 K after 1.5 h, with the dimer  $[Fe_2Cp_2(CO)_4]$  being the only new organometallic species detected in the solution at any time. Analogously, the photolysis of toluene solutions of **3b** from 243 to 293 K gave mainly the dimer  $[Fe_2Cp_2(CO)_4]$  in 0.5 h, along with trace amounts of other uncharacterized products.

In contrast, compound **3a** was found to be fairly robust thermally, because only a small amount of  $[Fe_2Cp_2(CO)_4]$ was formed after refluxing a toluene solution of the complex for 1 h. The full thermal degradation of **3a** under these conditions required about 5 h, but no other organometallic species (apart from the mentioned dimer) were present in the solution in significant amounts at any time. Fortunately, decarbonylation of **3a** could be accomplished photochemically, although it required prolonged reaction times (ca. 6 h) and gave modest yields of products, of which we have been able to isolate and characterize the tetranuclear cluster  $[Fe_4Cp_4(\mu_3-PCy)_2(\mu_3-CO)(\mu-CO)(CO)]$  (**4**) and the trinuclear isomers *syn*- and *anti*- $[Fe_3Cp_3(\mu_3-PCy)(\mu-PCyH)(\mu-CO)_2]$ (**5**) (Chart 3).

**Structural Characterization of Compound 4.** The structure of **4** in the crystal form (Figure 5 and Table 3) displays a central trimetal core built from three CpFe fragments defining an isosceles triangle, with a slightly asymmetric CO ligand bridging this triangle and a second CO ligand bridging the shorter edge. These carbonyl ligands and the Fe(2) atom are placed in a plane of symmetry containing the fourth





**Figure 5.** ORTEP diagram of compound 4, with H atoms and Cy groups (except the  $C^1$  atoms) omitted for clarity.

Table 3. Selected	Bond Lengths (Å)	and	Angles	(deg)	for
	Compound 4				

	1		
Fe(1)-Fe(2)	2.6115(7)	Fe(1)-C(1)	2.016(4)
Fe(1) - Fe(1)	2.5332(8)	Fe(2)-C(1)	1.956(5)
Fe(1) - P(1)	2.244(1)	Fe(1) - C(2)	1.903(4)
Fe(2) - P(1)	2.239(1)	Fe(4) - C(3)	1.727(5)
Fe(4)-P(1)	2.254(1)		
Fe(1) - P(1) - Fe(2)	71.3(1)	Fe(1) - C(1) - Fe(2)	82.2(2)
Fe(1) - P(1) - Fe(4)	125.1(1)	Fe(1) - C(1) - Fe(2)	77.8(2)
Fe(2)-P(1)-Fe(4)	105.2(1)		

metal fragment (Fe(CO)Cp). The corresponding metal atom (Fe(4)), however, is not directly bound to the metal triangle but is connected to it through two  $\mu_3$ -PCy ligands placed over the longest edges of the triangle. The phosphinidene-bridged Fe(1)-Fe(2) bonds have an intermetallic distance of 2.6115(7) Å, a figure comparable to the values measured for the phosphinidene derivatives **3b**,**d**, while the remaining Fe(1)-Fe(1) bond is considerably shorter (2.5332(8) Å), obviously because of the presence of two CO ligands bridging these metal atoms, with this figure being comparable to other intermetallic distances in complexes having a  $Fe_2(\mu$ - $CO_{2}$  core (cf. 2.534(2) and 2.531(2) Å for the trans and cis isomers of  $[Fe_2Cp_2(\mu-CO)_2(CO)_2]$ ).<sup>17</sup> All the Fe-P distances are almost identical (ca. 2.24 Å) and only marginally shorter than the single-bond figure measured for the binuclear phosphinidene complex 3b (ca. 2.26 Å), this indicating a fairly even distribution of the four bonding electrons of the PR ligands among the three metal centers in each case. Other structural parameters in this compound are as expected.

Spectroscopic data in solution for compound **4** are consistent with the solid-state structure discussed above. The retention of three carbonyls with different coordination modes is evident from the presence in the IR spectrum of three C–O stretching bands with very different frequencies, which can be respectively assigned to terminal (1898 cm<sup>-1</sup>),  $\mu_2$  (1746 cm<sup>-1</sup>), and  $\mu_3$  (1621 cm<sup>-1</sup>) carbonyl ligands. This is paralleled by the observation of very differently deshielded carbonyl resonances in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, at 303.0 ( $\mu_3$ -CO), 273.5 ( $\mu_2$ -CO), and 224.2 ppm (terminal CO), these being in the typical ranges for diiron complexes having

carbonyl ligands in those coordination modes.<sup>9,15c,15e,15f,30</sup> The phosphinidene ligands also remain equivalent in solution and give rise to a single <sup>31</sup>P resonance at 352.2 ppm, a chemical shift that falls in the expected range for phosphinidene ligands bridging three iron atoms.<sup>19,31</sup> Other spectroscopic data of **4** are as expected and deserve no detailed comment.

Structural Characterization of Compound 5. Spectroscopic data for the two isomers of compound 5 (Table 1 and Experimental Section) are similar to each other, thus indicating that these compounds share the same basic structure (Chart 3), which we propose to differ only in the relative conformation of the PHCy bridge with respect to the phosphinidene ligand, with the major isomer having the Cy groups away from each other (anti-5), presumably more favored on steric grounds. The relative arrangement proposed for the four bridging ligands (PCy, PHCy, and 2CO) present in both isomers of this 50-electron complex (therefore having only two metal-metal bonds according to the EAN formalism) is based on the solid-state structures found for related trinuclear clusters with two semibridging CO ligands, such as the carbyne-bridged complexes [MnMo<sub>2</sub>- $Cp_2Cp'(\mu_3-CH)(\mu-PCy_2)(CO)_4]$ , and  $[MnMo_2Cp_2Cp'(\mu_3-COMe)(\mu-PCy_2)(CO)_4]^{32}$  and the phosphinidene-bridged cluster  $[Fe_2MnCp(\mu_3-PPh)(CO)_8]$ ,<sup>33</sup> although all these species are 48-electron complexes with three intermetallic bonds. In the above Mo<sub>2</sub>Mn clusters, the phosphide ligand is placed close to the intermetallic plane, while the face-bridging ligand and the semibridging carbonyls are placed on different sides of the intermetallic plane, and this is the overall arrangement proposed for both isomers of 5.

The IR spectra for both isomers of 5 exhibit two C-O stretching bands at low frequencies that can be assigned to two CO ligands bridging two metal atoms an placed on the same side of the intermetallic plane, according to their relative intensities (very strong and weak in order of decreasing frequencies). Moreover, these ligands are related by symmetry, as deduced from the presence of a single and very deshielded carbonyl resonance at 281.2 ppm in the  ${}^{13}C{}^{1}H$ NMR spectrum of the major isomer. The <sup>31</sup>P NMR spectra show in each case a pair of mutually coupled resonances  $(J_{\rm PP} = \text{ca. 300 Hz})$ : a quite deshielded one at ca. 500 ppm, corresponding to a  $\mu_3$ -PCy ligand, and a strongly shielded one at around -30 ppm, corresponding to a PHCy ligand  $(J_{\rm PH} = \text{ca. } 250-300 \text{ Hz})$ . The low chemical shift of the latter resonance is characteristic of bridging phosphide ligands in the absence of metal-metal bonds,<sup>19,34</sup> while the observed P-P couplings are comparable to those measured for the related cluster  $[Fe_3(\mu-H)(\mu_3-PH)(\mu-PH_2)(CO)_9]$ .<sup>35</sup> The main



**Figure 6.** ORTEP diagram of compound **6**, with H atoms (except the P–H atom) and *p*-Me groups omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Compound 6

	1		
Fe(1)-Fe(2)	2.541(1)	Fe(1)-C(1)	1.912(5)
Fe(1) - P(1)	2.213(7)	Fe(1) - C(2)	1.905(6)
Fe(2)-P(2)	2.165(8)	Fe(2) - C(1)	1.906(5)
Fe(3) - P(1)	2.315(7)	Fe(2) - C(2)	1.934(6)
Fe(3) - P(2)	2.161(8)	Fe(3)-C(3)	1.729(6)
Fe(1) - P(1) - Fe(3)	122.4(3)	Fe(1) - Fe(2) - P(2)	93.0(1)
Fe(2) - P(2) - Fe(3)	132.5(4)	Fe(2)-Fe(1)-P(1)	100.4(1)
Fe(2) - P(2) - C(5)	111.2(4)	P(1)-Fe(3)-P(2)	83.5(3)
Fe(3) - P(2) - C(5)	114.9(4)		

spectroscopic differences between the syn and anti isomers of compound **5** are observed in the P-bound hydrogen resonance: the major isomer displays a quite shielded resonance exhibiting no coupling to the phosphinidene ligand ( $\delta$  0.49 ppm,  ${}^{1}J_{\rm HP} = 253$  Hz), while the minor isomer displays a less shielded resonance that is weakly coupled to the PCy ligand ( $\delta$  2.33 ppm,  ${}^{1}J_{\rm HP} = 304$  Hz,  ${}^{3}J_{\rm HP} = 7$  Hz). The observed differences in the  ${}^{3}J_{\rm PH}$  values are consistent with the assigned geometries by recalling the Karplus-type dependence with the dihedral angles usually observed for three-bond P–H couplings,  ${}^{36}$  this implying larger couplings for dihedral H–P–Fe–P angles close to 180° (*syn*-**5**).

**Decarbonylation Reactions of Compound 3c.** Surprisingly, the mesitylphosphinidene complex did not undergo photochemically induced decarbonylation or any other process at a significant extent under ordinary conditions. In contrast, refluxing a toluene solution of **3c** for ca. 6 h gave the trimetal complex  $[Fe_3Cp_3(\mu-PMes)(\mu-PMesH)(\mu-CO)_2(CO)]$  (6) in medium yield (ca. 40%), along with small amounts of the dimer  $[Fe_2Cp_2(CO)_4]$ .

The molecule of **6** (Figure 6 and Table 4) is built from three FeCp fragments, two of them connected through an intermetallic bond and two bridging CO ligands, while the third one is connected to the other metal atoms through either a bridging phosphide ligand (to Fe(1)) or a trigonal phosphinidene ligand (to Fe(2)) and completes its coordination sphere with a terminal carbonyl located opposite to the mesityl group of the phosphide ligand, presumably to minimize steric repulsions. In the crystal, the environments around the Fe(1)/Fe(2) and P(1)/P(2) atoms are disordered but could be satisfactorily refined with 0.5 occupancy factors (thus, the H(1) atom is actually disordered between P(1) and P(2)). The Fe(1)–Fe(2) length of 2.541(1) Å is almost

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syn-6



identical with the value of ca. 2.53 Å measured for both isomers of  $[Fe_2Cp_2(\mu-CO)_2(CO)_2]$ ,<sup>17a,b</sup> as expected. On the basis of simple electron counts, the phosphorus ligands in 6 should provide two electrons to each of the Fe(1) and Fe(2)atoms and a total of three electrons to the Fe(3) atom. In agreement with this, the phosphide ligand is quite asymmetrically placed, substantially closer to Fe(1)(2.213(7) Å) than to Fe(2) (2.315(7) Å), while the trigonal phosphinidene ligand (sum of X-P(2)-Y angles ca. 360°) behaves as a symmetrical four-electron donor and displays two short and comparable P-Fe lengths (2.165(8) and 2.161(8) Å). The latter distances are similar to the average Fe-P length in the trigonal phosphinidene complex  $[Fe_2(CO)_6(\mu-POR)_2]$  $(2.157(1) \text{ Å})^7$  and are significantly shorter (by 0.10-0.15) Å) than the values measured for the pyramidal phosphinidene complexes 3b,d. We notice that the only other reported diiron complex with a trigonal phosphinidene ligand displays a much longer Fe–P separation of ca. 2.45 Å.<sup>8</sup>

The spectroscopic data for 6 are consistent with the retention in solution of the essential features of the solidstate structure discussed above, although two isomers are present in a ratio of ca. 10:1 at room temperature in dichloromethane. These would follow from the two possible conformations (syn and anti) of the Cp ligand in the FeCp-CO fragment with respect to the mesityl group of the phosphide ligand (Chart 4). We trust that the syn isomer, that present in the crystal, would also be the major isomer in solution. In any case, both isomers display two similar and largely separated <sup>31</sup>P resonances, as found for 5. That corresponding to the PHMes ligand appears quite shielded (ca. 25 ppm), consistent with the lack of an intermetallic interaction between the implied iron atoms. In contrast, the resonance of the phosphinidene ligand now appears at ca. 750 ppm, some 350 ppm above the figure for the pyramidal phosphinidene complex 3c, this being consistent with the presence of a trigonal phosphinidene bridge.<sup>19</sup> Other spectroscopic features in the <sup>1</sup>H and <sup>13</sup>C NMR spectra of the major isomer (see the Experimental Section) are fully consistent with the structure found in the crystal and deserve no further comments, while most of the resonances for the minor isomer were obscured by those of the major isomer.

**Reaction Pathways in the Formation of Compounds 4–6.** The removal of a CO molecule from compounds 3 would be expected to give a dicarbonyl derivative of the type [Fe<sub>2</sub>Cp<sub>2</sub>- $(\mu$ -PR) $(\mu$ -CO)<sub>2</sub>, most likely with three bridging groups, one of them being a four-electron-donor, trigonal phosphinidene ligand. Such a structure would be comparable to that of the phosphinidene complex  $[Mo_2Cp_2(\mu-PMes^*)(\mu-CO)_2]^{37}$  and even to those of the isoelectronic phosphide complexes  $[Fe_2Cp_2(\mu-PR_2)(\mu-PR'_2)(\mu-CO)]$  (R = Ph, R' = Ph, Et).<sup>15f</sup> However, no evidence has been obtained for the presence of this species in the reaction mixtures after decarbonylation of compounds 3a,c. The formation of 4, however, can be viewed as resulting from the coupling of two of such units and a subsequent decarbonylation of the resulting  $[Fe_4Cp_4(\mu PR_{2}(CO)_{4}$  intermediate. On the other hand, the formation of 5 can be rationalized by assuming that, as a side process, homolytic fission of the Fe-Fe bond in 3a might take place at some extent, this yielding the  $FeCp(CO)_2$  and FeCp(CO)-(PCy) radicals, with the former explaining the appearance of  $[Fe_2Cp_2(CO)_4]$  in the corresponding reaction mixtures. The phosphinidene radical might then be able to couple to a molecule of  $[Fe_2Cp_2(\mu-PR)(\mu-CO)_2]$  to give the paramagnetic intermediate [Fe<sub>3</sub>Cp<sub>3</sub>(µ-PR)<sub>2</sub>(CO)<sub>4</sub>] that eventually would yield 5 after hydrogen abstraction (possibly from the solvent) and further loss of two CO molecules. Indeed, the formation of compound 6 might be rationalized in the same way, except that now only one CO ligand would be removed from the trimetallic intermediate after hydrogen abstraction.

Decarbonvlation Reactions of Compound 3d. This complex has only a limited thermal stability. In fact, it rearranges slowly (conversion ca. 80% after 4 day) in toluene solution at room temperature by undergoing intramolecular insertion of the P atom into a C-H bond of one of the close o-<sup>t</sup>Bu groups  $(\mathbf{P}\cdots\mathbf{H} = \mathbf{ca.} 2.55 \text{ \AA} \text{ in the crystal})$ , to give the phosphine derivative [Fe<sub>2</sub>Cp<sub>2</sub>( $\mu$ -CO)<sub>2</sub>(CO){PH(CH<sub>2</sub>CMe<sub>2</sub>)C<sub>6</sub>H<sub>2</sub><sup>t</sup>Bu<sub>2</sub>}] (7). As found for compounds 1c,d, complex 7 exists in solution as an equilibrium mixture of trans (major) and cis (minor) isomers, these differing in the relative orientation of the Cp or (CO/phosphine) ligands, and deserves no further discussion. Expectedly, the transformation leading to 7 is much faster at higher temperatures, and it can be completed in ca. 1 h at 338 K in toluene solution, but to our surprise this transformation could not be suppressed under photolytic conditions, even at low temperatures. In fact, all photolytic experiments carried out by us for 3d led to mixtures of compound 7 and the dicarbonyl hydrides  $[Fe_2Cp_2(\mu-H)]{\mu-1}$  $P(CH_2CMe_2)C_6H_2^{t}Bu_2\{(CO)_2\}$  (8) (cis and trans isomers), with the relative amount of hydride complexes increasing at prolonged reaction times, thus suggesting that they are generated photochemically from 7, as shown by independent tests (Scheme 4).

The structures of both isomers of compound 8 can be deduced easily from the corresponding spectroscopic data and their comparison with the data available for other diiron hydride complexes of the type  $[Fe_2Cp_2(\mu-H)(\mu-PRR') (CO)_2$ ].<sup>15c,f,38</sup> The major difference between the trans and cis isomers, of course, is found in the reversed pattern of the C-O stretching bands (Table 1), while the asymmetry of the trans isomer is readily apparent in the <sup>1</sup>H NMR spectrum, displaying separate resonances for each of the Cp or Me groups. In contrast, the isomer *cis*-8 has a symmetry plane relating both metal fragments, and accordingly it displays single Cp (4.29 ppm),  $CH_2$  (2.43 ppm), and  $CMe_2$  (1.53 ppm) resonances. Out of the two possible isomers having a cis arrangement of the terminal ligands in 8, the observed isomer most likely corresponds to that having its bulkier aryl

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<sup>(38) (</sup>a) Brunner, H.: Peter, H. J. Organomet. Chem. 1990, 393, 411. (b) Brunner, H.; Rötzer, M. J. Organomet. Chem. 1992, 425, 119.



fragment away from the Cp ligands (as observed for the phosphinidene complexes 3), more favored on steric grounds, although we have not investigated this matter in detail. Finally, we note that the hydride ligand in both isomers gives rise to a quite shielded resonance at ca. -18 ppm ( $J_{\rm HP} = 39$ ), comparable to those found in the literature for related complexes.

Reaction Pathways in the Formation of Compounds 7 and 8. The formation of compound 7 from 3d obviously requires the insertion of the P atom into the C-H bond of one of the closer o-'Bu groups at some stage. We recently reported that the dimolybdenum complex  $[Mo_2Cp_2(\mu-PR^*)(CO)_4]$ , having a trigonal (four-electron-donor) PR\* bridge, undergoes a related C-H bond cleavage reaction possibly via a photoexcited state having a pyramidal (two-electron-donor) PR\* bridge.<sup>37c</sup> On this basis, it could be assumed that the C-H cleavage step might take place directly at the phosphinidenebridged molecule of 3d (Scheme 5). This would yield the unstable intermediate F with a bridging phosphine that would rearrange into a terminal position, thus generating one of the isomers of compound 7. In any case, regardless of the isomer formed initially (cis or trans), they would interconvert afterward to reach the corresponding equilibrium ratio, as already discussed in previous sections. However, related activations of a 'Bu group in a compound with a PMes\* ligand to generate a PH(CH<sub>2</sub>CMe<sub>2</sub>)C<sub>6</sub>H<sub>2</sub><sup>t</sup>Bu<sub>2</sub> ligand have been previously reported to occur also on a few transient mononuclear complexes,<sup>39</sup> even with liberation of the free phosphine.<sup>39,40</sup> On this basis, then, one might conceive that such an activation reaction would surely be easier for a terminal bent phosphinidene, because of its higher coordinative unsaturation. Interestingly, we found recently that the oxophosphinidene derivative of compound 3d exists in solution as a mixture of isomers having either terminal or bridging oxophosphinidene ligands (P(O)R\*).<sup>10</sup> Taking all

Scheme 5. Reaction Pathways in the Formation of Compound 7



this information together, we might also conceive as a possible event for 3d the presence in solution of a tiny amount of terminal isomer T, that being perhaps the active species inducing the cleavage of the C-H bond, leading initially to the trans isomer of 7 (Scheme 5). At present, however, we cannot exclude any of the above proposals.

Once the phosphine complex **7** is formed, its photochemical decarbonylation to give the hydrides **8** seems completely analogous to the formation of the hydrides  $[Fe_2Cp_2(\mu-H)(\mu-PPh_2)(CO)_2]$  from the phosphine complex *trans*- $[Fe_2Cp_2(\mu-CO)_2(CO)(PPh_2H)]$  reported previously by us<sup>15f</sup> and does not need to be discussed in detail again. We just note that, according to this previous study, the trans isomer is formed first, in good agreement with the fact that *trans*-**8** is the only isomer obtained upon photolysis of **3d** using short reaction times, while the cis isomer would be photogenerated from the trans isomer at a lower rate (Scheme 4).

## **Concluding Remarks**

The diiron phosphinidene complexes **3** have been selectively synthesized from the corresponding  $PRH_2$  complexes **1** via the PRH-bridged cations **2**. The critical step is the formation of the phosphide complexes, this being oxidatively induced in two different ways: either though a one-electron oxidation followed by spontaneous dehydrogenation (R = Cy, Ph, Mes) or through a thermodynamically disfavored two-electron oxidation coupled with deprotonation (R = Mes\*). The final step is a conventional deprotonation of the bridging PRH ligand in the cationic complexes **2** to yield the corresponding derivatives with a pyramidal phosphinidene ligand. To our knowledge, this is a novel and highly efficient synthetic procedure to obtain pyramidal phosphinidene ligands bridging two metal atoms from the corresponding phosphine complexes.

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(b) Arif, A. M.; Cowley, A. H.; Pakulski, M.; Pearsall, M. A.; Clegg, W.; Norman, N. C.; Orpen, A. G. J. Chem. Soc., Dalton Trans. 1988, 2713.
(c) Hey-Hawkins, E.; Kurz, S. J. Organomet. Chem. 1994, 479, 125. (d) Masuda, J. D.; Hoskin, A. J.; Graham, T. W.; Beddie, C.; Fermin, M. C.; Etkin, N.; Stephan, D. W. Chem. Eur. J. 2006, 12, 8696. (e) Masuda, J. D.; Jantunen, K. C.; Ozerov, O. V.; Noonan, K. J. T.; Gates, D. P.; Scott, B. L.; Kiplinger, J. L. J. Am. Chem. Soc. 2008, 130, 2408.

 <sup>(40) (</sup>a) Shah, S.; Simpson, M. C.; Smith, R. C.; Protasiewicz, J. D. J.
 Am. Chem. Soc. 2001, 123, 6925. (b) Smith, R. C.; Shah, S.; Protasiewicz,
 J. D. J. Organomet. Chem. 2002, 646, 255.

Decarbonylation of the PR-bridged complexes **3** led to no stable complexes with trigonal phosphinidene bridges of the type  $[Fe_2Cp_2(\mu-PR)(\mu-CO)_2]$ , and the results were strongly dependent on the nature of R. While no stable derivatives were obtained when R = Ph, intramolecular insertion of the P atom into the C-H bond of an *o*-'Bu group dominated the reactions of the sterically congested PMes\* complex. In contrast, the decarbonylation reactions of the PCy and PMes complexes gave tetranuclear (Cy) or trinuclear (Cy, Mes) derivatives that might be formed from the putative  $[Fe_2Cp_2(\mu-PR)(\mu-CO)_2]$  intermediate through either dimerization or reaction with mononuclear radicals FeCpPR arising from thermally and photochemically induced homolytic cleavage of the metal-metal bond in the parent phosphinidene complexes.

### **Experimental Section**

General Procedures and Starting Materials. All manipulations and reactions were carried out under a nitrogen (99.995%) atmosphere using standard Schlenk techniques. Solvents were purified according to literature procedures and distilled prior to use.<sup>41</sup> Petroleum ether refers to that fraction distilling in the range 338–343 K. Compounds  $[FeCp_2]BF_4$ ,<sup>42</sup>  $[Fe_2Cp_2(\mu-CO)_2-(CO)(CNMe)]$ ,<sup>13</sup> PMesH<sub>2</sub>,<sup>39d</sup> and PMes\*H<sub>2</sub><sup>43</sup> were synthesized according to literature procedures. All other reagents were obtained from the usual commercial suppliers and used as received. Photochemical experiments were performed using jacketed guartz or Pyrex Schlenk tubes, cooled by tap water (ca. 288 K) or by a closed 2-propanol circuit kept at the desired temperature with a cryostat. A 400 W mercury lamp placed ca. 1 cm away from the Schlenk tube was used for all the experiments. Chromatographic separations were carried out using jacketed columns cooled by tap water (ca. 288 K) or by a closed 2-propanol circuit, kept at the desired temperature with a cryostat. Commercial aluminum oxide (activity I, 150 mesh) was degassed under vacuum prior to use. The latter was mixed afterward under nitrogen with the appropriate amount of water to reach the activity desired. IR C-O stretching frequencies were measured in solution and are referred to as  $\nu$ (CO). Nuclear magnetic resonance (NMR) spectra were routinely recorded at 300.13  $(^1H)$ , 121.50  $(^{31}P\{^1H\})$ , and 75.48 MHz  $(^{13}C\{^1H\})$  at 290 K in CD<sub>2</sub>Cl<sub>2</sub> solutions unless otherwise stated. Chemical shifts ( $\delta$ ) are given in ppm, relative to internal tetramethylsilane (<sup>1</sup>H, <sup>13</sup>C) or external 85% aqueous H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P). Coupling constants (J) are given in Hz. Cyclic voltammetry experiments were performed in an airtight custom-made electrolytic cell using a Pt working electrode, an Ag-wire reference electrode and a Ptwire auxiliary electrode. [NBu<sub>4</sub>][PF<sub>6</sub>] was used as the supporting electrolyte (0.1 M solutions). The analyte concentrations in a typical experiment were ca.  $10^{-3}$  M. All the potentials were referenced versus the ferrocene/ferrocenium couple ( $Cp_2Fe^{+/0}$ ), used as internal reference in all the experiments.

**Preparation of**  $[Fe_2Cp_2(\mu-CO)_2(CO)(PCyH_2)]$  (1a). An acetonitrile solution (50 mL) of  $[Fe_2Cp_2(\mu-CO)_2(CO)(CNMe)]$  was prepared in situ from  $[Fe_2Cp_2(CO)_4]$  (1.000 g, 2.825 mmol). The solvent was then removed under vacuum and the residue dissolved in dichloromethane (20 mL) and stirred with PCyH<sub>2</sub> (375  $\mu$ L, 2.825 mmol) at room temperature for 5 min to give a dark green solution, which was filtered. Solvent was then removed under vacuum from the filtrate, and the residue was washed with petroleum ether (5 × 10 mL) to give compound 1a as a dark green microcrystalline solid (1.125 g, 90%). Anal.

Calcd for C<sub>19</sub>H<sub>23</sub>Fe<sub>2</sub>O<sub>3</sub>P: C, 51.62; H, 5.24. Found: C, 51.23; H, 5.05. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  4.72 (s, 5H, Cp), 4.50 (d,  $J_{HP} = 1, 5H$ , Cp), 3.28 (dd,  $J_{HP} = 327, J_{HH} = 6, 2H, P-H$ ), 2.05–0.97 (m, 11H, Cy).

**Preparation of**  $[Fe_2Cp_2(\mu$ -CO)<sub>2</sub>(CO)(PPhH<sub>2</sub>)] (1b). The procedure is completely analogous to that described for 1a but using PPhH<sub>2</sub> instead (315  $\mu$ L, 2.864 mmol). Compound 1b was thus obtained as a dark green microcrystalline solid (1.108 g, 90%). Anal. Calcd for C<sub>19</sub>H<sub>17</sub>Fe<sub>2</sub>O<sub>3</sub>P: C, 52.34; H, 3.93. Found: C, 51.90; H, 3.65. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.70–7.30 (m, 5H, Ph), 4.76 (s, 5H, Cp), 4.47 (d,  $J_{HP}$  = 342, 2H, P–H), 4.45 (d,  $J_{HP}$  = 1, 5H, Cp).

Preparation of  $[Fe_2Cp_2(\mu-CO)_2(CO)(PMesH_2)]$  (1c). The procedure is completely analogous to that described for 1a, but using PMesH<sub>2</sub> instead (5 mL of a 0.62 M solution in CH<sub>2</sub>Cl<sub>2</sub>, 3.10 mmol). The green solid obtained after removal of solvent under vacuum from the reaction mixture was dissolved in the minimum amount of a dichloromethane/petroleum (1/2) mixture and chromatographed on alumina (activity II) at 288 K. Elution with dichloromethane/petroleum ether (1/4) gave a yellow fraction containing excess phosphine and related impurities and a red fraction containing some  $[Fe_2Cp_2(CO)_4]$ . Elution with dichloromethane/petroleum ether (1/4) gave a green fraction which gave, after removal of solvents under vacuum, compound **1c** as a green microcrystalline solid (1.120 g, 83%). This complex exists in solution as an equilibrium mixture of the corresponding trans and cis isomers. Anal. Calcd for  $C_{22}H_{23}Fe_2O_3P$ : C, 55.27; H, 4.85. Found: C, 55.23; H, 4.90. Spectroscopic data for *trans-lc* are as follows. <sup>1</sup>H NMR:  $\delta$  6.91 (s, 2H, C<sub>6</sub>H<sub>2</sub>), 4.74, 4.19 (2s,  $2 \times 5$ H, Cp), 3.87 (d,  $J_{\text{HP}} = 345$ , 2H, P-H), 2.45 (s, 6H, o-Me), 2.26 (s, 3H, p-Me). The resonances due to the isomer cis-1c were obscured by those of the major isomer in the <sup>1</sup>H NMR spectrum. Trans/cis ratio: ca. 20/1 (from the  ${}^{31}P{}^{1}H{}$  NMR spectrum).

Preparation of  $[Fe_2Cp_2(\mu$ -CO)<sub>2</sub>(CO)(PMes\*H<sub>2</sub>)] (1d). The procedure is completely analogous to that described for 1a, but using PMes\* $H_2$  instead (0.787 g, 2.827 mmol). The green residue obtained after removal of the solvent was washed with petroleum ether (6  $\times$  10 mL) to give compound 1d as a dark green microcrystalline solid. The petroleum ether fractions were collected and the solvent removed under vacuum. The residue was then dissolved in dichloromethane/petroleum ether (1/18)and chromatographed on alumina (activity IV) at 288 K. Elution with dichloromethane/petroleum ether (1/14) gave a red fraction containing some  $[Fe_2Cp_2(CO)_4]$  and then a green fraction which yielded, after removal of solvents, a second crop of compound 1d (combined yield: 1.520 g, 89%). This complex exists in solution as an equilibrium mixture of the corresponding trans and cis isomers. Anal. Calcd for C<sub>31</sub>H<sub>41</sub>Fe<sub>2</sub>O<sub>3</sub>P: C, 61.61; H, 6.84. Found: C, 61.49; H, 6.88. Spectroscopic data for *trans*-1d are as follows. <sup>1</sup>H NMR (400.13 MHz)  $\delta$  7.45 (s, 2H, C<sub>6</sub>H<sub>2</sub>), 4.71 (s, 5H, Cp), 4.44 (d,  $J_{\rm HP}$  = 343, 2H, P–H), 3.99 (s, 5H, Cp), 1.59 (s, 18H, o-'Bu), 1.31 (s, 9H, p-'Bu). Spectroscopic data for *cis*-1d are as follows. <sup>1</sup>H NMR (400.13 MHz): δ 4.71 (s, 5H, Cp), 4.51 (d,  $J_{\rm HP} = 343$ , 2H, P–H), 3.94 (s, 5H, Cp), 1.65 (s, 18H,  $o^{-t}$ Bu); other resonances of this isomer were obscured by those of the major isomer. Trans/cis ratio: 5/1.

**Preparation of** [Fe<sub>2</sub>Cp<sub>2</sub>( $\mu$ -PCyH)( $\mu$ -CO)(CO)<sub>2</sub>]BF<sub>4</sub> (2a). Solid [FeCp<sub>2</sub>]BF<sub>4</sub> (0.763 g, 2.798 mmol) was slowly added to a stirred dichloromethane solution (30 mL) of compound **1a** (1.125 g, 2.545 mmol) at 273 K, and the mixture was further stirred for 10 min to give a red solution. The solvent was then removed under vacuum, and the residue was washed with petroleum ether (7 × 10 mL) to give compound **2a** as a red microcrystalline solid (1.303 g, 97%). Anal. Calcd for C<sub>19</sub>H<sub>22</sub>BF<sub>4</sub>Fe<sub>2</sub>O<sub>3</sub>P: C, 43.23; H, 4.20. Found: C, 42.92; H, 3.89. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.13 (dd, J<sub>HP</sub> = 390, J<sub>HH</sub> = 10, 1H, P–H), 5.17 (s, 10H, Cp), 2.25–1.15 (m, 11H, Cy).

**Preparation of**  $[Fe_2Cp_2(\mu-PPhH)(\mu-CO)(CO)_2]BF_4$  (2b). The procedure is completely analogous to that described for 2a. With

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<sup>(43)</sup> Cowley, A. H.; Norman, N. C.; Pakulski, M. Inorg. Synth. 1990, 27, 253.

1.108 g (2.541 mmol) of compound **1b** as starting material and using 0.762 g of [FeCp<sub>2</sub>]BF<sub>4</sub> (2.795 mmol), compound **2b** was obtained as a red microcrystalline solid (1.272 g, 96%). Anal. Calcd for C<sub>19</sub>H<sub>16</sub>BF<sub>4</sub>Fe<sub>2</sub>O<sub>3</sub>P: C, 43.73; H, 3.09. Found: C, 43.45; H, 3.15. Spectroscopic data for *cis,anti-2b* are as follows. <sup>1</sup>H NMR:  $\delta$  9.10 (d, *J*<sub>HP</sub> = 413, 1H, P–H), 7.80–7.40 (m, 5H, Ph), 5.25 (s, 10H, Cp). The resonances due to the isomer *cis,sym*-**2b** were obscured by those of the major isomer in the <sup>1</sup>H NMR spectrum. Anti/syn ratio: ca. 10/1 (from the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum).

Preparation of [Fe<sub>2</sub>Cp<sub>2</sub>(µ-PMesH)(µ-CO)(CO)<sub>2</sub>]BF<sub>4</sub> (2c). Solid [FeCp<sub>2</sub>]BF<sub>4</sub> (0.703 g, 2.578 mmol) was slowly added to a stirred dichloromethane solution (30 mL) of compound 1c (1.120 g, 2.343 mmol) at 273 K, and the mixture was further stirred for 10 min to give a red solution. Excess KOH (ca. 0.5 g) was added to this solution, and the mixture was stirred for a further 10 min to give an orange solution containing compound 3c. The solvent was then evaporated under vacuum and the residue was dissolved in the minimum amount of dichloromethane/petroleum ether (1/1) and chromatographed on alumina (activity IV) at 288 K. Elution with dichloromethane/ petroleum ether (1/2) gave a yellow fraction containing [FeCp<sub>2</sub>], and elution with dichloromethane/petroleum ether (1/1) gave an orange fraction containing compound 3c. The solvents were removed under vacuum, and the residue was dissolved in  $CH_2Cl_2$  (20 mL). Then,  $HBF_4 \cdot OEt_2$  (325  $\mu$ L of a 54% solution in Et<sub>2</sub>O, 2.358 mmol) was added to the latter solution, and the mixture was stirred for 5 min to give a red solution. The solvent was then removed under vacuum, and the red residue was washed with Et<sub>2</sub>O (6  $\times$  8 mL) and then petroleum ether (4  $\times$  8 mL) to give compound 2c as a red microcrystalline solid (1.056 g, 80%). Anal. Calcd for C<sub>22</sub>H<sub>22</sub>BF<sub>4</sub>Fe<sub>2</sub>O<sub>3</sub>P: C, 46.86; H, 3.93. Found: C, 46.78; H, 3.80. <sup>1</sup>H NMR:  $\delta$  9.00 (d,  $J_{HP}$  = 397, 1H, P-H), 7.00 (d,  $J_{\text{HP}} = 4$ , 2H, C<sub>6</sub>H<sub>2</sub>), 5.39 (s, 10H, Cp), 2.73 (s, 6H, o-Me), 2.27 (s, 3H, p-Me).

Preparation of  $[Fe_2Cp_2(\mu-PMes^*H)(\mu-CO)(CO)_2]BF_4$  (2d). Solid [FeCp<sub>2</sub>]BF<sub>4</sub> (0.400 g, 1.467 mmol) was slowly added to a stirred suspension of NaHCO3 (1.0 g, 11.9 mmol) in a THF solution (22 mL) of compound 1d (0.400 g, 0.662 mmol) at 243 K, and the mixture was further stirred for 1 h at the same temperature to give a red solution containing compound 2d as the major species. The mixture was then allowed to reach room temperature (this causing a partial conversion of 2d into the phosphinidene complex 3d) and filtered with a canula. After  $HBF_4 \cdot OEt_2$  (150  $\mu$ L of a 54% solution in  $Et_2O$ , 1.32 mmol) was added to the filtrate, the mixture was stirred for 5 min to give a red solution. Removal of the solvent under vacuum from the latter solution and washing of the residue with petroleum ether  $(5 \times 20 \text{ mL})$  gave compound 2d as a red microcrystalline solid (0.360 g, 79%). Anal. Calcd for C<sub>31</sub>H<sub>40</sub>BF<sub>4</sub>Fe<sub>2</sub>O<sub>3</sub>P: C, 53.95; H, 5.84. Found: C, 54.00; H, 5.88. <sup>1</sup>H NMR (400.13 MHz): δ 9.88  $(d, J_{HP} = 385, 1H, P-H), 7.08 (s, 2H, C_6H_2), 5.32 (s, 10H, Cp),$ 1.64 (s, 18H, o-<sup>t</sup>Bu), 1.06 (s, 9H, p-<sup>t</sup>Bu).

**Preparation of**  $[Fe_2Cp_2(\mu-PCy)(\mu-CO)(CO)_2]$  (3a). Solid KOH (ca. 0.1 g, excess) was added to a dichloromethane solution (6 mL) of compound 2a (0.050 g, 0.095 mmol) at room temperature, and the mixture was vigorously stirred for 5 min to give a red-brown solution which was filtered using a cannula. The solvent was then removed under vacuum from the filtrate, and the residue was washed with petroleum ether (2 × 5 mL) to give compound 3a as a red-brown, air-sensitive microcrystalline solid (0.040 g, 95%). Anal. Calcd for C<sub>19</sub>H<sub>21</sub>Fe<sub>2</sub>O<sub>3</sub>P: C, 51.87; H, 4.81. Found: C, 51.38; H, 4.47. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  4.24 (s, 10H, Cp), 2.24–1.47 (m, 11H, Cy).

**Preparation of**  $[Fe_2Cp_2(\mu-PPh)(\mu-CO)(CO)_2]$  (3b). The procedure is completely analogous to that described for 3a. With 0.050 g (0.096 mmol) of compound 2b as starting material and using ca. 0.1 g of KOH (excess), compound 3b was obtained as a red-brown, air-sensitive microcrystalline solid (0.039 g, 93%). Anal. Calcd for C<sub>19</sub>H<sub>15</sub>Fe<sub>2</sub>O<sub>3</sub>P: C, 52.58; H, 3.48. Found: C,

52.13; H, 3.17. <sup>1</sup>H NMR: *δ* 7.60–7.20 (m, 5H, Ph), 4.90 (s, 10H, Cp).

Preparation of  $[Fe_2Cp_2(\mu$ -PMes)( $\mu$ -CO)(CO)<sub>2</sub>] (3c). Method A (Small Scale). This synthetic procedure is completely analogous to that described for 3a. With compound 2c (0.050 g, 0.093 mmol) as starting material and using KOH (ca. 0.1 g, excess), compound 3c was obtained as an orange, very air-sensitive microcrystalline solid (0.042 g, 95%).

Method B (Large Scale). This synthetic procedure is analogous to that described for 2c, but omitting the final step (protonation). Yield: 0.960 g (86%). Satisfactory elemental analysis could not be obtained for this very air-sensitive material. <sup>1</sup>H NMR:  $\delta$  6.85 (s, 2H, C<sub>6</sub>H<sub>2</sub>), 4.91 (s, 10H, Cp), 2.53 (s, 6H, *o*-Me), 2.25 (s, 3H, *p*-Me).

**Preparation of**  $[Fe_2Cp_2(\mu$ -PMes<sup>\*</sup>)( $\mu$ -CO)(CO)<sub>2</sub>] (3d). The procedure is completely analogous to that described for 3a. With compound 2d (0.050 g, 0.072 mmol) as starting material and using KOH (ca. 0.1 g, excess), compound 3d was obtained as a wine red, very air-sensitive microcrystalline solid (0.042 g, 95%). Satisfactory elemental analysis could not be obtained for this very air-sensitive material. <sup>1</sup>H NMR:  $\delta$  6.92 (s, 2H, C<sub>6</sub>H<sub>2</sub>), 4.86 (s, 10H, Cp), 1.58 (s, 18H, o-'Bu), 1.07 (s, 9H, p-'Bu).

Photolysis of Compound 3a. A toluene solution (8 mL) of compound 3a (0.200 g, 0.455 mmol) was irradiated with vis-UV light for 6 h at 288 K while N<sub>2</sub> was gently bubbled through the solution, to give a brown mixture. The solvent was then removed under vacuum, the residue was extracted with dichloromethane/ petroleum ether (1/1), and the extracts were chromatographed on alumina (activity IV) at 288 K. Elution with the same solvent mixture gave a green fraction yielding, upon removal of solvents under vacuum, the compound  $[Fe_4Cp_4(\mu_3-PCy)(\mu_3-CO)(\mu-CO)-$ (CO)] (4) as a green microcrystalline solid (0.040 g, 11%). The crystals of 4 used in the diffraction study were grown by the slow diffusion of a layer of petroleum ether into a CH2Cl2 solution of the complex at 253 K. Elution with dichloromethane/petroleum ether (3/1) gave a red-brown fraction yielding analogously the compound syn-[Fe<sub>3</sub>Cp<sub>3</sub>( $\mu_3$ -PCy)( $\mu$ -PCyH)( $\mu$ -CO)<sub>2</sub>] (syn-5) as a brown solid (0.021 g, 7%) and then a brown fraction yielding compound  $anti-[Fe_3Cp_3(\mu_3-PCy)(\mu-PCyH)(\mu-CO)_2]$  (anti-5) also as a brown solid (0.035 g, 12%). Data for compound 4 are as follows. Anal. Calcd for  $C_{35}H_{42}Fe_4O_3P_2$ : C, 52.81; H, 5.32. Found: C, 52.53; H, 5.03. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  4.71, 4.70 (2s,  $2 \times 5H$ , Cp), 4.62 (s, 10H, Cp), 2.07–1.25 (m, 22H, Cy). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  303.0 (s,  $\mu_3$ -CO), 273.5 (s,  $\mu$ -CO), 224.2 (t,  $J_{CP} = 28$ , FeCO), 90.5 (s, 2Cp), 87.3, 80.6 (2 s, Cp), 64.0 (false t,  $|J_{CP} + J_{CP}| = 17$ ,  $C^{1}(Cy)$ ), 34.5, 31.5 (2s,  $C^{2}(Cy)$ ), 26.6 (s, br,  $C^{3}(Cy)$ ), 25.5 (s,  $C^{4}(Cy)$ ).  ${}^{13}C{}^{1}H$  NMR (CDCl<sub>3</sub>, 233 K)  $\delta$  27.4, 27.3 (2s, C<sup>3</sup>(Cy)). Spectroscopic data for *syn-5* are as follows. <sup>1</sup>H NMR: δ 4.58 (s, 5H, Cp), 4.19 (s, 10H, Cp), 3.04 (m, 2H, Cy), 2.48 (m, 2H, Cy), 2.33 (dt,  $J_{HP} = 304$ ,  $J_{HH} = J_{HP} = 7$ , 1H, P-H), 2.23 (m, 2H, Cy), 2.06 (m, 1H, Cy), 1.90 (m, 2H, Cy), 1.78-1.50 (m, 8H, Cy), 1.29 (m, 2H, Cy), 1.14 (m, 2H, Cy), 1.01 (m, 1H, Cy). Data for anti-5 are as follows. Anal. Calcd for C<sub>29</sub>H<sub>38</sub>Fe<sub>3</sub>O<sub>2</sub>P<sub>2</sub>: C, 53.74; H, 5.91. Found: C, 53.41; H, 5.52. <sup>1</sup>H NMR: δ 4.61 (s, 5H, Cp), 4.11 (s, 10H, Cp), 3.11 (m, 2H, Cy), 2.25 (m, 2H, Cy), 2.08 (m, 1H, Cy), 1.92 (m, 2H, Cy), 1.81 (m, 2H, Cy), 1.78-1.66 (m, 5H, Cy), 1.56 (m, 1H, Cy), 1.29-1.15 (m, 7H, Cy), 0.49 (dd,  $J_{\rm HP} = 253$ ,  $J_{\rm HH} = 4$ , 1H, P–H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  281.2 (d,  $J_{CP} = 14, \mu$ -CO), 85.7 (s, Cp), 81.2 (s, 2Cp), 54.3 (d,  $J_{CP} = 25$ , C<sup>1</sup>(Cy)], 37.9 (d,  $J_{CP} = 12$ , C<sup>1</sup>(Cy)),  $35.4, 32.4 (2s, C^2(Cy)), 28.5 (d, J_{CP} = 11, C^3(Cy)), 27.7 (d, J_{CP} =$ 10, C<sup>3</sup>(Cy)), 27.1, 26.9 (2s, C<sup>4</sup>(Cy)).

**Preparation of**  $[Fe_3Cp_3(\mu-PMes)(\mu-PMesH)(\mu-CO)_2(CO)]$ (6). A solution of 3c (0.080 g, 0.168 mmol) in toluene (4 mL) was refluxed for 6.5 h to give a dark green-brown solution. After removal of the solvent under vacuum, the residue was extracted with dichloromethane/petroleum ether (1/2) and the extracts were chromatographed on alumina (activity IV) at 288 K. Elution with the same solvent mixture gave a yellow fraction containing [FeCp<sub>2</sub>], a red fraction containing some

Table 5. Crystal Data for New Compounds

	$4 \cdot 2 CH_2 Cl_2$	6
mol formula	$C_{37}H_{46}Cl_4Fe_4O_3P_2$	C <sub>36</sub> H <sub>38</sub> Fe <sub>3</sub> O <sub>3</sub> P <sub>2</sub>
mol wt	965.88	748.15
cryst syst	orthorhombic	monoclinic
space group	Pnma	C2/c
radiation $(\hat{\lambda}, \hat{A})$	0.71073	0.71073
a, Å	18.6619(7)	23.646(2)
b, Å	19.2134(6)	9.1154(9)
c, Å	10.4001(3)	33.408(3)
α, deg	90	90
$\beta$ , deg	90	104.087(5)
$\gamma$ , deg	90	90
$V, Å^{\overline{3}}$	3729.0(2)	6984.2(11)
Z	4	8
calcd density, $g \text{ cm}^{-3}$	1.720	1.423
abs coeff, $mm^{-1}$	1.935	1.355
temp, K	100(2)	100(2)
$\theta$ range, deg	2.12-26.38	1.78, 25.35
index ranges $(h, k, l)$	0-23; 0-24; 0-12	-28 to $+27, 0-10, 0-40$
no. of rflns collected	48 888	47 239
no. of indep rflns $(R_{int})$	3928 (0.0936)	6380 (0.1392)
no. of rflns with $I > 2\sigma(I)$	2758	3763
<i>R</i> indexes (data with $I > 2\sigma(I)$ ) <sup><i>a</i></sup>	$R1 = 0.0374, wR2 = 0.0613^{b}$	$R1 = 0.0593, wR2 = 0.1282^{\circ}$
R indexes (all data) <sup>a</sup>	$R1 = 0.0744, wR2 = 0.0715^{b}$	$R1 = 0.1176, wR2 = 0.146^{c}$
GOF	1.003	0.973
no. of restraints/params	0/225	1/427
$\Delta \rho(\max, \min), e \hat{A}^{-3}$	0.878, -0.633	0.736, -0.744
${}^{a}$ R1 = $\sum_{c}   F_{o}  -  F_{c}   / \sum_{c}  F_{o} $ . wR2 = [ $\sum w(6.7275)$ . ${}^{c}a = 0.0732$ , $b = 0.0000$ .	$  F_{\rm o} ^2 -  F_{\rm c} ^2$ $/\sum w  F_{\rm o} ^2$ $ ^{1/2} w = 1/[\sigma^2(F_{\rm o}^2) + (aP)^2 + bP] w$	where $P = (F_0^2 + 2F_c^2)/3$ . $^b a = 0.0206, b =$

[Fe<sub>2</sub>Cp<sub>2</sub>(CO)<sub>4</sub>], and a third green fraction. Removal of the solvents from the latter fraction under vacuum gave the green complex 6 (0.050 g, 40%) as a mixture of syn and anti isomers. The crystals of 6 (syn isomer) used in the diffraction study were grown by the slow diffusion of a layer of petroleum ether into a toluene solution of the complex at 253 K. Anal. Calcd for  $C_{36}H_{38}Fe_3O_3P_2$ : C, 57.79; H, 5.12. Found: C, 57.60; H, 5.10. Spectroscopic data for *syn-6* are as follows. <sup>1</sup>H NMR:  $\delta$  6.98, 6.92, 6.90, 6.81 (4s,  $4 \times 1$ H, C<sub>6</sub>H<sub>2</sub>), 6.44 (d,  $J_{\text{HP}} = 306$ , 1H, P-H), 4.46 (d, J<sub>HP</sub> = 1, 5H, Cp), 4.43 (s, 5H, Cp), 3.72 (d, J<sub>HP</sub> 1, 5H, Cp), 2.64, 2.38, 2.37, 2.26, 2.18, 2.14 (6s, 6 × 3H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  281.5 (dd,  $J_{CP}$  = 7, 11,  $\mu$ -CO), 279.5 (d,  $J_{CP} = 10, \mu$ -CO), 213.6 (dd,  $J_{CP} = 28, 19, FeCO$ ), 162.1 (dd,  $\begin{array}{l} (4, 5) \\ (4, 5$ 128.8 (s, C<sup>3</sup>(Mes)), 90.0, 88.9, 86.4 (3s, Cp), 24.6, 24.5, 21.9, 21.7, 21.2, 21.0 (6s, Me). Spectroscopic data for anti-6 are as follows. <sup>1</sup>H NMR:  $\delta$  4.39 (s, 5H, Cp), 4.36, 3.82 (2d,  $J_{HP} = 1, 2 \times 5H$ , Cp). Other resonances for *anti-6* in the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra could not be assigned, as they were masked by those of the major isomer. Syn/anti ratio: ca. 10/1.

Preparation of  $[Fe_2Cp_2(\mu-CO)_2(CO){PH(CH_2CMe_2)C_6H_2}]$ <sup>t</sup> $Bu_2$ ] (7). A toluene solution (5 mL) of compound 3d (0.050 g, 0.083 mmol) was placed in a Schlenk tube equipped with a Young valve, and it was stirred at 233 K for 1 h to give a brown-green mixture. The solvent was then removed under vacuum, and the residue was dissolved in a minimum of dichloromethane/petroleum ether (1/6) and chromatographed on alumina (activity IV). Elution with dichloromethane/petroleum ether (1/4) gave a red fraction containing the dimer [Fe<sub>2</sub>Cp<sub>2</sub>(CO)<sub>4</sub>]. Elution with dichloromethane/petroleum ether (1/1) gave a green fraction yielding, after removal of solvents, compound 7 as a dark green microcrystalline solid (0.036 g, 71%). This complex exists in solution as an equilibrium mixture of the corresponding trans and cis isomers. Anal. Calcd for C<sub>31</sub>H<sub>39</sub>Fe<sub>2</sub>O<sub>3</sub>P: C, 61.82; H, 6.53. Found: C, 61.67; H, 6.51. Spectroscopic data for trans-7 are as follows. <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  7.48, 7.06 (2 m, 2 × 1H,  $C_6H_2$ ), 4.56  $(dd, J_{HP} = 348, J_{HH} = 5, 1H, P-H), 4.47, 4.09 (2s, 2 \times 5H, Cp),$ 2.53, 1.99 (2 m, 2  $\times$  1H, CH<sub>2</sub>), 1.66 (s, 3H, Me), 1.64 (s, 9H,

o-<sup>t</sup>Bu), 1.20 (s, 9H, p-<sup>t</sup>Bu), 1.00 (s, 3H, Me). Spectroscopic data for *cis*-7 are as follows. <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  4.51, 4.20 (2s, 2 × 5H, Cp). Other resonances of this isomer were obscured by those of the major isomer. Trans/cis ratio: ca. 5/1.

**Photolysis of Compound 3d.** A toluene solution (8 mL) of compound 3d (0.100 g, 0.166 mmol) was irradiated with visible-UV light in a quartz Schlenk tube for 1 h while N<sub>2</sub> was gently bubbled through the solution, to give a green-brown mixture. After removal of the solvent under vacuum, the residue was extracted with dichloromethane/petroleum ether (1/15) and the extracts were chromatographed on alumina (activity IV) at 288 K. Elution with the same solvent mixture gave two orange fractions yielding respectively, after removal of solvents under vacuum, the complexes trans- $[Fe_2Cp_2(\mu-H){\mu-P(CH_2-\mu)}]$  $CMe_2)C_6H_2^{t}Bu_2\}(CO)_2$  (trans-8; 0.019 g, 20%) and cis-[Fe<sub>2</sub>Cp<sub>2</sub>- $(\mu-H){\mu-P(CH_2CMe_2)C_6H_2^{'}Bu_2}(CO)_2$  (*cis-8*; 0.012 g, 13%) as orange microcrystalline powders. Finally, elution with dichloromethane/petroleum ether (1/1) gave a green fraction analogously yielding compound 7 (0.060 g, 60%). Anal. Calcd for C<sub>30</sub>H<sub>39</sub>Fe<sub>2</sub>O<sub>2</sub>P (*trans-8*): C, 62.74; H, 6.84. Found: C, 62.60; H, 6.83. Anal. Calcd for C<sub>30</sub>H<sub>39</sub>Fe<sub>2</sub>O<sub>2</sub>P (*cis-8*): C, 62.74; H, 6.84. Found: C, 62.52; H, 6.61. Spectroscopic data for trans-8 are as follows. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.55 (dd,  $J_{HH} = 2$ ,  $J_{HP} = 4$ , 1H,  $C_6H_2$ ), 7.35 (d,  $J_{HH} = 2$ , 1H,  $C_6H_2$ ), 4.36, 4.24 (2s, 2 × 5H, Cp), 2.60 (t,  $J_{HH} = J_{HP} = 13$ , 1H, CH<sub>2</sub>), 2.03 (dd,  $J_{HH} = 13$ ,  $J_{HP} =$ 5, 1H, CH<sub>2</sub>), 1.88 (s, 3H, Me), 1.58 (s, 9H, o-<sup>t</sup>Bu), 1.40 (s, 3H, Me), 1.35 (s, 9H,  $p^{-1}$ Bu), -18.30 (d,  $J_{HP} = 39$ , 1H,  $\mu$ -H). Spectroscopic data for *cis*-8 are as follows. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.51 (dd,  $J_{\text{HH}} = 2, J_{\text{HP}} = 4, 1\text{H}, \text{C}_{6}\text{H}_{2}$ ), 7.27 (d,  $J_{\text{HH}} = 2, 1\text{H},$  $C_6H_2$ ), 4.29 (s, 10H, Cp), 2.43 (d,  $J_{HP} = 5, 2H, CH_2$ ), 1.53 (s, 6H, Me), 1.44 (s, 9H,  $o^{-t}$ Bu), 1.32 (s, 9H,  $p^{-t}$ Bu), -18.21 (d,  $J_{HP}$  = 39, 1H, µ-H).

X-ray Structure Determination for Compound 4. The X-ray intensity data for 4.2CH2Cl2 were collected on a Kappa-Apex-II Bruker diffractometer using graphite-monochromated Mo K $\alpha$  radiation at 100 K. The software APEX<sup>44</sup> was used for collecting frames with the  $\omega/\psi$  scan measurement method. The

<sup>(44)</sup> APEX 2, version 2.0-1; Bruker AXS Inc., Madison, WI, 2005.

Bruker SAINT<sup>45</sup> software was used for the data reduction, and a multiscan absorption correction was applied with SADABS.<sup>46</sup> Using the program suite WinGX,<sup>47</sup> the structure was solved by direct methods with SIR92<sup>48</sup> and refined with full-matrix least squares on  $F^2$  with SHELXL97.<sup>49</sup> During the solution process, the compound was found to be placed on the symmetry operation x,  $-y + \frac{3}{2}$ , z and to crystallize with two molecules of dichloromethane. All the positional parameters and the anisotropic temperature factors of all the non-H atoms were refined anisotropically, except for the carbon atoms C(14), C(21), C(31), and C(33), which were refined isotropically to prevent their temperature factors from becoming nonpositive definite. All hydrogen atoms were geometrically placed and refined using a riding model. Crystallographic data and structure refinement details for  $4 \cdot 2 CH_2 Cl_2$  are collected in Table 5.

X-ray Structure Determination for Compound 6. The acquisition of data, absorption corrections, and data reduction for 6 were performed as described for 4. Using the program suite WinGX,<sup>47</sup> the structure was solved by Patterson interpretation and phase expansion and refined with full-matrix least squares on  $F^2$  using SHELXL97.<sup>49</sup> During the solution stages the compound was found to crystallize with a molecule of solvent, possibly *n*-hexane, highly disordered and placed on a symmetry element. The refinement process made evident that both phosphorus atoms were disordered in two positions, but this disorder

(49) Sheldrick, G. M. Acta Crystallogr., Sect. A 2008, 64, 112.

could be modeled satisfactorily by introducing occupation factors of 0.5 in all atoms of both parts. During the final stages of the refinement, all the positional parameters and the anisotropic temperature factors of all the non-H atoms were refined anisotropically. All hydrogen atoms were geometrically placed and refined using a riding model, except for the hydrogen atoms H(1) and H(2), which were located in the Fourier map and refined isotropically; nevertheless, a restriction on the P-(2B)-H(2) distance (1.2 Å) had to be added for a satisfactory refinement. As the solvent molecule present in the asymmetric unit could not be conveniently modeled, the SQUEEZE<sup>50</sup> procedure, as implemented in PLATON,<sup>51</sup> was used. Upon SQUEEZE application and convergence the strongest residual peak (0.74 e Å<sup>-3</sup>) was located near the Fe(1) atom. Crystallographic data and structure refinement details for **6** are collected in Table 5.

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**Supporting Information Available:** A CIF file giving crystallographic data for the structural analysis of compounds **4** and **6**. This material is available free of charge via the Internet at http:// pubs.acs.org.

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