Silyl Migration from Iron to Platinum in dppm-Bridged Bimetallic Complexes[†]

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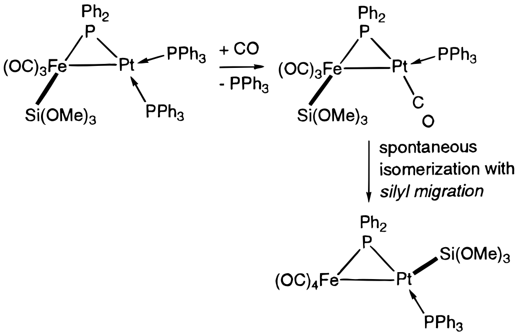
*Summary: The contrasting behavior of the trialkoxysilyl-substituted iron metalate [Et_3NH][Fe{Si(OMe)$_3$}(CO)$_3$(η^1-dppm)] toward [MCl_2(η^2-dppm)] (M = Pd, Pt) has been investigated. It reacts with [$PdCl_2$(η^2-dppm)] to give the known heterodinuclear complex [Fe(CO)$_3${μ-Si(OMe)$_2$(OMe)}(μ-dppm)PdCl] (**2**), although this requires displacement of the Pd-bound chelating dppm ligand. In contrast, reaction with [$PtCl_2$(η^2-dppm)] afforded [Fe(CO)$_3$(μ-dppm)$_2$Pt{Si(OMe)$_3$}Cl] (**3**), which results from silyl migration from Fe to Pt. This intermetallic silyl migration reaction has very few precedents and is observed here for the first time in bimetallic dppm complexes. Loss of the silyl ligand of **3** occurs slowly in CH_2Cl_2 and leads to [FeCl(CO)(μ-CO)(μ-dppm)$_2$PtCl] (**4**). This A-frame complex is protonated by HBF_4 to give [FeCl(CO)$_2$(μ-dppm)$_2$Pt(H)Cl][BF_4] (**5**).*

Introduction

Group transfer reactions between organometallics represent key steps in a number of metal-catalyzed organic reactions. Intramolecular versions of such reactions provide unique opportunities for studying how adjacent metals affect the course of a reaction promoted by a di- or multinuclear complex. Thus for example, transfer reactions of alkyl ligands from one metal center to another in bimetallic systems have been studied by several groups.[1] These reactions may involve the existence of intermediates or transition states with bridging alkyl groups possessing in some cases additional agostic C−H interactions with a metal center.[2]

We observed recently the first examples of intramolecular CO-induced transfer reactions of *silyl groups* in phosphido-bridged bimetallic Fe−Pt systems of the type [(OC)$_3$(R_3Si)Fe(μ-PPh$_2$)Pt(PPh$_3$)$_2$] or [(OC)$_3$(R_3Si)Fe(μ-PR$_2$)Pt(1,5-COD)].[3] The silyl group originally coordinated to iron migrated onto platinum (eq 1). In the case of the trimethoxysilyl ligand, the structure of the rearranged, isomeric product [(OC)$_4$Fe(μ-PPh$_2$)Pt{Si(OMe)$_3$}(PPh$_3$)] has been established by an X-ray diffraction study.[3a] The enhanced reactivity of the 1,5-COD complexes [(OC)$_3$(R_3Si)Fe(μ-PR$_2$)Pt(1,5-COD)] allowed the silyl transfer of a Fe-bound SiR_3 group to the adjacent platinum center to be promoted even with isonitriles CNR under mild conditions.[4]



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Subsequent NMR studies by Akita et al. and Girolami et al. on dinuclear $SiMe_3$-substituted Ru−Ru complexes have concluded that a silyl ligand could reversibly flip from one metal center to another via a μ_2-SiR_3 intermediate.[5] This unusual bridging bonding mode for a −SiR_3 group, which we have also postulated to account for our silyl transfer reaction, has already been structurally established in a borane[6] and, more recently, in the polynuclear copper complex[7] [Li(THF)$_4$][Cu$_5$Cl$_4${Si(SiMe$_3$)$_3$}$_2$] and in the dirhodium complex [P(^{i}Pr)$_3$Rh(H)(μ-Cl)(μ-SiAr$_2$)(μ-SiAr$_3$)Rh(H)P(^{i}Pr)$_3$].[8]

Our previous results on metal to metal silyl migration were all concerned with phosphido-bridged bimetallic

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[†] Dedicated to Professor H. Werner on the occasion of his 65th birthday (April 19, 1999), with our warmest congratulations and best wishes.

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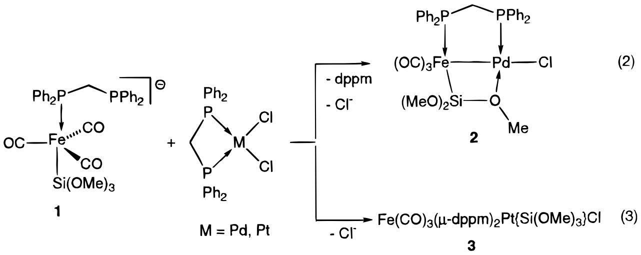
complexes, and we report now on the first example of an irreversible migration of a $Si(OMe)_3$ group from iron to platinum in a dppm-bridged (dppm = $Ph_2PCH_2PPh_2$) bimetallic system.

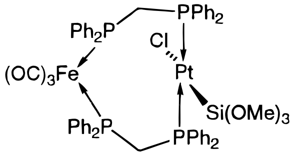
Results and Discussion

A route often used to access metal−metal bonded bimetallic complexes [$L_nM-M'L_n$] or larger cluster compounds is the reaction of a nucleophilic metalate [L_nM]$^-$ with a transition metal halide complex [$XM'L_n$]. We have applied it to the synthesis of dppm-bridged heterobimetallics or trimetallic clusters by reacting the dppm-chelated complexes [$MCl_2(\eta^2$-dppm)] (M = Pd, Pt) with various metalates such as [$CpMo(CO)_3$]$^-$, [$Co(CO)_4$]$^-$, or [$Mn(CO)_5$]$^-$.[9a,b,d] In the case of Na_2[$Fe(CO)_4$], this led to the triangulo clusters [$FePt_2(\mu$-dppm$)_2(CO)_4$] and [$Fe_2Pd(\mu$-dppm$)_2(CO)_6$].[9a,c]

As part of our studies on silyl-substituted heterobimetallics, a promising class of molecules,[10] we investigated also the reactivity of the $Si(OR)_3$-functionalized metalate[11a] [$HNEt_3$][$Fe\{Si(OMe)_3\}(CO)_3(\eta^1$-dppm)] (**1**) toward [$MCl_2(\eta^2$-dppm)] (M = Pd, Pt) with the hope of using the dangling phosphorus atom of the dppm ligand in the assembling process. Upon addition of an equimolar amount of **1** to a CH_2Cl_2 solution of [$PdCl_2(\eta^2$-dppm)] and stirring at ambient temperature, the reaction mixture became deep red. After workup we isolated the heterodinuclear complex [$Fe(CO)_3\{\mu$-$Si(OMe)_2(OMe)\}(\mu$-dppm)PdCl] (**2**). This complex has been previously prepared by reaction of K[$Fe\{Si(OMe)_3\}(CO)_3(\eta^1$-dppm)] with [$PdCl_2(NCPh)_2$] and has been structurally characterized.[11b] It is rather surprising that the tendency to form a four-membered Fe−Si−O−Pd cycle with a dative Si−O→Pd interaction leads to extrusion of the Pd-bound *chelating* dppm ligand (eq 2).



Unexpectedly, the reaction took a more complicated course when **1** was reacted with [$PtCl_2(\eta^2$-dppm)] in CH_2Cl_2 under similar reaction conditions (eq 3). After stirring for 19 h at ambient temperature and workup, the new rearranged dinuclear complex [$(OC)_3Fe(\mu$-dppm$)_2Pt\{Si(OMe)_3\}Cl$] (**3**) was isolated in high yields as an orange-red solid, which can be handled under air for several hours without any significant decomposition. The compound is soluble in CH_2Cl_2 or $CHCl_3$, but almost insoluble in Et_2O or hexane. Our structural proposal for this heterobimetallic complex with a trigonal bipyramidal Fe(0) center possessing a *cis*-arrangement of the phosphorous ligands and a square-planar Pt(II) center having a platinum-bound $Si(OMe)_3$ ligand, and a *trans*-arrangement of the dppm−phosphorous atoms depicted below is based on the combined IR and NMR data. To achieve the usual 18-electron count on iron and 16-electron count for the Pt(II) center with d^8 configuration, the presence of an additional metal−metal bond is not required for **3**. The ligand arrangement around the platinum center of **3** corresponds therefore to that reported for a range of mononuclear Pt(II) complexes of the type *trans*-[$PtCl(SiR_3)(PR_3)_2$].[12] Considering a possible rotation of the platinum square plane about an axis passing through the Fe and Pt atoms, the degree of twisting of the dppm ligands cannot be stated in the absence of a crystal structure. Such an oscillation may even occur in solution. There are precedents in the literature for bis-dppm dinuclear complexes in which the phosphorus atoms are far from being coplanar or pairwise *trans* oriented.[9b,13] A driving force for this ligand rearrangement may be the higher stability of a Pt−Si bond compared to a Fe−Si bond. Note however that we have prepared several stable silyl-substituted Fe−Pt complexes bridged by a single dppm ligand, which showed no tendency for silyl migration from Fe to Pt.[10b]



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Spectroscopic Studies. The presence of a platinum-bound silyl group was evidenced in particular from the ^{29}Si INEPT spectrum shown in Figure 1, which displays a broadened singlet centered at δ −46.7 (vs TMS), which is strongly coupled to the ^{195}Pt-nucleus with a ^1J(Pt−Si) coupling of 1821 Hz. A similar ^1J(Si−Pt) coupling of 2117 Hz has been measured in the rearranged phosphido complex [$(OC)_4Fe(\mu$-$PPh_2)Pt\{Si(OMe)_3\}(CO)$] ($\delta$ = −26.8), whereas a ^2J(Si−Pt) coupling of 49 Hz was found in the precursor complex [$(OC)_3\{(MeO)_3Si\}Fe(\mu$-$PPh_2)Pt(1,5$-COD)] ($\delta$ = 7.3), which contains an iron−silicon bond.[10b]

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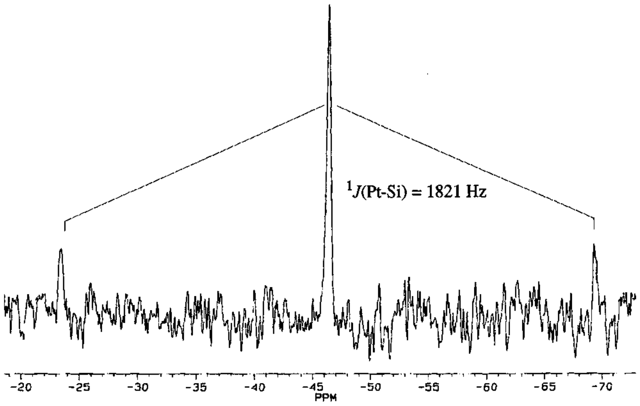
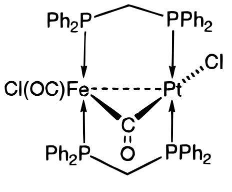


Figure 1. ^{29}Si INEPT spectrum of complex **3** in $CDCl_3$ at room temperature.

Further proof for our structural proposal is provided by the $^{13}C\{^1H\}$ NMR spectrum of **3**, which exhibits a singlet for the Pt-bound $Si(OMe)_3$ ligand at δ 49.6, which is flanked by platinum satellites due to a ^3J(Pt−C) coupling of 16 Hz. The observation of two distinct triplet resonances for the carbonyl ligands at δ 215.1 (^2J(P−C) = 22 Hz) and 208.3 (^2J(P−C) = 35 Hz) in a 2:1 ratio rules out a *trans*-arrangement of the two phosphorous nuclei on iron, as known for numerous mononuclear trigonal-bipyramidal complexes of the type *trans*-[Fe(CO)$_3$(PR$_3$)$_2$]. In this case only *one* ^{13}C carbonyl resonance should be expected owing to the equivalence of the three iron carbonyls. The $^{31}P\{^1H\}$ NMR spectrum displays a AA′XX′ type pattern showing a pseudo-triplet for the Fe-bound phosphorus at δ 63.6 with N = 72 Hz [$N = |^2J(P_AP_X) + {}^4J(P_{A'}P_{X'})|$] (no additional ^{2+3}J(Pt−P) coupling was found, consistent with the absence of a metal−metal bond) and a second triplet at δ 21.6. The latter is flanked with platinum satellites (^1J(Pt−P) = 2910 Hz). As expected, the same ^1J(Pt−P) coupling of 2910 Hz is also observed in the ^{195}Pt NMR spectrum of **3**, where a triplet is found at δ −3158 due to the equivalence of the two phosphorus nuclei ligated on platinum. The broad ^{1}H NMR signal observed for the PCH_2P protons suggests a dynamic behavior of the molecule. The IR spectrum (in KBr) displays three carbonyl stretches at 1982 (m), 1921 (s), and 1884 (s) cm^{-1} ruling out any (semi)bridging interactions of the carbonyl ligands. This finding again supports a *cisoid*-arrangement of the phosphorus atoms bound to iron comparable to that of the chelate complexes [Fe(CO)$_3$-{Ph$_2$P(CH$_2$)$_n$PPh$_2$}] (n = 1−5).[14] In contrast, complexes of the type *trans*-[Fe(CO)$_3$(PR$_3$)$_2$] exhibit in general a very weak A_1 stretch and a very intense E-mode vibration in the ν(CO) region. For instance, a very intense absorption is observed for *trans*-[Fe(CO)$_3$(PPh$_3$)-(η^1-dppm)] at 1875 cm^{-1}.[11c] A sharp vibration at 2839 cm^{-1} diagnostic for a ν(C−H) vibration of a $Si(OMe)_3$ group and a ν(Pt−Cl) stretch at 274 cm^{-1} confirmed also the presence of a silyl moiety and of a covalent platinum−halide bond.

Cleavage of the Pt−Si Bond. Upon attempts to purify the product by crystallization from CH_2Cl_2 (without exclusion of day light), the orange solution became progressively red. After layering with hexane, air-stable deep red crystals were formed in 27% isolated yield. This compound was characterized by elemental analysis, IR spectroscopy, and ^{31}P and ^{195}Pt NMR techniques as the A-frame type complex [(OC)(Cl)Fe(μ-CO)(μ-dppm)$_2$PtCl]-(**4**), which contains a carbonyl bridge.



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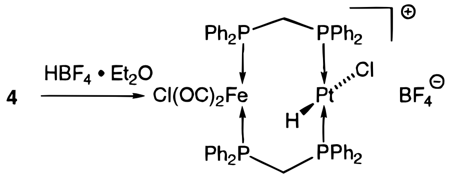
We believe that the loss of the silyl and carbonyl ligands is caused by radicals and/or traces of HCl stemming from the dichloromethane used as solvent. Analogous palladium complexes [(OC)$_2$(X)Fe(μ-dppm)$_2$-PdX](X = Cl, Br, I) containing a semibridging carbonyl ligand have been prepared by Shaw in very low yields.[15a] For example the iodo derivative has been synthesized by reaction of the metallophosphine [FeI$_2$(CO)(η^2-dppm)-(η^1-dppm)] with [Pd(dba)$_2$] (dba = dibenzylideneacetone). According to the authors, an extension of their method to the preparation of iron−platinum bimetallics was unsuccessful.

On the basis of the IR data for [(OC)$_2$(X)Fe(μ-dppm)$_2$PdX] Shaw concluded that in these iron−palladium complexes one carbonyl ligand could be *semibridging*. For instance, two ν(CO) vibrations 1912 and 1824 cm^{-1} have been observed for the chloro-derivative [(OC)$_2$(Cl)Fe(μ-dppm)$_2$PdCl].[15a] In the IR spectrum of **4** a strong terminal ν(CO) vibration is found at 1895 cm^{-1} and a second vibration of medium intensity at 1764 cm^{-1}. We assign the latter absorption to a *bridging* carbonyl. An almost identical value (1760 cm^{-1}) has been reported for the structurally characterized complex [(OC)$_3$Fe(μ-CO)(μ-dppm)Pt(PPh$_3$)], which contains a symmetrically bridging carbonyl ligand.[15b] The $^{195}Pt\{^1H\}$ NMR spectrum consists of a triplet of triplets centered at δ − 2771 with a ^1J(Pt−P) coupling of 3066 Hz and a ^3J(Pt−P) coupling of 116 Hz. The large magnitude of this latter coupling, which is absent in the spectrum of the precursor **3**, may be indicative of the presence of a (weak) interaction between the two metal centers. These couplings are also found in the AA′MM′X (A, M = ^{31}P, X = ^{195}Pt) type $^{31}P\{^1H\}$ NMR spectrum, where two multiplets are observed at δ 56.0 and 22.2, the latter resonance being assigned to the phosphorus nuclei on platinum.

Protonation of 4. In an NMR tube experiment, the electron-rich complex **4** was instantaneously protonated upon addition of excess $HBF_4 \cdot Et_2O$ to a CD_2Cl_2 solution, yielding the cationic hydride complex [(OC)$_2$(Cl)Fe(μ-dppm)$_2$Pt(H)Cl][BF$_4$] (**5**) (eq 4). The presence of a terminal hydride ligand was inferred from both the



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chemical shift value of δ −17.0 and the magnitude of the ^1J(Pt−H) coupling (860 Hz) in the ^{1}H NMR spectrum, which compare with those found in *trans*-[PtCl(PPh$_3$)$_2$] ($\delta = -16.2$, ^1J(Pt−H) = 1206 Hz), [(OC)$_4$Fe(μ-dppm)Pt(H)(PPh$_3$)][BF$_4$] ($\delta = -5.53$, ^1J(Pt−H) = 713 Hz),[15b] and in other dppm-bridged dinuclear complexes.[15c,d] Protonation of [(OC)$_2$(Cl)Fe(μ-dppm)$_2$PdCl] occurred with formation of a bridging hydride ligand,[15a] but this seems unlikely for **5**, since in this case a ^1J(Pt−H) coupling would be expected in the range 200−300 Hz.[3b,15b,c,16] The quintet pattern for this hydride resonance originates from accidental equivalence of ^2J(P−H) and ^4J(P−H) couplings.[15c] Finally, the FAB$^+$ mass spectrum (NBA matrix) displays the peak for the molecular ion at *m/e* 1146, of which the experimental distribution pattern is in perfect agreement with the simulation.

In conclusion, we have shown that silyl migration reactions from one metal to another that is chemically different are not limited to the phosphido-bridged bimetallic complexes previously described.[3] This illustrates further that novel and unforseen reactivity patterns of transition metal−silicon bonds may occur in di- and polynuclear complexes, thus extending the well-established chemistry of mononuclear silyl complexes.[10b]

Experimental Section

All reactions were performed in Schlenk tubes under purified nitrogen. Solvents were dried and distilled under nitrogen before use: toluene and hexane, over sodium and dichloromethane over P$_4$O$_{10}$. Nitrogen was passed through BASF R3-11 catalyst and molecular sieve columns to remove residual oxygen or water. The ^{1}H, ^{31}P{^{1}H}, ^{29}Si INEPT, and ^{13}C{^{1}H} NMR spectra were recorded at 200.13, 81.01, 39.76, and 50.32 MHz, respectively, on a Bruker ACP 200 or Bruker WP 200 SY instrument. Phosphorus chemical shifts were referenced to 85% H$_3$PO$_4$ in H$_2$O with downfield shifts reported as positive. ^{195}Pt chemical shifts were measured on a Bruker ACP 200 instrument (42.95 MHz) and externally referenced to K$_2$PtCl$_4$ in water with downfield chemical shifts reported as positive. The presence and amount of CH$_2$Cl$_2$ in **4** have been determined from the ^{1}H NMR spectrum. The reactions were generally monitored by IR spectroscopy in the ν(CO) region. [MCl$_2$(η^2-dppm)] was prepared as described in the literature.[17]

Preparation of [Fe(CO)$_3${μ-Si(OMe)$_2$(OMe)}(μ-dppm)PdCl] (2). To a stirred solution of **1** (prepared in situ by addition of 1 mL of NEt$_3$ to 0.645 g of the hydride complex [HFe{Si(OMe)$_3$}(CO)$_3$(η^1-dppm)]) in CH$_2$Cl$_2$ (20 mL) was added at −20 °C [PdCl$_2$(η^2-dppm)] (0.562 g, 1 mmol). Upon slowly warming to room temperature, the mixture turned dark red. The solution was filtered after 30 min, and the solvent was concentrated under reduced pressure to ca. 10 mL. Addition of hexane (40 mL) caused precipitation of a red solid, which was filtered and dried under vacuum. IR and ^{31}P NMR data revealed the presence of **2** as the sole metal complex.[11b] Free dppm and minor amounts of Ph$_2$PCH$_2$P(O)Ph$_2$ and Ph$_2$P(O)CH$_2$P(O)Ph$_2$ were found in the filtrate.

Preparation of [Fe(CO)$_3$(μ-dppm)$_2$Pt{Si(OMe)$_3$}Cl] (3). To a stirred solution of **1** (prepared in situ by addition of 1 mL of NEt$_3$ to 0.645 g of the hydride complex [HFe{Si(OMe)$_3$}(CO)$_3$(η^1-dppm)]) in CH$_2$Cl$_2$ (30 mL) was added [PtCl$_2$(η^2-dppm)] (0.651 g, 1.0 mmol). After the mixture was stirred for 19 h at room temperature, the volume of the solution was reduced to ca. 15 mL under reduced pressure and the precipitated ammonium salt was filtered. The solution was further concentrated to 5 mL. Addition of hexane (30−40 mL) caused precipitation of an orange solid, which was filtered and dried in vacuo. Yield: 1.196 g, 95%. IR (KBr): ν = 2833 m cm^{-1} (CH$_{\mathrm{SiOMe}}$); 1982 m, 1921 s, 1884 s cm^{-1} (CO). FIR (polyethylene): ν = 274 cm^{-1} (PtCl). ^{1}H NMR (CD$_2$Cl$_2$): δ = 2.50 (s, 9 H, Si(OMe)$_3$), 4.10 (m, not resolved, vbr, 4 H, PCH$_2$P), 7.00−8.11 (m, 40 H aromatic). ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 44.0 (m, br, not resolved, 2 C, PCP), 49.6 (s, 3 C, ^3J(C,Pt) = 16 Hz, Si(OMe)$_3$), 208.3 (t, 1 C, ^2J(C,P) = 35 Hz, Fe(CO)), 215.1 (t, 2 C, ^2J(C,P) = 22 Hz, Fe(CO)$_2$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 21.6 (virt. t, P(Pt), *N* = 72 Hz, ^1J(P,Pt) = 2910 Hz), 63.6 (virt. t, P(Fe), *N* = 72 Hz). ^{29}Si{^{1}H} INEPT NMR (CDCl$_3$): δ = −46.7 (s, ^1J(Si,Pt) = 1821 Hz). ^{195}Pt{^{1}H} δ = −3158 (t, ^1J(Pt,P) = 2910 Hz). C$_{56}$H$_{53}$ClFeO$_6$P$_4$PtSi (1260.40) Calcd: C, 53.37; H, 4.24. Found: C, 53.64; H, 4.47.

Preparation of [FeCl(CO)(μ-CO)(μ-dppm)$_2$PtCl] (4). An orange-yellow dichloromethane solution of **3** (0.630 g, 0.5 mmol) was stirred for three days and exposed to sunlight. During this period the solution became more and more red. After reducing the volume to ca. 10 mL, the solution was layered with hexane. On the wall of the Schlenk flask red crystals of **4** were formed, which were separated after two days from a insoluble precipitate. Yield: 0.166 g, 27%. IR (CH$_2$Cl$_2$): ν = 1895 s, 1764 m cm^{-1} (CO). ^{1}H NMR (CD$_2$Cl$_2$): δ = 3.85 (m, 2 H, PCH$_2$P), 4.40 (m, 2 H, PCH$_2$P), 7.05−7.89 (m, 40 H, phenyl). ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 56.0 (m, P(Fe), *N* = 94, ^3J(Pt−P) = 116 Hz), 22.2 (m, *N* = 94 Hz, P(Pt), ^1J(P−Pt) = 3066 Hz). ^{195}Pt{^{1}H}: δ = −2771 (tt, ^1J(Pt−P) = 3066, ^3J(Pt−P) = 116 Hz). C$_{52}$H$_{44}$Cl$_2$FeO$_2$P$_4$Pt·CH$_2$Cl$_2$ (1231.58) Calcd: C, 51.69; H, 3.76; Cl, 11.51; Fe, 4.53; Pt, 15.84. Found: C, 51.43; H, 3.67; Cl, 11.09; Fe, 4.32; Pt, 15.69.

Preparation of [FeCl(CO)$_2$(μ-dppm)$_2$Pt(H)Cl] (5). A NMR tube containing a solution of **4** (0.037 g, 0.03 mmol) in CD$_2$Cl$_2$ was cooled to 273 K, and then HBF$_4$·Et$_2$O was added in excess. The solution changed immediately from dark red to yellow-orange. After recording of the NMR spectrum the solvent was removed and the residue was dried in vacuo. IR (CH$_2$Cl$_2$): ν = 2035 ms, 1965 s cm^{-1} (CO). ^{1}H NMR: δ = −16.99 (q, 1 H, ^2J(P,H) ≈ ^4J(P,H) = 11 Hz, ^1J(Pt,H) = 860 Hz, hydride). ^{31}P{^{1}H} NMR: δ = 65.0 (virt. t, P(Fe), *N* = 95 Hz, ^4J(Pt,P) = 86 Hz), 22.5 (virt. t, *N* = 95 Hz, P(Pt), ^1J(P,Pt) = 2524 Hz). MS (FAB$^+$): *m/z* 1146 (M$^+$).

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