P−C and C−H Bond Cleavages in the Photochemical Reactions of [$Fe_2(\eta^5-C_5H_5)_2(CO)_4$] with Bis(diphenylphosphino)methane

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The photochemical reactions of [$Fe_2Cp_2(CO)_4$] (Cp = η^5-C_5H_5) and the bidentate ligand $Ph_2PCH_2PPh_2$ give a complex mixture of products. These include the known complexes [$Fe_2Cp_2(\mu$-$CO)_2(\mu$-$Ph_2PCH_2PPh_2)$] and *cis*-[$Fe_2Cp_2(\mu$-$PPh_2)_2(CO)_2$], as well as the new species [$Fe_2Cp(\mu$-η^5:κ^1-$C_5H_4CH_2PPh_2)(\mu$-$CO)_2(CO)$], *cis*-[$Fe_2Cp_2(\mu$-$H)(\mu$-$PPh_2)(CO)_2$], [$Fe_2Cp(\mu$-η^5:κ^1-$C_5H_4CH_2PPh_2)(\mu$-$H)(\mu$-$PPh_2)(CO)$], *trans*-[$Fe_2Cp_2(\mu$-$H)(\mu$-$PPh_2)(CO)(PMePh_2)$], and [$Fe_2Cp_2(\mu$-$PPh_2)_2(\mu$-$CO)$]. An intermediate species, *trans*-[$Fe_2Cp_2(\mu$-$CO)_2(CO)(\kappa^1$-$Ph_2PCH_2PPh_2)$], having an intact diphosphine ligand coordinated through one of the P atoms, can be detected at the early stages of the reaction. Separate experiments indicate that the latter species is the precursor of the unique diphosphine-bridged complex, but of none of the other products. The above results indicate that different P−C (diphosphine) and C−H (cyclopentadienyl) bond cleavage processes are operative under the conditions examined, as well as novel C−C bond formations. The structures of the new complexes are analyzed on the basis of the corresponding IR and NMR (^{1}H, ^{31}P, and ^{13}C) data, as well as a single-crystal X-ray study on the (diphenylphosphinomethyl)cyclopentadienyl complex [$Fe_2Cp(\mu$-η^5:κ^1-$C_5H_4CH_2PPh_2)(\mu$-$CO)_2(CO)$]. A reassessment of the ^{31}P chemical shifts for *cis*- and *trans*-[$Fe_2Cp_2(\mu$-$PPh_2)_2(CO)_2$] is also made.

Introduction

We have recently reported our studies on the thermal and photochemical reactions of the metal−metal bonded dimer [$Fe_2Cp_2(CO)_4$] (**1**; Cp = η^5-C_5H_5) and the bidentate phosphite $(EtO)_2POP(OEt)_2$ (tedip).[1] From these studies we concluded that these reactions seem to proceed mainly through the radical intermediates [$FeCp(CO)_2$] and [$FeCp(CO)(\kappa^1$-tedip)], which then evolve in different ways, always implying either C−O (ethoxy) or P−O (backbone) bond cleavages of the diphosphite ligand, but never involving activation of the C−H bonds in the cyclopentadienyl ligands. These results are in contrast with our studies on the thermal or photochemical reactions of the binuclear Mo and W compounds [$M_2Cp_2(CO)_4(\mu$-$A_2PXPA_2)$] [$A_2PXPA_2 = Ph_2PCH_2PPh_2$ (dppm) or $Me_2PCH_2PMe_2$ (dmpm); $M_2 = W_2$,[2] Mo_2.[3] or MoW;[4] $A_2PXPA_2 = (EtO)_2POP(OEt)_2$; $M_2 = Mo_2$ or W_2[5]]. In the latter we found that bond cleavages of the backbone of the bidentate phosphorus ligands (P−O or P−C bonds) are processes in competition with the oxidative addition of C−H bonds of the cyclopentadienyl ligands. However, we noticed that P−C bond cleavage of the diphosphine ligands required higher thermal activation than P−O bond cleavages in the diphosphite, so that the former could be suppressed at low temperatures, thus allowing the C−H bond cleavages to occur as a dominant process. As far as the above trends would hold at diiron centers, we could then make the hypothesis that chances to observe cyclopentadienyl C−H bond cleavages during decarbonylation reactions would be higher in the presence of diphosphines rather than diphosphites. We thus decided to study the reaction between [$Fe_2Cp_2(CO)_4$] and dppm.

First, we examined the thermal reaction of [$Fe_2Cp_2(CO)_4$] with dppm, studied originally by Haines et al.,[6] but we found no evidence of any ligand bond cleavage

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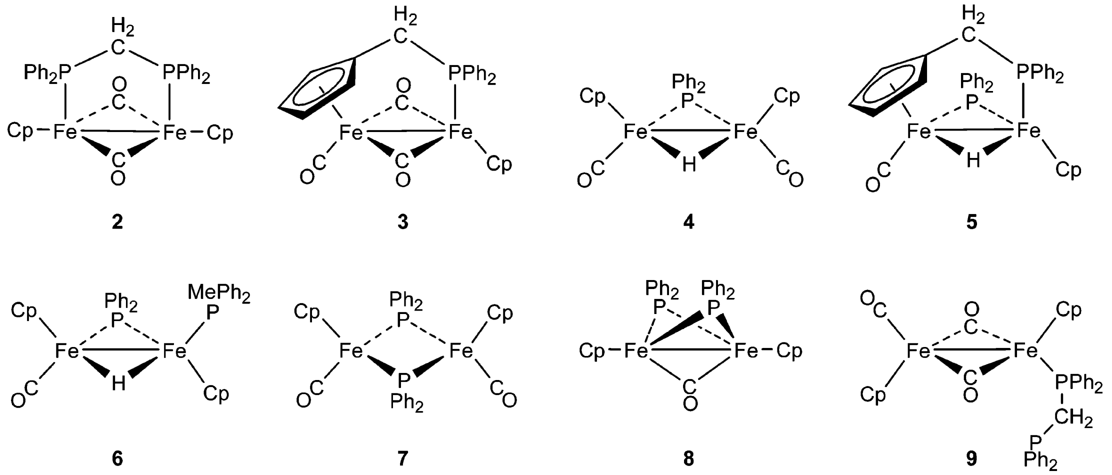
Chart 1



in the pathway to the final product [$Fe_2Cp_2(\mu\text{-}CO)_2(\mu\text{-}$dppm)] (**2**). Then we turned to the photochemical reactions, and the results thus obtained are the focus of the present paper. The photochemical reactions of [$Fe_2L_2(CO)_4$] complexes (L = cyclopentadienyl or related ligands) have been extensively studied,[7,8] but none of the reactive intermediates thus generated appear to have been recognized as being involved in the activation of ligands. We note, however, that Shade et al. have reported a cyclopentadienyl C−H activation during the photolysis of the dppm-bridged complex **2** in chloroform solutions to yield [$Fe_2Cp\{C_5H_4(CHO)\}(\mu\text{-}CO)_2(\mu\text{-}$dppm)].[9] Surprisingly, no new products could be isolated during the photolysis of **2** in benzene solutions. A photoinduced electron transfer to the solvent has been proposed to explain the above observations. We also note that related work on [$Ru_2Cp_2(CO)_4$] has shown the involvement of C−H (Cp) bond cleavage steps under photochemical conditions.[10] There is also at least one precedent of a C−H bond cleavage of an iron-bound cyclopentadienyl ligand under "dark" conditions, this occurring in the reaction between [$NbCp_2H$] and [$FeCp(Me)(CO)_2$] to give [$NbCp_2H(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5H_4)Fe(CO)_2$] after extrusion of methane.[11] As we will next discuss, the photochemical reactions of **1** with dppm are rather complex, and not only C−H (Cp) or P−C (dppm) bond cleavages have been detected, but also unexpected reductive C−C couplings between the fragments generated after the initial bond cleavage steps.

Results and Discussion

Photochemical Reactions of Compound 1 with Dppm. Irradiation with UV−visible light of solutions having stoichiometric amounts of **1** and dppm leads to a complex mixture of different species, with seven of them having been fully identified or characterized. These are the reported product of the thermal reaction, compound **2**,[6] and the new species [$Fe_2Cp(\mu\text{-}\eta^5{:}\kappa^1\text{-}C_5H_4CH_2PPh_2)(\mu\text{-}CO)_2(CO)$] (**3**), *cis*-[$Fe_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_2$] (**4**), [$Fe_2Cp(\mu\text{-}\eta^5{:}\kappa^1\text{-}C_5H_4CH_2PPh_2)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)$] (**5**), *trans*-[$Fe_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)(PMePh_2)$] (**6**), *cis*-[$Fe_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2$] (**7**), and [$Fe_2Cp_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)$] (**8**) (Chart 1). Compound **7** was first described by Hayter[12] and has been prepared also by other authors.[13,14] In fact, it is a minor product in our photochemical reaction that cannot be completely separated from other minor and unidentified products present in the reaction mixture. However, several aspects of its spectroscopic characterization have to be revised, as will be discussed later on.

The ratio among the above products in the final mixture is dependent on the reaction conditions (solvent, temperature, irradiation time, and glassware used). For example, we have found that the amount of **2** in the final mixture is increased when the photolysis experiment is carried out at room temperature, while compounds **5** and **6** are somewhat favored upon increasing the reaction time. On the other hand, formation of the dppm compound **2** is also favored when using Pyrex rather than quartz vessels, this indicating that UV light favors the bond cleavage processes required to form compounds **3**−**8**. The highest relative amounts of the new complexes **3**−**8** are obtained when the reaction is carried out at low temperatures (−25 °C) and using THF as solvent. In any case, we could not find experimental conditions to make more selective the photochemical reaction between **1** and dppm. In addition, spectroscopic monitoring of the photolytic experiments allowed us to detect the new complex *trans*-[$Fe_2Cp_2(\mu\text{-}CO)_2(CO)(\kappa^1\text{-}$dppm)] (**9**) as an intermediate species, which transforms into the dppm-bridged **2** at longer reaction times. Finally, as would be expected, the carbonyl-bridged compound **8** can be selectively prepared from dicarbonyl **7** under similar conditions, as shown by a separate experiment.

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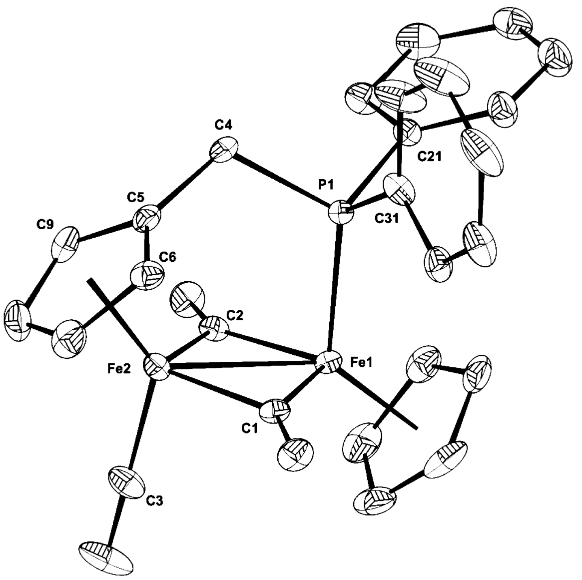

Figure 1. CAMERON view of the molecular structure of $[Fe_2Cp(\mu\text{-}\eta^5{:}\kappa^1\text{-}C_5H_4CH_2PPh_2)(\mu\text{-}CO)_2(CO)]$ (**3**). Ellipsoids represent 30% probability.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 3

	d (Å)		*θ* (deg)
Fe(1)−Fe(2)	2.504(1)	Fe(2)−Fe(1)−P(1)	90.02(5)
Fe(1)−P(1)	2.190(2)	Fe(1)−Fe(2)−C(3)	99.1(2)
Fe(1)−C(1)	1.888(5)	Fe(1)−C(1)−Fe(2)	82.1(2)
Fe(1)−C(2)	1.883(5)	Fe(1)−C(2)−Fe(2)	81.7(2)
Fe(2)−C(1)	1.923(5)	C(5)−C(4)−P(1)	111.2(4)
Fe(2)−C(2)	1.943(5)	C(4)−C(5)−C(6)	126.6(6)
Fe(2)−C(3)	1.737(7)	C(4)−C(5)−C(9)	124.9(6)
P(1)−C(4)	1.851(5)	C(4)−P(1)−Fe(1)	113.8(2)
P(1)−C(21)	1.829(4)	C(21)−P(1)−C(31)	102.7(2)
P(1)−C(31)	1.830(5)	C(4)−P(1)−C(21)	102.9(3)
C(5)−C(4)	1.500(8)	C(4)−P(1)−C(31)	102.3(3)

Crystal and Solution Structure of Compound 3. The structure of **3** has been determined through an X-ray study. There are two independent but almost identical molecules in the unit cell. Only one of them is depicted in Figure 1, while Table 1 lists the most relevant bond distances and angles. The molecule displays two iron cyclopentadienyl fragments bridged by a new seven-electron (diphenylphosphinomethyl)-cyclopentadienyl ligand ($C_5H_4CH_2PPh_2$) and two carbonyl ligands. A third carbonyl ligand is terminally bound to one of the iron atoms, thus completing the pseudotetrahedral coordination around the metal atoms (Cp assumed to occupy a single coordination position). Although different complexes containing the above phosphinomethylcyclopentadienyl bridging group have been previously described,[15] the presence of this ligand in **3** has two novel aspects: (a) previous complexes have been typically obtained through reactions that used a precursor already containing this ligand, such as $[FeCp(\mu\text{-}\eta^5{:}\kappa^1\text{-}C_5H_4CH_2PPh_2)]$[16] or $[TiCl_2(\mu\text{-}\eta^5{:}\kappa^1\text{-}C_5H_4CH_2PPh_2)_2]$,[17] and not through a C−C coupling reaction from metal-coordinated Cp and alkyl ligands; (b) complex **3** seems to be the first example structurally characterized where the phosphinomethylcyclopentadienyl ligand bridges two metal atoms that are also connected by a metal−metal bond. The presence of this metal−metal interaction, however, has little influence on the structural parameters in the ligand; thus the C4−P1−Fe1 and C5−C4−P1 angles (ca. 110°, Table 1) are similar to those in previous $C_5H_4CH_2PPh_2$ complexes.[15] The reverse is not true, and the presence of this bridging ligand seems to have a genuine shortening effect on the intermetallic separation. In fact, compound **3** can be considered a “linked” cyclopentadienyl derivative of the general family of phosphine complexes of the type $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)(PR_3)]$ first reported by Haynes et al. (R = alkyl, aryl, alkoxy, etc.).[18] However, the intermetallic distances in these complexes are significantly longer than the value of 2.504(1) Å found for **3**: for example, the complexes $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)\{P(OPh)_3\}]$[19a] and $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)\{PPh_2(CH_2Ph)\}]$[19b] exhibit intermetallic bond lengths of 2.545(2) and 2.540(2) Å, respectively. This shortening effect on the iron−iron distance is observed when other bridging ligands are present. For example, the diphosphine- or diphosphite-bridged compounds $[Fe_2Cp_2(\mu\text{-}CO)_2(\mu\text{-}L_2)]$ (L_2 = tedip,[1] dppe[9]) display similar short Fe−Fe distances (ca. 2.51 Å).

Spectroscopic data in solution for **3** are in agreement with the structure observed in the solid state. The IR spectrum of **3** (Table 2) exhibits two bands (weak and strong, in order of decreasing frequency) in the region of the C−O stretches of bridging carbonyls, as expected for two CO ligands defining almost a 180° relative angle.[20] There is also a strong band at 1939 cm^{-1} corresponding to the terminal carbonyl. Its frequency is characteristic of *trans*-$[Fe_2Cp_2(\mu\text{-}CO)_2(CO)(PR_3)]$ geometries. For example, the *trans*-complex having PEtPh$_2$ exhibits a terminal stretch at 1940 cm^{-1}.[18] The $^{31}P\{^1H\}$ NMR spectrum of **3** exhibits just one signal at 114.2 ppm (Table 2) in the usual region of phosphine ligands coordinated to iron centers. For example, the diphosphine-bridged compound **2** displays a ^{31}P resonance at 86.56 ppm.[9] The ^1H NMR spectrum of **3** exhibits a singlet for the cyclopentadienyl protons and two multiplets for the hydrogen atoms of the second ring ligand, as expected for monosubstituted cyclopentadienyls in general,[21] and also observed for previous $C_5H_4CH_2PPh_2$ complexes.[15] The presence of a mirror plane defined by the C5, C4, and P1 atoms makes the methylene protons equivalent, thus explaining their appearance as a doublet at 2.02 ppm (J_{PH} = 8 Hz).

Structural Characterization of Compound 4. The structure of compound **4** can be deduced unambiguously from the corresponding spectroscopic data. The $^{31}P\{^1H\}$ NMR spectrum of **4** exhibits just one signal at 187.3 ppm in the range expected for diarylphosphide ligands

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Table 2. IR and NMR Data for Compounds 3−8

compound	$\nu_{st}(CO)^a$	$\delta(P)^b$	$J_{PP}{}^c$
$[Fe_2Cp(\mu\text{-}\eta^5{:}\kappa^1\text{-}C_5H_4CH_2PPh_2)(\mu\text{-}CO)_2(CO)]$ (**3**)	1939(s), 1771(w), 1727(vs)	114.2	
cis-$[Fe_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_2]$ (**4**)	1950(vs)	187.3^d	
$[Fe_2Cp(\mu\text{-}\eta^5{:}\kappa^1\text{-}C_5H_4CH_2PPh_2)(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)]$ (**5**)	1898(vs)	193.3, 89.4	29
trans-$[Fe_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)(PMePh_2)]$ (**6**)	1898(vs)	180.3, 61.9	37
cis-$[Fe_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2]$ (**7**)	1951(vs)	−8.1	
$[Fe_2Cp_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)]$ (**8**)	1747(s)	116.9^d	
trans-$[Fe_2Cp_2(\mu\text{-}CO)_2(CO)(\kappa^1\text{-}dppm)]$ (**9**)	1929(s), 1725(vs)	65.4, −23.7^e	29

[a] Recorded in CH_2Cl_2 solution, unless otherwise stated, ν in cm^{-1}. [b] Recorded in C_6D_6 solution at 290 K and 81.01 MHz, unless otherwise stated; δ in ppm relative to external 85% aqueous H_3PO_4. [c] Coupling constants in hertz. [d] Recorded in CD_2Cl_2 and 121.49 MHz. [e] Recorded at 121.49 MHz.

bridging two iron atoms connected by a metal−metal bond.[22] Its ^1H NMR spectrum indicates the equivalence of both cyclopentadienyl ligands (just a resonance at 4.60 ppm) and the presence of a hydride ligand (−19.24 ppm). The chemical shift of the latter signal, much lower than the usual values for terminal hydride ligands, and the P−H coupling to the phosphide group (J_{HP} = 43 Hz) are consistent with a bridging coordination of the hydride ligand. These spectroscopic parameters are comparable to those measured for the diphenylphosphide-hydride $[Fe_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}dppm)]$, a complex isolated from the reaction of $[FeCl_2(dppm)]$ with activated Mg and C_5H_6,[23] which exhibits δ (μ-P) = 172.3 ppm, δ (μ-H) = −22.00 ppm, and J_{PH} = 42.2 Hz. The IR spectrum of **4** displays one band in the region of the terminal C−O stretches. Its frequency (1950 cm^{-1} in CH_2Cl_2) falls in the range observed (1963−1943 cm^{-1}) for isoelectronic and isostructural dicarbonyl complexes having a *cis*-disposition of the carbonyl ligands, *cis*-$[Ru_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_2]$[24] and *cis*-$[Fe_2Cp_2(\mu\text{-}H)(\mu\text{-}PR_2)(CO)_2]$ (R = menthyl and related hydrocarbon chains).[25] The presence of just one band rather than the expected strong and weak bands in the CO stretching region is not attributed to a low intensity (perfect parallelism between the CO ligands) of the asymmetric stretch,[20] but to an almost identical frequency (small value of the interaction constant). The *cis* relative position of the carbonyl ligands in **4** is confirmed by its $^{13}C\{^1H\}$ NMR spectrum, which exhibits two different sets of signals for the phenyl groups. This is an indication of different environments at both sides of the approximate plane defined by the iron and phosphorus atoms, which is caused by the presence of both carbonyls ligands at the same side of that plane (Chart 1). We should note that a compound with the same formulation as **4** was reported by Hayter to be formed in very low yield (5%) from the thermal reaction of $[Fe_2Cp_2(CO)_4]$ with Ph_2P-PPh_2,[12] but this product was not fully characterized at the time. In the same paper the complex $[Fe_2Cp_2(\mu\text{-}H)(\mu\text{-}PMe_2)(CO)_2]$ was also described, but, surprisingly, the only related phosphide hydride diiron complexes described in the literature since Hayter's original report have been prepared by Brunner et al. from the thermal reaction of secondary phosphines HPR_2 (R_2 = menthyl and related hydrocarbon chains).[25] Under these conditions, a mixture of *cis*- and *trans*-$[Fe_2Cp_2(\mu\text{-}H)(\mu\text{-}PR_2)(CO)_2]$ could be prepared in moderate to good yields. Our photochemical preparation of **4**, although quite unsatisfactory from a synthetic point of view, gives specifically the *cis* isomer of the diphenylphosphide-hydride derivative, thus allowing its full spectroscopic characterization. As will be seen, the formation of **4** in our photochemical reaction also explains the presence of compound **6** in the reaction mixture.

Structural Characterization of Compounds 5 and 6. Compound **5** combines the structural elements present in complexes **3** (diphenylphosphinomethylcyclopentadienyl) and **4** (diphenylphosphide and hydride ligands). Thus, the spectroscopic data for **5** are very similar to those previously discussed for compounds **3** and **4** (Table 2 and Experimental Section). For example, the $^{31}P\{^1H\}$ NMR spectrum exhibits two signals at 193.3 and 89.4 ppm in the usual range for iron-bonded diarylphosphide (187.3 ppm for **4**)[22,25] or phosphine ligands (114.2 ppm for **3**), respectively. The ^1H NMR spectrum of **5** exhibits as most relevant features a triplet hydride resonance at −18.70 ppm (J_{PH} = 37 Hz), indicative of a bridging hydride defining similar H−Fe−P angles with the phosphide and phosphine P atoms. As a result, the symmetry plane bisecting the phosphinomethylcyclopentadienyl ligand in **3** is no longer present in **5**, thus yielding all the C_5H_4 and methylene protons to be unequivalent. This asymmetry is also evident from the $^{13}C\{^1H\}$ NMR spectrum of **5**, which exhibits independent resonances for the four phenyl groups or the C_5H_4 ring atoms.

The structure of complex **6** is shown in Chart 1. It is formally derived from **4** after replacement of a CO ligand by methyldiphenylphosphine. In fact, we have shown through a separate experiment that **4** reacts with $PMePh_2$ under the usual photochemical conditions to give **6** as the major product. The spectroscopic data for **6** (Table 2) totally support that structure. The presence of diphenylphosphide and hydride ligands similar to those in **4** is indicated by the appearance of resonances at δ (μ-P) = 180.3 ppm and δ (μ-H) = −21.38 ppm. On the other hand, the incorporation of a $PMePh_2$ phosphine to the iron center is clearly revealed by the appearance of a ^{31}P resonance at 61.9 ppm and a ^1H doublet resonance at 0.67 ppm (J_{HP} = 7 Hz) assigned to the methyl group of the phosphine. The coupling between P atoms (J_{PP} = 37 Hz) is similar to that found for **5** (J_{PP} = 29 Hz), as expected from their similar relative positions. The same applies to the hydride resonance, which exhibits H−P couplings of 33 and 48 Hz, in the range found for **5** (J_{HP} = 37 Hz). Finally, the

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(24) Caffyn, A. J. M.; Mays, M. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1991**, 2349−2356.

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exact coincidence of the C−O stretching frequencies exhibited by **5** and **6** proves that the CO and the phosphine ligands in the latter lie on opposite sides of the plane defined by the bridging groups (*trans* isomer), as it necessarily happens in the case of **5**.

Identification and NMR Properties of Compound 7. In our photochemical reaction, compound **7** is just a minor compound that is formed in very low yield and is difficult to purify even after laborious chromatographic work. However, its presence in the reaction mixture is relevant in order to understand the reaction pathways under operation. Complex **7** has been identified as the *cis* isomer of the phosphide complex $[Fe_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2]$, first reported by Hayter,[12] and structurally characterized through an X-ray study.[26] Although only the IR and ^1H NMR spectra for this product were originally recorded, thus precluding a more complete comparison with our data, we have independently prepared compound **7** as well as its *trans* isomer by the Hayter's route (thermal reaction of **1** with Ph_2P-PPh_2). In our hands, the ν(CO) stretching frequencies for *cis* and *trans* isomers of $[Fe_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2]$ are respectively 1949 and 1927 cm^{-1}, both in CH_2Cl_2 solution. These figures compare well with the values 1961 and 1917 cm^{-1} reported in CS_2 solution.[12] The ^1H NMR spectrum of **7** in C_6D_6 solution exhibits the expected phenyl resonances and a singlet cyclopentadienyl resonance at 3.93 ppm, in agreement with the symmetry of the complex and the reported shift of 3.99 ppm in CS_2.[12] The $^{31}P\{^1H\}$ NMR spectrum of **7** exhibits a resonance at −8.1 ppm in C_6D_6. This chemical shift must be viewed as normal by considering that there is no metal−metal bond in this molecule. Usually, the absence of metal−metal bonds causes a strong shielding of the ^{31}P resonances of diphenylphosphide ligands.[22] Indeed, this is also the case of the *trans* isomer of **7**. For this *trans* isomer we have measured a ^{31}P chemical shift of −11.6 ppm in C_6D_6 solution, to be compared with shifts of ca. 190 ppm for the metal−metal bonded phosphide compounds **4**−**6**. There is, however, a conflict involving the ^{31}P shifts of these compounds. As part of a general study on the spectroscopic properties of *cis* and *trans* diiron complexes of general formula $[Fe_2Cp_2(\mu\text{-}PX_2)_2(CO)_2]$, with X being electronegative substituents of type OR, SR, or NR_2, Verkade and co-workers reported ^{31}P chemical shifts of 206.6 and 212.0 ppm for the *cis* and *trans* isomers of compound $[Fe_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2]$, respectively.[14] Those values are in radical disagreement with our own data for the same compounds (−8.1 and −11.6 ppm, respectively), but we cannot explain this strong discrepancy in these NMR data.

Synthesis and Structural Characterization of Compound 8. The IR spectrum of compound **8** displays a single band at 1747 cm^{-1} in CH_2Cl_2 solution, thus clearly indicating its bridging character. This is corroborated by the appearance of a highly deshielded resonance at 276.4 ppm in the $^{13}C\{^1H\}$ NMR spectrum. The latter resonance appears as a triplet ($J_{PC} = 21$ Hz) due to coupling with two equivalent phosphorus atoms. Other features in the $^{13}C\{^1H\}$ and ^1H NMR spectra (see Experimental Section) are indicative of a rather symmetric molecule having equivalent phosphorus and Cp ligands, while the four phenyl rings are related pairwise, in agreement with a $(CpFe)_2$ moiety bridged symmetrically by two diphenylphosphide groups and one carbonyl ligand (Chart 1). The chemical shift of the phosphide P atoms ($\delta = 116.9$ ppm) can be considered as somewhat low, when compared to the shifts of ca. 190 ppm for other metal−metal bonded complexes in this work. Although we are not sure about the origin of this low shift, we suspect that this could be an indication of strain in the Fe_2P cycle or steric congestion around the dimetal unit, all of which could have definite effects on the Fe_2P or PC_2 angles.[22] In fact, compound **8** is not very stable, and prolonged manipulation of its solution causes its progressive decomposition. In line with this idea we note that, to our surprise, no other carbonyl-bridged phosphide complex of type $[Fe_2Cp_2(\mu\text{-}PX_2)_2(\mu\text{-}CO)]$ appears to have been reported in the literature. Interestingly, Bitterwolf et al. have recently reported the detection of similar thiolate-bridged complexes $[Fe_2Cp_2(\mu\text{-}SR)_2(\mu\text{-}CO)]$ as transient intermediates in the photolytic isomerization between *cis* and *tran*s dicarbonyls $[Fe_2Cp_2(\mu\text{-}SR)_2(CO)_2]$, both in solution and in frozen matrix supports.[27]

Once the structure of **8** was firmly established, it could be anticipated that **8** was very likely to be a photoproduct derived from dicarbonyl **7**. Indeed, when a mixture of *cis* and *trans* isomers of **7** (as directly obtained by Hayter's method) is photolyzed in THF solution at − 25 °C, it slowly but cleanly transforms into the monocarbonyl compound **8**. No other side products were formed in significant amounts, as verified by recording a ^{31}P NMR spectrum of the reaction mixture.

Synthesis and Structural Characterization of Compound 9. As we have stated above, complex **9** is detected by IR and ^{31}P NMR during the photolysis of **1** in the presence of dppm, but it gradually disappears from the reaction mixture. To prepare this compound selectively, we considered the same strategy used before to obtain the isostructural complex $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)(\kappa^1\text{-tedip})]$,[1] based on the fact that the acetonitrile ligand in $[Fe_2Cp_2(CO)_3(NCMe)]$[28] is easily displaced by two-electron donor ligands. As expected, $[Fe_2Cp_2(CO)_3(NCMe)]$ reacts rapidly with dppm in toluene even at 0 °C to give **9** in very good yield. The presence of a unidentate dppm ligand in **9** is clearly shown in its $^{31}P\{^1H\}$ NMR spectrum, which exhibits two coupled resonances. The doublet at 65.4 ppm (Table 2) has a chemical shift in the region observed for arylphosphines bonded to iron complexes, while the signal at −23.7 ppm has a chemical shift very close to that for the free dppm ligand (−23.2 ppm in C_6D_6). Compound **9** is then another member of the large family of phosphine derivatives of compound **1** having the general formula $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)(PR_3)]$.[18] For these compounds, *cis* and *trans* isomers are possible, as defined by the relative positions of the terminal ligands with respect to the average $Fe_2(\mu\text{-}C)_2$ plane. When both isomers of the same compound are known, it is always found that the *cis* isomers exhibit ν(CO) stretching frequencies around 20 cm^{-1} higher than the *trans* isomers. Therefore, by recalling that *trans*-$[Fe_2Cp_2(\mu\text{-}CO)_2(CO)(PEtPh_2)]$ ex-

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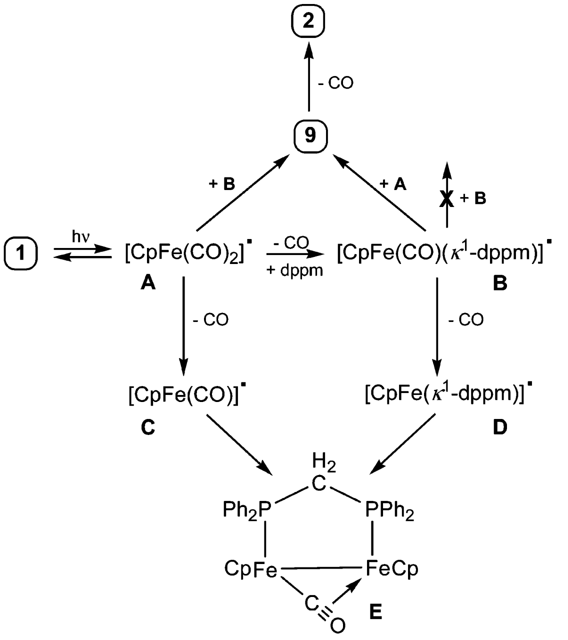
[28] Labinger, J. A.; Madhaven, S. *J. Organomet. Chem.* **1977**, *134*, 381−389.

Scheme 1. Initial Reaction Pathways Proposed to Occur in the Photochemical Reaction of 1 with Dppm



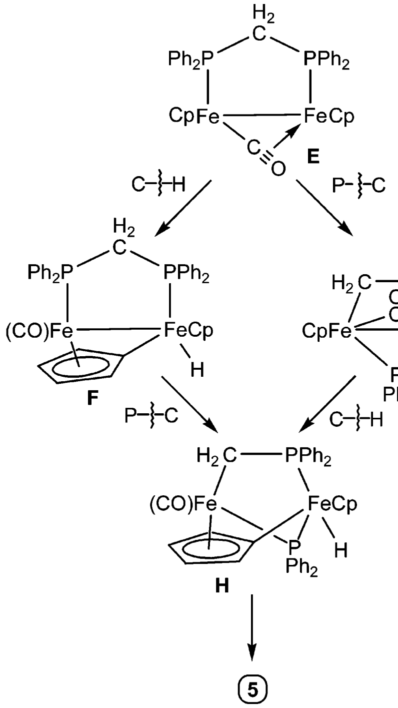
hibits a terminal C−O stretch at 1940 cm^{-1} (cyclohexane solution)[18] and that the terminal C−O band of **9** appears at 1929 cm^{-1} (CH_2Cl_2 solution), we can safely assign a *trans* structure to the latter complex (Chart 1).

When toluene or tetrahydrofuran solutions of compound **9** were exposed to UV light at −25 °C for 1 h, a clean transformation into the dppm-bridged **2** occurred. No other P-containing species were present in the crude reaction mixture, a result that is of relevance when analyzing the pathways under operation in these photochemical experiments, as we will next discuss.

Reaction Pathways of Dppm at Diiron Centers. As it can be deduced from the results discussed above, the photochemical reaction between **1** and the diphosphine ligand dppm cannot be a simple process. This is readily apparent by just considering the large number and structural variety of the complexes formed. Although the detailed reaction pathways in operation cannot be revealed from our synthetic work, we have enough information to propose rational steps that could explain some of the processes likely to be responsible for the formation of compounds **2**−**9** (Schemes 1−3). These necessarily involve different P−C and C−H bond cleavages, as well as some C−C couplings, in order to explain the nature of the compounds isolated.

The photochemical reaction between **1** and dppm would be mainly initiated by the homolytic cleavage of the Fe−Fe bond to give the [FeCp(CO)$_2$] radical **A**[7,8] (Scheme 1), which is well known to experience easy substitution of CO by ligands.[8d,e,29] In our case, **A** would thus easily give the 17-electron dppm derivative [FeCp(CO)(κ^1-dppm)], **B**. At this point, three radical recombinations can occur: **A**−**A**, **A**−**B**, or **B**−**B**. The first one affords the starting complex **1**, which obviously must be in equilibrium with radical **A** under photolytic conditions. Reaction **A** + **B** would give compound **9**, and this is surely the main reaction pathway leading to **2**. Indeed, pure compound **9** transforms cleanly into **2** under similar photolytic conditions, as we have discussed above. However, this also means that compound **9** is not a precursor of compounds **3**−**8**. Finally, the dimerization process **B** + **B** could happen as well, but this is expected to be slow, as shown for other phosphine-substituted radicals of type [FeCp(CO)L]. As a result, further evolution of the radicals **A** and **B**, different from simple recombination, must be involved in order to justify the formation of compounds **3**−**8**.

Scheme 2. Oxidative Additions and C−C Reductive Coupling Proposed to Occur during the Photochemical Formation of Compound 5



As we have proposed for the photolytic reactions of **1** in the presence of diphosphite tedip,[1] it is likely that either radical **A** or **B** could experience further decarbonylation to give 15-electron radicals (Scheme 1).[8f] In our case, this would lead to radicals **C** and **D**, the combination of which (**A** + **D** or **B** + **C**) would give the monocarbonyl intermediate **E**, isoelectronic to compound [$Fe_2Cp_2(\mu\text{-}\eta^1,\eta^2\text{-}CO)(CO)_2$][8b,30] and also having probably a μ-η^1:η^2 bridging CO ligand. This intermediate could lead to the formation of complex **5** by stepwise intramolecular oxidative additions of a P−C bond of the dppm ligand and a C−H bond of the cyclopentadienyl ligand, via intermediates **F** or **G**, followed by a C−C coupling (reductive elimination) that would generate the (diphenylphosphinomethyl)cyclopentadienyl ligand (Scheme 2). Both types of oxidative additions have been previously observed for related binuclear complexes such as [$Fe_2(CO)_5(\mu\text{-dppm})_2$] (thermal P−C cleavage)[31] or [$M_2Cp_2(CO)_4(\mu\text{-dppm})$] (M = Mo, W; thermal P−C and photochemical C−H cleavages).[2−4] We note, however, that previous examples of P−C cleavages are always

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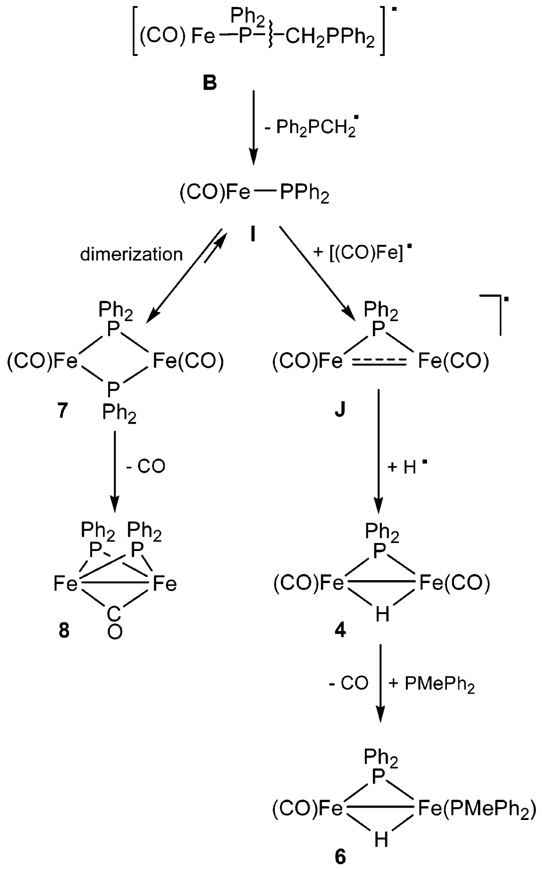
Scheme 3. Proposed Reaction Pathways in the Photochemical Formation of the Diphenylphosphide Derivatives 4, 6, 7, and 8 (Fe = FeCp)



induced thermally, not photochemically. On the other hand, we should stress that precedents for related reductive C−C couplings are extremely scarce. In fact, we have been able to find just one example of a related coupling involving cyclopentadienyl and phosphine ligands. Thus, refluxing xylene solutions of **1** and PPh_3 to yield $[Fe_4Cp_4(CO)_4]$ has been reported to give the C−C coupling product $[Fe_4Cp_3(C_5H_4Ph)(CO)_4]$ in 3% yield.[32] On the other hand, it is also likely that similar bond cleavage and forming processes are involved in the buildup of tricarbonyl **3**, although the sequence of events is more unclear to us at the moment.

Intermediate **B** could alternatively evolve through the homolytic cleavage of a C−P bond in the unidentate dppm ligand to give the diphenylphosphide intermediate **I** and the phosphinomethyl radical CH_2PPh_2 (Scheme 3). The dimerization of **I** then would lead to the formation of complexes **7** and **8**, while the combination of this intermediate with radical **C** would form the paramagnetic dicarbonyl **J**. The latter is a 33-electron radical isoelectronic with $[Mo_2Cp_2(\mu\text{-}PPh_2)(CO)_4]$ and therefore is expected to abstract easily an H atom either from the solvent or from traces of water present in the reaction mixture.[33] In this way the formation of the hydride complex **4** can be explained. A similar H atom abstraction from the phosphinomethyl radical would yield methyldiphenylphosphine, which under photolytic conditions does react with **4** to give **6**, as we have shown through separate experiments. The key step to explain the formation of compounds **4**, **6**, **7**, and **8** then is the P−C cleavage of the backbone of the dppm ligand at the mononuclear radical $[FeCp(CO)(\kappa^1\text{-dppm})]$, **B**. Unfortunately, we have not been able to find previous reports of P−C bond cleavages occurring at paramagnetic iron phosphine complexes that would provide further support to our hypothesis. In any case, we should stress that the influence of the reaction time on the relative amounts of compounds **4**, **6**, **7**, and **8** is in full agreement with the above proposal. It is experimentally observed that on prolonged photolysis the yield of **6** is somewhat increased, and that of **8** is decreased while the yields of **4** or **7** are almost reduced to zero. This is in agreement with our proposal, which implies the generation of stoichometric amounts of $PMePh_2$ relative to the overall **J** + **7**, that is, **4** + **6** + **7** + **8**. Moreover, the fact that the yields in **7** and **8** are reduced upon extended photolysis suggests that the dimerization from intermediate **I** is a reversible step.

In any case the results just discussed indicate that the intermediates generated during the photolysis of mixtures of **1** and dppm are much more reactive than the unsaturated species generated through decarbonylation of the Mo and W complexes $[Mo_2Cp_2(CO)_4(\mu\text{-}L_2)]$. This is deduced from the observation that the P−C bond cleavage of the dppm ligand at the iron centers cannot be suppressed even at −25 °C under photolytic conditions.

Concluding Remarks

The photochemical reactions between $[Fe_2Cp_2(CO)_4]$ and the diphosphine ligand $Ph_2PCH_2PPh_2$ seem to proceed through the radical intermediates $[FeCp(CO)_2]$ and $[FeCp(CO)(\kappa^1\text{-dppm})]$, which then evolve and experience C−H (cyclopentadienyl) or P−C (backbone of dppm) bond cleavages even at −25 °C. These bond cleavages are responsible for the appearance of diphenylphosphide and methyldiphenylphosphine ligands in the reaction products and may be followed by reductive C−C coupling involving cyclopentadienylidene intermediates, thus leading to products with a seven-electron-donor (diphenylphosphinomethyl)cyclopentadienyl bridging ligand.

Experimental Section

General Comments. All manipulations and reactions were carried out using standard Schlenk techniques under an atmosphere of dry, oxygen-free nitrogen. Solvents were purified according to standard literature procedures[34] and distilled under nitrogen prior to use. Petroleum ether refers to the fraction distilling in the range 60−65 °C. The compounds dppm[35] and $[Fe_2Cp_2(CO)_3(NCMe)]$[28] were prepared as described previously. Compound $[Fe_2Cp_2(CO)_4]$ was obtained from the usual commercial suppliers and used without further purification. Photochemical experiments were preformed using jacketed Pyrex or quartz Schlenk tubes, refrigerated by a closed 2-propanol circuit kept at the desired temperature with a cryostat or by tap water. A 400 W mercury lamp (Applied

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[34] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, U.K., 1988.

[35] Aguiar, A. M.; Beisler, J. *J. Org. Chem.* **1964**, *29*, 1660−1662.

Photophysics), placed ca. 1 cm away from the Schlenk tube, was used for these experiments. Low-temperature chromatographic separations were carried out analogously using jacketed columns. Commercial aluminum oxide (alumina, Aldrich, 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. NMR spectra were recorded at 300.13 (^1H), 81.01 ($^{31}P\{^1H\}$), or 50.32 MHz ($^{13}C\{^1H\}$), at room temperature unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal TMS (^1H, ^{13}C) or external 85% H_3PO_4 aqueous solution (^{31}P), with positive values for frequencies higher than that of the reference. Coupling constants (J) are given in hertz. $^{13}C\{^1H\}$ NMR spectra were routinely recorded on solutions containing a small amount of tris(acetylacetonate) chromium(III) as a relaxation reagent.

Photochemical Reaction of [$Fe_2Cp_2(CO)_4$] (1) with Dppm. A tetrahydrofuran solution (20 mL) of **1** (0.250 g, 0.707 mmol) and dppm (0.275 g, 0.716 mmol) was placed in a refrigerated quartz Schlenk tube. This solution was photolyzed at −25 °C for 5 h while bubbling N_2 (99.9995%) through the solution to give a brown solution. Solvent was then removed under vacuum and the residue dissolved in a minimum of petroleum ether/CH_2Cl_2 (2/1). This solution was chromatographed at −15 °C on an alumina column (activity III, 50 × 3 cm) prepared in petroleum ether. After washing the column with petroleum ether, elution with a petroleum ether/CH_2Cl_2 (5/1) mixture gave an orange fraction containing a small amount of compound **7** and some other unidentified species, which was discarded. Elution with a petroleum ether/CH_2Cl_2 (4/1) mixture gave two light brown fractions containing complexes **4** and **8**, respectively, followed by a third dark brown fraction containing complex **6**. Elution with petroleum ether/CH_2Cl_2 (3/1) gave a red fraction containing compound **5**, and elution with petroleum ether/CH_2Cl_2 (1/1) gave a light green fraction containing compound **3**. Finally, a dark green fraction of **2** was collected when a petroleum ether/CH_2Cl_2 (1/4) mixture was used as eluant. Removal of solvents under vacuum from the above fractions gave respectively compounds **4** (red-brown, 0.051 g, 15%), **8** (yellow-orange, 0.066 g, 14%), **6** (brown, 0.014 g, 3%), **5** (brown, 0.018 g, 4%), **3** (green, 0.063 g, 17%), and **2** (green, 0.066 g, 15%) as microcrystalline powders. The crystals used in the X-ray diffraction study of compound **3** were grown by slow diffusion of petroleum ether into a solution of this complex in CH_2Cl_2 at −20 °C. The use of longer reaction times causes a significant change in the relative amounts of the above complexes. For example, using a photolysis time of 8 h increases the amount of compounds **5** and **6**, while the yields of compounds **3** and **8** are lower and compounds **4** and **7** disappear from the final reaction mixture. The yield of complex **2** remains roughly unchanged.

Data for Compound 3. Anal. Calcd for $C_{26}H_{21}O_3PFe_2$: C, 59.58; H, 4.04. Found: C, 59.12; H, 3.95. ^1H NMR (C_6D_6): δ 7.80−6.80 (m, 20H, Ph), 4.76 (t, AA′XX′, $J_{AX} + J_{AX'} = 4$, 2H, C_5H_4), 4.40 (s, br, 2H, C_5H_4), 4.24 (s, 5H, Cp), 2.02 (d, $J_{HP} = 8$, 2H, CH_2). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 114.2 (s, CH_2PPh_2).

Data for Compound 4. Anal. Calcd for $C_{24}H_{21}O_2PFe_2$: C, 59.55; H, 4.37. Found: C, 59.46; H, 4.31. ^1H NMR (CD_2Cl_2): δ 7.80−7.15 (m, 10H, Ph), 4.60 (s, 10H, Cp), −19.24 (d, $J_{HP} = 43$, 1H, μ-H). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2): δ 187.3 (s, μ-PPh_2). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2): δ 215.8 (d, $J_{CP} = 20$, CO), 147.8 [d, $J_{CP} = 12$, $^1C(Ph)$], 140.8 [d, $J_{CP} = 39$, $^1C(Ph)$], 135.8 [d, $J_{CP} = 9$, $^2C(Ph)$], 132.3 [d, $J_{CP} = 9$, $^2C(Ph)$], 128.9 [s, $^4C(Ph)$], 128.2 [d, $J_{CP} = 9$, $^3C(Ph)$], 128.1 [s, $^4C(Ph)$], 127.8 [d, $J_{CP} = 9$, $^3C(Ph)$], 80.6 (s, Cp).

Data for Compound 5. Anal. Calcd for $C_{36}H_{32}OP_2Fe_2$: C, 66.09; H, 4.93. Found: C, 66.18; H, 4.95. ^1H NMR (C_6D_6): δ 8.20−6.90 (m, 20H, Ph), 4.99, 4.72, 4.61 (3 × s, 3 × 1H, C_5H_4), 4.13 (s, 5H, Cp), 4.02 (s, br, 1H, C_5H_4), 1.87 (t, $J_{HH} = J_{HP} = 13$, 1H, CH_2), 1.00 (dd, $J_{HH} = 13$, $J_{HP} = 5$, 1H, CH_2), −18.70 (t, $J_{HP} = 37$, 1H, μ-H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 193.3 (d, $J_{PP} = 29$, μ-PPh_2), 89.4 (d, $J_{PP} = 29$, μ-CH_2PPh_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 219.5 (d, $J_{CP} = 16$, CO), 148.7 [d, $J_{CP} = 28$, $^1C(Ph)$], 147.5 [d, $J_{CP} = 18$, $^1C(Ph)$], 144.6 [d, $J_{CP} = 28$, $^1C(Ph)$], 142.2 [d, $J_{CP} = 25$, $^1C(Ph)$], 135−126 (Ph), 97.2 (d, $J_{CP} = 4$, C_5H_4), 82.3 (s, C_5H_4), 82.1 (s, C_5H_4), 77.1 (s, Cp), 71.2 (s, C_5H_4), 28.7 (d, $J_{CP} = 23$, CH_2).

Table 3. Crystal Data for Compound 3

mol formula	$C_{26}H_{21}Fe_2O_3P$
mol wt	524.12
cryst syst	orthorhombic
space group	$P2_1cn$
cryst color	dark green
radiation (λ, Å)	Mo Kα ($\lambda = 0.71069$ Å)
a, Å	8.510(2)
b, Å	13.070(4)
c, Å	39.411(19)
V, Å^3	4383(3)
Z	8
calcd density, g cm^{-3}	1.59
μ(Mo Kα), cm^{-1}	14.21
diffractometer	CAD4 Enraf-Nonius
temperature, K	295
scan type	$\omega/2\theta$
θ limits, deg	1−30
scan width	$0.8 + 0.345 \tan\theta$
total no. of data	7131
no. of total unique data	6766
no. of unique data used	3850 [$(F_o)^2 > 3\sigma(F_o)^2$]
R^a	0.0394
$R_w{}^b$	0.0487
GOF	0.94
octants collected	0,11; 0,18; 0,55
decay %	< 5
extinction param	855
no. of variables	580
$\Delta\rho_{min}$ (e/Å^3)	−0.46
$\Delta\rho_{max}$ (e/Å^3)	0.38

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = w'[1 - (||F_o| - |F_c||/6\sigma F_o)^2]^2$, with $w' = 1/\sum r A_r T_r(X)$ with 3 coefficients 8.29, −0.232, and 6.65 for a Chebyshev series, for which X is F_c/F_c(max).

Data for Compound 6. Anal. Calcd for $C_{36}H_{34}OP_2Fe_2$: C, 65.88; H, 5.22. Found: C, 65.53; H, 5.45. ^1H NMR (200.13 MHz, C_6D_6): δ 8.30−6.80 (m, 20H, Ph), 4.35, 3.91 (2 × s, 2 × 5H, Cp), 0.67 (d, $J_{HP} = 7$, 3H, Me), −21.38 (dd, $J_{HP} = 48$, 33, 1H, μ-H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 180.3 (d, $J_{PP} = 37$, μ-PPh_2), 61.9 (d, $J_{PP} = 37$, PPh_2Me).

Preparation of [$Fe_2Cp_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)$] (8). A mixture of *cis* and *trans* isomers of compound **7**, obtained as described in ref 12 (0.050 g, 0.08 mmol), was dissolved in tetrahydrofuran (15 mL) and photolyzed at −25 °C for 2 h in a quartz Schlenk tube while keeping a strong bubbling of N_2 through the solution. The resulting dark brown solution was filtered and the solvent removed from the filtrate under vacuum. Washing of the residue with petroleum ether (3 × 5 mL) gave compound **8** as a brown powder (0.041 g, 80%). Anal. Calcd for $C_{35}H_{30}OP_2Fe_2$: C, 65.66; H, 4.72. Found: C, 65.38; H, 4.49. ^1H NMR (400.13 MHz, C_6D_6): δ 7.30−6.70 (m, 20H, Ph), 4.54 (s, 10H, Cp). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2): δ 116.9 (s). $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2): δ 276.4 (t, $J_{CP} = 21$, μ-CO), 149.9 [false t, $J_{CP} + J_{CP'} = 32$, $^1C(Ph)$], 135.0 [m, $^2C(Ph)$], 134.6 [false t, $J_{CP} + J_{CP'} = 34$, $^1C(Ph)$], 131.9 [m, $^2C(Ph)$], 129.2, 128.3 [2 × s, $^4C(Ph)$], 127.7, 127.4 [2 × m, $^3C(Ph)$], 86.0 (s, Cp).

Preparation of *trans*-[$Fe_2Cp_2(\mu\text{-}CO)_2(CO)(\kappa^1\text{-}dppm)$] (9). A cold (0 °C) toluene solution (20 mL) of dppm (0.100 g, 0.26 mmol) was transferred over [$Fe_2Cp_2(CO)_3(NCMe)$][28] (0.095 g, 0.26 mmol), previously placed in a refrigerated flask at 0 °C, and the mixture was stirred at this temperature for 15 min to yield a green solution. Solvent was then removed under vacuum, and the residue was dissolved in CH_2Cl_2/petroleum ether (1/2) and chromatographed at −15 °C on an alumina column (activity 3.5, 12 × 1.5 cm) prepared in petroleum ether. Elution with the same solvent mixture gave a red fraction, containing **1**, followed by a green fraction that contains complex **9**. Removal of solvents from the latter fraction yielded compound **9** (0.162 g, 88%) as a microcrystalline green solid. Anal. Calcd for $C_{38}H_{32}O_3P_2Fe_2$: C, 64.26; H, 4.54. Found: C, 64.95; H, 5.10. ^1H NMR (200.13 MHz, C_6D_6): δ 7.90 (m, 4H, Ph), 7.22−6.88 (m, 16H, Ph), 4.43, 4.13 (2 × s, 2 × 5H, Cp), 2.57 (br, 2H, CH_2). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6): δ 65.4 (d, $J_{PP} = 29$, P−Fe), −23.7 (d, $J_{PP} = 29$, P).

X-ray Structure Determination for Compound 3. The selected crystal was stuck on a glass fiber and mounted on a Enraf-Nonius CAD4 automatic diffractometer. Accurate cell dimensions and orientation matrix were obtained by least-squares refinements of 25 accurately centered reflections. No significant variations were observed in the intensities of two checked reflections during data collection. Complete crystallographic data and collection parameters are listed in Table 3. The data were corrected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS.[36] Scattering factors and corrections for anomalous absorption were taken from the International Tables for Crystallography.[37] The structure was solved by direct methods (SHELXS),[38] completed by Fourier techniques, and refined by full-matrix least-squares. All non hydrogen atoms were anisotropically refined. Hydrogen atoms were introduced in calculated positions in the last least-squares refinements; they were allocated an overall isotropic thermal parameter. Two independent molecules are present in the asymmetric unit, having no significant differences in their structural parameters. The main bond lengths and bond angles are summarized in Table 1. Figure 1 contains a CAMERON[39] view of one of the molecules.

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Supporting Information Available: Tables of fractional atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for compound **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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