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Activation of H−H and H−O Bonds at Phosphorus with Diiron Complexes Bearing Pyramidal Phosphinidene Ligands

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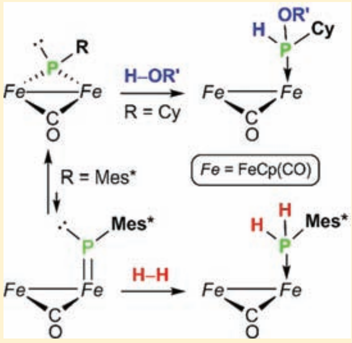
Ⓢ *Supporting Information*

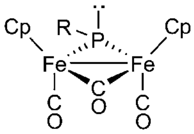


ABSTRACT: The complex $[Fe_2Cp_2(\mu\text{-PMes*})(\mu\text{-CO})(CO)_2]$ (Mes* = 2,4,6-$C_6H_2{}^tBu_3$), which in the solid state displays a pyramidal phosphinidene bridge, reacted at room temperature with H_2 (ca. 4 atm) to give the known phosphine complex $[Fe_2Cp_2(\mu\text{-CO})_2(CO)(PH_2Mes*)]$ as the major product, along with small amounts of other byproducts arising from the thermal degradation of the starting material, such as the phosphindole complex $[Fe_2Cp_2(\mu\text{-CO})_2(CO)\{PH(CH_2CMe_2)C_6H_2{}^tBu_2\}]$, the dimer $[Fe_2Cp_2(CO)_4]$, and free phosphine PH_2Mes*. During the course of the reaction, trace amounts of the mononuclear phosphide complex $[FeCp(CO)_2(PHMes*)]$ were also detected, a compound later found to be the major product in the carbonylation of the parent phosphinidene complex, with this reaction also yielding the dimer $[Fe_2Cp_2(CO)_4]$ and the known diphosphene Mes*P═PMes*. The outcome of the carbonylation reactions of the title complex could be rationalized by assuming the formation of an unstable tetracarbonyl intermediate $[Fe_2Cp_2(\mu\text{-PMes*})(CO)_4]$ (undetected) that would undergo a fast homolytic cleavage of a Fe−P bond, this being followed by subsequent evolution of the radical species so generated through either dimerization or reaction with trace amounts of water present in the reaction media. A more rational synthetic procedure for the phosphide complex was accomplished through deprotonation of the phosphine compound $[FeCp(CO)_2(PH_2Mes*)](BF_4)$ with Na(OH), the latter in turn being prepared via oxidation of $[Fe_2Cp_2(CO)_4]$ with $[FeCp_2](BF_4)$ in the presence of PH_2Mes*. To account for the hydrogenation of the parent phosphinidene complex it was assumed that, in solution, small amounts of an isomer displaying a terminal phosphinidene ligand would coexist with the more stable bridged form, a proposal supported by density functional theory (DFT) calculations of both isomers, with the latter also revealing that the frontier orbitals of the terminal isomer (only 5.7 kJ mol^{-1} above of the bridged isomer, in toluene solution) have the right shapes to interact with the H_2 molecule. In contrast to the above behavior, the cyclohexylphosphinidene complex $[Fe_2Cp_2(\mu\text{-PCy})(\mu\text{-CO})(CO)_2]$ failed to react with H_2 under conditions comparable to those of its PMes* analogue. Instead, it slowly reacted with HOR (R = H, Et) to give the corresponding phosphinous acid (or ethyl phosphinite) complexes $[Fe_2Cp_2(\mu\text{-CO})_2(CO)\{PH(OR)Mes*\}]$, a behavior not observed for the PMes* complex. The presence of BEt_3 increased significantly the rate of the above reaction, thus pointing to a pathway initiated with deprotonation of an O−H bond of the reagent by the basic P center of the phosphinidene complex, this being followed by the nucleophilic attack of the OR^- anion at the P site of the transient cationic phosphide thus formed. The solid-state structure of the cis isomer of the ethanol derivative was determined through a single crystal X-ray diffraction study (Fe−Fe = 2.5112(8) Å, Fe−P = 2.149(1) Å).

■ INTRODUCTION

The chemistry of phosphinidene (PR) complexes has been a very active area of research during the past three decades.[1] Most of this work has been focused on terminal complexes having bent-phosphinidene ligands, which are usually compared to carbenes and can also be classified as electrophilic or nucleophilic. In contrast, the chemistry of binuclear complexes bearing bridging phosphinidene ligands has been comparatively less developed. Recently we implemented a high-yield route to the stable diiron compounds $[Fe_2Cp_2(\mu\text{-PR})(\mu\text{-CO})(CO)_2]$ (R= Cy (**1a**), Ph (**1b**), Chart 1), having a phosphinidene bridge with a pyramidal environment and displaying a strong nucleophilic behavior.[2] We noticed at the time that there were only a few diiron phosphinidene complexes previously described in the literature, with most of them being either thermally unstable (as the cyclopentadienyl complex $[Fe_2Cp_2(\mu\text{-PPh})(CO)_4]$),[3] or transient species generated from suitable precursors, such as $[Fe_2\{\mu\text{-P}(N^iPr_2)\}_2(CO)_6]$,[4] $[Fe_2(\mu\text{-P}^tBu)(CO)_6]$,[5] or $[Fe_2(\mu\text{-PPh})_2(CO)_6]^{2-}$.[6] We can quote also a couple of isolable diiron phosphinidene complexes,

Chart 1



R = Cy(**1a**), Ph(**1b**), Mes*(**1c**)

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$[Fe_2\{\mu\text{-}P(OR)\}_2(CO)_6]$[7] and $[Fe_2(\mu\text{-}PPh)_2(L_2)_2]$,[8] both of them having bulky protecting groups (R = 4,2,6-$C_6H_2Me^tBu_2$, L_2 = $HC(CMeNC_6H_3{}^iPr_2)_2$) and a trigonal geometry at phosphorus, although no reactivity appears to have been developed around these complexes. We then started a detailed study of the reactivity of our diiron complexes and found that the cyclohexylphosphinidene complex **1a** was quite reactive toward a great variety of reagents, including alkyl halides, chalcogens, alkynes, diazoalkanes, organic azides, and metal carbonyl complexes, to give a variety of organophosphorus derivatives and heterometallic clusters.[2,9]

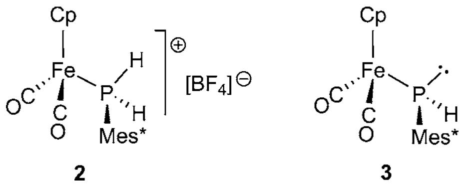
To examine the influence of steric factors on all this rich chemistry we later prepared the complex $[Fe_2Cp_2(\mu\text{-}PMes^*)(\mu\text{-}CO)(CO)_2]$ (**1c**), with Mes* being the bulky group 2,4,6-$C_6H_2{}^tBu_3$, and found that the steric pressure introduced by the Mes* group had pronounced effects concerning its synthesis, structure, thermal stability, and general reactivity.[10] Particularly intriguing was the remarkable ability of this complex to react with dihydrogen at room temperature, to give the phosphine complex $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)(PH_2Mes^*)]$ as the major product.[10a] This behavior was quite noticeable since no other phosphinidene complex of any type had been reported previously to be hydrogenated under similar conditions, while phosphines and related organophosphorus molecules (also having an electron pair and the ability to increase the coordination number at phosphorus) equally fail to react easily with hydrogen (except under Frustrated Lewis Pair conditions).[11] Noticeably, Bertrand et al. had recently reported the first example of hydrogenation of a free carbene molecule.[12] In this paper we report a detailed study of the hydrogenation reaction of compounds **1a,c** including the analysis of some side processes such as the reaction of **1c** with CO. We have also examined the ability of these compounds to activate the H–O bonds of water and ethanol. As it will be shown, the pathways involved in the activation of these two types of bonds (H–H vs H–O) seem to be completely different, with the hydrogenation of **1c** following from the ability of this crowded molecule to rearrange into an isomer having a terminal bent-phosphinidene ligand, an hypothesis supported by density functional theory (DFT) calculations on both **1c** and its phenyl analogue **1b**. Interestingly, while this paper was being finished, Mathey et al. reported that the transient bent-phosphinidene complexes $[Mo(PR)(CO)_5]$ (R = Me, Ph) were hydrogenated under more forcing conditions (20 bar, $T > 393$ K) to give the phosphine derivatives $[Mo(CO)_5(PH_2R)]$ via the corresponding diphosphine complexes $[Mo_2(\mu\text{-}PhHPPHPh)(CO)_{10}]$.[13]

■ RESULTS AND DISCUSSION

Hydrogenation of Compound 1c. The reactivity of compounds **1a,c** toward H_2 was tested under mild conditions (room temperature, ca. 4 atm). While the cyclohexylphosphinidene complex **1a** failed to react after 6 d in toluene solution, we found that the more congested compound **1c** did react with H_2 under the same conditions, the reaction being completed in about 16 h, to give the phosphine complex $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)(PH_2Mes^*)]$ (actually, the synthetic precursor of **1c**)[10] as the major compound (ca. 50% by ^1H NMR). Other products detected in the reaction mixture were free phosphine PH_2Mes^* (20%), the dimer $[Fe_2Cp_2(CO)_4]$ (15%), the oxophosphinidene complex $[Fe_2Cp_2(CO)_3\{P(O)Mes^*\}]$[10a] (10%), and the phosphindole derivative $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)\{PH(CH_2CMe_2)C_6H_2{}^tBu_2\}]$[10] (5%). The presence of all these minor products can be rationalized by taking into account the known degradation processes of **1c** in solution. Thus, we have previously shown that **1c** slowly decomposes at room temperature in toluene solution (ca. 80% conversion after 4 days) to give $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)\{PH(CH_2CMe_2)C_6H_2{}^tBu_2\}]$, following from the intramolecular addition of a C–H bond of an *o*-^tBu group at the P center, and also some $[Fe_2Cp_2(CO)_4]$.[10b] In addition, the phosphine complex $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)(PH_2Mes^*)]$ is also known to decompose slowly in solution to give free phosphine (PH_2Mes^*) and more $[Fe_2Cp_2(CO)_4]$.[10b] Finally, the phosphinidene oxide complex obviously arises from the reaction of **1c** with trace amounts of O_2 present in the reaction media.[10a]

To detect possible intermediates, we also carried out the hydrogenation of **1c** (C_6D_6 solution) within an NMR tube equipped with a Young's valve and pressurized with about 3 atm of H_2, to monitor the reaction by NMR spectroscopy. A blank experiment was also carried out with another aliquot of **1c** in C_6D_6 solution, under a N_2 atmosphere. The hydrogenation reaction was significantly slower under these conditions, probably because of the slower incorporation of dihydrogen into the solution in the absence of stirring, coupled to the progressive loss of H_2 pressure within the NMR tube (overall reaction time of ca. 4 weeks). As a result, the relative amount of byproducts increased significantly, especially those derived from the thermal degradation of **1c**: the dimer $[Fe_2Cp_2(CO)_4]$ (30%) and the phosphindole complex $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)\{PH(CH_2CMe_2)C_6H_2{}^tBu_2\}]$ (25%), whereas the yield of the hydrogenation product $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)(PH_2Mes^*)]$ decreased considerably (12%). Unexpectedly, at early stages in both experiments (H_2 or N_2 atmosphere) we detected the presence of small amounts of a species that we have later identified as the mononuclear phosphide complex $[FeCp(CO)_2(PHMes^*)]$ (**3**) (ca. 5% by ^1H NMR analysis), a degradation product of **1c** which had previously gone undetected (Chart 2).[10] In the hydrogenation experiment, however, complex **3** disappeared from the reaction mixture once the starting material was totally consumed, whereas it remained steady in the blank experiment as the amount of the other products coming from the thermal degradation of **1b** increased. The final product distribution in the blank experiment was $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)\{PH(CH_2CMe_2)C_6H_2{}^tBu_2\}]$ (55%), $[Fe_2Cp_2(CO)_4]$ (15%), complex **3** (5%), PH_2Mes^* (traces), and other unidentified products (15%).

Chart 2



Carbonylation of Compound 1c. While searching for alternative degradation processes of **1c** that could account for the formation of the phosphide complex **3**, we found that this complex could be obtained in good yield through the reaction of **1c** with CO. Different carbonylation experiments were carried out for **1c** in different solvents (CH_2Cl_2 or toluene) and reaction times (from 15 to 20 h), usually at a pressure of about 4 atm of CO, to give essentially the same product distribution: the phosphide complex **3** (55%), the dimer $[Fe_2Cp_2(CO)_4]$

(40%), and the diphosphene Mes*P═PMes* (5%), the latter being identified by its ^{31}P NMR resonance in C_6D_6 at 492 ppm.[14] As discussed later on, the hydrogen needed to form **3** seems to arise from traces of water present in the solvent and gas used.

Rational Synthesis of Compound 3. The phosphide complex **3** could be more selectively prepared through a two-step procedure starting from $[Fe_2Cp_2(CO)_4]$. First, the phosphine complex $[FeCp(CO)_2(PH_2Mes^*)][BF_4]$ (**2**) was prepared in 56% yield through the oxidation of $[Fe_2Cp_2(CO)_4]$ with $[FeCp_2]BF_4$ (2 equiv) in the presence of PH_2Mes^* (2 equiv), a procedure previously implemented by Schumann to prepare the related PPh_3 complex.[15] Then, compound **2** was deprotonated with Na(OH) to give compound **3** in 60% yield. The spectroscopic data in solution for compounds **2** and **3** are completely analogous to those of related primary phosphine and phosphide complexes reported by Malisch and co-workers,[16] and therefore deserve no detailed comments, except to note that the IR spectra of these complexes in dichloromethane solution show two strong C−O stretches (Table 1), as anticipated for cisoid $M(CO)_2$ oscillators in a pseudooctahedral coordination environment.[17] The bands of the cationic **2** are shifted significantly to higher frequencies (by ca. 60 cm^{-1}) with respect to those of the neutral **3**, as expected. Yet, the most informative spectroscopic features are found in the ^{31}P and ^{1}H NMR resonances corresponding to the PH_x moieties of these compounds. These appear in the case of **2** ($x = 2$) as a triplet at −49.2 ppm (^{31}P) and a doublet at 6.71 ppm (^{1}H) with a large coupling constant ($^{1}J_{PH}$) of 392 Hz, whereas for compound **3** ($x = 1$) these resonances appear as two more shielded doublets, at −91.8 ppm (^{31}P) and 5.02 ppm (^{1}H) respectively, with a largely reduced coupling constant ($^{1}J_{PH}$) of 179 Hz, a diagnostic effect of the presence of the lone electron pair at phosphorus in the neutral phosphide complex.[18]

Table 1. Selected IR and ^{31}P NMR Data for New Compounds

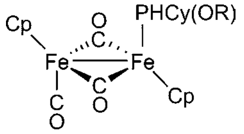
compound	ν(CO)^a	$\delta_P(J_{HP})^b$
$[FeCp(CO)_2(PH_2Mes^*)]BF_4$ (**2**)	2065 (vs), 2021 (s)	−49.2 (392)
$[FeCp(CO)_2(PHMes^*)]$ (**3**)	2007 (vs), 1955 (s)	−91.8 (179)
$[Fe_2Cp_2(\mu\text{-}CO)_2(CO)\{PHCy(OH)\}]$ (**4**)	1941 (s), 1769 (w), 1720 (vs)	171.3 (345)^c
$[Fe_2Cp_2(\mu\text{-}CO)_2(CO)\{PHCy(OEt)\}]$ (***trans*-5**)	1935 (s), 1767 (w), 1729 (vs)	192.4 (337)
$[Fe_2Cp_2(\mu\text{-}CO)_2(CO)\{PHCy(OEt)\}]$ (***cis*-5**)		189.9 (333)

^{a}Recorded in dichloromethane solution, with C−O stretching bands (ν(CO)) in cm^{-1}. ^{b}Recorded in CD_2Cl_2 solutions at 290 K and 121.50 MHz unless otherwise stated; δ in ppm relative to external 85% aqueous H_3PO_4 and coupling constants (J) in hertz. ^{c}Recorded in CH_2Cl_2 with a D_2O insert.

Reactions of Compounds 1a,c with H_2O and EtOH. The behavior of our phosphinidene complexes was completely reversed when faced to the polar single O−H bonds of water or alcohols. Thus, the PMes* complex **1c** failed to react with these reagents, even when using H_2O as cosolvent (H_2O/THF ratio = 1/5) or ethanol as solvent. Only a progressive thermal degradation of **1c** to give the phosphindole complex $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)\{PH(CH_2CMe_2)C_6H_2{}^tBu\}]$ was observed in these experiments. We noticed, however, that the rate of this degradation was much lower than that observed in toluene solution. For instance, the amount of phosphindole complex formed after 3 d in ethanol solution at room temperature was lower than 5%. Clearly, some kind of interaction between **1c** and the EtOH molecules must take place to suppress the intramolecular C−H cleavage leading to the phosphindole derivative. A comparable suppression of a related C−H cleavage has been previously observed in the photochemical reactions of the trigonal phosphinidene complex $[Mo_2Cp_2(\mu\text{-}PMes^*)(CO)_4]$ when carried out in the presence of acetonitrile.[19]

As opposed to **1c**, the less crowded and more basic PCy-bridged complex **1a** did react slowly with both substrates. The reaction with H_2O (ca. 500 equiv.) in toluene was completed in about 5 h at room temperature to give the phosphinous acid complex $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)\{PHCy(OH)\}]$ (**4**), a rather unstable species decomposing easily upon manipulation (Chart 3). Interestingly, this reaction proceeded more rapidly in the presence of 1 equiv of BEt_3, then being completed in only 45 min when using just 20 equiv of H_2O. A similar effect took place for the reaction of **1a** with ethanol, this being used both as solvent and reagent, then leading to the more stable phosphinite complex $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)\{PHCy(OEt)\}]$ (**5**). In the absence of BEt_3, only 50% conversion was obtained after 3 days at room temperature, whereas full conversion was achieved in the same reaction time after addition of 1 equiv of BEt_3. In the latter case, however, variable amounts of compound **4** (up to 25%, measured by ^{31}P NMR) were also generated, probably arising from the reaction with traces of H_2O present in the solvent. We finally note that the above reactions of the diiron complex **1a** are reminiscent of the reactions reported by Mathey and co-workers between transient electrophilic phosphinidenes of the type $[M(CO)_n(PPh)]$ (M = Cr, Mo, W; $n = 5$;[20a,b] M = Fe, $n = 4$[20c]) with water or simple alcohols to give the corresponding phosphinite derivatives $[M(CO)_n\{PHPh(OR)\}]$ (R = H, alkyl group).

Chart 3



R = H (**4**), Et (**5**)

Structural Characterization of Compounds 4 and 5. The solid-state structure of ***cis*-5** was determined through a single-crystal X-ray diffraction analysis (Figure 1 and Table 2). The structure of ***cis*-5** is built from two CpFe fragments in a cisoid arrangement bridged by two carbonyl ligands in an almost symmetric fashion. The coordination sphere of each metal center is completed by a carbonyl and a phosphinite ligand, respectively. The bridging CO ligands are almost coplanar, with the angle between the corresponding Fe_2C planes being about 160°, in the range found for related complexes of the formula *cis*-$[Fe_2Cp_2(\mu\text{-}CO)_2(CO)L]$ (L = $P(OPh)_3$,[21] $PPh_2(CH_2Ph)$,[22] $P(Ph)C_4H_2Me_2$[23]). The intermetallic length of 2.5112(8) Å in ***cis*-5** is consistent with the formulation of a single metal−metal bond, and it is only marginally shorter than the average distance measured for the mentioned complexes (ca. 2.54 Å), while the Fe2−P1 distance of 2.149(1) Å is also comparable to the iron-phosphite or iron-phosphine separations in these species.

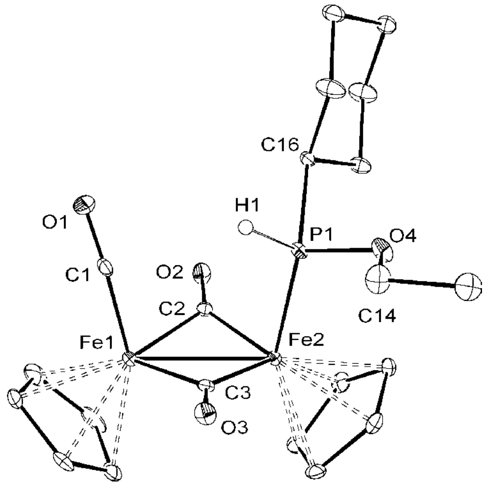


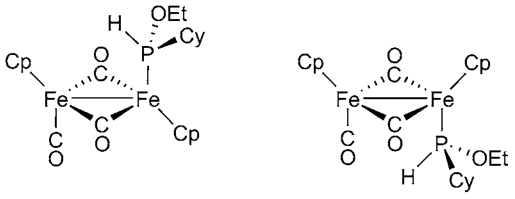
Figure 1. ORTEP diagram of compound ***cis*-5**, with H atoms (except H1) omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound *cis*-5

Fe(1)−Fe(2)	2.5112(8)	Fe(2)−C(2)−Fe(1)	82.2(1)
Fe(2)−P(1)	2.149(1)	Fe(2)−C(3)−Fe(1)	81.8(1)
Fe(1)−C(1)	1.744(4)	P(1)−Fe(2)−Fe(1)	100.06(4)
Fe(1)−C(2)	1.952(3)	C(1)−Fe(1)−Fe(2)	103.1(1)
Fe(1)−C(3)	1.947(3)		
Fe(2)−C(2)	1.866(3)		
Fe(2)−C(3)	1.887(3)		

The spectroscopic data for compound **5** reveal the presence of a solvent-dependent equilibrium mixture of cis and trans isomers in solution (Chart 4 and Experimental Section), a common feature for this type of compound. The IR spectrum exhibits three C−O stretching bands with the expected pattern, with the two bridging CO ligands in a transoid arrangement giving rise to bands at 1769 (w) and 1729 (vs) cm^{-1}, and the terminal CO ligand yielding a strong band at 1935 cm^{-1}. The IR spectra of different compounds of the formula [$Fe_2Cp_2(\mu$-$CO)_2(CO)L$] (L = phosphine,[16] phosphite,[16,17] κ^1-$(EtO)_2POP(EtO)_2$[18]) exhibit a terminal C−O stretching band in the range 1973−1951 cm^{-1} for the cis isomers, and 1950−1929 cm^{-1} for the trans isomers. On this basis we propose a transoid arrangement of the FeCp(CO) fragments for the major isomer of **5**, as opposed to the conformation found in the solid state (cis). The ^{31}P NMR spectrum of **5** exhibits two doublets, at 192.4 ppm (trans isomer, $^1J_{PH}$ = 337 Hz) and 189.9 ppm (cis isomer, $^1J_{PH}$ = 334 Hz) respectively. These chemical shifts are reasonable for a phosphinite ligand coordinated to an iron center, and not far from that measured for the mononuclear complex [$Fe(CO)_4\{PHPh(OEt)\}$] (153.3 ppm).[20c]

Chart 4

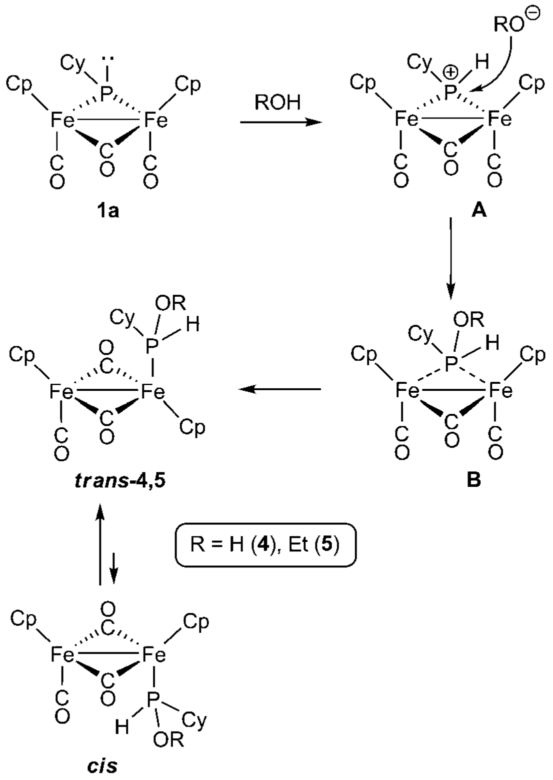


***trans*-5** ***cis*-5**

The phosphinous acid complex **4** could only be characterized through the IR and ^{31}P NMR spectra of the crude reaction mixture, because of its low stability. All attempts to isolate it as a pure material resulted in its progressive decomposition. Its IR spectrum in solution is comparable to that of compound **5** (Table 1), thus suggesting that the trans isomer is also the major (or unique) species in solution. Its ^{31}P NMR spectrum exhibited only a broad doublet resonance at 171.3 ppm ($^1J_{PH}$ ca. 345 Hz), not far from that of **5**. The broadness of this resonance, however, would prevent the detection of a second isomer, if only present in small amounts.

Pathways for the Reactions of 1a with H_2O and EtOH. To account for the formation of the PHCy(OR) complexes **4** and **5** we can propose a first step in which the nucleophilic P atom of the phosphinidene ligand in **1a** would deprotonate a molecule of H_2O or EtOH to give the corresponding cationic phosphide intermediates [$Fe_2Cp_2(\mu$-$CO)(\mu$-$PCyH)(CO)_2$][OR] (**A** in Scheme 1). These species were not detected spectroscopically in the reaction mixtures, but the corresponding cation has been previously isolated as the [BF_4]$^-$ salt (actually, that salt is the synthetic precursor of **1a**).[10b] In the case of salts **A**, however, the P atom in the cation would undergo a fast nucleophilic attack of the alkoxide (or hydroxide) counterion to give the corresponding PHCy(OR)-bridged derivates [$Fe_2Cp_2(\mu$-$CO)\{\mu$-$PCyH(OR)\}(CO)_2$] (**B**), these in turn rapidly rearranging into the more stable terminal coordination mode, thus yielding the complexes **4** and **5**. We note that this pathway is different from that proposed for the reactions of water or alcohols with transient electrophilic phosphinidenes of Cr, Mo, W, and Fe mentioned above,[20] the latter involving first a nucleophilic attack of the OR$^-$ anion

Scheme 1



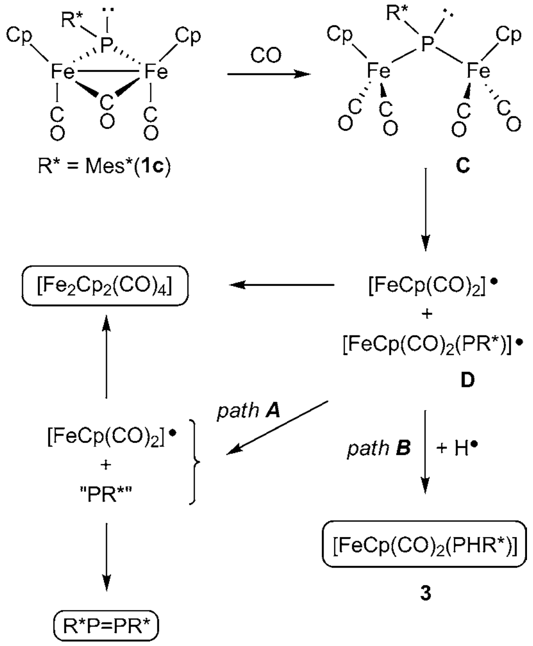
followed by the protonation of the (undetected) resulting anionic phosphide intermediate. This difference of course follows from the strong nucleophilic nature of the phosphinidene ligand in **1a**. We finally note that a concerted mechanism from **A** to **4**/**5** (i.e., not involving the intermediacy of **B**) cannot be ruled out in any case.

The limiting step in the reactions of **1a** with H_2O or EtOH surely is the proton transfer step, because of the low acidity of the H atoms involved, and a stronger acid would probably react more easily. To check this hypothesis we tested the reaction with HSPh. Indeed, just stoichiometric amounts of the thiol were enough to react instantaneously with **1a** at 273 K to give a deep green solution containing the expected thiolophosphine complex $[Fe_2Cp_2(\mu\text{-CO})_2(CO)\{PHCy(SPh)\}]$, as deduced from its IR (ν(CO) (CH_2Cl_2): 1938 (m), 1775 (w), 1735 (vs)) and ^{31}P NMR spectra (δ_P 113.5 ppm, J_{HP} = 348 Hz, in CD_2Cl_2). This compound, however, was a rather unstable species that could not be isolated or fully characterized because of its progressive decomposition upon manipulation. A second piece of evidence in favor of deprotonation as the limiting step in the reactions of **1a** under discussion is the observed increase in the reaction rate when BEt_3 is present. Presumably, this effect would follow from the formation of small amounts of the corresponding adducts $R(H)O-BEt_3$, these in turn having O-bound hydrogens of increased acidity. Although these adducts appear to have been never reported in the literature, the methanol−BEt_3 adduct has been proposed as an intermediate species in the methanolysis of BEt_3 to give $Et_2B(OMe)$.[27] In fact, in the course of the reactions of **1a** with excess H_2O or EtOH in the presence of BEt_3, the alcoholysis or hydrolysis products $Et_2B(OR)$ and $EtB(OR)_2$ were detected by ^{11}B NMR, these giving rise to diagnostic resonances at about 55 ppm and 30 ppm respectively, which compare well to the values reported in the literature for these or analogous compounds.[27,28]

We are aware of only one other report involving a borane-mediated reaction of water with a phosphinidene complex, even if the results are different. Thus, the ruthenium complexes $[Ru(\eta^6\text{-Ar})(PCy_3)(PMes^*)]$ (Ar = *p*-cymene, benzene) have been reported to react with H_2O in the presence of BPh_3 to give the corresponding phosphide species $[Ru(\eta^6\text{-Ar})(PCy_3)(PHMes^*)][BPh_3OH]$.[29] For comparison purposes, we also carried out the reaction of **1a** with water in the presence of BPh_3. This led to a complex mixture containing the cation $[Fe_2Cp_2(\mu\text{-CO})(\mu\text{-PHCy})(CO)_2]^+$ and other uncharacterized products, as deduced from the analysis of the IR and ^{31}P NMR spectra of the reaction mixture. It thus seems that the hydroxoborate ion $[(OH)BPh_3]^-$ presumably formed in these reactions would be a nucleophile weaker than its triethyl counterpart, not strong enough to attack the cationic species **A** formed in the first step of these reactions.

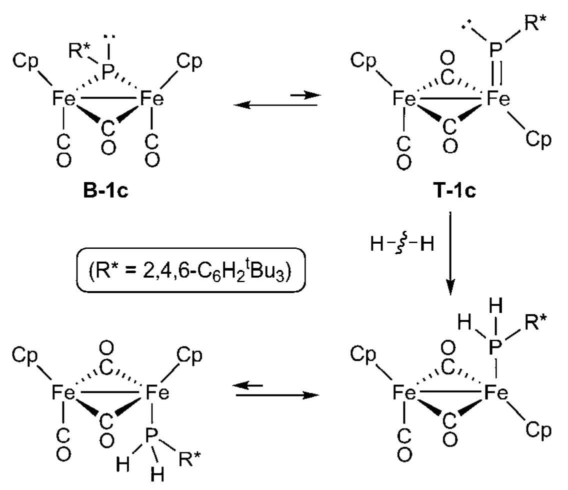
Pathways in the Carbonylation Reaction of 1c. As mentioned above, three products (the phosphide complex **3**, the dimer $[Fe_2Cp_2(CO)_4]$, and the diphosphene Mes*P=PMes*) were obtained in the room temperature carbonylation of **1c**, with little dependence on the reaction conditions (solvent, reaction time). To account for the formation of all of them we assume that the first step in this reaction would involve the addition of a CO molecule to the dimetal center, to give a transient (undetected) tetracarbonyl derivative $[Fe_2Cp_2(\mu\text{-PMes}^*)(CO)_4]$ with no direct Fe−Fe interaction (**C** in Scheme 2). Interestingly, the isostructural phenylphosphinidene complex $[Fe_2Cp_2(\mu\text{-PPh})(CO)_4]$ has been previously reported by Lorenz and co-workers, and found to be thermally unstable.[3] Intermediate **C** could then undergo an homolytic fission of one of its Fe−P bonds, to give the mononuclear radicals $[FeCp(CO)_2]$ and $[FeCp(CO)_2(PMes^*)]$ (**D**), with the first of them rapidly dimerizing to render $[Fe_2Cp_2(CO)_4]$. In contrast, the phosphinidene radical **D**, perhaps unable to dimerize rapidly because of steric hindrance, might follow two mutually competitive reaction pathways: (a) A thermal degradation to give the radical $[FeCp(CO)_2]$ and free phosphinidene "PMes*" (path A in Scheme 2), with these species rapidly dimerizing to yield more $[Fe_2Cp_2(CO)_4]$ and the diphosphene Mes*P=PMes* respectively. (b) An H-atom abstraction (presumably at its P atom) from traces of water present in the solvent (and in the gas used) to give the phosphide complex **3** (path B in Scheme 2). We note that H-atom abstraction is a typical reaction of organometallic radicals,[30] while the formation of the mentioned diphosphene upon dimerization of the transient phosphinidene PMes* has been also recognized previously.[31] From the observed product distribution it is obvious that the second route is faster, accounting for about 85% of the evolution of the radical **D**, a conclusion not surprising in view of the high reactivity of organometallic radicals.[30]

Scheme 2



The Role of a Terminal Isomer. Pathways in the Hydrogenation Reaction of 1c. To account for the formation of the phosphine derivative $[Fe_2Cp_2(\mu\text{-CO})_2(CO)(PH_2Mes^*)]$ upon hydrogenation of **1c** we propose for the latter complex the presence in solution of small amounts of a terminal isomer **T-1c** in equilibrium with the dominant, PMes*-bridged isomer **B-1c** (Scheme 3). This would be analogous to the observed equilibrium in the corresponding oxophosphinidene complex $[Fe_2Cp_2(CO)_3\{P(O)Mes^*\}]$,[10a] and perhaps it is also behind the thermal degradation of **1c** to give the phosphindole complex $[Fe_2Cp_2(\mu\text{-CO})_2(CO)\{PH(CH_2CMe_2)C_6H_2{}^tBu_2\}]$.[10b] The isomer **T-1c** is expected to be more reactive than its bridged isomer because of both the lower steric hindrance around the P atom and its more favorable electronic structure (see below), then becoming able to induce the required homolytic cleavage of H_2 at the P site. We have

Scheme 3



carried out DFT[32] calculations for both isomers of **1c** and also for the phenylphosphinidene complex **1b**, for comparative purposes (see the Experimental Section and the Supporting Information for further details).

The gas phase Gibbs energy for the isomerization **B-1c** to **T-1c** was computed to be only 0.97 kcal mol^{-1} (K_{eq} (**B→T**) about 0.19), this rising to 1.37 kcal mol^{-1} when the solvation correction for toluene was applied (K_{eq} ca. 0.10). In contrast, the terminal isomer of the phenylphosphinidene complex **1b** was computed to be much higher in energy than its bridged isomer in the gas phase (ΔG_{gas} = 21.1 kcal mol^{-1}; K_{eq} (**B→T**) = 3.4×10^{-16}). From this we conclude that the presence of small amounts of the terminal isomer in the solutions of **1c** is feasible and mainly derived from the steric congestion induced by the bulky Mes* group. Although we failed to detect the presence of such a terminal isomer in the low-temperature $^{31}P\{^{1}H\}$ NMR spectra of **1c** we note that the anomalous upfield shift (ca. 20 ppm) of the resonance from 298 to 193 K would be consistent with the above calculations, these predicting higher prevalence of the bridged isomer (with much lower ^{31}P chemical shift than the terminal isomer) at lower temperatures, because of its lower entropy content (ΔS_{gas} = 9 cal mol^{-1} K^{-1}).

The DFT-optimized geometries for **B-1c** and **T-1c** (Figure 2) display unremarkable geometric parameters (Table 3) except for the Fe−P distance in the terminal isomer, about 0.2 Å shorter than the Fe−P separations in the bridged isomer, therefore indicative of a significant multiplicity in that bond. Indeed the presence of a small π component in the Fe−P bond of **T-1c** can be grasped through the nature of its HOMO−4 orbital (Figure 3). In agreement with this, an analysis of the topology of the electron density (ρ) of the molecule under the Atoms in Molecules scheme (AIM)[33] revealed a substantially increased value of ρ at the Mo−P bond critical point (0.72 eÅ^{-3}, to be compared with an average value of 0.50 eÅ^{-3} in the bridged isomer).

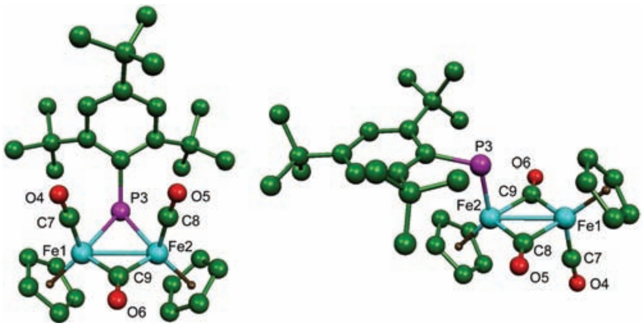


Figure 2. DFT optimized geometries of **B-1c** (left) and **T-1c** (right).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for B-1c and T-1c

parameter	B-1c	T-1c
Fe(1)−Fe(2)	2.586	2.578
Fe(1)−P(3)	2.320	
Fe(1)−C(7)	1.755	1.757
Fe(1)−C(8)		1.902
Fe(1)−C(9)	1.912	1.920
Fe(2)−P(3)	2.332	2.129
Fe(2)−C(8)	1.758	1.938
Fe(2)−C(9)	1.903	1.929
Fe(2)−P(3)−C(Ar)	116.1	111.9

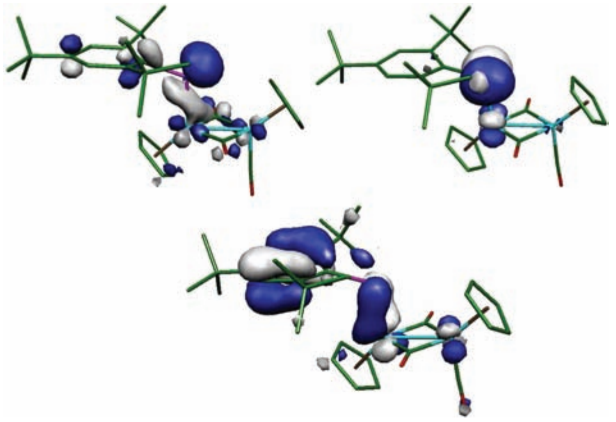


Figure 3. DFT-computed HOMO (−5.15 eV, left), LUMO (−2.43 eV, right), and HOMO−4 (−6.33 eV, down) orbitals in **T-1c**.

Recent work by Power and other researchers has proved the ability of different types of main-group compounds (ER$_2$, E$_2$R$_2$, etc., with E = Si−Pb) to activate the single bonds of hydrogen and related molecules.[34] This transition-metal-like reactivity relies on the presence in the main-group compounds of suitable frontier orbitals, an empty one able to interact with the σ-orbital of H$_2$, and an occupied one able to provide back-donation to the σ* orbital of H$_2$. In the case of **T-1c**, this role clearly would be played respectively by the lowest unoccupied molecular orbital (LUMO) (largely located at P, with π*(Fe−P) character) and the highest occupied molecular orbital (HOMO) (also largely located at P, with dominant lone pair character), this accounting for its hydrogenation to give the phosphine derivative [Fe$_2$Cp$_2$(μ-CO)$_2$(CO)(PH$_2$Mes*)] in a straightforward way. Interestingly, a recent report has shown the ability of the mononuclear phosphinidene complex [FeCp(CO)$_2$(PN^{i}Pr$_2$)][AlCl$_4$] to activate the Si−H bond of different silanes under mild conditions, to give the corresponding silylphosphine derivatives.[35]

■ CONCLUDING REMARKS

The ability of the supermesitylphosphinidene complex **1c** to react at room temperature with H$_2$ at a single P center, a unique behavior to date, is attributed to the presence in solution of small amounts of an isomer bearing a terminal phosphinidene ligand, estimated to be in toluene solution only 1.4 kcal mol^{-1} less stable than the major, PMes*-bridged isomer, according to DFT calculations. This is ultimately a steric effect, since the analogous phenylphosphinidene complex **1b** (inert toward H_2) exists only in the bridged form. The presence of CO induces the cleavage of the Fe−Fe bond of **1c**, to give the mononuclear phosphide complex $[FeCp(CO)_2(PHMes^*)]$ as major product, this following from an H-atom abstraction by the radical $[FeCp(CO)_2(PMes^*)]$ presumably generated in the process. In contrast to the above behavior, the cyclohexylphosphinidene complex **1a**, which fails to react with H_2 presumably because of the absence of significant amounts of the terminal isomer in solution, is able to activate the polar O−H bonds of H_2O or EtOH to give the corresponding derivatives $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)\{PH(OR)Mes^*\}]$. This, however, takes place via a two step mechanism initiated with the deprotonation of the O-bound hydrogen by the basic P atom of the phosphinidene ligand, followed by a nucleophilic attack of the OR^- anion at the P atom in the cationic phosphide complex first formed.

■ EXPERIMENTAL SECTION

General Procedures and Starting Materials. All manipulations and reactions were carried out under a nitrogen (99.995%) atmosphere using standard Schlenk techniques. Solvents were purified according to literature procedures and distilled prior to use.[36] Petroleum ether refers to that fraction distilling in the range 338−343 K. Compounds $[FeCp_2]BF_4$,[37] and PH_2Mes^*,[38] were synthesized according to literature procedures. Solutions of the phosphinidene complexes $[Fe_2Cp_2(\mu\text{-}PR)(\mu\text{-}CO)(CO)_2]$ (R = Cy (**1a**), Mes* (**1c**)) were prepared in situ as described previously.[10b] All other reagents were obtained from the usual commercial suppliers and used as received. Chromatographic separations were carried out using jacketed columns cooled by tap water (ca. 288 K). Commercial aluminum oxide (activity I, 150 mesh) was degassed under vacuum prior to use. The latter was afterward mixed under nitrogen with the appropriate amount of water to reach the activity desired. IR C−O stretching frequencies were measured in solution and are referred to as ν (CO). Nuclear Magnetic Resonance (NMR) spectra were routinely recorded at 300.13 (^1H), 121.50 ($^{31}P\{^1H\}$), 75.48 ($^{13}C\{^1H\}$) or 121.52 MHz (^{11}B) at 290 K in CD_2Cl_2 solutions unless otherwise stated. Chemical shifts (δ) are given in parts per million (ppm), relative to internal tetramethylsilane (^1H, ^{13}C), external 85% aqueous H_3PO_4 (^{31}P) or external $BF_3{\cdot}OEt_2$ (^{11}B). Coupling constants (J) are given in hertz (Hz).

Hydrogenation of Compound 1c. In a typical experiment, a Schlenk tube equipped with a Young's valve containing a solution of compound **1c** (ca. 0.05 mmol) in toluene (5 mL) was frozen with liquid N_2. The tube was degassed under vacuum, and then refilled with H_2. The valve was then closed, and the mixture was allowed to reach room temperature (P_{H2} ca. 4 atm). The solution was then stirred for 16 h to yield a brown-greenish solution containing $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)(PH_2Mes^*)]$,[10b] as an equilibrium mixture of the cis and trans isomers (50%), PH_2Mes^* (20%), $[Fe_2Cp_2(CO)_4]$ (15%), $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)\{P(O)Mes^*\}]$ (10%),[10a] and $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)\{PH(CH_2CMe_2)C_6H_2{}^tBu_2\}]$ (5%).[10b] The relative ratio of the above compounds in the reaction mixture was determined through ^1H NMR measurements in C_6D_6.

Carbonylation of Compound 1c. In a typical experiment, a Schlenk tube equipped with a Young's valve containing a solution of compound **1c** (ca. 0.05 mmol) in toluene (5 mL) was frozen with liquid N_2. The tube was degassed under vacuum, and then refilled with CO. The valve was then closed, and the mixture was allowed to reach room temperature (P_{CO} ca. 4 atm). The solution was then stirred for 16 h to yield an orange solution containing $[FeCp(CO)_2(PHMes^*)]$ (**3**) (55%), $[Fe_2Cp_2(CO)_4]$ (40%), and Mes*P═PMes* (5%), as determined through the ^1H NMR spectra of the mixture. The same product distribution was reached when using dichloromethane as solvent.

Preparation of $[FeCp(CO)_2(PH_2Mes^*)](BF_4)$ (2). A mixture of $[Fe_2Cp_2(CO)_4]$ (0.035 g, 0.099 mmol), $[FeCp_2]BF_4$ (0.055 g, 0.202 mmol) and PH_2Mes^* (0.055 g, 0.198 mmol) in dichloromethane (7 mL) was stirred for 4 h at room temperature to give a green solution. The solvent was then removed under vacuum and the green residue was washed with diethyl ether (4 × 6 mL) to give compound **2** as a green microcrystalline solid (0.060 g, 56%). Anal. Calcd for $C_{25}H_{36}BF_4FeO_2P$: C, 55.38; H, 6.69. Found: C, 55.26; H, 6.88. ^1H NMR: δ 7.54 (d, J_{HP} = 4, 2H, C_6H_2), 6.71 (d, J_{HP} = 392, 2H, PH_2), 5.09 (d, J_{HP} = 1, 5H, Cp), 1.57 (s, 18H, o-^{t}Bu), 1.31 (s, 9H, p-^{t}Bu).

Preparation of $[FeCp(CO)_2(PHMes^*)]$ (3). Solid NaOH (ca. 0.1 g, excess) was added to a solution of compound **2** (0.060 g, 0.111 mmol) in dichloromethane (7 mL), and the mixture was stirred for 5 min to give a dark orange solution. The solvent was then removed under vacuum, and the residue was dissolved in the minimum amount of petroleum ether and chromatographed on alumina (activity IV) at 288 K. Elution with a dichloromethane/petroleum ether (1/9) mixture gave an orange fraction yielding, upon removal of solvents under vacuum, compound **3** as a dark orange microcrystalline solid (0.030 g, 60%). Anal. Calcd for $C_{25}H_{35}FeO_2P$: C, 66.09; H, 7.76. Found: C, 66.35; H, 7.90. ^1H NMR (C_6D_6): δ 7.43 (s, 2H, C_6H_2), 5.02 (d, J_{HP} = 179, 1H, PH), 3.87 (s, 5H, Cp), 1.88, 1.73, 1.30 (3s, 3 × 9H, ^{t}Bu).

Preparation of $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)\{PHCy(OH)\}]$ (4). A 1 M solution of BEt_3 in hexane (300 μL, 0.3 mmol) and degassed water (100 μL, 5.55 mmol) were added to a solution of compound **1a** (ca. 0.28 mmol) in dichloromethane (10 mL). The reaction mixture was stirred for 45 min to give a brown solution containing compound **4** as the major compound. All the attempts to isolate it as a pure species led invariably to its progressive decomposition.

Preparation of $[Fe_2Cp_2(\mu\text{-}CO)_2(CO)\{PHCy(OEt)\}]$ (5). A 1 M solution of BEt_3 in hexane (200 μL, 0.2 mmol) was added to an ethanol suspension (7 mL) of compound **1a** (ca. 0.2 mmol), and the mixture was stirred for 3 d at room temperature to give a brown solution containing compounds **5** and **4** (ratio **5**/**4**: 3/1, as determined from the $^{31}P\{^1H\}$ NMR spectrum of the mixture). After removal of the solvent under vacuum, the residue was dissolved in dichloromethane/petroleum ether (1/9), and the extract was chromatographed on alumina (activity IV) at 288 K. Elution with dichloromethane/petroleum ether (1/2) gave a brown fraction yielding, upon removal of solvents under vacuum, compound **5** as a red-brownish microcrystalline solid (0.040 g, 41%). This compound exists in solution as an equilibrium mixture of the corresponding cis and trans isomers, with the trans/cis ratio being 10/1 in CD_2Cl_2 and 13/1 in C_6D_6, as determined from the $^{31}P\{^1H\}$ NMR spectra. Brown crystals suitable for an X-ray analysis of the cis isomer were grown from a concentrated solution of the mixture of isomers in petroleum ether at 253 K. Anal. Calcd for $C_{21}H_{27}Fe_2O_4P$: C, 51.89; H, 5.60. Found: C, 51.86; H, 5.93. *Spectroscopic data for **trans-5***: ^1H NMR: δ 4.82 (d, J_{HP} = 337, 1H, PH), 4.72, 4.52 (2s, 2 × 5H, Cp), 3.94 (dq, J_{HH} = 15, 7, 1H, CH_2), 3.74 (dq, J_{HH} = 15, 7, 1H, CH_2), 2.2−1.0 (m, 11H, Cy), 1.22 (t, J_{HH} = 7, 3H, Me). The proton resonances of the minor isomer ***cis*-5** were masked by those of the major isomer.

X-ray Structure Determination of Compound 5. The X-ray intensity data for ***cis*-5** were collected on a Smart-CCD-1000 Bruker diffractometer using graphite-monochromated MoK_α radiation at 120 K. Cell dimensions and orientation matrices were initially determined from least-squares refinements on reflections measured in 3 sets of 30 exposures collected in 3 different ω regions and eventually refined against all reflections. The software SMART[39] was used for collecting frames of data, indexing reflections, and determining lattice parameters. The collected frames were then processed for integration by the software SAINT,[39] and a multiscan absorption correction was applied with SADABS.[40] Using the program suite WinGX,[41] the structure was solved by Patterson interpretation and phase expansion using SHELXL97,[42] and refined with full-matrix least-squares on F^2 using SHELXL97. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were geometrically placed and refined using a riding model except for H(1), which was located in the Fourier Maps and refined isotropically. Crystallographic data and structure refinement details for ***cis*-5** are collected in Table 4.

Table 4. Crystal Data for Compound *cis*-5

	cis-5
mol formula	$C_{21}H_{27}Fe_2O_4P$
mol wt	486.1
cryst syst	orthorhombic
space group	*Pbca*
radiation (λ, Å)	0.71073
a, Å	15.293(4)
b, Å	11.795(3)
c, Å	23.293(6)
α, deg	90
β, deg	90
γ, deg	90
V, Å^3	4202(2)
Z	8
calcd density, g cm^{-3}	1.537
absorp coeff, mm^{-1}	1.481
temperature, K	120(2)
θ range (deg)	1.75−26.37
index ranges (h, k, l)	0, 19; 0, 14; 0, 29
no. of reflns collected	35866
no. of indep reflns (R_{int})	4290 (0.0699)
reflns with $I > 2\sigma(I)$	3062
R indexes [data with $I > 2\sigma(I)$]^a	$R_1 = 0.0368$; $wR_2 = 0.0761^b$
R indexes (all data)^a	$R_1 = 0.073$; $wR_2 = 0.0943^b$
GOF	1.121
no. of restraints/params	0/258
$\Delta\rho$(max., min.), e Å^{-3}	0.497, −0.44

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $wR = [\sum w(F_o^2 - F_c^2)^2/\sum|F_o|^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. [b] $a = 0.0276$, $b = 10.7231$.

DFT Analysis of Phosphinidene Complexes. All computations described in this work were carried out with the GAUSSIAN03 package,[43] in which the hybrid method B3LYP was applied with the Becke three parameters exchange functional[44] and the Lee−Yang−Parr correlation functional.[45] Effective core potentials (ECP) and their associated double-ζ LANL2DZ basis set were used for the iron centers.[46] The light elements (O, C, P, and H) were described with 6-31G* basis.[47] Geometry optimizations were performed under no symmetry restrictions, using initial coordinates derived from X-ray data of the same or comparable complexes, and frequency analyses were performed to ensure that a minimum structure with no imaginary frequencies was achieved. For interpretation purposes, Mulliken charges were computed as usual,[48] and natural population analysis (NPA) charges were derived from the natural bond order (NBO) analysis of the data.[49] Molecular orbitals and vibrational modes were visualized using the Molekel program.[50] The topological analysis of ρ was carried out with the *Xaim* routine.[51] Solvent effects (toluene, ε = 2.3741) were modeled using the polarized-continuum-model (PCM),[52] and the B3LYP optimized structures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures and tables of data from the DFT calculations (pdf), and a CIF file giving the crystallographic data for the structural analysis of compound ***cis*-5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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