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Diphenylphosphide-Bridged Diiron Derivatives of $[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_2]$

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The complex *trans*-$[Fe_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_2]$ is obtained in 91% yield by refluxing toluene solutions of $[Fe_2Cp_2(CO)_4]$ ($Cp = \eta^5\text{-}C_5H_5$) and the secondary phosphine PPh_2H. This compound isomerizes upon irradiation with visible−UV light under a CO atmosphere to yield *cis*-$[Fe_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_2]$. The above hydride complexes react under photochemical conditions with 1 equiv of secondary phosphines PR_2H ($R = Et$, Ph) to give the corresponding monocarbonyl compounds $[Fe_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}PR_2)(\mu\text{-}CO)]$ via the hydride intermediates $[Fe_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)(PR_2H)]$ (detected and isolated for $R = Et$). Deprotonation of *trans*-$[Fe_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_2]$ with LiBu gives the binuclear anion $[Fe_2Cp_2(\mu\text{-}PPh_2)(CO)_2]^-$. This highly nucleophilic carbonylate reacts rapidly with $[AuCl(P^iPr_3)]$ or MeI to give the corresponding gold diiron cluster $[AuFe_2Cp_2(\mu\text{-}PPh_2)(CO)_2(P^iPr_3)]$ or methyl derivative $[Fe_2Cp_2(Me)(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_2]$, respectively. Both hydrides *cis*- and *trans*-$[Fe_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_2]$ can be reversibly oxidized at low temperature to the corresponding cation radicals *cis*- and *trans*-$[Fe_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_2]^+$. At room temperature, however, the trans dicarbonyl cation isomerizes to its cis isomer, which in turn experiences a degradation process involving the reductive elimination of the bridging groups. The structures of the new complexes are analyzed on the basis of the corresponding IR and NMR (^1H, ^{31}P and ^{13}C) spectroscopic data. The nature of the new radical cations is analyzed also on the basis of cyclic voltammetry and ESR measurements.

Introduction

We have recently reported our results on the thermal and photochemical reactions of the metal−metal-bonded dimer $[Fe_2Cp_2(CO)_4]$ (**1**; $Cp = \eta^5\text{-}C_5H_5$) with the bidentate phosphorus ligands $(EtO)_2POP(OEt)_2$ (tedip)[1] and $Ph_2PCH_2PPh_2$ (dppm).[2] In these reactions, several bond ligand activations (C−H, C−O, P−O, and P−C) have been discovered, thus explaining the formation of a wide variety of binuclear iron complexes exhibiting very different bridging groups such as $P(OEt)_2$, $OP(OEt)_2$, H, PPh_2, and $C_5H_4CH_2PPh_2$.[1,2] Among those complexes we noticed the presence of two simple complexes exhibiting bridging diphenylphosphide ligands, the hydride *cis*-$[Fe_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_2]$ (*cis*-**2**) and the carbonyl-bridged $[Fe_2Cp_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)]$ (**3**). During the past few years we have been studying the reactions of related dimolybdenum and tungsten complexes $[M_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4]$ and $[M_2Cp_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)]$.[3] From these studies we have concluded that the diphenylphosphide ligand acts as a robust and flexible bridge, able to keep the integrity of the dimetal center through a great variety of elemental reactions including decarbonylation,[3a] oxidation,[3b] and protonation,[3c] thus leading to new and reactive metal−metal-bonded substrates. We thus considered the possibility of exploring the potential of the hydride **2** as a synthetic precursor of new diphenylphosphide-bridged diiron complexes. Noticeably, only a few related hydride−phosphide diiron complexes have been described so far, these being limited to several alkylphosphide complexes $[Fe_2Cp_2(\mu\text{-}H)(\mu\text{-}PR_2)(CO)_2]$ ($R =$ menthyl and related hydrocarbon chains)[4] and the diphenylphosphide-bridged $[Fe_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(\mu\text{-}dppm)]$.[5] Moreover, the chemistry of these phosphide compounds has not been explored in detail.

First, we faced the problem of finding an efficient synthetic route to *cis*-**2**, because the photochemical reaction between **1** and dppm was clearly inappropriate (the yield was only 15%).[2] Different methods to prepare cyclopentadienyliron complexes having phosphide bridging ligands have been described in the literature. The classical cleavage of a P−P bond in the reactions of

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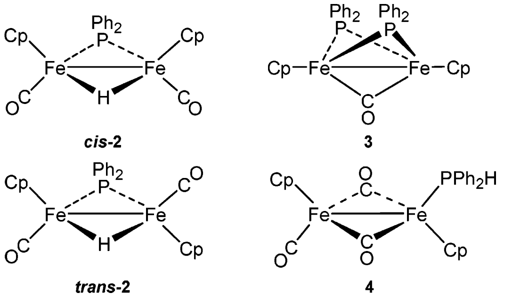
Table 1. IR and ^{31}P NMR Spectroscopic Data for Compounds 2−10

compd	ν_{st}(CO)[a]	δ(P)[b]	J_{PP}[c]
trans-[$Fe_2Cp_2(\mu$-H)(μ-PPh_2)$(CO)_2$] (*trans*-**2**)	1912 (vs)[d]	194.6[e]	
cis-[$Fe_2Cp_2(\mu$-H)(μ-PPh_2)$(CO)_2$] (*cis*-**2**)[f]	1950 (vs)	187.3	
[$Fe_2Cp_2(\mu$-$PPh_2)_2(\mu$-CO)] (**3**)[f]	1747 (vs)	116.9	
[$Fe_2Cp_2(\mu$-$CO)_2$(CO)(PPh_2H)] (**4**)	1936 (s), 1731 (vs)	60.3[e]	
[$Fe_2Cp_2(\mu$-PEt_2)(μ-PPh_2)(μ-CO)] (**5**)	1746 (vs)	142.7, 119.2*	34
[$Fe_2Cp_2(\mu$-H)(μ-PPh_2)(CO)(PEt_2H)] (**6**)	1896 (vs)	180.2*, 59.9	41
Li[$Fe_2Cp_2(\mu$-PPh_2)$(CO)_2$] (**7**)	1821 (vs)[g]	109.2[g,h]	
trans-[$AuFe_2Cp_2(\mu$-PPh_2)$(CO)_2$(P^iPr_3)] (*trans*-**8**)	1899 (vs)	208.4, 80.0	14
cis-[$AuFe_2Cp_2(\mu$-PPh_2)$(CO)_2$(P^iPr_3)] (*cis*-**8**)	1945 (vs)	201.3*, 77.9	12
[Fe_2Cp_2(Me)(μ-PPh_2)(μ-CO)(CO)] (**9**)	1953 (m), 1787 (vs)	205.0[e,i]	
trans-[$Fe_2Cp_2(\mu$-H)(μ-PPh_2)$(CO)_2$]PF_6 (*trans*-**10**)	1998 (w, sh), 1982 (vs)		
cis-[$Fe_2Cp_2(\mu$-H)(μ-PPh_2)$(CO)_2$]PF_6 (*cis*-**10**)	2020 (vs), 2003 (w, sh)		

[a] Recorded in CH_2Cl_2 solution, unless otherwise stated; ν in cm^{-1}. [b] Recorded in CD_2Cl_2 solution at 290 K and 121.50 MHz, unless otherwise stated; δ in ppm relative to external 85% aqueous H_3PO_4. An asterisk denotes the resonance assigned to the μ-PPh_2 group when two resonances are present. [c] Coupling constants in hertz. [d] 1932 (sh), 1923 (vs) cm^{-1} in petroleum ether solution. [e] Recorded at 80.01 MHz. [f] Data from ref 2. [g] Recorded in THF. [h] Recorded at 165.97 MHz. [i] Recorded in C_6D_6.

Chart 1



diphosphines P_2R_4 with carbonyl complexes has been successfully used to obtain bis(phosphide) complexes of the type [$Fe_2Cp_2(\mu$-$PR_2)_2(CO)_2$] (R = Ph,[6] Me,[6] CF_3[7]) and might be considered as an useful synthetic entry to complex **3**.[2] However, the only useful synthetic route to hydride **2** has been found to rely on the P−H bond cleavage occurring in the thermal reaction between PPh_2H and **1**, thus paralleling the synthetic method used in the above-mentioned diiron hydrides[4,5] or dimolybdenum and ditungten complexes.[3a] The thermal reaction, however, produces the trans isomer of **2**. In any case this product has been found to be a suitable precursor for new neutral, anionic, and cationic phosphide-bridged diiron complexes, as discussed below.

Results and Discussion

Thermal Reaction of Compound 1 with PPh_2H. Compound **1** reacts readily with the secondary phosphine PPh_2H in refluxing toluene to give the complex *trans*-[$Fe_2Cp_2(\mu$-H)(μ-PPh_2)$(CO)_2$] (*trans*-**2**; Chart 1) as a major product, along with trace amounts of its isomer *cis*-[$Fe_2Cp_2(\mu$-H)(μ-PPh_2)$(CO)_2$] (*cis*-**2**;[2] Chart 1). IR monitoring of the above reaction allowed us to detect the tricarbonyl complex [$Fe_2Cp_2(\mu$-$CO)_2$(CO)(PPh_2H)] (**4**; Chart 1) as an intermediate (see below).

trans-**2** was first identified by Hayter in 1963 as a low-yield (5%) byproduct in the reaction between P_2Ph_4 and **1**,[6] although its structure was not accurately determined at the time. The IR spectrum of *trans*-**2** exhibits two bands (1932 (sh) and 1923 (vs) cm^{-1} in petroleum ether) in the region of C−O stretches,[8] with the relative intensities expected for a trans configuration of the carbonyl ligands in these binuclear complexes. As usually found, these absorption frequencies are lower for trans isomers than for the corresponding cis isomers.[2,4] The ^{31}P{^{1}H} NMR spectrum of *trans*-**2** exhibits a strongly deshielded resonance at 194.6 ppm (Table 1), as expected for arylphosphide ligands bridging metal−metal bonds.[9] This shift is similar to the values found for *cis*-**2**,[2] [$Fe_2Cp_2(\mu$-H)(μ-PPh_2)(μ-dppm)],[5] and [$Fe_2Cp_2(\mu$-H)(μ-$PMen_2$)$(CO)_2$],[4b] which are 187.3, 172.3, and 191.7 ppm, respectively. The ^{1}H NMR spectrum of *trans*-**2** displays a high-field doublet at −18.89 ppm (J_{HP} = 40 Hz) assigned to the bridging hydride ligand. The chemical shift and coupling constant of this resonance are in agreement with the proposed structure and the data originally reported for the complex (δ −18.67 ppm, J_{HP} = 41 Hz in CS_2)[6] or related complexes. The ^{13}C{^{1}H} NMR spectrum of *trans*-**2** provides definitive proof for the stereochemistry of the complex. Thus, the presence of just one set of phenyl carbon resonances for the diphenylphosphide bridge is only compatible with the trans arrangement of the terminal carbonyl and cyclopentadienyl ligands.

As stated above, several related alkylphosphide complexes of the type [$Fe_2Cp_2(\mu$-H)(μ-PR_2)$(CO)_2$] were previously synthesized through the thermal reaction between PR_2H and **1**.[4] These reactions also led to the trans isomer as the major product. Surprisingly, the yields obtained were high only when the phosphorus atom was part of a five-membered ring derived from phospholane [P(C_4H_8)H], whereas the use of the related acyclic ligand μ-$PMen_2$ (Men = menthyl, 2-isopropyl-4-methylcyclohexyl) led to low yields of the hydride complex (40%). This suggests that the above reactions are governed by the steric rather than electronic properties of the phosphorus ligands. By considering the cone angle of model phosphines,[10] we can estimate the steric demands on the involved phosphines to follow the order P(C_4H_8)H (similar to PMe_2H, 108°) < PPh_2H (126°) < $PMen_2$H (similar to PCy_2H, 143°). From these figures we can conclude that the steric demands of the PR_2H ligands might hinder the oxidative addition of the P−H bond to the metal during reaction with **1**.

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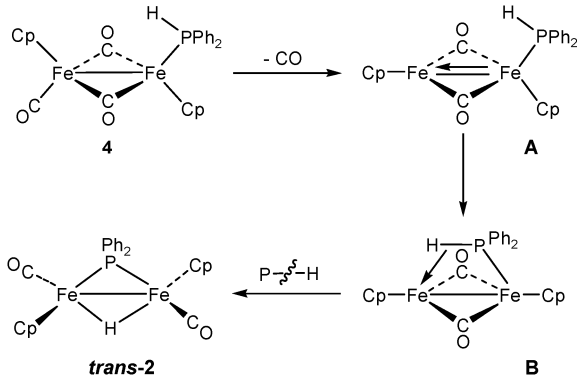
Synthesis and Structural Characterization of Compound 4. As stated above, complex **4** is detected as an intermediate during the IR and NMR spectroscopic monitoring of the thermal reaction of **1** with PPh_2H. To prepare this compound selectively, we considered the same strategy used before to obtain the isostructural complexes $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)(\kappa^1\text{-}L)]$ (L = tedip,[1] dppm[2]), based on the fact that the acetonitrile ligand in $[Fe_2Cp_2(CO)_3(NCMe)]$[11] is easily displaced by two-electron-donor ligands. As expected, $[Fe_2Cp_2(CO)_3(NCMe)]$ reacts rapidly with PPh_2H in toluene even at 0 °C to give compound **4** in very good yield.

When a toluene solution of pure compound **4** was heated under reflux for 1 h, clean transformation into *trans*-**2** occurred. This proves that complex **4** is a genuine intermediate in the formation of **2** from **1** and PPh_2H.

The presence of the PPh_2H ligand in **4** is easily deduced from its $^{31}P\{^1H\}$ NMR spectrum, which exhibits a singlet at 60.3 ppm (Table 1). This chemical shift is in the usual region observed for arylphosphines bonded to iron complexes.[12] The ^1H NMR spectrum of **4** exhibits, as expected, two signals due to the nonequivalent cyclopentadienyl ligands. The resonance of the P-bonded hydrogen atom appears at 4.70 ppm (CD_2Cl_2) as a strongly coupled doublet (J_{PH} = 353 Hz). The IR spectrum of **4** in THF exhibits three bands in the C−O stretching region at 1935 (m), 1777 (w), and 1731 (vs) cm^{-1} with the pattern expected for this geometry, having one terminal and two transoid bridging carbonyls. In agreement with this, the $^{13}C\{^1H\}$ NMR spectrum of this complex exhibits two carbonyl resonances at δ 280.0 ppm (J_{CP} = 15 Hz, two equivalent bridging CO ligands) and 214.6 ppm (J_{CP} = 11 Hz, terminal CO). Compound **4** is thus another member of the large family of phosphine derivatives of compound **1** having the general formula $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)(PR_3)]$.[13] For these compounds, cis and trans isomers are possible, depending on the relative positions of the terminal ligands with respect to the average plane defined by the Fe atoms and bridging CO ligands. When both isomers of the same compound are known, it is always found that the cis isomer exhibits ν(CO) stretching frequencies around 20 cm^{-1} higher than the trans isomer. Therefore, by recalling that *trans*-$[Fe_2Cp_2(\mu\text{-}CO)_2(CO)(PEtPh_2)]$ exhibits a terminal C−O stretch at 1940 cm^{-1} (cyclohexane solution)[13] and that the terminal C−O band of **4** appears at 1935 cm^{-1} (THF solution), we can safely assign a trans structure to the latter complex.

It should be noted that, once formed, *cis*-**2** and *trans*-**2** do not interconvert in refluxing toluene. Therefore, the stereoselectivity in the formation of these hydride derivatives must be kinetic in origin. It can be imagined that decarbonylation of tricarbonyl **4** would initially generate the unsaturated intermediate **A** (Scheme 1), which would induce the oxidative addition of a P−H bond of the phosphine through the “agostic” intermediate **B** to yield specifically *trans*-**2** as a consequence of the trans arrangement of the bridging carbonyls in the latter species (Scheme 1). Actually, intermediate **B** could be isostructural with the diphosphine-bridged $[Fe_2Cp_2(\mu\text{-}CO)_2(\mu\text{-}L_2)]$ (L_2 = dppm,[14] tedip[1]). We note that the oxidative addition of P−H bonds to multiple metal−metal bonds is a process well established at dimolybdenum, ditungsten, and diosmium centers.[3a,15,16] Furthermore, a precedent involving diiron complexes can be found in the reaction of the unsaturated $[Fe_2Cp^*_2(\mu\text{-}H)_4]$ with PPh_2H.[17] Moreover, it is noteworthy that the “agostic” bridging coordination mode of a PR_2H ligand proposed for intermediate **B** has been found at dipalladium centers.[18]

Scheme 1. Proposed Reaction Pathway in the Formation of the Diphenylphosphide Complex *trans*-2



Photochemical Reactions of the Compound *trans*-2. The irradiation with UV−visible light of a THF solution of compound *trans*-**2** at low temperature (−15 °C) causes its transformation to the cis isomer *cis*-**2**. However, when the photolysis is carried out at room temperature, the bis(phosphide) compound $[Fe_2Cp_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)]$ (**3**; Chart 1) is obtained in medium yield. As stated in the Introduction, both *cis*-**2** and **3** have been previously obtained in low yields (15% and 14%, respectively) through the photochemical reaction of complex **1** with dppm.[2] Interestingly, yields above 80% can be obtained for these complexes by appropriate adjustment of the photolytic conditions of *trans*-**2**. Thus, when irradiation of *trans*-**2** is carried out at low temperature under a CO atmosphere, *cis*-**2** is obtained in high yield (83%). On the other hand, when irradiation of *trans*-**2** is carried out in the presence of 1 equiv of PPh_2H at room temperature, then the yield of compound **3** increases up to 80%. Noticeably, the monitoring of this reaction by IR revealed that substantial amounts of *cis*-**2** are first formed, which then gradually transform into the final product **3**. From this we conclude that the photochemical trans to cis isomerization of compound **2** is not suppressed by the presence of PPh_2H to a significant extent.

The reaction leading to the phosphide complex **3** turned out to be a useful synthetic method to prepare mixed bis(phosphide) complexes. Thus, when *trans*-**2** is irradiated at room temperature in the presence of the

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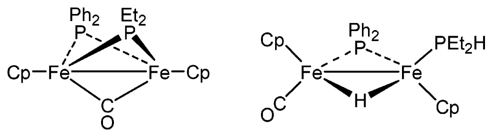
Chart 2



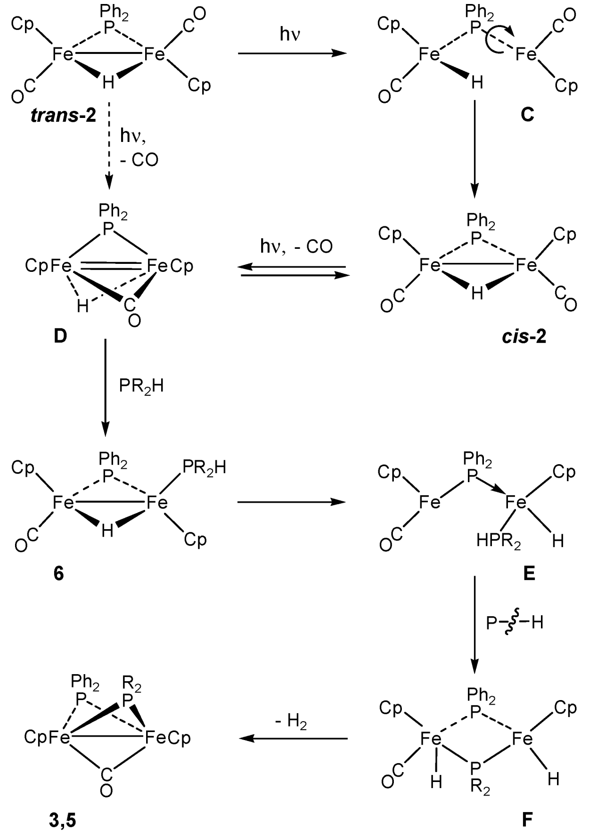
5 **6**

different phosphine PEt_2H, the mixed-phosphide complex $[Fe_2Cp_2(\mu\text{-}PEt_2)(\mu\text{-}PPh_2)(\mu\text{-}CO)]$ (**5**; Chart 2) is formed in high yield. This complex is isostructural with compound **3**. For example, its IR spectrum displays a single C−O stretching band at 1746 cm^{-1} in CH_2Cl_2 solution, this indicating the bridging character of the carbonyl ligand, as observed for **3** (Table 1). Two doublet resonances at 142.7 and 119.2 ppm (Table 1) in the $^{31}P\{^1H\}$ NMR spectrum indicate the presence of the two different phosphide ligands bridging identical metal fragments, the latter being denoted by the chemical equivalence of the cyclopentadienyl groups in the ^1H NMR spectrum. As is the case for **3**, the chemical shifts of the phosphorus atoms in **5** can be considered as unusually low for metal−metal-bonded phosphide bridges, and this is thought to be an indication of strain in the Fe_2P cycle or steric congestion around the dimetal unit.[2] Although complexes **3** and **5** are not very stable, it should be noted that no other carbonyl-bridged phosphide complexes of the type $[Fe_2Cp_2(\mu\text{-}PX_2)_2(\mu\text{-}CO)]$ appear to have been reported in the literature. Interestingly, similar thiolate-bridged complexes $[Fe_2Cp_2(\mu\text{-}SR)_2(\mu\text{-}CO)]$ have been recently detected as transient intermediates in the photolytic isomerization *cis*- to *trans*-$[Fe_2Cp_2(\mu\text{-}SR)_2(CO)_2]$.[19]

If the irradiation of compound *trans*-**2** in the presence of PEt_2H is carried out at −20 °C, the hydride *trans*-$[Fe_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)(PEt_2H)]$ (**6**; Chart 2) is obtained in high yield. This compound formally results from substitution of carbonyl by phosphine at *trans*-**2** and is an important intermediate in the formation of the mixed-phosphide complex **5**. Indeed, a separate experiment showed that photolysis of **6** at room temperature yields **5** as the major product. Analysis of the spectroscopic data for **6** (Table 1 and Experimental Section) indicates that this compound is isostructural with the monocarbonyl complex *trans*-$[Fe_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)(PPh_2Me)]$, previously prepared through the photochemical reaction of *cis*-**2** with PPh_2Me.[2] The structure of *trans*-$[Fe_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)(PPh_2Me)]$ has been discussed in detail previously, and therefore no further comments are needed in the case of compound **6**.

Reaction Pathways in the Photochemical Reactions of the Iron Complex *trans*-2. As discussed above, depending on the experimental conditions the irradiation of *trans*-**2** with UV−visible light can induce several processes such as isomerization, CO substitution, and P−H bond cleavage. Our synthetic data suggest that the dominant reaction pathway should be close to that depicted in Scheme 2. The fastest photochemical process in all cases would be the trans to cis isomerization of the terminal ligands of the starting material. This process seems not to involve CO dissociation to a significant extent, as the presence of neither CO nor PR_2H suppresses this isomerization in a noticeable way. Therefore, we propose that reversible opening of the hydride bridge occurs at the transient stage **C**, this being followed by rotation of the FeCp(CO) moiety around an Fe−P bond, allowing the formation of the isomer *cis*-**2**. This bridge-opening mechanism is similar to that proposed to explain cis/trans isomerization in the thiolate-bridged dimolybdenum complexes $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}SR)(CO)_4]$.[20] We note, however, that Brunner et al. also reported photochemical trans to cis isomerization at the alkylphosphide diiron complexes $[Fe_2Cp_2(\mu\text{-}H)(\mu\text{-}PR_2)(CO)_2]$. A CO-dissociative mechanism was envisaged there[4] and cannot be completely excluded in the case of the trans to cis isomerization of compound **2** (dashed arrow in Scheme 2). However, the fact that this isomerization is not suppressed to a significant extent by the presence of PR_2H leads us to think that the nondissociative pathway must be dominant. In this context, it is important to note that a recent and detailed mechanistic study on the photochemical cis to trans isomerization in the thiolate complexes $[Fe_2Cp_2(\mu\text{-}SR)_2(CO)_2]$ led to the conclusion that both CO-loss and non-CO-loss pathways were operative.[19]

Scheme 2. Proposed Reaction Pathways in the Photochemical Reactions of *trans*-2



The fact that the cis geometry is favored for compound **2** under UV−visible light irradiation might be a more general property of diiron dicarbonyls having two bridges and a metal−metal bond. For example, a similar (photochemically favored) trans to cis isomerization has been reported for the silylene-bridged complex [Fe₂(*η*-

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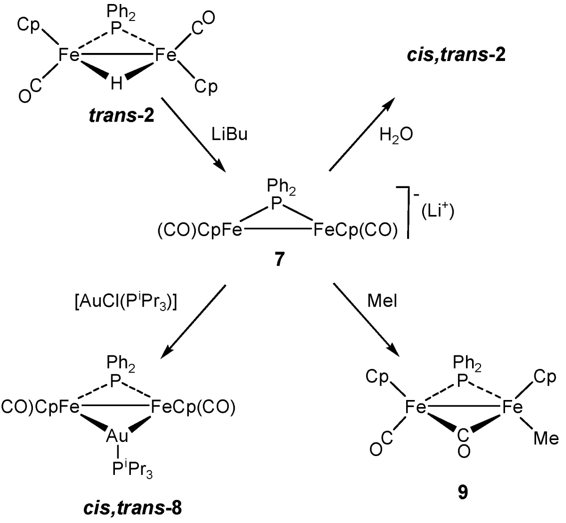
Scheme 3. Reactions of Anion 7 with Different Electrophiles



$C_5Me_5)_2\{\mu\text{-}SiH(C_6H_4Me)\}(\mu\text{-}CO)(CO)_2]$.[21] The isomer *cis*-**2** is relatively stable under UV–visible light, although the low yield of monocarbonyl **3** upon extended photolysis at room temperature suggests that some slow decarbonylation is induced under these conditions. In fact, this can be put to good use by performing the photolysis of **2** in the presence of 1 equiv of PR_2H, in which case the bis(phosphide) monocarbonyls **3** and **5** are formed in good yield. It is assumed that initial decarbonylation would give the unsaturated intermediate **D**, which then would rapidly add a molecule of phosphine to give compound **6** or its PPh_2H analogue (not detected). This is a well-established reaction pathway for the photochemical substitution of CO by phosphines at $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)_2]$[22] and $[Fe_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}CO)(\mu\text{-}CHMe)(CO)_2]$.[23]

The final steps connecting the hydrides of type **6** and the bis(phosphide) derivatives **3** and **5** are less straightforward. Under photochemical conditions, a hydride-bridge-opening process would generate a 16-electron metal center (intermediate **E**), on which the oxidative addition of a P–H bond would readily occur to give the dihydride intermediate **F**. This step would be similar to the addition of P–H bonds from coordinated phosphines to coordinatively unsaturated PtL_2 centers to afford phosphide-bridged heterometallic derivatives.[24] Finally, dehydrogenation from the overcrowded intermediate **F** would yield the bis(phosphide) complexes **3** and **5** after rearrangement.

Synthesis and Structural Characterization of the Anion $[Fe_2Cp_2(\mu\text{-}PPh_2)(CO)_2]^-$ (7). Treatment of a THF solution of *trans*-**2** with 1 equiv of LiBu yields $Li[Fe_2Cp_2(\mu\text{-}PPh_2)(CO)_2]$ (**7**) almost instantaneously (Scheme 3). This anion is extremely reactive toward water, which makes its manipulation very difficult in a relatively hydrophilic solvent such as tetrahydrofuran. The IR spectrum of the anion **7** exhibits only one C–O stretching band at 1821 cm^{-1}, some 100 cm^{-1} lower than that in its neutral precursor *trans*-**2** (Table 1). This large decrease in the C–O stretching frequency is characteristic of metal carbonylates and is similar to the ca. 90 cm^{-1} decrease observed for the anion $[Mo_2Cp_2(\mu\text{-}PPh_2)(CO)_4]^-$ when obtained from neutral $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4]$.[25] The $^{31}P\{^1H\}$ NMR spectrum of **7** exhibits only one signal at 109.2 ppm (Table 1), which appears considerably upfield with respect to the usual values found for bridging diphenylphosphide ligands. However, analysis of the spectroscopic data for different dinuclear phosphide-bridged complexes indicates that a change in the overall charge of a compound, as happens in protonation/deprotonation reactions of hydride-bridged complexes, can induce either upfield or downfield changes in the chemical shift of the phosphide ^{31}P nucleus.[9] Unfortunately, no additional spectroscopic data could be obtained for **7** because of its easy protonation during manipulation. Nevertheless, the structures of some of its derivatives, discussed next, suggest that anion **7** would exist in solution as an equilibrium mixture of cis and trans isomers.

Despite the relatively simple nature of compound **7**, we note that this anion is a rare example of a binuclear iron carbonylate having cyclopentadienyl ligands. In fact, there are only relatively few diiron anions, none of them having Cp ligands as, for example, the diphenylphosphide-bridged anions $[Fe_2(\mu\text{-}PPh_2)(CO)_n]^-$ (n = 6, 7),[26] the related alkenyl and thiolate anions $[Fe_2(\mu\text{-}X)(\mu\text{-}CO)(CO)_6]^-$ (X = RCCHR,[27] SR),[28] and the octocarbonyl complexes $[Fe_2(CO)_8]^{2-}$ and $[Fe_2(\mu\text{-}H)(CO)_8]^-$.[29]

Reaction of Anion 7 with $[AuCl(P^iPr_3)]$. As expected, compound **7** easily displaces chloride ions from $[AuCl(P^iPr_3)]$. However, this reaction yields almost instantaneously a mixture of the isomers *cis*- and *trans*-$[AuFe_2Cp_2(\mu\text{-}PPh_2)(CO)_2(P^iPr_3)]$ (**8**; Scheme 3) in a 1:4 ratio. These two isomers could not be separated by using either chromatography or crystallization techniques. The IR spectrum of the mixture of isomers in the C–O stretching frequency region is very similar to those of isomers **2** but is displaced by ca. 10 cm^{-1} toward lower frequency (Table 1). This is expected, due to the lower electronegativity of the $Au(P^iPr_3)$ fragment with respect to the H atom.[30] The $^{31}P\{^1H\}$ NMR spectrum shows two doublets for each isomer (Table 1). The signal of the bridging phosphide atom (ca. 200 ppm, Table 1) appears in the expected region for this kind of ligand.[9] Again, as was observed for hydrides **2**, the trans isomer gives rise to a more deshielded resonance. Finally, the resonances of the phosphorus atoms coordinated to Au atoms appear around 80 ppm, as expected.

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The reaction of carbonyl anions with chlorogold complexes is a general synthetic method to generate heterometallic clusters combining Au and transition-metal atoms.[31] Its use with dinuclear anions having $M_2(\mu\text{-}PR_2)$ backbones to give phosphide-bridged M_2Au clusters has been reported for different metals, including Mo, Re, and Mn.[25,32]

A point yet to be addressed is the formation of a mixture of cis and trans Fe_2Au clusters apparently from the single anion **7**. In this respect, the observation that protonation of **7** with H_2O also gives a mixture of cis and trans hydrides **2**, in a ratio (ca. 1:4) identical with the ratio observed for the gold clusters **8**, is revealing. There are two possible explanations for these observations. First, it is conceivable that two rapidly interconverting (so as to give a single ^{31}P resonance) isomers of the anion **7** coexist in solution in a 1:4 ratio. Second, it is possible that only one static structure for **7** is present in solution, having two nonequivalent reaction sites, each leading to a different isomer. In the latter case, however, it is difficult to understand why the reaction with two electrophiles so different in size, namely H^+ and $(AuPR_3)^+$, would lead to the same ratio of isomers. By exclusion, then, we favor the coexistence of cis and trans isomers in the THF solutions of complex **7**.

Reaction of Anion 7 with MeI. Anion **7** is nucleophilic enough so as to react with MeI in THF to give the methyl complex $[Fe_2Cp_2(Me)(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_2]$ (**9**; Scheme 3) in good yield. The vacant site at anion **7** is located between the iron atoms as it is, presumably, the HOMO of the molecule, as calculated for the related dimolybdenum anion $[Mo_2Cp_2(\mu\text{-}Cl)(CO)_4]^-$.[33] The methyl group is therefore expected to be incorporated as a bridging ligand, as observed in the reaction of the unsaturated anion $[Mo_2Cp_2(\mu\text{-}PCy_2)(CO)_2]^-$ with MeI.[34] Apparently, however, a bridging μ,η^1 coordination for the methyl group at this diiron center is not stable; thus, the product would rapidly rearrange, by exchanging Me and CO positions, to yield a CO-bridged complex with a terminal methyl ligand (see below).

The presence of both terminal and bridging carbonyl ligands in **9** is readily apparent from its IR spectrum in solution (Table 1), which exhibits two C−O stretching bands at 1953 cm^{-1} (terminal C−O) and at 1787 cm^{-1} (bridging C−O). The $^{31}P\{^1H\}$ NMR spectrum of compound **9** shows a resonance at 205.0 ppm (Table 1), in the region expected for diphenylphosphide ligands bridging metal−metal bonds. Its ^1H NMR spectrum shows two resonances at 4.34 and 4.30 ppm corresponding to the nonequivalent cyclopentadienyl ligands, whereas the methyl protons give rise to a doublet resonance at −1.13 ppm ($J_{HP} = 8$ Hz). The latter data are similar to those for the methyl complex $[FeCp(Me)(CO)(PPh_3)]$ (δ −0.17 ppm; $J_{HP} = 7$ Hz),[35] thus supporting the terminal coordination proposed for the methyl ligand in complex **9**.

Scheme 4. Proposed Reaction Pathways in the Formation of the Methyl Complex 9

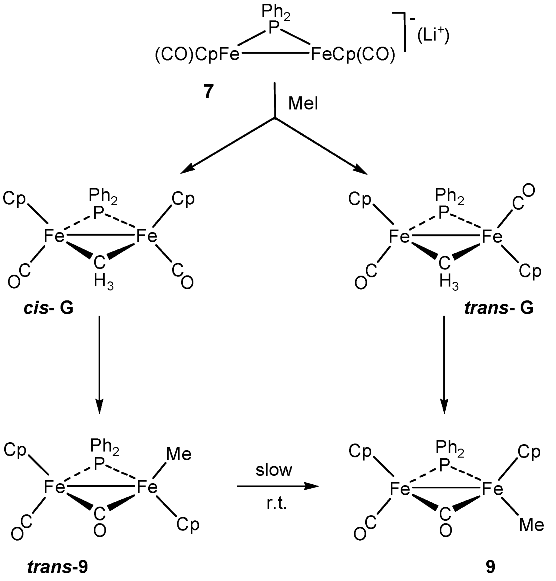
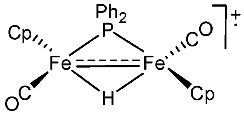
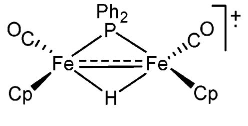


Chart 3



trans-**10**



cis-**10**

Early in the reaction leading to **9**, a weak C−O band is observed at 1937 cm^{-1} (in THF) in the IR spectrum of the reaction mixture, this disappearing during the reaction. It is reasonable to suggest that this unstable species is an isomer of **9** (Scheme 4). Thus, as observed for the protonation or "aurification" reaction of anion **7**, it is likely that both cis (minor) and trans (major) μ-methyl derivatives (**G**) are initially formed; they rearrange to trans (minor) and cis (major) terminal methyl complexes, respectively. By analogy with the IR spectroscopic data for cis and trans complexes of the type $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)(PR_3)]$,[13] the band at 1937 cm^{-1} can be assigned to the trans isomer, while the higher frequency of the C−O stretching band in the final compound **9** would identify it as the cis isomer. These data thus imply that the trans isomer rearranges to the cis isomer in solution at room temperature.

Synthesis and Structural Characterization of the Paramagnetic Cations $[Fe_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_2]^+$ (*cis*- and *trans*-10). The hydride complexes *cis*-**2** and *trans*-**2** can be oxidized with 1 equiv of $[FeCp_2]PF_6$ in THF at −60 °C to form the 33-electron species *cis*- and *trans*-$[Fe_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_2]^+$ (*cis*-**10** and *trans*-**10**; Chart 3), respectively. These cations have been characterized by IR and ESR spectroscopy and cyclic voltammetry (CV). All the data indicate that oxidation takes place with retention of the stereochemistry of the neutral precursors.

Each of the isomers of compound **10** displays two C−O stretching bands in its IR spectrum (Table 1). The relative intensities of the two bands point respectively to the presence of $[M(CO)]_2$ oscillators with transoid or

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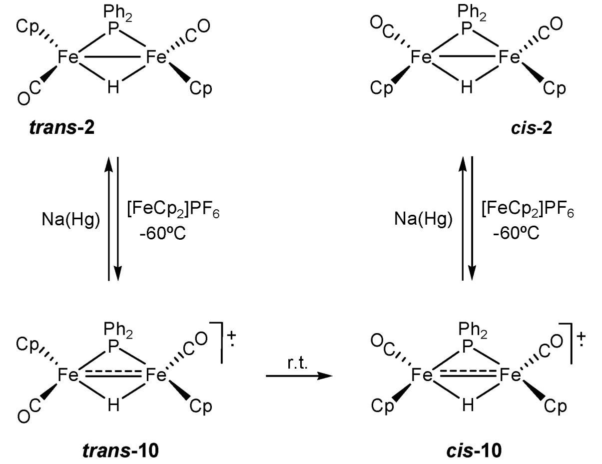
Scheme 5. Redox Transformations of Hydride Complexes 2



almost parallel CO ligands.[8] In addition, the frequencies for those bands are shifted ca. 70 cm^{-1} higher than those of the neutral precursors, as expected for the change from neutral to cationic species. The fact that both C−O stretching bands (symmetric and asymmetric) experience a similar increase on going from compounds **2** to **10** indicates that the unpaired electron in the cations is delocalized over both iron atoms. Thus, both cis and trans cations **10** should be classified as class III mixed-valence complexes.[36] The room-temperature ESR spectra of CH_2Cl_2 solutions of cations **10** exhibit in each case a single resonance displaying no coupling to the phosphorus atom. This observation suggests that in both isomers the singly occupied molecular orbital (SOMO) has a very low participation of the phosphorus atomic orbitals.

Cyclic voltammetry studies in CH_2Cl_2 indicate that both isomers undergo reversible one-electron oxidation at 0.24 V (cis isomer) and 0.36 V (trans isomer). In agreement with this reversibility, both isomers **10** are reduced by sodium amalgam in tetrahydrofuran to regenerate the corresponding neutral precursors **2** (Scheme 5).

trans-**10** is thermally unstable, and complete isomerization to *cis*-**10** takes place in ca. 15 min in CH_2Cl_2 solution at room temperature (Scheme 5). This process can be monitored by either IR spectroscopy or cyclic voltammetry. If, during cyclic voltammetry of *trans*-**2** from −0.2 to 0.5 to −0.2 V, the potential is held for a short time (15−30 s) at 0.5 V, an additional wave is observed on the return scan corresponding to the reduction *cis*-**10** to *cis*-**2**.

Electron-transfer-induced isomerizations of organometallic complexes are not unusual,[37,38] but we have found no precedents for the above isomerization in related diiron complexes. For example, the bis(diphenylphosphide) isomers *cis*- and *trans*-$[Fe_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2]$ can be readily oxidized to the corresponding mono- and dications without isomerization.[39,40] This suggests that, in the case of cations **10**, the observed trans/cis isomerization might be facilitated by the presence of a weakly bound hydride ligand, perhaps involved in a bridge-opening mechanism similar to that operating in the photochemical isomerization of the neutral hydride **2** (Scheme 2). In line with this, isomer *cis*-**10** is also not very stable at room temperature. In fact, this complex decomposes slowly at room temperature to give the mononuclear species $[FeCp(CO)_2(PPh_2H)]PF_6$ as the only carbonyl-containing product.[41]

The paramagnetic cations **10** also give mononuclear species readily in their reactions with classical radical traps such as I_2 and S_2Ph_2. In both cases, mononuclear cations of the type $[FeCp(CO)_2(PPh_2X)]^+$ (X = I, SPh) were obtained, as judged from the IR and NMR spectra of the corresponding reaction mixtures. No attempts were made to characterize these products fully. However, it seems clear that the diphenylphosphide bridge is not strong enough so as to preserve the nuclearity of the paramagnetic cations **10**.

We note finally that compounds **10** are among the very few 33-electron diiron complexes synthesized so far. Previous examples are limited to the phosphide-bridged $[Fe_2(\mu\text{-}PPh_2)(CO)_7]$[42] and the diphosphine-bridged cations $[Fe_2Cp_2(\mu\text{-}CO)_2(\mu\text{-}Ph_2PXPPh_2)]^+$ ($X = C_nH_{2n}$; $n = 1-3$)[43] and $[Fe_2Cp_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\mu\text{-}dppm)]^+$.[44] Unfortunately, the low stability of the diphenylphosphide bridge in **10** precludes a detailed study of their chemical behavior.

Concluding Remarks

The thermally induced oxidative addition of the P−H bond of PPh_2H to $[Fe_2Cp_2(CO)_4]$ provides a highly efficient and stereoselective route to *trans*-$[Fe_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_2]$ (*trans*-**2**). The diphenylphosphide bridge in *trans*-**2** acts as an efficient support of the dimetallic center through a number of different reactions, including photochemical decarbonylation, reduction, and oxidation, thus allowing the synthesis of new cyclopentadienyldiiron derivatives. Under photochemical conditions, trans to cis isomerization of compound **2** is faster than CO dissociation, but the latter generates unsaturated intermediates able to induce new P−H bond activations which eventually allow the synthesis of bis(phosphide) derivatives of the type $[Fe_2Cp_2(\mu\text{-}PPh_2)(\mu\text{-}PR_2)(\mu\text{-}CO)]$. Trans to cis isomerization is also thermodynamically favored for the 33-electron cations $[Fe_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_2]^+$, which are stereospecifically generated upon 1-electron oxidation of isomers **2**. These cations, however, are unstable with respect to P−H reductive elimination and degrade to mononuclear species at room temperature. In contrast, the diphenylphosphide ligand behaves as a more robust bridging group under reducing conditions, thus allowing the formation of the new binuclear carbonylate $[Fe_2Cp_2(\mu\text{-}PPh_2)(CO)_2]^-$. The latter is a strong nucleophile, and it reacts readily with either metal-based or carbon-based electrophiles and

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might therefore have significant potential in the synthesis of new diiron cyclopentadienyl derivatives.

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[45] and distilled under nitrogen prior to use. Petroleum ether refers to that fraction distilling in the range 60−65 °C. Compounds $[Fe_2Cp_2(CO)_3(NCMe)]$,[11] and $[FeCp_2]PF_6$[46] were prepared as described previously. $[AuCl(P^iPr_3)]$ was prepared from $[AuCl(SC_4H_8)]$[47] and P^iPr_3. Compounds $[Fe_2Cp_2(CO)_4]$, PR_2H (R = Et, Ph), LiBu, and CH_3I were obtained from the usual commercial suppliers and used without further purification. Photochemical experiments were performed using jacketed Pyrex or quartz Schlenk tubes, refrigerated by a closed propan-2-ol circuit kept at the desired temperature with a cryostat or by tap water. A 400 W mercury lamp (Applied Photophysics), placed ca. 1 cm away from the Schlenk tube, was used for these experiments. Low-temperature chromatographic separations were carried out 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), 121.50 ($^{31}P\{^1H\}$), 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. X-Band ESR spectra were recorded on a Bruker ESP300 spectrometer equipped with a Bruker variable-temperature accessory and a Hewlett-Packard 5350B microwave frequency counter. The field calibration was checked by measuring the resonance of the diphenylpicrylhydrazyl (dpph) radical before each series of spectra. Electrochemical studies were carried out using an EG&G Model 273A potentiostat linked to a computer using EG&G Model 270 Research Electrochemistry software in conjunction with a three-electrode cell. The auxiliary electrode was a platinum wire and the working electrode a platinum disk. The reference was an aqueous saturated calomel electrode separated from the test solution by a fine-porosity frit and an agar bridge saturated with KCl. Solutions were 5.0×10^{-4} or 1.0×10^{-3} mol dm^{-3} in the test compound and 0.1 mol dm^{-3} in $[N^nBu_4][PF_6]$ as the supporting electrolyte in CH_2Cl_2. Under the conditions used, $E^{\circ\prime}$ for the one-electron oxidation of $[Fe(\eta^5\text{-}C_5H_5)_2]$, added to the test solutions as an internal calibrant, is 0.47 V.

Preparation of *trans*-$[Fe_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_2]$ (*trans*-2). A mixture of compound **1** (0.200 g, 0.565 mmol) and PPh_2H (100 μL, 0.574 mmol) was heated under reflux in toluene (25 mL) for 1 h to give a reddish solution. Solvent was then removed under vacuum and the residue dissolved in a minimum of CH_2Cl_2. This solution was chromatographed at 15 °C on an alumina column (activity II, 20 × 2 cm) prepared in petroleum ether. After the column was washed with petroleum ether, elution with petroleum ether/CH_2Cl_2 (4/1) gave a small brown fraction containing trace amounts of *cis*-**2** and then a red-brown fraction containing the complex *trans*-**2**. Elution with CH_2Cl_2 gave a green fraction containing a very small amount of compound **4**. Removal of solvents under vacuum from the main fraction gave compound *trans*-**2** (0.248 g, 91%) as a brown crystalline solid. Anal. Calcd for $C_{24}H_{21}O_2PFe_2$: C, 59.55; H, 4.37. Found: C, 59.38; H, 4.29. ^1H NMR (200.13 MHz, CD_2Cl_2): δ 7.80−7.70 (m, 4H, Ph), 7.50−7.15 (m, 6H, Ph), 4.37 (s, 10H, Cp), −18.89 (d, J_{HP} = 40, 1H, μ-H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 216.4 (d, J_{CP} = 18, CO), 143.8 (d, J_{CP} = 28, C^1(Ph)), 132.8 (d, J_{CP} = 9, C^2(Ph)), 127.4 (d, J_{CP} = 2, C^4(Ph)), 126.9 (d, J_{CP} = 10, C^3(Ph)), 80.5 (s, Cp).

Preparation of *cis*-$[Fe_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_2]$ (*cis*-2). A THF solution (10 mL) of compound *trans*-**2** (0.030 g, 0.062 mmol) was irradiated with visible−UV light in a quartz Schlenk tube at −15 °C under a CO atmosphere for 1 h to give a red solution. The latter was then filtered and the solvent removed under vacuum to give *cis*-**2** as a brown-red powder (0.025 g, 83%). Spectroscopic data for *cis*-**2** were identical with those reported for this complex in ref 2.

Preparation of $[Fe_2Cp_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)]$ (3). A tetrahydrofuran solution (10 mL) of *trans*-**2** (0.030 g, 0.062 mmol) and PPh_2H (13 μL, 0.074 mmol) was irradiated with visible−UV light for 90 min in a quartz Schlenk tube at 15 °C while nitrogen was bubbled through the solution. The resulting red solution was then filtered, the solvent removed under vacuum, and the resulting residue washed with petroleum ether (2 × 3 mL) to give compound **3** as a brown solid (0.032 g, 80%). Spectroscopic data for compound **3** were identical with those previously reported for this complex in ref 2.

Preparation of $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)(PPh_2H)]$ (4). A dichloromethane solution (15 mL) of $[Fe_2Cp_2(CO)_3(NCMe)]$[11] (0.155 g, 0.26 mmol) and PPh_2H (74 μL, 0.425 mmol) was stirred at 0 °C for 5 min to yield a green solution. The latter was then filtered, the solvent removed under vacuum, and the resulting residue washed with petroleum ether (2 × 3 mL) to give compound **4** as a green powder (0.190 g, 87%). Anal. Calcd for $C_{25}H_{21}O_3PFe_2$: C, 58.64; H, 4.13. Found: C, 58.39; H, 4.02. ^1H NMR (200.13 MHz, CD_2Cl_2): δ 7.60−7.20 (m, 10H, Ph), 4.79 (s, 5H, Cp), 4.70 (d, J_{HP} = 353, 1H, PH), 4.61 (s, 5H, Cp). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 280.0 (d, J_{CP} = 15, μ-CO), 214.6 (d, J_{CP} = 11, CO), 134.6−128.2 (m, Ph), 86.9 (s, Cp), 85.7 (s, Cp).

Preparation of $[Fe_2Cp_2(\mu\text{-}PEt_2)(\mu\text{-}PPh_2)(\mu\text{-}CO)]$ (5). A tetrahydrofuran solution (10 mL) of *trans*-**2** (0.030 g, 0.062 mmol) and PEt_2H (8 μL, 0.070 mmol) was irradiated with visible−UV light for 90 min in a quartz Schlenk tube at 15 °C while nitrogen was bubbled through the solution. The resulting red solution was then filtered, the solvent removed under vacuum, and the resulting residue washed with petroleum ether (2 × 3 mL) to give compound **5** as a brown solid (0.023 g, 77%). Anal. Calcd for $C_{27}H_{30}OP_2Fe_2$: C, 59.59; H, 5.56. Found: C, 59.68; H, 5.60. ^1H NMR (CD_2Cl_2): δ 7.80−7.15 (m, 10H, Ph), 4.50 (s, 10H, Cp), 1.64 (dq, J_{HP} = 12, J_{HH} = 7, 2H, CH_2), 1.42 (dq, J_{HP} = 10, J_{HH} = 7, 2H, CH_2), 1.05 (dt, J_{HP} = 16, J_{HH} = 7, 3H, CH_3), 0.66 (dt, J_{HP} = 14, J_{HH} = 7, 3H, CH_3).

Preparation of $[Fe_2Cp_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)(PEt_2H)]$ (6). A tetrahydrofuran solution (10 mL) of *trans*-**2** (0.030 g, 0.062 mmol) and PEt_2H (8 μL, 0.070 mmol) was irradiated with visible−UV light in a quartz Schlenk tube at −20 °C for 45 min to give a reddish solution. The latter was then filtered, the solvent was removed under vacuum, and the resulting residue was dissolved in petroleum ether/CH_2Cl_2 (19/1) and chromatographed at 15 °C on an alumina column (activity II, 20 × 2 cm) prepared in petroleum ether. Elution with the same solvent mixture gave a green fraction containing a very small amount of an uncharacterized complex. Elution with petroleum ether/CH_2Cl_2 (9/1) gave a brown fraction containing compound **6**. Elution with petroleum ether/CH_2Cl_2 (3/1) gave a brown fraction containing a small amount of *cis*-**2**. Removal of solvents under vacuum from the second fraction gave compound **6** as a brown crystalline solid (0.027 g, 81%). Anal. Calcd for $C_{27}H_{32}OP_2Fe_2$: C, 59.37; H, 5.91. Found: C, 59.38; H, 5.49. ^1H NMR (CD_2Cl_2): δ 7.70 (m, 2H, Ph), 7.44 (m, 2H, Ph), 7.30−7.15 (m, 6H, Ph), 4.40 (d, J_{HP} = 1, 5H, Cp), 4.20 (d, J_{HP} = 1, 5H, Cp), 1.70 (m, 2H, CH_2), 1.53 (m, 1H, CH_2), 1.55 (d of m, J_{HP} = 321, 1H, HP), 1.41 (m, 1H, CH_2), 1.22 (dt, J_{HP} = 15, J_{HH} = 7, 3H, CH_3), 0.71 (dt, J_{HP} = 13, J_{HH} = 7, 3H, CH_3), −18.89

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(d, $J_{HP} = 40$, 1H, μ-H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 219.8 (d, $J_{CP} = 26$, CO), 151.1 (d, $J_{CP} = 13$, C^1(Ph)), 140.8 (dd, $J_{CP} = 27$, 5, C^1(Ph)), 136.3 (d, $J_{CP} = 9$, C^2(Ph)), 133.0 (d, $J_{CP} = 9$, C^2(Ph)), 127.8 (s, C^4(Ph)), 127.7 (d, $J_{CP} = 9$, C^3(Ph)), 127.3 (d, $J_{CP} = 9$, C^3(Ph)), 126.9 (d, $J_{CP} = 2$, C^4(Ph)), 80.8 (s, Cp), 74.0 (s, Cp), 21.8 (dd, $J_{CP} = 25$, 4, CH_2), 21.3 (d, $J_{CP} = 25$, CH_2), 12.9 (d, $J_{CP} = 8$, CH_3), 11.4 (s, CH_3).

Preparation of Tetrahydrofuran Solutions of Li[Fe_2Cp_2(μ-PPh_2)$(CO)_2$] (7). Rigorously dried solvent is required for this preparation. A petroleum ether solution of LiBu (45 μL of an 1.6 M solution, 0.072 mmol) was added over a THF solution (10 mL) of compound *trans*-**2** (0.030 g, 0.062 mmol) at room temperature. This mixture was stirred for 5 min to give a brown solution shown by IR and $^{31}P\{^1H\}$ NMR to contain the complex **7** as major species.

Preparation of *cis*- and *trans*-[$AuFe_2Cp_2$(μ-PPh_2)$(CO)_2$(P^iPr_3)] (*cis*- and *trans*-8). [AuCl(P^iPr_3)] (0.024 g, 0.062 mmol) was added to a THF solution of compound **7**, prepared in situ as described above (ca. 0.062 mmol), and the mixture was stirred at room temperature for 5 min to give a brown solution. Solvent was then removed under vacuum, and the resulting residue was extracted with CH_2Cl_2/petroleum ether (1/1) and chromatographed on alumina (activity IV) at 15 °C. After the column was washed with petroleum ether, a brown fraction was eluted using CH_2Cl_2/petroleum ether (1/1). Removal of solvents from this fraction gave compound **8** as a brown solid (0.039 g, 75%). This product was shown by NMR to be a mixture of cis and trans isomers (in a ca. 1/4 ratio), which could not be separated by either crystallization or chromatography. Anal. Calcd for $C_{33}H_{41}O_2P_2AuFe_2$: C, 47.17; H, 4.92. Found: C, 47.29; H, 5.11. ^1H NMR (CD_2Cl_2): δ 7.80−7.10 (m, Ph), 4.55 (s, Cp, isomer trans), 4.33 (s, Cp, isomer cis), 2.36 (m, 3H, CH), 1.37 (dd, $J_{HP} = 15$, $J_{HH} = 7$, CH_3, isomer trans), 1.30 (dd, $J_{HP} = 15$, $J_{HH} = 7$, CH_3, isomer cis). cis/trans = 1/4.

Preparation of [Fe_2Cp_2(μ-PPh_2)(Me)(μ-CO)(CO)] (9). An excess of CH_3I (10 μL, 0.160 mmol) was added to a THF solution of compound **7**, prepared in situ as described above (ca. 0.062 mmol), and the mixture was stirred at room temperature for 5 min to give a brown solution. Solvent was then removed under vacuum, and the resulting residue was extracted with toluene (2 × 5 mL) and filtered. Removal of solvent from the filtrate and washing of the residue with petroleum ether (2 × 3 mL) gave compound **9** as a dark brown solid (0.020 g, 66%). The solutions of this complex decompose progressively, even at low temperature. ^1H NMR (200.13 MHz, C_6D_6): δ 7.90−7.08 (m, 10H, Ph), 4.34 (s, 5H, Cp), 4.30 (s, 5H, Cp), −1.13 (d, $J_{HP} = 8$, 3H, Me).

Preparation of Solutions of *trans*-[Fe_2Cp_2(μ-H)(μ-PPh_2)$(CO)_2$]PF_6 (*trans*-10). Solid [$FeCp_2$]PF_6 (0.023 g, 0.064 mmol) was added to a dichloromethane solution (8 mL) of the compound *trans*-**2** (0.030 g, 0.062 mmol) at −60 °C, and the mixture was stirred at the same temperature for 5 min to give a brown-green solution containing complex *trans*-**10** as the major species. This compound is quite air-sensitive and decomposes easily at room temperature. ESR (CH_2Cl_2, 300 K): $g = 2.0036$. $E°'$(*trans*-**10**/*trans*-**2**) = 0.36 V.

Preparation of Solutions of *cis*-[Fe_2Cp_2(μ-H)(μ-PPh_2)$(CO)_2$]PF_6 (*cis*-10). The procedure is analogous to that described for *trans*-**10** but using *cis*-**2** as starting material. This compound is also quite air-sensitive and decomposes easily at room temperature. ESR (CH_2Cl_2, 300 K): $g = 2.0038$. $E°'$(*cis*-**10**/*cis*-**2**) = 0.24 V.

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