

**Cyclopentadienyldicarbonyliron Halides as Electrophiles:
Reactions of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ with RLi in the Presence of
PPh₃ To Produce $(\eta^4\text{-}exo\text{-RC}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_3)$ and
Preparation of
 $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{C}(\text{O})\text{Me}](\mu,\eta^1,\eta^1\text{-dppf})[(\eta^4\text{-}exo\text{-MeC}_5\text{H}_5)\text{Fe}(\text{CO})_2]$**

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The reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ (X = Cl, Br, I) with RLi (R = Me, *n*-Bu, *s*-Bu, Ph) in the presence of PPh₃ at low temperature changes the $\eta^5\text{-C}_5\text{H}_5$ bonding mode in $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ to an $\eta^4\text{-RC}_5\text{H}_5$ bonding mode in $(\eta^4\text{-RC}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_3)$. The X-ray results of $(\eta^4\text{-BuC}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_3)$ reveal an *exo*-Bu group at the cyclopentadiene ring. The nucleophilic addition of R⁻ is therefore a direct one, without the Fe mediation. Generated in situ, $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ is believed to be the catalyst in the conversion of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ and PPh₃ to the cationic intermediate $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_3)]^+$ which is much more electrophilic toward R⁻ to produce $(\eta^4\text{-}exo\text{-RC}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_3)$. The conformation of $(\eta^4\text{-}exo\text{-RC}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_3)$ may be described as a pseudo-square-pyramid with one of the CO ligands at the apical position. Refluxing 1:2 $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Me}$, and dppf gives $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\eta^1\text{-dppf})\text{C}(\text{O})\text{Me}$ which, upon treatment of MeLi at low temperature, yields $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{C}(\text{O})\text{Me}](\mu,\eta^1,\eta^1\text{-dppf})[(\eta^4\text{-}exo\text{-MeC}_5\text{H}_5)\text{Fe}(\text{CO})_2]$, a complex with a dppf linking two isomeric, methylated $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$ units, one end in the form of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{C}(\text{O})\text{Me}$ and the other end in the form of $(\eta^4\text{-}exo\text{-MeC}_5\text{H}_5)\text{Fe}(\text{CO})_2$.

Introduction

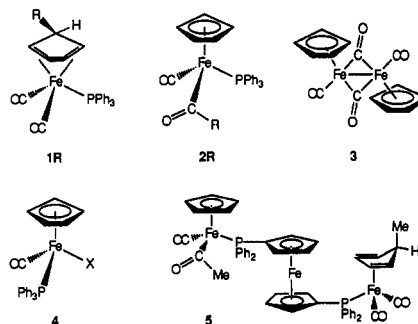
Treatment of carbon nucleophiles such as alkyl anion R⁻ with the half-sandwich compounds $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ (X = Cl, Br, I) produces metal alkyls $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{R}$.¹ The PR'₃ (R'₃ = Ph₃, Ph₂Me, PhMe₂ (OPh)₃, etc.) induced alkyl migration of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{R}$ (R = Me, Et, *i*-Pr, etc.) gives high yields of metal acyls $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PR}'_3)\text{C}(\text{O})\text{R}$, Fe becoming a chiral center.² Being configurationally stable³ and readily resolvable into optically pure forms,⁴ $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{C}(\text{O})\text{CH}_2\text{R}$ has been used extensively in organic synthesis and in mechanistic studies.⁵

In our attempts, the reactions of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ with RLi in the presence of PPh₃ at low temperature have been studied. The reaction pattern found is a facile three-component reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$, PPh₃, and RLi,

which effectively changes the $\eta^5\text{-C}_5\text{H}_5$ bonding mode in $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ to an $\eta^4\text{-RC}_5\text{H}_5$ bonding mode in $(\eta^4\text{-RC}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_3)$, instead of a summation of the metal-halide exchange and the phosphine-assisted migratory insertion mentioned above.

Results and Discussion

Product Analysis. Treatment of an equimolar amount of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ and PPh₃ in THF at -78 °C dropwise with slightly more than 1 molar equiv of RLi produces an array of products: $(\eta^4\text{-RC}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_3)$ (**1R**), $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{C}(\text{O})\text{R}$ (**2R**), $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ (**3**),⁶ and a trace amount of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{X}$ (**4**).⁷ The



results of the three-component reaction are listed in Table 1, varying halides $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ (X = Cl, Br, I) and organolithium reagents RLi (R = Me, *n*-Bu, *s*-Bu, Ph). All

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Table 1. Yields for Products Obtained in the Reaction of 1:1 ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)₂X/PPh₃ with RLi

halide	RLi	product ^a			
		1R	2R	3	4
($\eta^5\text{-C}_5\text{H}_5$)Fe(CO) ₂ Cl	MeLi	63.7	6.3	trace	trace
($\eta^5\text{-C}_5\text{H}_5$)Fe(CO) ₂ Br	MeLi	69.8	3.8	trace	trace
($\eta^5\text{-C}_5\text{H}_5$)Fe(CO) ₂ I	MeLi	77.8	1.2	trace	trace
($\eta^5\text{-C}_5\text{H}_5$)Fe(CO) ₂ Cl	<i>n</i> -BuLi	58.2	11.5	5	trace
($\eta^5\text{-C}_5\text{H}_5$)Fe(CO) ₂ Br	<i>n</i> -BuLi	68.8	3.5	5	trace
($\eta^5\text{-C}_5\text{H}_5$)Fe(CO) ₂ I	<i>n</i> -BuLi	82.9	<1	5	trace
($\eta^5\text{-C}_5\text{H}_5$)Fe(CO) ₂ Cl	<i>s</i> -BuLi	53.0	0.7	5.7	trace
($\eta^5\text{-C}_5\text{H}_5$)Fe(CO) ₂ Br	<i>s</i> -BuLi	57.2	0.9	4.8	trace
($\eta^5\text{-C}_5\text{H}_5$)Fe(CO) ₂ I	<i>s</i> -BuLi	64.9	0.7	4.3	trace
($\eta^5\text{-C}_5\text{H}_5$)Fe(CO) ₂ Cl	PhLi	47.2	19.1	trace	trace
($\eta^5\text{-C}_5\text{H}_5$)Fe(CO) ₂ Br	PhLi	59.1	7.8	trace	trace
($\eta^5\text{-C}_5\text{H}_5$)Fe(CO) ₂ I	PhLi	70.9	3.6	trace	trace

^a In addition to the array of products 1R, 2R, 3, and 4, sometimes ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)R was also collected in trace amount.

entries conform to a very similar reaction pattern, indicating that the reaction is a general one for a wide range of lithiated carbon nucleophiles, among which PhLi is the least favorable. Complex 1R is always the major product with yields in the range from 47.2% to 82.9% whereas complex 2R is a byproduct with yields between less than 1% and 19.1%. Complex 3 is isolated in a trace amount to less than 5.7% yield. For ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)₂I, the reaction produces mostly 1R whereas for ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)₂Cl, the yield of 1R decreases and that of 2R increases. For ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)₂Br, the results are between those for ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)₂I and ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)₂Cl. Apparently, the yield of 2R increases at the expense of 1R in changing from I to Br to Cl.

All complexes 1R and 2R have been characterized by spectroscopic methods. The ¹H NMR data of 1R generally shows three peaks for five-ring protons of RC₅H₅, i.e., the chemical shifts of the inner diene H atoms, the outer diene H atoms, and the *endo* H atom with ratios 2:2:1. Since the electron-donating tendency of substituents increases in the order Ph < Me < *n*-Bu < *s*-Bu, the chemical shift of the neighboring *endo* H atom in 1R should clearly reveal such an electronic influence. Parallel to the electron-donating tendency, the observed δ values of the *endo* H atoms are in the following order 1Ph > 1Me > 1Bu > 1*s*-Bu, with that of 1*s*-Bu being at the most upfield. Compounds 1Bu and 2Bu have been studied with X-ray diffraction to establish the molecular connectivities of 1R and 2R. Complex 1Bu has an Fe center coordinated by $\eta^4\text{-BuC}_5\text{H}_5$, PPh₃, and two CO ligands. On the other hand, 2Bu has an Fe center coordinated by $\eta^5\text{-C}_5\text{H}_5$, PPh₃, CO, and C(O)Bu. If the nucleophile R⁻ attacks the Fe center followed by a rearrangement to the $\eta^5\text{-C}_5\text{H}_5$ ring, the resulting 1R should be ($\eta^4\text{-endo-RC}_5\text{H}_5$)Fe(CO)₂(PPh₃). A direct attack at the $\eta^5\text{-C}_5\text{H}_5$ ring should result in an ($\eta^4\text{-exo-RC}_5\text{H}_5$)Fe(CO)₂(PPh₃). The *exo/endo* ambiguity of 1R has also been cleared with the results of X-ray structure of 1Bu. As seen in Figure 1, compound 1Bu has an *exo*-Bu group at the cyclopentadiene ring. Retrochemically, the nucleophilic addition of R⁻ is therefore a direct one, without the Fe mediation.

Out of a handful of ($\eta^4\text{-RC}_5\text{H}_5$)Fe(CO)₂(PPh₃) complexes known in the literature, complex 1Ph has been synthesized *via* the reaction of [($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)₂(PPh₃)]⁺I⁻ with PhLi in 14% yield.⁸ Compounds 1Me, 1Bu, and 1*s*-Bu have not been reported, however. Compound 2Me has been

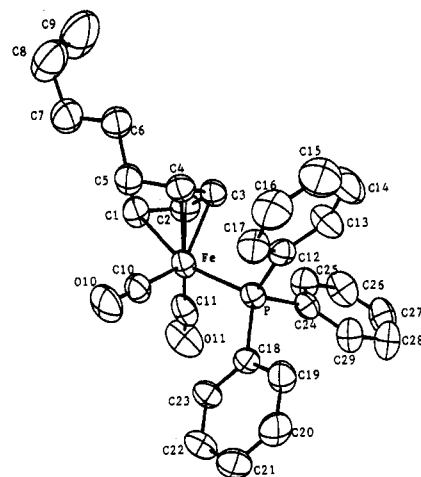


Figure 1. Molecular plot of ($\eta^4\text{-BuC}_5\text{H}_5$)Fe(CO)₂(PPh₃) (1Bu). Selected bond lengths: Fe–P 2.211(1); Fe–C(10) 1.796(5); Fe–C(11) 1.752(6); O(10)–C(10) 1.129(5); O(11)–C(11) 1.158(7) Å. Selected bond angles: P–Fe–C(10) 98.35(13); P–Fe–C(11) 92.06(15); Fe–C(10)–O(10) 178.9(4); Fe–C(11)–O(11) 178.4(4)°. Selected interplanar angle: [C1, C2, C3, C4]–[C1, C4, C5] 34.9(4)°.

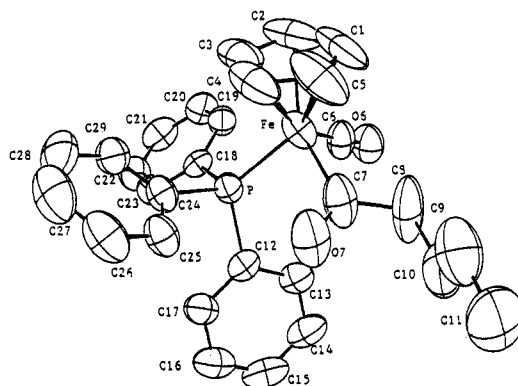


Figure 2. Molecular plot of ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)(PPh₃)C(O)Bu (2Bu). Selected structural parameters: Fe–P 2.198(2), Fe–C(6) 1.723(9), Fe–C(7) 1.992(8), O(6)–C(6) 1.158(10), O(7)–C(7) 1.221(10), C(7)–C(8) 1.503(12) Å; P–Fe–C(6) 95.9(3), P–Fe–C(7) 91.3(3), C(6)–Fe–C(7) 92.1(4), Fe–C(6)–O(6) 177.1(7), Fe–C(7)–O(7) 121.0(6), Fe–C(7)–C(8) 118.9(6)°; P–Fe–C(7)–O(7) –48.4(4), P–Fe–C(7)–C(8) 134.9(6), C(6)–Fe–C(7)–O(7) –144.4(7), C(6)–Fe–C(7)–C(8) 38.9(5)°.

synthesized easily *via* the PPh₃-assisted methyl migration reaction of ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)₂Me.² Complex 2Bu has previously been synthesized *via* deprotonation of ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)(PPh₃)C(O)Me with *n*-BuLi and then trapped with *n*-PrBr⁹ or *via* repetitive catalytic hydrosilylation.¹⁰ Complex 2*s*-Bu has been synthesized from ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)(PPh₃)C(O)Me deprotonation with *n*-BuLi, trapping with MeI, deprotonation with *n*-BuLi one more time, and then trapping with EtI.¹¹ Complex 2Ph has been synthesized *via* the PPh₃-assisted migratory insertion reaction of ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)₂Ph or *via* the PPh₃ substitution of CO in ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)₂C(O)Ph.¹²

X-ray Structures. A molecular plot of 1Bu is shown in Figure 1. The original $\eta^5\text{-C}_5\text{H}_5$ bonding in ($\eta^5\text{-C}_5\text{H}_5$)-

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Fe(CO)₂X changes to η⁴-BuC₅H₅ bonding in 1Bu. C1, C2, C3, and C4 are coplanar within 0.001 Å. The plane of C5, C6, Fe, C10, and O10 (deviations within 0.026 Å) is perpendicular to the plane of C1–C4, the interplanar angle being 90.6(2)°. The distance between C5 and the plane of C1–C4 is 0.582(9) Å. The three atom plane of C1, C4, and C5 is tilted by 34.9(4)° away from Fe to the other side of the diene plane. The available (η⁴-RC₅H₅)Fe(CO)₂(PPh₃) structures for comparison are 1Ph¹³ and (η⁴-*exo*-PhCH₂C₅H₅)Fe(CO)₂(PPh₃),¹⁴ the latter being obtained from a photolytic reaction of (η⁵-C₅H₅)Fe(CO)₂CH₂Ph with PPh₃.¹⁵ The corresponding angles are 34.1° in 1Ph and 34.7° and 32.9° in the two independent molecules of (η⁴-*exo*-PhCH₂C₅H₅)Fe(CO)₂(PPh₃). Both structures also show a planar diene skeleton which is orthogonal to the plane made of the unique C atom of the cyclopentadiene ring, the neighboring *exo*-C atom, Fe, and one of the CO groups—86.4(1)° for 1Ph and 93.1° and 89.8° for two the independent molecules of (η⁴-*exo*-PhCH₂C₅H₅)Fe(CO)₂(PPh₃). On the basis of the structural parameters of 1Bu, 1Ph, and (η⁴-*exo*-PhCH₂C₅H₅)Fe(CO)₂(PPh₃), the minimum energy conformation of (η⁴-RC₅H₅)Fe(CO)₂(PPh₃) may reasonably be described as a pseudo-square-pyramid with one of the CO ligands at the apical position, PPh₃ in the basal plane *trans* to one of the double bonds, and the second CO ligand *trans* to the second double bond.

Shown in Figure 2, the acyl compound 2Bu has the Bu group placed away from PPh₃. The torsion angle of P–Fe–C7–C8 is 134.9(6)°. Because of the dipole–dipole repulsion, the acyl CO group is in an *anti* position to the carbonyl CO group where the torsion angle of C6–Fe–C7–O7 is –144.4(7)°, smaller than that in 2Ph,^{13a} 158.0(3)°, and that in (η⁵-C₅H₅)Fe(CO)(PPh₃)C(O)Me,¹⁶ –168°. The coordination sphere around Fe atom conforms to a piano stool with the bonding geometry characteristic to a pseudo-octahedron, the η⁵-C₅H₅ ring occupying the *fac* sites.¹⁷ The angles of P–Fe–C6, P–Fe–C7, and C6–Fe–C7 are 95.9(3)°, 91.3(3)°, and 92.1(4)°, respectively—closer to 90° than 109.5°. Out of 24 crystal structures having the common fragment of (η⁵-C₅H₅)Fe(CO)(PR'₃)(acyl) as retrieved from the Cambridge Structural Database¹⁸ together with the crystal structure of 2Ph, details about the bond angles among the piano stool legs and the torsion angles of P–Fe–C7–O7 and C6–Fe–C7–O7 are given in Table 2. The medians of the bond angles are 93.0°, 90.3°, and 94.6°, respectively, and the medians of the torsion angles are 63.0 and 155.9°, respectively. These values compare well with the structural parameters of 2Bu.

Reaction Pathways. The electrophile (η⁵-C₅H₅)Fe(CO)₂X is expected to receive RLi at the coordinated CO

site rather than the Fe center or the η⁵-C₅H₅ ligand initially.¹⁹ If followed by the Fe–X bond cleavage, the immediately product (η⁵-C₅H₅)Fe(CO)C(O)R—or its alkyl migrated, 18-e⁻ equivalent, (η⁵-C₅H₅)Fe(CO)₂R—is then attacked by a second R⁻ resulting in 3, with reduction probably via a direct coupling, an Fe hydride mechanism, or an Fe radical pathway.²⁰

A neutral (η⁵-C₅H₅)Fe skeleton is resistive to modification in bonding such that an anionic alkyl usually deprotonates, not adds to, a η⁵-C₅H₅ ring. One example is the reaction of *n*-BuLi and (η⁵-C₅H₅)₂Fe, the product being (η⁵-C₅H₄Li)Fe(η⁵-C₅H₅)²¹ or, in the presence of TMEDA, (η⁵-C₅H₄Li)₂Fe.²² The carbonyl systems (η⁵-C₅H₅)Fe(CO)₂R giving evidence to the activity of (η⁵-C₅H₅)Fe deprotonations are reported in the literature as well, e.g., the numerous migrations *via* such a deprotonation.²³ Generated *in situ*, 3 is believed to be the catalyst triggering the above-mentioned one-flask reaction in which the aromatic η⁵-C₅H₅ in (η⁵-C₅H₅)Fe(CO)₂X changes to the nonaromatic cyclopentadiene in 1R. The catalytic property of 3 has been reported in the replacement reaction of CO or I⁻ of (η⁵-C₅H₅)Fe(CO)₂I with ligands, e.g., PPh₃, *t*-BuNC.²⁴ Shown in Scheme 1, complex 3 catalyzes the formation of cation [(η⁵-C₅H₅)Fe(CO)₂(PPh₃)]⁺ from (η⁵-C₅H₅)Fe(CO)₂X and PPh₃. In this catalytic cycle, complex 3 is considered a better electrophile toward PPh₃ than (η⁵-C₅H₅)Fe(CO)₂X and the resulting (η⁵-C₅H₅)Fe(CO)₂⁻ is considered a better nucleophile toward (η⁵-C₅H₅)Fe(CO)₂X than PPh₃. The radical mechanism is not ruled out, however. The cation [(η⁵-C₅H₅)Fe(CO)₂(PPh₃)]⁺ is much more electrophilic toward R⁻ than the neutral complex (η⁵-C₅H₅)Fe(CO)₂X. The cationic complexes (η⁵-C₅H₅)FeL₃⁺, where L₃ = (CO)₃, (CO)₂(PPh₃), or [P(OPh)₃]₃, have been reported to undergo the nucleophilic addition on η⁵-C₅H₅ ring with PhLi or NaBH₄ to give η⁴-cyclopentadiene complexes.⁸

The IR spectrum of an equimolar mixture of (η⁵-C₅H₅)Fe(CO)₂I and PPh₃ in THF at –78 °C (Figure 3b) is identical with that of only (η⁵-C₅H₅)Fe(CO)₂I (ν_{CO} 2035, 1988 cm⁻¹ in THF, Figure 3a), that is, there is no detectable concentration of the cation [(η⁵-C₅H₅)Fe(CO)₂(PPh₃)]⁺ (ν_{CO} 2058(s), 2013(s) cm⁻¹ in THF) in the 1:1 mixture before *n*-BuLi is added.

When a few drops of *n*-BuLi are added to the mixture of 1:1 (η⁵-C₅H₅)Fe(CO)₂I/PPh₃, complex 3 (ν_{CO} 1994, 1957, 1781 cm⁻¹ in THF) rapidly builds up to an observable concentration as shown in Figure 3c. Also exhibited are the small bands due to the cation [(η⁵-C₅H₅)Fe(CO)₂(PPh₃)]⁺, giving evidence to the presence of the cation shortly after the initial introduction of *n*-BuLi. To test the catalytic activity of 3, a mixture of (η⁵-C₅H₅)Fe(CO)₂I, PPh₃, and 0.05 mol % of 3 in THF has been found to

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Table 2. Summary of the Relevant Bond Angles and Torsion Angles of Compounds with the Common Fragment $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PR}'_3)\text{C}(\text{O})\text{R}$. The Atomic Numbering Scheme Used is That of 2Bu

compound	bond angle, deg			torsion angle, deg	
	$\angle\text{PFcC}_6$	$\angle\text{PFcC}_7$	$\angle\text{C}_6\text{FcC}_7$	PFcC_7O_2	$\text{C}_6\text{FcC}_7\text{O}_2$
2Bu	95.9(3)	91.3(3)	92.1(4)	-48.4(4)	-144.4(7)
2Ph	91.6(1)	89.4(1)	95.1(1)	-66.2(2)	-158.0(3)
ACMPFE ^a	94.6	90.6	92.4	-42.4	-137.0
BAPYEM ^b	93.2	84.8	88.8	-69.2	-155.9
CALWAN ^c	92.1	89.3	94.8	-74.1	-166.2
CUXBIG ^d	93.1	90.1	96.2	-63.0	-156.1
DAWDUA ^e	93.4	88.1	95.6	-81.1	-174.3
DOKHOA ^f	91.7	91.0	94.1	-95.2	-173.7
DUHXOT ^g	91.8	89.1	95.1	-69.2	-160.9
FAMNAI ^h	94.8	88.9	95.4	-79.5	-174.3
FEHTUH ⁱ	91.8	90.9	94.1	62.2	154.0
FELFOR ^j	92.5	91.3	93.1	-57.0	-149.6
FUXHUB ^k	91.4	91.7	94.6	74.4	165.9
GADWEN2 ^l	92.6	90.3	92.4	69.8	162.5
GAKJEH ^m	93.5	89.2	97.3	74.9	168.3
GEGHEF ⁿ	93.0	88.2	95.0	-69.7	-162.5
GIBTUG ^o	90.1	92.1	93.3	67.9	158.1
JUDNEB ^p	93.6	90.1	95.7	-60.4	-154.0
KALTOG ^q	94.8	92.3	93.6	-43.1	-138.0
KAVVOS ^r	94.3	91.7	93.8	-42.1	-136.5
KEWSEK ^s	92.4	94.3	94.1	48.3	-141.0
KITVEO ^t	94.2	90.0	94.9	-50.7	-144.9
SOGXOB ^u	91.9	90.3	94.7	-59.6	-151.6
SOTYEF ^v	94.2	90.0	93.1	-54.6	-148.8
VIVTEZ ^w	91.7	90.1	95.1	-73.8	-165.6
VOWVAE ^x	90.7	92.4	97.2	-53.2	-144.2

^a ACMPFE = acetylcarbonyl(η^5 -1-methyl-3-phenylcyclopentadienyl)(triphenylphosphine)iron: Attig, T. G.; Teller, R. G.; Wu, S.-M.; Bau, R.; Wojcicki, A. *J. Am. Chem. Soc.* **1979**, *101*, 619. ^b BAPYEM = acetylcarbonyl(η^5 -cyclopentadienyl)((1-(phenylethyl)amino)diphenylphosphine)iron: Korp, J. D.; Bernal, I. *J. Organomet. Chem.* **1981**, *220*, 355. ^c CALWAN = (*sec*-butylcarbonyl)carbonyl(η^5 -cyclopentadienyl)(triphenylphosphine)iron: Baird, G. J.; Bandy, J. A.; Davies, S. G.; Prout, K. *J. Chem. Soc., Chem. Comm.* **1983**, 1202. ^d CUXBIG = carbonyl(η^5 -cyclopentadienyl)(3-hydroxy-1-oxo-3-phenylpropyl)(triphenylphosphine)iron: Liebeskind, L. S.; Welker, M. E. *Tetrahedron Lett.* **1984**, *25*, 4341. ^e DAWDUA = (*RS,S*R)-carbonyl(η^5 -cyclopentadienyl)((3-hydroxybutylcarbonyl-C)(triphenylphosphine)iron: Brown, S. L.; Davies, S. G.; Warner, P.; Jones, R. H.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1985**, 1446. ^f DOKHOA = carbonyl(η^5 -cyclopentadienyl)(α,β -dimethylcinnamoyl)(triphenyl phosphite)iron: Reger, D. L.; Mintz, E.; Lebioda, L. *J. Am. Chem. Soc.* **1986**, *108*, 1940. ^g DUHXOT = (*R,S*)-(E)-carbonylcyclopentadienyl(η^5 -cyclopentadienyl)(triphenylphosphine)iron: Davies, S. G.; Dordor-Hedgecock, I. M.; Sutton, K. H.; Walker, J. C.; Jones, R. H.; Prout, K. *Tetrahedron* **1986**, *42*, 5123. ^h FAMNAI = carbonyl(η^5 -cyclopentadienyl)(3-phenyl-3-(phenylamino)-1-oxopropionyl)(triphenylphosphine)iron: Liebeskind, L. S.; Welker, M. E.; Fengl, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 6328. ⁱ FEHTUH = carbonyl(η^5 -cyclopentadienyl)(2-cyclopropylacetyl)(triphenylphosphine)iron: Pannell, K. H.; Kapoor, R. N.; Wells, M.; Giasolli, T.; Parkanyi, L. *Organometallics* **1987**, *6*, 663. ^j FELFOR = *cis*-(*RS*)-(Z)-carbonylcyclopentadienyl(η^5 -cyclopentadienyl)(triphenylphosphine)iron: Davies, S. G.; Easton, R. C. J.; Sutton, K. H.; Walker, J. C.; Jones, R. H. *J. Chem. Soc., Perkin Trans. 1* **1987**, 489. ^k FUXHUB = carbonyl(η^5 -cyclopentadienyl)((2-methyl-1-(methoxymethyl)-2-phenylethyl)carbonyl)(triphenyl phosphite)iron: Reger, D. L.; Klaeren, S. A.; Babin, J. E.; Adams, R. D. *Organometallics* **1988**, *7*, 181. ^l GADWEN2 = acetylcarbonyl(η^5 -methylcyclopentadienyl)(triphenylphosphine)iron: Liu, H. Y.; Koh, L. L.; Eriks, K.; Giering, W. P.; Prock, A. *Acta Crystallogr.* **1990**, *C46*, 51. ^m GAKJEH = *rac*-(*S*^{*},*S*^{*},*S*^{*})(η^5 -cyclopentadienyl)carbonyl-(triphenylphosphine)(3'-(benzoyloxy)-2'-methyl-1'-oxohept-6'-enyl)iron: Capon, R. J.; MacLeod, J. K.; Coote, S. J.; Davies, S. G.; Gravatt, G. L.; Dordor-Hedgecock, I. M.; Whittaker, M. *Tetrahedron* **1988**, *44*, 1637. ⁿ GEGHEF = acetylcarbonyl(η^5 -cyclopentadienyl)(dimethylphenylphosphine)iron: Herndon, J. W.; Wu, C.; Ammon, H. L. *J. Org. Chem.* **1988**, *53*, 2873. ^o GIBTUG = carbonyl(η^5 -cyclopentadienyl)((6-methyl-3-cyclohexene-4,5-dicarboxylic anhydride)acetyl)iron: Lee, G.-H.; Peng, S.-M.; Lush, S.-F.; Liu, R.-S. *J. Organomet. Chem.* **1988**, *349*, 219. ^p JUDNEB = (η^5 -cyclopentadienyl)benzoylcarbonyl(triphenylphosphine)iron: Krajewski, J. W.; Gluzinski, P.; Zamojski, A.; Mishnyov, A.; Kemme, A.; Guo, Z.-W. *J. Cryst. Spectrosc.* **1992**, *22*, 213. ^q KALTOG = (μ^2 - η^5 -(diphenylphosphino)cyclopentadienyl)acetyl(η^5 -cyclopentadienyl)methyltetracarbonyliron: Stille, J. K.; Smith, C.; Anderson, O. P.; Miller, M. M. *Organometallics* **1989**, *8*, 1040. ^r KAVVOS = acetylcarbonyl(η^5 -methylcyclopentadienyl)-(diphenylethylphosphine)iron: Liu, H. Y.; Rahman, M. M.; Koh, L. L.; Eriks, K.; Giering, W. P.; Prock, A. *Acta Crystallogr.* **1989**, *C45*, 1683. ^s KEWSEK = (2-phenyl-4-oxo-1-oxabutane-1,4-diyl)(carbonyl(η^5 -cyclopentadienyl)(triphenylphosphine)iron)-chlorobis(η^5 -cyclopentadienyl)titanium: Berno, P.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1990**, *9*, 1995. ^t KITVEO = (*R*)-(+)-carbonyl(η^5 -cyclopentadienyl)nicotinoyl-(((--)-menthyloxy)diphenylphosphine)iron: Davies, S. G.; Edwards, A. J.; Skerlj, R. T.; Sutton, K. H.; Whittaker, M. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1027. ^u SOGXOB = (η^5 -cyclopentadienyl)methoxyacetyl(triphenylphosphine)iron: Krajewski, J. W.; Gluzinski, P.; Zamojski, A.; Mishnyov, A.; Kemme, A.; Guo, Z.-W. *J. Cryst. Spectrosc.* **1991**, *21*, 271. ^v SOTYEF = acetylcarbonyl(η^5 -methylcyclopentadienyl)(methyl)diphenylphosphine)iron: Liu, H. Y.; Rahman, M. M.; Eriks, K.; Giering, W. P.; Prock, A. *Acta Crystallogr.* **1992**, *C48*, 433. ^w VIVTEZ = (η^5 -cyclopentadienyl)carbonyl-((diphenylphosphino)acetyl)(triphenylphosphine)iron: Berno, P.; Braunstein, P.; Floriano, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1991**, *30*, 1407. ^x VOWVAE = (2-(benzoyloxy)-2-methylheptanoyl)(η^5 -cyclopentadienyl)carbonyl(triphenylphosphine)iron(II): Stolz, F.; Strazewski, P.; Tamm, C.; Neuberger, M.; Zehnder, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 193.

produce yellow precipitates of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_3)]^+\text{I}^-$ (70%) after being stirred for 2 h. The 1:1 mixture without externally added 3 gave only 4 even after a prolonged stirring, although it would give both 4 and $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_3)]^+\text{I}^-$ under refluxing conditions.²⁵ Figure 3d shows the IR spectrum at the end of addition of 1 molar equiv of *n*-BuLi. Besides the ν_{CO} stretching frequencies due to 3, the dominating ν_{CO} bands at 1962, 1902 cm^{-1} are due to the product 1Bu.

In varying the halides, the product ratios of 1R/2R have been found to decrease drastically (I > Br > Cl) as revealed

in Table 1. Since the bond energy of Fe-I is the smallest (in complexes FeX_2 , 279, 340, and 400 KJ/mol for Fe-I, Fe-Br, and Fe-Cl, respectively),²⁶ the catalytic process to shift $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ to the cation $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_3)]^+$ is the easiest one among three halides ($\eta^5\text{-C}_5\text{H}_5$)- $\text{Fe}(\text{CO})_2\text{X}$. The possibility of the R⁻ attack at CO of the cation $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_3)]^+$ to produce 2R is likely of less importance, judged from the $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ results. The initial R⁻ attack at a CO site of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$, followed by PPh₃ ligation with simultaneous Fe-X bond dissociation, would also produce 2R. For $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$

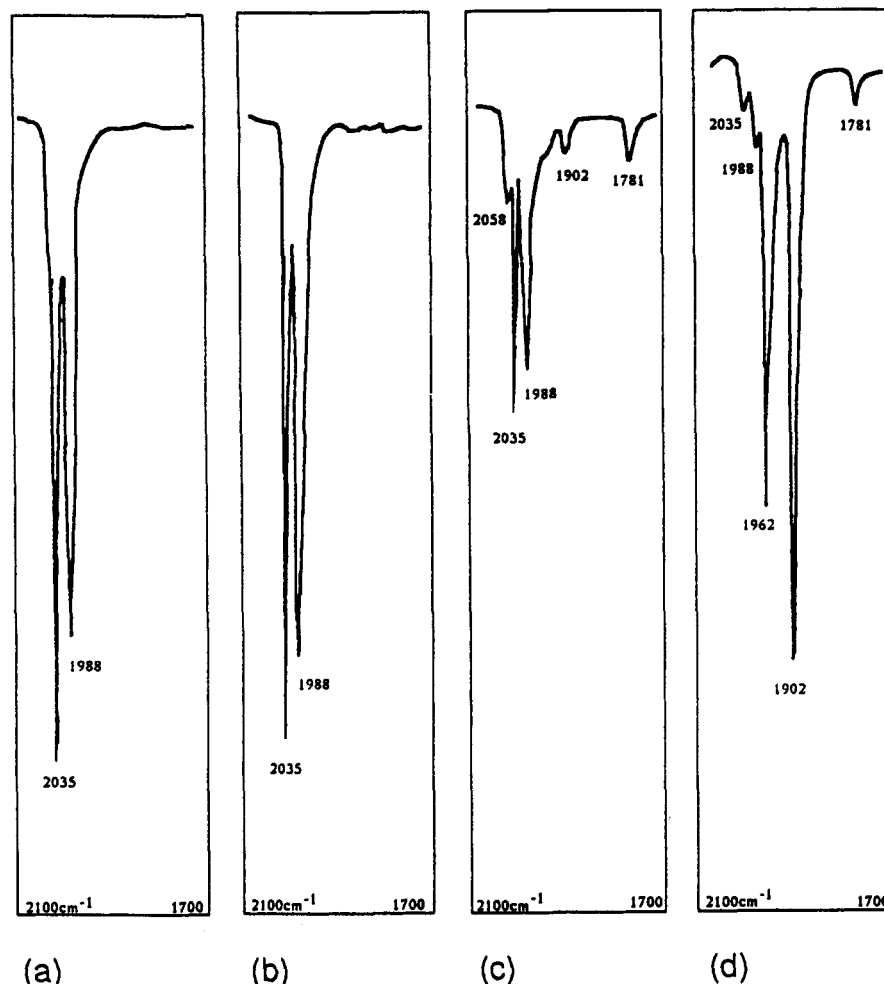
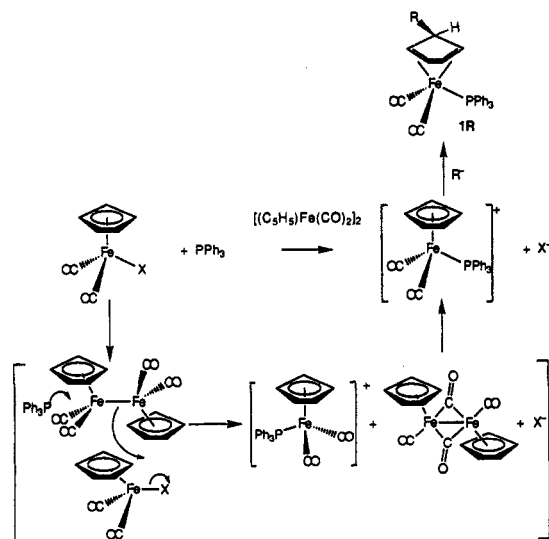


Figure 3. IR monitoring for the reaction of 1:1 $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}/\text{PPh}_3$ with $n\text{-BuLi}$. (a) IR spectrum of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ in THF at $-78\text{ }^\circ\text{C}$. (b) IR spectrum of an equimolar mixture of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ and PPh_3 in THF at $-78\text{ }^\circ\text{C}$. (c) Adding a few drops of $n\text{-BuLi}$ to (b). (d) Adding 1 molar equiv of $n\text{-BuLi}$ to (b).

Scheme 1



$\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Cl}$, with its higher barrier in steps involving Fe–Cl bond dissociation, the rate of 3-catalyzed reaction

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(26) Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*, 3rd ed.; Harper and Row: New York, 1983; Appendix 3.

is lowered, making the associative ligand substitution of Cl^- in the intermediate $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{C}(\text{O})\text{R}\text{-Cl}^-$ by PPh_3 competitive, giving an additional, important route to the increased production of **2R**. The PPh_3 ligand in the cation $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_3)]^+$ directs the incoming nucleophile R^- to the $\eta^5\text{-C}_5\text{H}_5$ site. Without PPh_3 , $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{THF})]^+$ simply reacts with a nucleophilic alkyl R^- to give $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{R}$ in enhanced yields.¹⁶

Preparation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{C}(\text{O})\text{Me}](\mu, \eta^1, \eta^1\text{-dppf})[(\eta^4\text{-exo-MeC}_5\text{H}_5)\text{Fe}(\text{CO})_2]$. The unidentate complex $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\eta^1\text{-dppf})\text{C}(\text{O})\text{Me}$ has been produced in refluxing 1:2 $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Me}$ and dppf [$\text{dppf} = (\eta^5\text{-C}_5\text{H}_4\text{PPh}_2)_2\text{Fe}$]. A small amount of the bridging product $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{C}(\text{O})\text{Me}]_2(\mu, \eta^1, \eta^1\text{-dppf})$ is also obtained. Contrasted to the dppf -assisted methyl migration reaction, those of $\text{PPh}_2(\text{CH})_n\text{PPh}_2$ ($n = 2\text{--}4$) have been found to easily yield complexes derived from double assistance instead, i.e., the bridging products $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{C}(\text{O})\text{Me}]_2[\mu, \eta^1, \eta^1\text{-PPh}_2(\text{CH})_n\text{PPh}_2]$ being major.²⁷ The 1:1 $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\eta^1\text{-dppf})\text{C}(\text{O})\text{Me}$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ are allowed to slowly react with dropping MeLi at $-78\text{ }^\circ\text{C}$ to create the novel complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{C}(\text{O})\text{Me}](\mu, \eta^1, \eta^1\text{-dppf})[(\eta^4\text{-exo-MeC}_5\text{H}_5)\text{Fe}(\text{CO})_2]$ (**5**), whose molecular connectivity is readily derived from the spectroscopic data: the IR ν_{CO} bands of 1908 and 1596 cm^{-1} and a ^{31}P NMR chemical shift of δ 71.3 are typical of a $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{C}(\text{O})\text{Me}$ linked to dppf ; on the other hand,

(27) Ni, R. S.; Luh, L. S.; Liu, L.-K. Manuscript in preparation.

the IR ν_{CO} bands of 1966 and 1908 (overlapped) cm^{-1} , a ^{31}P NMR chemical shift of δ 67.2, and the ^1H NMR shifts at δ 4.92, 2.52, and 2.11 (integration 2:1:2) are indicative for the presence of a $(\eta^4\text{-RC}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PR}_3)$ fragment in **5** as well, in good comparison with $(\eta^4\text{-MeC}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_3)$ which shows relevant IR ν_{CO} bands of 1964 and 1904 cm^{-1} and chemical shifts at δ 73.2 (^{31}P) and δ 5.03, 2.72, 2.41 (^1H , integration 2:1:2). Thus, a dppf linking two isomeric, methylated $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2]$ units has been obtained, one end in the form of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{C}(\text{O})\text{Me}$ and the other end in the form of $(\eta^4\text{-MeC}_5\text{H}_5)\text{Fe}(\text{CO})_2$.

The elaboration of the acyl Me group in $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{C}(\text{O})\text{Me}$ is well known.⁵ With a similar chirality center on the half sandwich Fe, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\eta^1\text{-dppf})\text{C}(\text{O})\text{Me}$ has been expected to proceed with a deprotonation by MeLi to give the anionic intermediate $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\eta^1\text{-dppf})\text{C}(\text{O})\text{CH}_2^-$ to be trapped by the electrophile $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$. On the basis of the results, the deprotonation pathway has been judged to be less important than the three-component reaction. Treating $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\eta^1\text{-dppf})\text{C}(\text{O})\text{Me}$ sequentially with MeLi and then $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ has produced very complex Fe-containing species which are not resolved. Within reasonable extension, Scheme 2 is a plausible mechanism toward the preparation of **5**—the dangling PPh₂ group of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\eta^1\text{-dppf})\text{C}(\text{O})\text{Me}$ coordinates to $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ to first form a cationic intermediate that is attacked by Me⁻ immediately, the methylation on $\eta^5\text{-C}_5\text{H}_5$ occurring via an *exo* direction.

Experimental Section

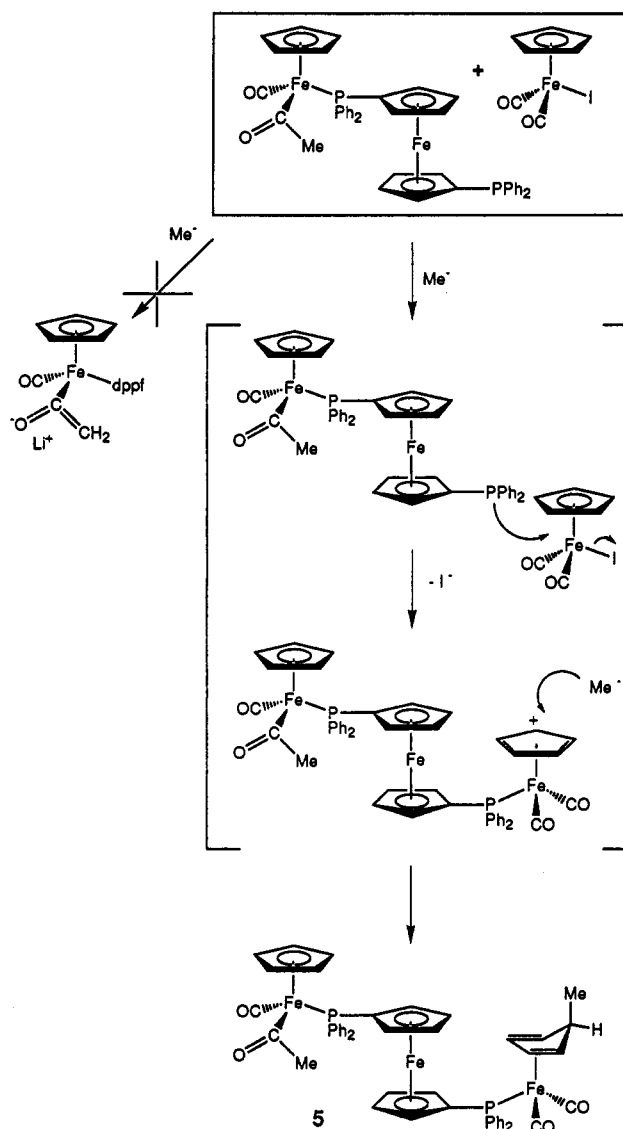
General. All manipulations were performed under an atmosphere of prepurified nitrogen with standard Schlenk techniques, and all solvents were distilled from an appropriate drying agent.²⁸ Infrared spectra were recorded in CH_2Cl_2 using CaF_2 optics on a Perkin-Elmer 882 spectrophotometer. The ^1H NMR spectra were obtained on Bruker AC200/AC300 spectrometers, with chemical shifts reported in δ values relative to the residual solvent resonance of CDCl_3 (7.24 ppm). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were obtained on Bruker MSL200/AC200/AC300 spectrometers using 85% H_3PO_4 as an external standard. The halides $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ (X = Cl, Br, I) and $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Me}$ were prepared according to the literature procedures.²⁹ Other reagents were obtained from commercial sources, e.g., Aldrich, Merck, and used without further purification.

Reaction of 1:1 $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ and PPh_3 with MeLi. $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ (X = Cl, Br, or I, respectively, 5 mmol) and PPh_3 (1.312 g, 5 mmol) were dissolved in THF (150 mL) and maintained at -78°C . MeLi (1.6 M, 3.75 mL, 6 mmol) in 30 mL of ether at -78°C was added dropwise to the solution. The mixture was stirred for an additional 1 h before being warmed up to room temperature and stirred overnight. The solution was then quenched with water. The organic layer was combined with the benzene extracts of the water layer, dried over MgSO_4 , and then evaporated to dryness under vacuum. The resulting oil-like concentrates were mixed well with 5 g of silica gel and 10 mL of CH_2Cl_2 and then pumped dry before being packed to the top of a SiO_2 column. The purification by column chromatography eluting with 1:10–1:7 EtOAc/*n*-hexane gave, according to the order of appearance, four products: the yellow $(\eta^4\text{-MeC}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_3)$ (**1Me**), the orange $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{C}(\text{O})\text{Me}$ (**2Me**),⁵ the purple **3**, and a trace amount of greenish **4**. The product distribution and the respective yields are listed in Table 1.

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(29) (a) Dombek, B. D.; Angelici, R. J. *Inorg. Chim. Acta* 1973, 7, 345. (b) Meyer, T. J.; Johnson, E. C.; Winterton, N. *Inorg. Chem.* 1971, 10, 1673. (c) *Inorg. Synth.* 1971, 12, 36. (d) *Inorg. Synth.* 1963, 7, 110. (e) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* 1964, 2, 15.

Scheme 2



1Me: mp 131–133 $^\circ\text{C}$; IR (CH_2Cl_2) ν_{CO} 1964 (s), 1904 (s) cm^{-1} ; ^1H NMR (CDCl_3) δ 0.33 (d, $J = 6$ Hz, 3H, Me), 2.41 (b, 2H, $-\text{CH}=\text{CHCHMe}-$), 2.72 (b, 1H, $-\text{CH}=\text{CHCHMe}-$), 5.03 (b, 2H, $-\text{CH}=\text{CHCHMe}-$), 7.32–7.42 (m, 15H, Ph); ^{13}C NMR (CDCl_3) δ 28.2 (s, Me), 50.8 (s, $-\text{CH}=\text{CHCHMe}-$), 57.6 (s, $-\text{CH}=\text{CHCHMe}-$), 82.0 (s, $-\text{CH}=\text{CHCHMe}-$), 128.0–136.7 (m, Ph), 219.8 (d, $^2J_{\text{P-C}} = 10.1$ Hz, CO); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ 73.2 (s); MS (m/z) M^+ 454 (parent ion). Anal. Calcd for $\text{C}_{28}\text{H}_{25}\text{FeO}_2$: C, 68.74; H, 5.10. Found: C, 69.04; H, 5.19.

Reaction of 1:1 $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ and PPh_3 with *n*-BuLi. $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$ (X = Cl, Br, or I, respectively, 2 mmol) and PPh_3 (525 mg, 2 mmol) were dissolved in THF (75 mL) and maintained at -78°C . *n*-BuLi (1.6 M, 1.5 mL, 2.4 mmol) in 20 mL of *n*-hexane at -78°C was added dropwise to the solution. The mixture was stirred for an additional 1 h before being warmed up to room temperature and stirred overnight. The solution was then filtered and the filtrate was evaporated to dryness under vacuum. The resulting oil-like concentrates were mixed with 5 g of silica gel and 10 mL of CH_2Cl_2 and pumped dry before being packed to the top of a SiO_2 column. The purification by column chromatography eluting with 1:15–1:10 EtOAc/*n*-hexane gave, according to the order of appearance, four products: the yellow $(\eta^4\text{-BuC}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{PPh}_3)$ (**1Bu**), the orange $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{C}(\text{O})\text{Bu}$ (**2Bu**), the purple **3**, and trace amount of greenish **4**. The product distribution and the respective yields are listed in Table 1. For **1Bu** and **2Bu**, the crystals suitable for X-ray diffraction were grown from CH_2Cl_2 /*n*-hexane by a slow evaporation method.

1Bu: mp 123–124 °C; IR (CH₂Cl₂) ν_{CO} 1962 (s), 1902 (s) cm⁻¹; ¹H NMR (CDCl₃) δ 0.73–1.11 (m, 9H, Bu), 2.46 (b, 2H, —CH=CHCHBu—), 2.61 (b, 1H, —CH=CHCHBu—), 5.06 (b, 2H, —CH=CHCHBu—), 7.36–7.44 (m, 15H, Ph); ¹³C NMR (CDCl₃) δ 14.0 (s, CH₂CH₂CH₂Me), 22.7 (s, CH₂CH₂CH₂Me), 28.3 (s, CH₂CH₂CH₂Me), 42.9 (d, $J = 5$ Hz, CH₂CH₂CH₂Me), 56.0 (s, —CH=CHCHBu—), 56.5 (s, —CH=CHCHBu—), 82.3 (s, —CH=CHCHBu—), 128.0–136.7 (m, Ph), 219.8 (d, ² $J_{\text{P-C}} = 10.1$ Hz, CO); ³¹P{¹H} NMR (CDCl₃) δ 73.32 (s); MS (m/z) M⁺ 496 (parent ion). Anal. Calcd for C₂₉H₂₉FeO₂P: C, 70.17; H, 5.89. Found: C, 70.16; H, 5.81.

2Bu: mp 126–127 °C; IR (CH₂Cl₂) ν_{CO} 1912 (s), 1602 (m) cm⁻¹; ³¹P{¹H} NMR (CDCl₃) δ 76.24 (s); MS (m/z) M⁺ 496 (parent ion). Anal. Calcd for C₂₉H₂₉FeO₂P: C, 70.17; H, 5.89. Found: C, 70.19; H, 5.86.

Reaction of 1:1 ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)₂I and PPh₃ and 0.05 Equiv of 3. Under a N₂ atmosphere, ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)₂I (1.52 g, 5 mmol), PPh₃ (1.312 g, 5 mmol), and 0.05 equiv of **3** were mixed completely and stirred for 2 h in THF (100 mL). The color of solution changed from black to green **4**, producing at the same time yellow precipitates that were later filtered, washed with THF for several times, and then dried *in vacuo*. The yellow crystallines of [($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)₂(PPh₃)]⁺I⁻ were collected (ca. 2 g, 70% yields): IR (CH₂Cl₂) ν_{CO} 2058 (s), 2013 (s) cm⁻¹ (lit. 2045, 2005 cm⁻¹ in CHCl₃); mp 203–204 °C (lit.⁷ mp 205 °C). Reactions running at -78 °C and room temperature gave similar results, the rate for the latter being faster. The same reaction without 0.05 equiv of externally added **3** in the reaction mixture was also performed and mainly resulted in green ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)(PPh₃)I under prolonged stirring.

Reaction of 1:1 ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)₂X and PPh₃ with *s*-BuLi. ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)₂X (X = Cl, Br, or I, respectively, 5 mmol) and PPh₃ (1.312 g, 5 mmol) were dissolved in THF (150 mL) and maintained at -78 °C. *s*-BuLi (1.3 M in cyclohexane, 4.0 mL, 5.2 mmol) in 30 mL of *n*-hexane at -78 °C was added dropwise to the solution. The mixture was stirred for an additional 1 h before being warmed up to room temperature and stirred overnight. The solution was then quenched with water. The organic layer was combined with the benzene extracts of the water layer, dried over MgSO₄, and then evaporated to dryness under vacuum. The resulting oil-like concentrates were mixed with 5 g of silica gel and 10 mL of CH₂Cl₂ and pumped dry before being packed to the top of a SiO₂ column. Purification by column chromatography eluting with 1:10 EtOAc/*n*-hexane gave, according to the order of appearance, four products: the yellow ($\eta^4\text{-s-BuC}_5\text{H}_5$)Fe(CO)₂(PPh₃) (**1s-Bu**), the orange ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)(PPh₃)C(O)*s*-Bu (**2s-Bu**),¹¹ the purple **3**, and a trace amount of greenish **4**. The product distribution and the respective yields are listed in Table 1.

1s-Bu: mp 125–126 °C; IR (CH₂Cl₂) ν_{CO} 1969 (s), 1909 (s) cm⁻¹; ¹H NMR (CDCl₃) δ 0.48–1.26 (m, 9H, *s*-Bu), 2.36 (b, 1H, —CH=CHCH*s*-Bu—), 2.51 (b, 2H, —CH=CHCH*s*-Bu—), 5.03 (b, 2H, —CH=CHCH*s*-Bu—), 7.30–7.44 (m, 15H, Ph); ¹³C NMR (CDCl₃) δ 11.3 (s, CHMeCH₂Me), 15.2 (s, CHMeCH₂), 25.6 (s, CHMeCH₂Me), 46.2 (d, $J = 5$ Hz, CHMeCH₂Me), 54.6 (s, —CH=CHCH*s*-Bu—), 62.4 (s, —CH=CHCH*s*-Bu—), 82.5 (s, —CH=CHCH*s*-Bu—), 128.0–136.8 (m, Ph), 219.7 (d, ² $J_{\text{P-C}} = 10.1$ Hz, CO); ³¹P{¹H} NMR (CDCl₃) δ 73.21 (s); MS (m/z) M⁺ 516 (parent ion). Anal. Calcd for C₃₁H₂₅FeO₂P: C, 72.11; H, 4.88. Found: C, 72.01; H, 4.70.

Reaction of 1:1 ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)₂X and PPh₃ with PhLi. ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)₂X (X = Cl, Br, or I, respectively, 5 mmol) and PPh₃ (1.312 g, 5 mmol) were dissolved in THF (100 mL) and maintained at -78 °C. PhLi (1.8 M in 3:7 ether/cyclohexane, 3.0 mL, 5.4 mmol) in 20 mL of ether/cyclohexane at -40 °C was added dropwise to the solution. The mixture was stirred for an additional 1 h before being warmed up to room temperature and stirred overnight. The solution was then quenched with water. The organic layer was combined with the benzene extracts of the water layer, dried over MgSO₄, and then evaporated to dryness under vacuum. The resulting oil-like concentrates were mixed with 5 g of silica gel and 10 mL of CH₂Cl₂ and pumped dry before being packed to the top of a SiO₂ column. Purification by column

Table 3. Crystal Data and Structure Refinement Details for ($\eta^4\text{-exo-BuC}_5\text{H}_5$)Fe(CO)₂(PPh₃) (1Bu**) and ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)(PPh₃)C(O)Bu (**2Bu**)**

	1Bu	2Bu
crystal system	triclinic	monoclinic
space group	P1	P2 ₁ /c
cell dimensions		
<i>a</i> , Å	8.870(3)	15.277(3)
<i>b</i> , Å	11.333(2)	9.851(2)
<i>c</i> , Å	13.509(3)	16.674(4)
α , deg	90.82(2)	90
β , deg	106.93(2)	91.87(2)
γ , deg	97.36(2)	90
volume, Å ³	1286.5(6)	2508.0(9)
reflins for cell params.	25	25
2θ range, deg.	15.60–32.90	15.24–30.32
crystal dimen., mm	0.31 × 0.43 × 0.44	0.31 × 0.37 × 0.23
empirical formula	C ₂₉ H ₂₉ FeO ₂ P	C ₂₉ H ₂₉ FeO ₂ P
formula weight	496.37	496.37
<i>F</i> (000)	519.93	1039.86
<i>Z</i>	2	4
<i>D</i> _{calc} , g/cm ³	1.281	1.315
μ , mm ⁻¹	0.67	0.68
radiation	Mo K α	Mo K α
λ , Å	0.70930	0.70930
diffractometer	Nonius CAD4	Nonius CAD4
scan mode	$\theta/2\theta$	$\theta/2\theta$
2θ (max)	44.9	44.8
<i>h, k, l</i> ranges	-9 < <i>h</i> < 9 0 < <i>k</i> < 12 -14 < <i>l</i> < 14	-10 < <i>h</i> < 10 0 < <i>k</i> < 10 0 < <i>l</i> < 17
no. reflins measd	3618	2845
no. unique reflins	3358	2703
no. observations	2774[<i>I</i> ₀ < 2.5 σ (<i>I</i> ₀)]	1732[<i>I</i> ₀ < 2.5 σ (<i>I</i> ₀)]
absorption corr	yes	yes
min and max trans factor	0.789–0.998	0.930–0.999
least squares		
no. atoms	62	62
no. parameters	299	298
weights	counting statistics	counting statistics
<i>R</i> ^a	0.040	0.048
<i>R</i> _w ^b	0.049	0.052
GOF ^c	2.45	2.19
max Δ /s	0.231	0.016
D-map		
highest peak	0.290	0.380
deepest hole	-0.330	-0.330
secondary ext. coeff.	0.495(40)	

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. ^c GOF = $[\sum w(|F_o| - |F_c|)^2 / (n - v)]^{1/2}$, *n* = no. of observations, *v* = no. of parameters.

chromatography eluting with 1:20 EtOAc/*n*-hexane gave, according to the order of appearance, four products: the yellow ($\eta^4\text{-PhC}_5\text{H}_5$)Fe(CO)₂(PPh₃) (**1Ph**), the orange ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)(PPh₃)C(O)Ph (**2Ph**), the purple **3**, and a trace amount of greenish **4**. The product distribution and the respective yields are listed in Table 1.

1Ph: mp 179–180 °C (lit.^{8a} mp 172 °C); IR (CH₂Cl₂) ν_{CO} 1969 (s), 1909 (s) cm⁻¹; ¹H NMR (CDCl₃) δ 2.63 (b, 2H), 3.88 (b, 1H), 5.18 (b, 2H), 6.91–7.42 (m, 20H); ¹³C NMR (CDCl₃) δ 55.2 (s, —CH=CHCHPh—), 59.7 (s, —CH=CHCHPh—), 82.5 (s, —CH=CHCHPh—), 128.0–147.7 (m, Ph), 219.4 (d, ² $J_{\text{P-C}} = 15.1$ Hz, CO); ³¹P{¹H} NMR (CDCl₃) δ 73.21 (s); MS (m/z) M⁺ 516 (parent ion). Anal. Calcd for C₃₁H₂₅FeO₂P: C, 72.11; H, 4.88. Found: C, 72.01; H, 4.70.

2Ph: mp 170–171 °C (lit.¹² mp 164 °C); IR (CH₂Cl₂) ν_{CO} 1919 (s), 1558 (m) cm⁻¹; ³¹P{¹H} NMR (CDCl₃) δ 75.42 (s); IR (CH₂Cl₂) ν_{CO} 1919 (s), 1558 (m) cm⁻¹; MS (m/z) M⁺ 516 (parent ion). Anal. Calcd for C₃₁H₂₅FeO₂P: C, 72.11; H, 4.88. Found: C, 71.98; H, 5.10.

Preparation of ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)($\eta^1\text{-dppf}$)C(O)Me. ($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)₂Me (0.32 g, 1.7 mmol) and dppf (1.83 g, 3.3 mmol) were dissolved in a mixture of THF (10 mL) and MeCN (50 mL) and then refluxed for 48 h to give an orange-red solution. The solvent was removed, column chromatography (SiO₂, eluting with 1:2 EtOAc/*n*-hexane) was applied to separate the unidentate

Table 4. Fractional Coordinates for Non-Hydrogen Atoms in 1Bu

atom	x	y	z	B _{iso}
Fe	0.51470(8)	0.38684(5)	0.21370(4)	3.86(3)
P	0.53409(13)	0.24393(8)	0.32462(8)	3.37(5)
O10	0.3657(4)	0.2405(3)	0.0215(2)	6.9(2)
O11	0.8514(4)	0.4095(3)	0.2292(3)	7.5(2)
C1	0.4616(7)	0.5488(3)	0.1459(4)	5.2(3)
C2	0.5277(6)	0.5634(3)	0.2550(4)	5.1(3)
C3	0.4210(6)	0.4951(4)	0.2971(3)	4.9(3)
C4	0.2924(6)	0.4406(4)	0.2126(4)	4.9(3)
C5	0.2843(6)	0.5148(4)	0.1201(3)	5.3(3)
C6	0.1852(6)	0.6188(4)	0.1144(4)	6.3(3)
C7	0.1820(7)	0.6928(4)	0.0246(4)	7.9(4)
C8	0.0701(8)	0.7883(5)	0.0062(5)	9.4(4)
C9	0.1062(11)	0.8769(6)	0.0845(5)	15.3(7)
C10	0.4231(6)	0.2960(3)	0.0962(3)	4.7(3)
C11	0.7174(7)	0.3987(4)	0.2231(3)	5.0(3)
C12	0.3540(5)	0.2057(3)	0.3619(3)	3.8(2)
C13	0.3387(6)	0.2365(4)	0.4577(4)	5.7(3)
C14	0.1950(7)	0.2105(6)	0.4781(4)	8.1(4)
C15	0.0638(7)	0.1548(6)	0.4043(5)	8.4(4)
C16	0.0770(6)	0.1224(5)	0.3085(4)	6.8(3)
C17	0.2182(6)	0.1481(4)	0.2865(3)	5.1(3)
C18	0.5641(4)	0.0985(3)	0.2778(3)	3.2(2)
C19	0.5130(5)	-0.0080(3)	0.3153(3)	4.3(2)
C20	0.5343(6)	-0.1163(3)	0.2775(3)	5.3(3)
C21	0.6105(6)	-0.1204(4)	0.2020(4)	5.5(3)
C22	0.6614(5)	-0.0165(4)	0.1631(3)	5.0(2)
C23	0.6395(5)	0.0932(3)	0.2005(3)	4.1(2)
C24	0.6897(5)	0.2719(3)	0.4505(3)	3.6(2)
C25	0.7607(5)	0.3882(4)	0.4804(3)	4.8(2)
C26	0.8780(6)	0.4127(4)	0.5766(4)	6.0(3)
C27	0.9219(6)	0.3238(5)	0.6409(3)	6.1(3)
C28	0.8521(6)	0.2067(5)	0.6109(4)	6.2(3)
C29	0.7351(5)	0.1816(4)	0.5156(3)	4.8(2)

complex ($\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\eta^1\text{-dppf})\text{C}(\text{O})\text{Me}$) (0.49 g, 40%) and the byproduct $[(\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\text{C}(\text{O})\text{Me})_2(\mu, \eta^1, \eta^1\text{-dppf})]$ (6.19 mg, 0.4%).

$(\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\eta^1\text{-dppf})\text{C}(\text{O})\text{Me})$: mp 140–141 °C; IR (CH_2Cl_2) ν_{CO} 1912 (s), 1598 (m) cm^{-1} ; ^{31}P NMR (CDCl_3) δ 71.2, -17.26. Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{O}_2\text{Fe}_2\text{P}_2$: C, 67.59; H, 4.86. Found: C, 67.18; H, 4.88.

$[(\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\text{C}(\text{O})\text{Me})_2(\mu, \eta^1, \eta^1\text{-dppf})]$: mp 175–176 °C; IR (CH_2Cl_2) ν_{CO} 1912 (s), 1597 (m) cm^{-1} ; ^{31}P NMR (CDCl_3) δ 71.50, 71.38. Anal. Calcd for $\text{C}_{20}\text{H}_{14}\text{O}_4\text{Fe}_2\text{P}_2$: C, 64.0; H, 4.73. Found: C, 63.84; H, 4.93.

Preparation of $[(\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\text{C}(\text{O})\text{Me})_2(\mu, \eta^1, \eta^1\text{-dppf})]$ - $[(\eta^4\text{-exo-MeC}_5\text{H}_5\text{Fe}(\text{CO})_2)]$. ($\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\eta^1\text{-dppf})\text{C}(\text{O})\text{Me}$) (1.493 g, 2 mmol) and ($\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$) (0.608 g, 2 mmol) were dissolved in THF (100 mL) and maintained at -78 °C. MeLi (1.6 M, 1.5 mL, 2.4 mmol) in 20 mL of ether at -78 °C was added dropwise to the solution. The mixture was stirred for an additional 1 h before being warmed to room temperature and stirred overnight. The solution was then quenched with water. The organic layer was combined with the benzene extracts of the water layer, dried over MgSO_4 , and then evaporated to dryness under vacuum. The resulting oil-like concentrates were mixed with 5 g of silica gel and 10 mL of CH_2Cl_2 and pumped dry before being packed to the top of a SiO_2 column. The purification by column chromatography eluting with 1:6 EtOAc/*n*-hexane gave, according to the order of appearance, two products: the yellow $[(\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\text{C}(\text{O})\text{Me})_2(\mu, \eta^1, \eta^1\text{-dppf})]$ - $[(\eta^4\text{-exo-MeC}_5\text{H}_5\text{Fe}(\text{CO})_2)]$ (5) in 80.7% yield and a trace amount of purple 3.

5: mp 177–178 °C; IR (CH_2Cl_2) ν_{CO} 1966 (s), 1908 (s), 1596 (w) cm^{-1} ; ^1H NMR (CDCl_3) δ 0.26 (b, 3H, Me), 2.11 (b, 2H, -CH=CHCHMe-), 2.44 (b, 3H, C(O)Me), 2.56 (b, 1H, -CH=CHCHMe-), 3.83 (b, 8H, C_5H_4), 4.21 (b, 5H, C_5H_5), 4.92 (b, 2H, -CH=CHCHMe), 7.30 (b, 20H, Ph); ^{13}C NMR (CDCl_3) δ 28.0 (s, Me), 50.7 (s, -CH=CHCHMe-), 51.9 (s, C(O)Me), 57.7 (s, -CH=CHCHMe-), 72.8–81.5 (m, C_5H_4), 82.2 (s, -CH=CHCHMe-), 85.2 (s, C_5H_5), 127.6–133.6 (m, Ph), 220.1 ($d, ^2J_{\text{P-C}} = 15.1$ Hz, CO), 275.7 (s, -C(O)Me); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ 71.26 (s), 67.24 (s); MS (*m/z*) M^+ 938 (parent ion).

Table 5. Fractional Coordinates for Non-Hydrogen Atoms of 2Bu

atom	x	y	z	B _{iso}
FE	0.76633(8)	0.17985(11)	0.06432(7)	5.03(6)
P	0.73278(13)	0.37880(18)	0.11441(10)	3.65(9)
O6	0.5896(4)	0.0872(5)	0.0339(3)	6.0(3)
O7	0.8132(4)	0.1516(5)	0.2285(3)	8.0(3)
C1	0.8255(9)	0.0410(12)	-0.0128(8)	10.0(8)
C2	0.8066(7)	0.1610(16)	-0.0568(6)	8.8(7)
C3	0.8498(7)	0.2667(10)	-0.0211(7)	7.7(6)
C4	0.8998(6)	0.2116(13)	0.0451(7)	8.4(7)
C5	0.8844(8)	0.0737(13)	0.0487(7)	9.9(8)
C6	0.6599(6)	0.1265(7)	0.0476(4)	4.8(4)
C7	0.7721(6)	0.0971(8)	0.1734(5)	6.8(5)
C8	0.7290(7)	-0.0380(9)	0.1859(6)	10.4(7)
C9	0.7423(7)	-0.1013(9)	0.2745(6)	9.0(7)
C10	0.8236(7)	-0.1600(10)	0.2778(7)	10.5(8)
C11	0.8388(8)	-0.2172(11)	0.3665(5)	13.7(9)
C12	0.6656(5)	0.3875(7)	0.2042(4)	3.7(4)
C13	0.6014(5)	0.2900(18)	0.2158(4)	4.6(4)
C14	0.5448(5)	0.3002(9)	0.2792(5)	6.1(5)
C15	0.5527(6)	0.4093(11)	0.3318(5)	6.6(6)
C16	0.6156(6)	0.5052(9)	0.3206(5)	6.2(5)
C17	0.6730(5)	0.4964(7)	0.2581(4)	4.9(4)
C18	0.6681(5)	0.4928(7)	0.0460(4)	3.6(4)
C19	0.6340(5)	0.4429(7)	-0.0276(4)	4.4(4)
C20	0.5834(5)	0.5269(8)	-0.0761(4)	5.3(4)
C21	0.5681(5)	0.6588(9)	-0.0539(4)	5.6(5)
C22	0.6024(6)	0.7098(7)	0.0170(5)	5.7(5)
C23	0.6520(5)	0.6266(7)	0.0677(4)	4.9(4)
C24	0.8289(5)	0.4822(7)	0.1415(4)	4.2(4)
C25	0.8614(6)	0.5770(8)	0.0898(4)	5.3(5)
C26	0.9389(7)	0.6443(9)	0.1071(6)	7.2(6)
C27	0.9863(6)	0.6148(10)	0.1767(7)	7.9(7)
C28	0.9543(6)	0.5231(10)	0.2293(5)	6.8(6)
C29	0.8759(6)	0.4538(7)	0.2128(4)	5.0(4)

Anal. Calcd for $\text{C}_{50}\text{H}_{44}\text{Fe}_3\text{O}_4\text{P}_2$: C, 64.00; H, 4.73. Found: C, 64.36; H, 4.54.

X-ray Structure Analysis. The single-crystal X-ray diffraction measurements were performed on a Nonius CAD-4 automated diffractometer using graphite-monochromated Mo $\text{K}\alpha$ radiation; 25 high-angle reflections were used in a least-squares fit to obtain accurate cell constants. Diffraction intensities were collected up to $2\theta < 45^\circ$ using the $\theta/2\theta$ scan technique, with background counts made for half the total scan time on each side of the peak. Three standard reflections, remeasured every hour, showed no significant decrease in intensity during data collection. The reflections with $I_0 > 2.5\sigma(I_0)$ were judged as observations and were used for solution and structure refinement. Data were corrected for Lorentz-polarization factors. An empirical absorption correction based on a series of ψ scans was applied to the data. The structure was solved by direct methods³⁰ and refined by a full-matrix least-squares routine³¹ with anisotropic thermal parameters for all non-hydrogen atoms (weight = $1/[\sigma(F_o)^2 + 0.0001(F_o)^2]$, $\sigma(F_o)$ from counting statistics). All of the hydrogen atoms were placed isotropically at their calculated positions (C-H = 1.00 Å) and fixed in the calculations. Atomic scattering factor curves f_o , $\Delta f'$, and $\Delta f''$ of Fe, P, O, and C and f_o of H were taken from International Tables.³² For a summary of crystal data and refinement details, see Table 3. Selected bond distances and angles for 1Bu and 2Bu are given in the captions of Figures 1 and 2, respectively, with respective final atomic fractional coordinates in Tables 4 and 5.

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Supplementary Material Available: For the structures of 1Bu and 2Bu, listings of crystallographic data, positional and anisotropic thermal parameters, and bond distances, angles, and structural parameters (19 pages). Ordering information is given on any current masthead page.

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