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MeLi Reactions with the Electrophile System of (η^5-C_5H_5)Fe(CO)$_2$I/P(OMe)$_3$: The Roles of MeLi as Reductant, Nucleophile, and Base

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The three roles of MeLi—nucleophile, base and reductant—could be revealed by the electrophile system of (η^5-C_5H_5)Fe(CO)$_2$I (**1**) and P(OMe)$_3$. The addition of MeLi dropwise without delay to the 1:1 mixture results in (η^4-*exo*-MeC_5H_5)Fe(CO)$_2$P(OMe)$_3$ (**3**), where MeLi is a reductant at the first stage and then a nucleophile at the second stage. On the other hand, the addition of a catalytic amount of MeLi to the mixture of **1** and excess P(OMe)$_3$, followed by the MeLi/MeI sequence after a delay time, results in the formation of [η^5-C_5H_4-{P(O)(OMe)$_2$}]-Fe(CO){P(OMe)$_3$}Me (**7**), where MeLi is a reductant at the initial stage and a base at the latter stage.

Introduction

A lithiated reagent serves as a nucleophile and a base.[1] Occasionally, the lithiated reagent works as a reductant.[2] In this paper, we report these various roles of MeLi[3] in its reaction with a mixture of (η^5-C_5H_5)Fe(CO)$_2$I (**1**) and P(OMe)$_3$. Depending upon the molar ratio of **1**/P(OMe)$_3$ and the delay time, MeLi acts as a reductant and then a nucleophile or as a reductant and then a base. In the latter case, for the first time electron-transfer chain catalysis (ETC)[4] of two levels has been observed on the P(OMe)$_3$ substitution reactions, one for the iodide and one for the CO ligand in sequence.

Results and Discussion

The addition of MeLi dropwise to a 1:1 mixture of **1**/P(OMe)$_3$ at −78 °C gives in 45% isolated yields the ring-methylation product (η^4-*exo*-MeC_5H_5)Fe(CO)$_2$P(OMe)$_3$ (**3**), analogous to the reaction of MeLi with a 1:1 mixture of **1**/PR_3 at −78 °C (where PR_3 is a phosphine).[5] This η^5-C_5H_5 ring methylation changes the bonding of the ring to metal from η^5-C_5H_5 to η^4-*exo*-MeC_5H_5 and the oxidation state of Fe from +2 to 0; i.e., the aromaticity of the ring is lost. The facile formation of **3** from **1**, P(OMe)$_3$, and MeLi is the sum of two sequential reactions, as shown in Scheme 1. The first reaction is an ETC initiated by the initial, small amount of MeLi, bringing **1** and P(OMe)$_3$ together to form [(η^5-C_5H_5)Fe(CO)$_2$P(OMe)$_3^+$][I^-] (**2·I**) (vide infra). Such an ETC pathway initiated by a strong reductant has been established for the substitution reaction of (η^5-C_5H_5)-Fe(CO)$_2$X, with PPh$_3$ replacing halide X^-.[6] The second reaction is the nucleophilic addition of stoichiometric MeLi to the η^5-C_5H_5 ring of **2** from an *exo* side to Fe. The *exo* addition has been established for the similar complex (η^4-*exo*-MeC_5H_5)Fe(CO)$_2$PMePh$_2$[7] and (η^4-*exo*-MeC_5H_5)Fe(CO)$_2$PPh$_3$[8] by single-crystal X-ray diffraction.

As the 1:1 mixture of **1** and P(OMe)$_3$ gives the same IR ν_{CO} features as **1** alone, compound **1** does not interact with P(OMe)$_3$ at −78 °C. Only after the addition of a few drops of MeLi does the mixture reveal a rapid conversion to **2**, which can be isolated as a PF_6^- salt (**2·PF$_6$**) in 68% isolated yield if immediately anion-exchanged in ca. 2 min (or in ca. 5 min for the (η^5-C_5H_5)Fe(CO)$_2$Cl reaction) after introduction of a few drops of MeLi to the mixture. The delay time between the introduction of initial catalytic MeLi to the mixture and the addition of stoichiometric MeLi is an important factor, because the rapidly formed **2·I** will proceed with

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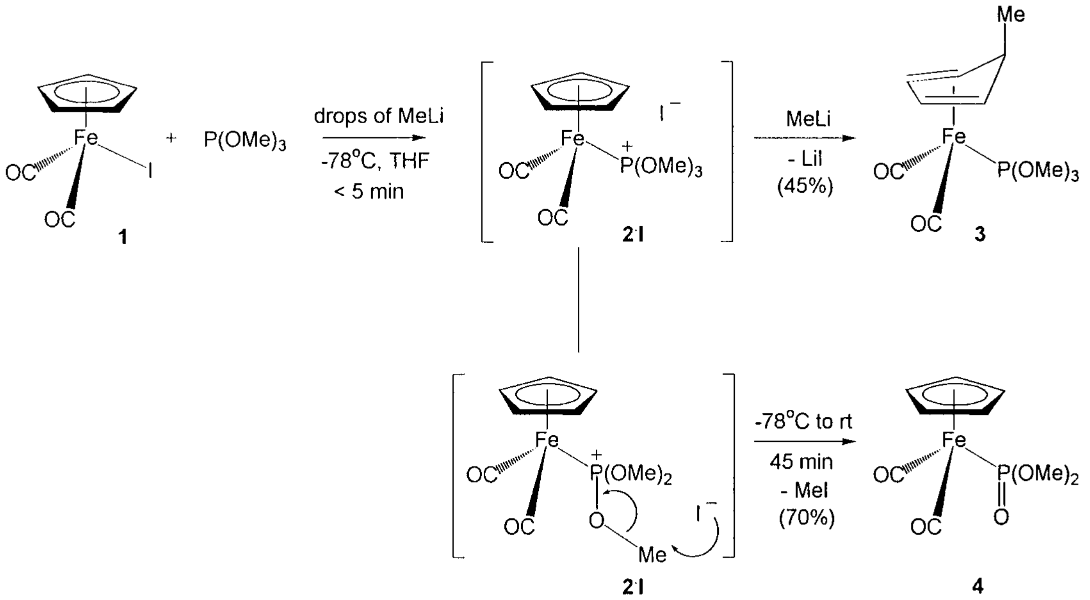
10.1021/om981001r CCC: $18.00

Scheme 1



the well-known Arbuzov-like reaction[9] on standing for 45 min and produces in 70% yields the phosphonate complex $(\eta^5\text{-}C_5H_5)Fe(CO)_2P(O)(OMe)_2$ (**4**) when the solution is warmed from −78 °C to room temperature, also presented in Scheme 1. In the literature, the preparation of **4** from $(\eta^5\text{-}C_5H_5)Fe(CO)_2X$ (X = Cl, I) and $P(OMe)_3$ requires a long stirring at reflux or at room temperature with a large quantity of byproducts $(\eta^5\text{-}C_5H_5)Fe(CO)\{P(OMe)_3\}\{P(O)(OMe)_2\}$ (**6**) and $(\eta^5\text{-}C_5H_5)Fe(CO)\{P(OMe)_3\}X$.[10] Compound **4** could also be prepared from the treatment of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2\{P(NC_4H_8)(OMe)_2\}^+][Cl^-]$ with KOH.[11] Thus, the procedure employing a catalytic amount of MeLi improves the method of preparation in that the reaction is at a low temperature, requires a short time, and gives a high yield. MeLi could not add at the $\eta^5\text{-}C_5H_5$ ring of **4** but could seemingly add at the CO ligand. On the basis of ν_{CO} 1922, 1560 cm^{-1} in the IR spectrum and δ 160.8 in ^{31}P NMR detected from the mixture, a $(\eta^5\text{-}C_5H_5)Fe(CO)C(O)Me\{P(O)(OMe)_2\}^-$ anion has been assumed, which is resistant to our attempted isolation, however.[12] Employing LDA, which is just a base and not a nucleophile at all, Nakazawa observed a $-P(O)(OEt)_2$ migration from Fe to the $\eta^5\text{-}C_5H_5$ ring in $(\eta^5\text{-}C_5H_5)Fe(CO)_2P(O)(OEt)_2$.[13] More studies with the metastable solution of the $(\eta^5\text{-}C_5H_5)Fe(CO)C(O)Me\{P(O)(OMe)_2\}^-$ anion are now underway.

The addition of 1 equiv of MeLi dropwise to a mixture of **1** and *excess* $P(OMe)_3$ at −78 °C produces the same **3** as the addition to a 1:1 mixture of **1**/$P(OMe)_3$ at −78 °C. However, when the mixture of **1** and *excess* $P(OMe)_3$ at −78 °C is treated with just a few drops of MeLi and then allowed to return to room temperature, the bubbling of CO gas could be observed. After 2 h, the phosphite−phosphonate complex **6** could be isolated in 92% yield (Scheme 2). An intermediate, the $(\eta^5\text{-}C_5H_5)Fe(CO)\{P(OMe)_3\}_2^+$ cation (**5**), could be isolated as a PF_6^- salt (**5·PF$_6$**; 27%, not optimized)[14] whose characterization data are consistent with those reported by Schuman[15] and Coville.[16] The low yield of **5·PF$_6$** here is due to the decomposition of the cationic complex during workup. Cation **5** then proceeds with the Arbuzov-like reaction. It is clear that prior to the Arbuzov-like reaction, there are two levels of ETC reactions: one is the $P(OMe)_3$ substitution for I^-, as shown at the top of Scheme 3, and the other is the $P(OMe)_3$ substitution for CO, as shown at the bottom of Scheme 3. The former ETC is initiated by a few drops of MeLi at −78 °C, and the latter is a continuation, requiring a slightly higher temperature, in addition to the second equivalent of $P(OMe)_3$. Due to trace MeLi, it is believed that an electron transfer occurs from MeLi to **1** to give the 19e $(\eta^5\text{-}C_5H_5)Fe(CO)_2I^{\bullet-}$ radical anion (**1re**), followed by a dissociation of I^- and the formation of the 17e $(\eta^5\text{-}C_5H_5)Fe(CO)_2^{\bullet}$ radical, to which $P(OMe)_3$ is coordinated to give the 19e $(\eta^5\text{-}C_5H_5)Fe(CO)_2P(OMe)_3^{\bullet}$ radical (**2re**), which reduces another molecule of **1** and is itself oxidized to **2** (see Scheme 3, a 17e−19e mechanism). This process goes on in cycles until all the I^- ions are replaced by $P(OMe)_3$. The driving force is believed to be the electronegative iodine taking away the negative charge to dissociate from **1re**. When the temperature is increased from −78 °C to between −60 and −40 °C, the catalytic electron allows a rapid ligand exchange of free $P(OMe)_3$ with the ligands in **2**. The $P(OMe)_3$ substitution for $P(OMe)_3$ may be kinetically more favored but gives products that are the same as the reactants. The $P(OMe)_3$ substitution for CO may be kinetically less favored, but the release of CO to the gaseous phase serves as a driving force for the second level of ETC, in

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[14] $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ works better than **1** in producing **2**: the chloride is a weaker nucleophile than the iodide.

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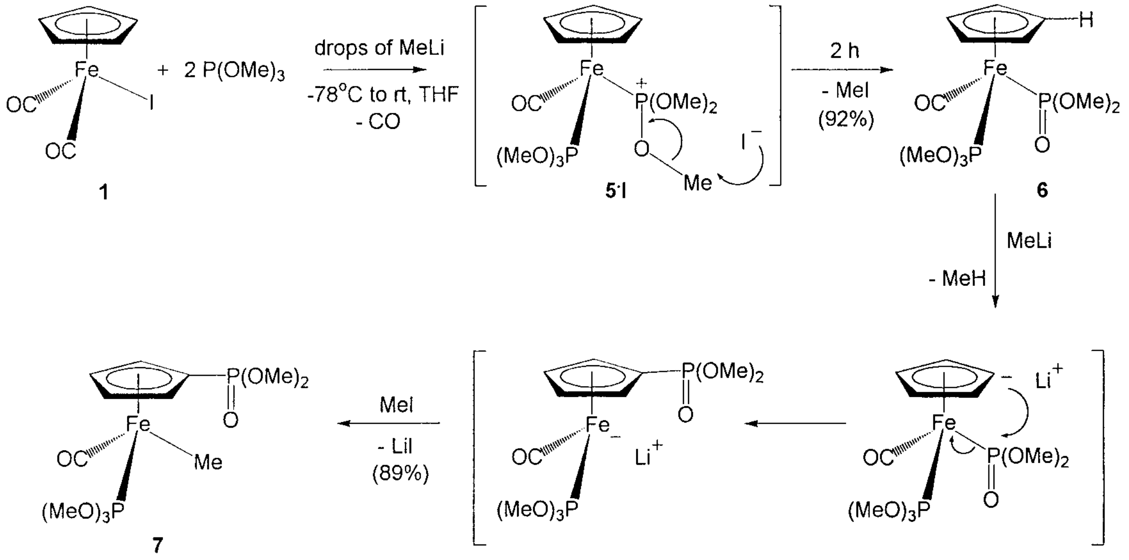
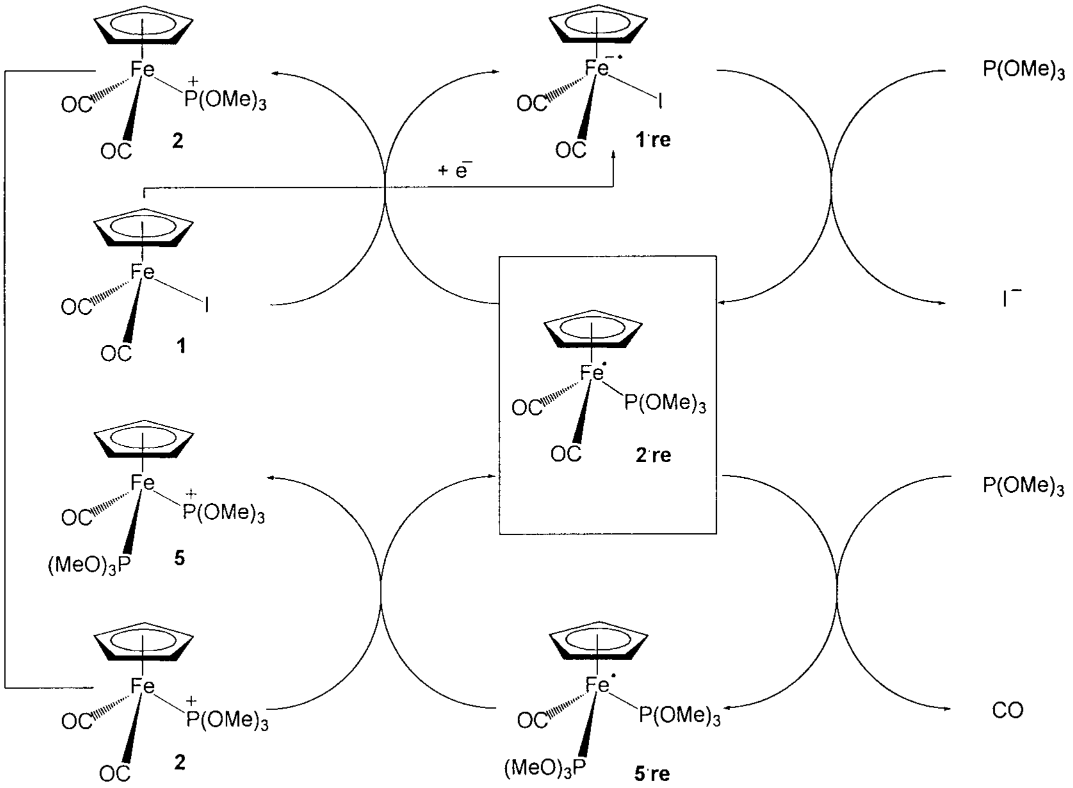
Scheme 2



Scheme 3



which the formed $(\eta^5\text{-}C_5H_5)Fe(CO)\{P(OMe)_3\}_2^{\bullet}$ radical (**5re**) is also better than **2re** as a reducing agent. In the literature, Tyler reported that the excess $P(OEt)_3$ substitution for CO in $(\eta^5\text{-}C_5H_5)Fe(CO)_2\{P(OEt)_3\}^+$ is catalyzed by the chemical reducing agent $(\eta^5\text{-}C_5H_5)_2Co$.[17] The last CO is not activated in the 17e−19e mechanism at room temperature and is rationalized from the IR ν_{CO} stretching frequencies—that of **5** (1999 cm^{-1}) is shifted toward low enough wavenumbers from those of **2** (2072, 2025 cm^{-1}), the former having a much stronger Fe−C(CO) bond.

The Arbuzov-like reaction with **5** to give **6** is limited to just one $P(OMe)_3$ and does not involve a second $P(OMe)_3$, partially because the phosphonium structure which assists the I^- counterattack is much higher in energy for **6**. Attempts to bring about a further Arbuzov-like reaction of **6** in the same sense by using extra NH_4I was unsuccessful in the present case. In the literature, excess iodide had furnished bis- and tris(phosphonate) complexes of a variety of transition-metal moieties.[18] Koelle reported that the Arbuzov-like reaction of $(\eta^5\text{-}C_5Me_5)Ru\{P(OMe)_3\}_3$ proceeds with only one $P(OMe)_3$.[19]

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Also shown in Scheme 2, the **6** reaction with MeLi at −78 °C is the deprotonation and not the methylation of the η^5-C_5H_5 ring; i.e., MeLi works as a base rather than a nucleophile. An intramolecular migration of the $-P(O)(OMe)_2$ group from Fe to the η^5-C_5H_5 ring follows, effectively making the Fe anion instead of the C anion the site for a MeI quench to produce $[\eta^5\text{-}C_5H_4P\{(O)(OMe)_2\}]Fe(CO)\{P(OMe)_3\}Me$ (**7**; 89%). Nakazawa reported the $-P(O)Ph_2$ group migration in $(\eta^5\text{-}C_5H_5)Fe(CO)\{P(OMe)Ph_2\}\{P(O)Ph_2\}$ employing a LDA/MeI sequence.[13]

The difference in MeLi reactions toward **4** and **6** could be rationalized by the Fe back-bonding to CO ligands, as revealed from the IR ν_{CO} stretching frequencies—2040, 1990 cm^{-1} for **4** and 1964 cm^{-1} for **6**. The higher IR ν_{CO} stretching frequencies associated with **4** suggest that there is less back-bonding and hence there is more positive charge on the CO carbon atoms, in favor of receiving MeLi as a nucleophile. Compound **6**, on the other hand, has more back-bonding from Fe and hence has less positive charge on the CO carbon atom, disfavoring the reception of MeLi at the CO site. MeLi works as a base as a consequence. The fact that MeLi attacks one of the CO sites in **4** and the η^5-C_5H_5 ring in **6** could be attributed to a steric affect as well.

Overall **7** could be prepared in one flask, starting from a mixture of **1** and excess $P(OMe)_3$, plus trace MeLi as an initiator at −78 °C. With evolution time, temperature increase, and decrease, and then the MeLi/MeI sequence, the reaction gives **7** in yields comparable to the stepwise operation. The MeI produced at the Arbuzov-like reaction stage could be removed under vacuum for use as a quencher in the end or simply destroyed with extra MeLi during deprotonation in the MeLi/MeI sequence.

In summary, a mixture of **1** and $P(OMe)_3$ detects the three roles of MeLi. The addition of MeLi dropwise without delay to the 1:1 mixture results in **3**, where MeLi is both a reductant and a nucleophile. On the other hand, the addition of a catalytic amount of MeLi to the mixture of **1** and excess $P(OMe)_3$, with a delay time applied before the MeLi/MeI sequence, results in **7**, where MeLi is both a reductant and a base.

Experimental Section

General Considerations. All manipulations were performed under an atmosphere of prepurified nitrogen with standard Schlenk techniques. All solvents were distilled from an appropriate drying agent.[20] Infrared spectra were recorded in CH_2Cl_2 using CaF_2 optics on a Perkin-Elmer 852 spectrophotometer. The ^1H NMR and ^{13}C NMR spectra were obtained on Bruker AC200/AC300 spectrometers, with chemical shifts reported in δ values, downfield positive, relative to the residual solvent resonance of $CDCl_3$ (^1H δ 7.24, ^{13}C δ 77.0). The ^{31}P NMR spectra were obtained on Bruker AC200/AC300 spectrometers using 85% H_3PO_4 as an external standard (δ 0.00). The melting points were determined on a Yanaco MPL melting-point apparatus and are uncorrected. $(\eta^5\text{-}C_5H_5)Fe(CO)_2X$ (X = Cl, I) was prepared according to the literature procedure.[21] Other reagents were obtained from commercial sources and used without further purification.

Synthesis of $(\eta^4\text{-}\textit{exo}\text{-}MeC_5H_5)Fe(CO)_2P(OMe)_3$ (3). Compound **1** (1.519 g, 5.0 mmol) and $P(OMe)_3$ (0.60 mL, 0.621 g, 5.0 mmol) were taken up in dry THF (90 mL), and the solution was chilled to −78 °C. Excess MeLi (5.0 mL, 15% ether solution) in ether (30 mL) maintained at −78 °C was added dropwise to the stirred mixture over a period of 15 min. The stirring was continued at −78 °C for 1 h before the mixture was warmed gradually to room temperature and continuously stirred for another 1 h. The reaction mixture was filtered through a glass frit containing a short column of alumina to obtain a clear yellow solution. The solvent was then removed by rotary evaporation. The resultant oily concentrates were packed on a column of nonactivated alumina by dry packing and then eluted with 10% ethyl acetate in hexane. Only one yellow band separated on the column. The fraction was collected, and after solvent removal, the resultant yellow oil was frozen in liquid nitrogen for 1 h to obtain yellow solids of **3** (0.711 g, 44.9%). Mp: 38−39 °C. IR (CH_2Cl_2): ν_{CO} 1979 vs, 1916 vs cm^{-1}. ^{31}P NMR ($CDCl_3$): δ 189.5. ^1H NMR ($CDCl_3$): δ 5.2 (b, 2H, $-\mathrm{C}H{=}\mathrm{CHCHMe}-$), 3.52 (d, $^3J_{PH}$ = 12 Hz, 9H, $\mathrm{O}Me$), 2.80−2.79 (b, 3H, $-\mathrm{CH{=}C}H\mathrm{C}H\mathrm{Me}-$), 0.41 (d, $^4J_{PH}$ = 6 Hz, 3H, Me). ^{13}C NMR ($CDCl_3$): δ 217.5 (d, $^2J_{PC}$ = 21.2 Hz, CO), 81.1 (s, $-C\mathrm{H{=}CHCHMe}-$), 57.7 (b, OMe), 51.3 (s, $-\mathrm{CH{=}CH}C\mathrm{HMe}-$), 51.2 (s, $-\mathrm{CH{=}}C\mathrm{HCHMe}-$), 28.5 (d, $^3J_{PC}$ = 6.6 Hz, Me). MS (FAB): *m/z* 316 (M^+). Anal. Calcd for $C_{11}H_{17}FeO_5P$: C, 41.79; H, 5.43. Found: C, 41.72; H, 5.35.

Synthesis of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2P(OMe)_3{}^+][PF_6{}^-]$ (2·PF$_6$). $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$ (0.50 g, 2.35 mmol) and $P(OMe)_3$ (0.29 g, 2.35 mmol) were dissolved in THF (50 mL) and the solution was maintained at −78 °C. A few drops of MeLi in ether were added to the solution, resulting in a yellow precipitate in 5 min. NH_4PF_6 (0.38 g, 2.35 mmol) was then added to the suspension. After 30 min, the temperature of the mixture was slowly raised to room temperature over ca. 1 h. After filtration, the filtrate was removed in vacuo. The yellow residue was extracted with CH_2Cl_2 (30 mL) and reprecipitated on dilution with hexane to give yellow crystals of **2·PF$_6$** (0.71 g, 68%). IR (CH_2Cl_2): ν_{CO} 2072, 2025 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.76 (s, 5H, Cp), 3.95 (d, $^3J_{PH}$ = 12 Hz, 9H, Me). ^{31}P NMR (acetone-d_6): δ 160.8 (s, $P(OMe)_3$), −145.0 (hep, $^1J_{PF}$ = 706 Hz, PF_6). (lit.[10] IR (CH_2Cl_2) ν_{CO} 2073, 2032 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.64 (d, $^3J_{PH}$ = 1.1 Hz, 5H, Cp)).

Synthesis of $(\eta^5\text{-}C_5H_5)Fe(CO)_2P(O)(OMe)_2$ (4). Compound **1** (0.51 g, 1.7 mmol) was mixed with $P(OMe)_3$ (0.21 g, 1.7 mmol) in THF (30 mL) at −78 °C. A few drops of MeLi in ether were then added to the solution. After about 2 min, a pale yellow precipitate formed that slowly disappeared to finally give a yellow solution when the temperature was raised from −78 °C to room temperature over a period of 45 min. The solvent was removed *in vacuo*. The yellow oily residue was dissolved in minimum amount of CH_2Cl_2 and transferred to a silica gel column made up with CH_2Cl_2. A yellow band, obtained on elution with CH_2Cl_2, was a mixture of **3** and $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$ (70 mg). The second yellow band, collected on elution with 1:1 acetone/MeOH, gave after the solvent removal yellow solids of **4** (0.35 g, 1.2 mmol, 70%). IR (CH_2Cl_2): ν_{CO} 2040, 1990 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.99 (s, 5H, Cp), 3.51 (d, $^3J_{PH}$ = 11.5 Hz, 6H, Me). ^{31}P NMR ($CDCl_3$): δ 111.81. ^{13}C NMR ($CDCl_3$): δ 210.86 (d, $^2J_{PC}$ = 40.5 Hz, CO), 85.74 (Cp), 51.14 (d, $^2J_{PC}$ = 7.9 Hz, Me) (lit.[11] IR (CH_2Cl_2) ν_{CO} 2040, 1990 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.08 (d, $^3J_{PH}$ = 1.8 Hz, 5H, Cp), 3.63 (d, $^3J_{PH}$ = 11.0, 6H, Me); ^{31}P NMR ($CDCl_3$) δ 109.2).

Reaction of 4 with MeLi. Compound **4** (0.30 g, 1.05 mmol) was suspended in THF (30 mL) at −78 °C. MeLi in THF/cumene (1:9) solution (1.2 mL × 1 M) was added dropwise to the mixture. The temperature of the mixture was slowly raised to room temperature for 30 min to give a yellow solution: IR ν_{CO} 1922, 1560 cm^{-1}; ^{31}P NMR δ 160.8. After the solvent was removed in vacuo, an air-sensitive and hygroscopic yellow solid was obtained that was resistant to purification nonetheless.

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Synthesis of [(η^5-C_5H_5)Fe(CO){P(OMe)$_3$}$_2^+$][PF$_6^-$] (5·PF$_6$). (η^5-C_5H_5)Fe(CO)$_2$Cl (0.5 g, 2.35 mmol) and P(OMe)$_3$ (0.7 mL, 5.92 mmol) were dissolved in THF (35 mL) at −78 °C. A few drops of MeLi (1.4 M in ether, ca. 3 drops) were added to the mixture. A yellow precipitate formed in 2 min at −78 °C. The reaction mixture was stirred for another 10 min at −40 °C until the bubbling ceased. Following addition of NH_4PF_6 (0.42 g, 3.33 mmol), the reaction mixture was stirred for another 30 min at room temperature. The volatiles were removed in vacuo to give a yellow solid. After two precipitations from MeOH/H_2O and CH_2Cl_2/hexane, a yellow oil was obtained. Removal of the solvents gave a yellow solid of **5·PF$_6$** (0.35 g, 0.65 mmol, 28%). IR (CH_2Cl_2): ν_{CO} 1999 cm^{-1} (lit.[15,16] IR ν_{CO} 1993 cm^{-1}). ^{1}H NMR (acetone-d_6): δ 5.27 (s, 5H, Cp), 3.84 (d, $^3J_{PH}$ = 11.4 Hz, 18H, OMe) (lit. ^{1}H NMR δ 5.23 (Cp), 3.87 (OMe)). ^{31}P NMR (acetone-d_6): δ 168.5 (s, P(OMe)$_3$), −145 (hep, $^1J_{PF}$ = 706 Hz, PF$_6$) (lit. ^{31}P NMR δ 168.8 (P(OMe)$_3$)).

Synthesis of (η^5-C_5H_5)Fe(CO){P(OMe)$_3$}{P(O)(OMe)$_2$} (6). Compound **1** (0.60 g, 1.97 mmol) and P(OMe)$_3$ (0.6 mL, 5.07 mmol) were dissolved in THF (40 mL) at −78 °C. A few drops of MeLi (1.4 M in ether) were added to the reaction mixture. Initially a yellow precipitate formed that was followed by gas evolving from solution when the reaction temperature was raised from −78 °C to room temperature. The reaction carried on at room temperature for another 2 h until all the precipitate redissolved to give a clear yellow solution. The solvents together with excess P(OMe)$_3$ were then removed in vacuo. The resultant yellow residue was dissolved in acetone (10 mL) and transferred to the top of a silica gel column. The polarity of the eluent was slowly increased from acetone to 30% methanol in acetone. A major yellow band was collected which, after removal of the solvents, gave a yellow oil of **6** (0.70 g, 1.83 mmol; 92%). IR (THF): ν_{CO} 1964 cm^{-1} (lit.[22] IR (KBr disk) ν_{CO} 1960 cm^{-1}). ^{1}H NMR (CDCl$_3$): δ 4.69 (s, 5H, Cp), 3.62 (d, $^3J_{PH}$ = 11.5 Hz, 9H, P(OMe)$_3$), 3.46 (d, $^3J_{PH}$ = 11.1 Hz, 6H, P(O)(OMe)$_2$) (lit. ^{1}H NMR (CDCl$_3$) δ 4.75 (s, 5H, Cp), 3.62 (dd, J_{PH} = 11.7 Hz, 2.0 Hz, 9H, P(OMe)$_3$), 3.46 (d, J_{PH} = 11.2 Hz, 6H, P(O)(OMe)$_2$)). ^{31}P NMR (CDCl$_3$): δ 175.0 (d, $^2J_{PP}$ = 139 Hz, P(OMe)$_3$), 118.0 (d, $^2J_{PP}$ = 139 Hz, PO(OMe)$_2$) (lit. ^{31}P NMR (CH$_2$Cl$_2$) δ 181.8 (d, J_{PP} = 140.3 Hz, P(OMe)$_3$), 124.9 (d, J_{PP} = 140.3 Hz, P(O)(OMe)$_2$)). ^{13}C NMR (CDCl$_3$): δ 216.1 (dd, $^2J_{PC}$ = 41.2 Hz, $^2J_{PC}$ = 44.2 Hz, CO), 83.6 (s, Cp), 52.5 (d, $^2J_{PC}$ = 4.9 Hz, P(OMe)$_3$), 50.0, 49.8 (d × 2, $^2J_{PC}$ = 7.5 Hz, 8.4 Hz, P(O)(OMe)$_2$). FAB MS: *m*/*z* 383 (M + 1)$^+$.

Synthesis of [η^5-C_5H_4{P(O)(OMe)$_2$}]Fe(CO){P(OMe)$_3$}Me (7). Compound **6** (0.70 g, 1.83 mmol) was dissolved in THF (40 mL) at −78 °C. MeLi in THF/cumene (1:9) (1.0 M × 3.5 mL, 3.50 mmol) was added dropwise to the solution, which was maintained at −78 °C for 30 min, at which point the color changed from yellow to orange-red. MeI (0.2 mL, 3.2 mmol) was then added via a syringe to the solution before the temperature was slowly raised from −78 °C to room temperature. The color returned to yellow. Upon removal of the solvents and the volatiles, the yellow residue dissolved in a minimum volume of THF was transferred to the top of a silica gel column made up with a CH_2Cl_2 solution. The polarity of the eluent increased from CH_2Cl_2 to 30% acetone in CH_2Cl_2. A major yellow fraction was collected which, upon removal of solvents, gave a yellow oil of **7** (0.64 g, 1.62 mmol, 89%). IR (CH_2Cl_2): ν_{CO} 1939 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 4.85, 4.80, 4.64, 4.50 (br s × 4, 1H × 4, Cp), 3.77 (d, $^3J_{PH}$ = 5.9 Hz, 6H, PO(OMe)$_2$), 3.56 (d, $^3J_{PH}$ = 11.2 Hz, 9H, P(OMe)$_3$), −0.04 (d, $^3J_{PH}$ = 4.0 Hz, 3H, FeMe). ^{31}P NMR (CDCl$_3$): δ 188.7 (s, P(OMe)$_3$), 23 (br, PO(OMe)$_2$). ^{13}C NMR (CDCl$_3$): δ 219.22 (d, $^2J_{PC}$ = 50 Hz, CO), 95.06, 86.44, 85.34, 82.16 (d × 4, J_{PC} = 14 Hz, Cp), 52.74 (br s, PO(OMe)$_2$), 51.84 (d, $^3J_{PC}$ = 4 Hz, P(OMe)$_3$), −25.17 (d, $^2J_{PC}$ = 33 Hz, FeMe). FAB MS: *m*/*z* 396 (M$^+$). Anal. Calcd for $C_{12}H_{22}FeO_7P_2$: C, 36.4; H, 5.6. Found: C, 36.6; H, 5.7.

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