Cyclopentadienyldicarbonyliron Halides as Electrophiles: Reactions of (η^5-C_5H_5)Fe(CO)$_2$X with RLi in the Presence of PPh$_3$ To Produce (η^4-*exo*-RC$_5$H$_5$)Fe(CO)$_2$(PPh$_3$) and Preparation of [(η^5-C_5H_5)Fe(CO)C(O)Me](μ,η^1,η^1-dppf)[(η^4-*exo*-MeC$_5$H$_5$)Fe(CO)$_2$]

Ling-Kang Liu* and Lung-Shiang Luh

Institute of Chemistry, Academia Sinica, Taipei, Taiwan 11529, Republic of China, and
Department of Chemistry, National Taiwan University,
Taipei, Taiwan 10767, Republic of China

Received March 14, 1994®

The reaction of (η^5-C_5H_5)Fe(CO)$_2$X (X = Cl, Br, I) with RLi (R = Me, *n*-Bu, *s*-Bu, Ph) in the presence of PPh$_3$ at low temperature changes the η^5-C_5H_5 bonding mode in (η^5-C_5H_5)Fe(CO)$_2$X to an η^4-RC$_5$H$_5$ bonding mode in (η^4-RC$_5$H$_5$)Fe(CO)$_2$(PPh$_3$). The X-ray results of (η^4-BuC$_5$H$_5$)Fe(CO)$_2$(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, [(η^5-C_5H_5)Fe(CO)$_2$]$_2$ is believed to be the catalyst in the conversion of (η^5-C_5H_5)Fe(CO)$_2$X and PPh$_3$ to the cationic intermediate [(η^5-C_5H_5)Fe(CO)$_2$(PPh$_3$)]$^+$ which is much more electrophilic toward R$^-$ to produce (η^4-*exo*-RC$_5$H$_5$)Fe(CO)$_2$(PPh$_3$). The conformation of (η^4-*exo*-RC$_5$H$_5$)Fe(CO)$_2$(PPh$_3$) may be described as a pseudo-square-pyramid with one of the CO ligands at the apical position. Refluxing 1:2 (η^5-C_5H_5)Fe(CO)$_2$Me, and dppf gives (η^5-C_5H_5)Fe(CO)(η^1-dppf)C(O)Me which, upon treatment of MeLi at low temperature, yields [(η^5-C_5H_5)Fe(CO)C(O)Me](μ,η^1,η^1-dppf)[(η^4-*exo*-MeC$_5$H$_5$)Fe(CO)$_2$], a complex with a dppf linking two iosmeric, methylated [(C$_5$H$_5$)Fe(CO)$_2$]units, one end in the form of (η^5-C_5H_5)Fe(CO)C(O)Me and the other end in the form of (η^4-*exo*-MeC$_5$H$_5$)Fe(CO)$_2$.

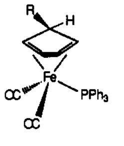
Introduction

Treatment of carbon nucleophiles such as alkyl anion R$^-$ with the half-sandwich compounds (η^5-C_5H_5)Fe(CO)$_2$X (X = Cl, Br, I) produces metal alkyls (η^5-C_5H_5)Fe(CO)$_2$R.[1] The PR$'_3$ [R$'_3$ = Ph$_3$, Ph$_2$Me, PhMe$_2$ (OPh)$_3$, etc.] induced alkyl migration of (η^5-C_5H_5)Fe(CO)$_2$R (R = Me, Et, *i*-Pr, etc.) gives high yields of metal acyls (η^5-C_5H_5)Fe(CO)(PR$'_3$)C(O)R, Fe becoming a chiral center.[2] Being configurationally stable[3] and readily resolvable into optically pure forms,[4] (η^5-C_5H_5)Fe(CO)(PPh$_3$)C(O)CH$_2$R has been used extensively in organic synthesis and in mechanistic studies.[5]

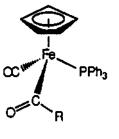
In our attempts, the reactions of (η^5-C_5H_5)Fe(CO)$_2$X with RLi in the presence of PPh$_3$ at low temperature have been studied. The reaction pattern found is a facile three-component reaction of (η^5-C_5H_5)Fe(CO)$_2$X, PPh$_3$, and RLi, which effectively changes the η^5-C_5H_5 bonding mode in (η^5-C_5H_5)Fe(CO)$_2$X to an η^4-RC$_5$H$_5$ bonding mode in (η^4-RC$_5$H$_5$)Fe(CO)$_2$(PPh$_3$), instead of a summation of the metal–halide exchange and the phosphine-assisted migratory insertion mentioned above.

Results and Discussion

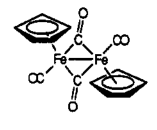
Product Analysis. Treatment of an equimolar amount of (η^5-C_5H_5)Fe(CO)$_2$X and PPh$_3$ in THF at −78 °C dropwise with slightly more than 1 molar equiv of RLi produces an array of products: (η^4-RC$_5$H$_5$)Fe(CO)$_2$(PPh$_3$) (**1R**), (η^5-C_5H_5)Fe(CO)(PPh$_3$)C(O)R (**2R**), [(η^5-C_5H_5)Fe(CO)$_2$]$_2$ (**3**),[6] and a trace amount of (η^5-C_5H_5)Fe(CO)(PPh$_3$)X (**4**).[7] The results of the three-component reaction are listed in Table 1, varying halides (η^5-C_5H_5)Fe(CO)$_2$X (X = Cl, Br, I) and organolithium reagents RLi (R = Me, *n*-Bu, *s*-Bu, Ph). All



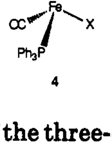
1R



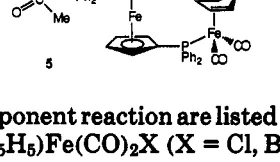
2R



3



4



5

[•] Abstract published in *Advance ACS Abstracts*, June 1, 1994.

(1) (a) Koerner von Gustorf, E. A., Grevels, F.-W., Fischler, I., Eds. *The Organic Chemistry of Iron*, Volume 1; Academic Press: New York, 1978; p 352. (b) Davies, S. G. *Organotransition Metal Chemistry: Applications to Organic Synthesis*; Pergamon Press: Oxford, 1982; pp 24–25. (c) Pearson, A. J. *Metallic-organic Chemistry*; John Wiley & Sons: Chichester, 1985; p 333. (d) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104. (e) Li, H.-J.; Turnbull, M. M. *J. Organomet. Chem.* **1991**, *419*, 245. (f) Chukwu, R.; Hunter, A. D.; Santarsiero, B. D.; Bott, S. G.; Atwood, J. L.; Chassaignac, J. *Organometallics* **1992**, *11*, 589. (g) Akita, M.; Terada, M.; Moro-oka, Y. *Organometallics* **1992**, *11*, 1825.

(2) (a) Bibler, J. P.; Wojcicki, A. *Inorg. Chem.* **1966**, *5*, 889. (b) Butler, I. S.; Basolo, F.; Pearson, R. G. *Inorg. Chem.* **1967**, *6*, 2074. (c) Green, M.; Westlake, D. J. *J. Chem. Soc. A* **1971**, 367.

(3) Pannell, K. H. *J. Chem. Soc., Chem. Commun.* **1969**, 1346.

(4) For example: Case-Green, S. C.; Costello, J. F.; Davies, S. G.; Heaton, N.; Hedgecock, C. J. R.; Prime, J. C. *J. Chem. Soc., Chem. Commun.* **1993**, 1621.

(5) (a) Libeskind, L. S.; Welker, M. E.; Fengl, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 6328. (b) Davies, S. G. *Organotransition Metal Chemistry: Applications to Organic Synthesis*; Pergamon Press: Oxford, 1982. (c) Davies, S. G. *Aldrichimica Acta* **1990**, *23*, 31.

(6) (a) Adams, R. D.; Cotton., F. A. *J. Am. Chem. Soc.* **1973**, *95*, 6589. (b) Manning, A. R. *J. Chem. Soc. A* 1968, 1319.

(7) Treichel, P. M.; Shubkin, R. L.; Barnett, K. W.; Reichard, D. *Inorg. Chem.* **1966**, *5*, 1177.

0276-7333/94/2313-2816$04.50/0

Table 1. Yields for Products Obtained in the Reaction of 1:1 $(\eta^5\text{-}C_5H_5)Fe(CO)_2X/PPh_3$ with RLi

halide	RLi	product[a] 1R	2R	3	4
$(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$	MeLi	63.7	6.3	trace	trace
$(\eta^5\text{-}C_5H_5)Fe(CO)_2Br$	MeLi	69.8	3.8	trace	trace
$(\eta^5\text{-}C_5H_5)Fe(CO)_2I$	MeLi	77.8	1.2	trace	trace
$(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$	*n*-BuLi	58.2	11.5	5	trace
$(\eta^5\text{-}C_5H_5)Fe(CO)_2Br$	*n*-BuLi	68.8	3.5	5	trace
$(\eta^5\text{-}C_5H_5)Fe(CO)_2I$	*n*-BuLi	82.9	<1	5	trace
$(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$	*s*-BuLi	53.0	0.7	5.7	trace
$(\eta^5\text{-}C_5H_5)Fe(CO)_2Br$	*s*-BuLi	57.2	0.9	4.8	trace
$(\eta^5\text{-}C_5H_5)Fe(CO)_2I$	*s*-BuLi	64.9	0.7	4.3	trace
$(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$	PhLi	47.2	19.1	trace	trace
$(\eta^5\text{-}C_5H_5)Fe(CO)_2Br$	PhLi	59.1	7.8	trace	trace
$(\eta^5\text{-}C_5H_5)Fe(CO)_2I$	PhLi	70.9	3.6	trace	trace

[a] In addition to the array of products **1R**, **2R**, **3**, and **4**, sometimes $(\eta^5\text{-}C_5H_5)Fe(CO)R$ 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 $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$, the reaction produces mostly **1R** whereas for $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$, the yield of **1R** decreases and that of **2R** increases. For $(\eta^5\text{-}C_5H_5)Fe(CO)_2Br$, the results are between those for $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$. 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 RC_5H_5, 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 $\eta^4\text{-}BuC_5H_5$, PPh_3, and two CO ligands. On the other hand, **2Bu** has an Fe center coordinated by $\eta^5\text{-}C_5H_5$, PPh_3, CO, and C(O)Bu. If the nucleophile R^- attacks the Fe center followed by a rearrangement to the $\eta^5\text{-}C_5H_5$ ring, the resulting **1R** should be $(\eta^4\text{-}endo\text{-}RC_5H_5)Fe(CO)_2(PPh_3)$. A direct attack at the $\eta^5\text{-}C_5H_5$ ring should result in an $(\eta^4\text{-}exo\text{-}RC_5H_5)Fe(CO)_2(PPh_3)$. 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 $(\eta^4\text{-}RC_5H_5)Fe(CO)_2(PPh_3)$ complexes known in the literature, complex **1Ph** has been synthesized *via* the reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)]^+I^-$ with PhLi in 14% yield.[8] Compounds **1Me**, **1Bu**, and **1*s*-Bu** have not been reported, however. Compound **2Me** has been synthesized easily *via* the PPh_3-assisted methyl migration reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$.[2] Complex **2Bu** has previously been synthesized *via* deprotonation of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)C(O)Me$ with *n*-BuLi and then trapped with *n*-PrBr[9] or *via* repetitive catalytic hydrosilylation.[10] Complex **2*s*-Bu** has been synthesized from $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)C(O)Me$ 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 PPh_3-assisted migratory insertion reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Ph$ or *via* the PPh_3 substitution of CO in $(\eta^5\text{-}C_5H_5)Fe(CO)_2C(O)Ph$.[12]

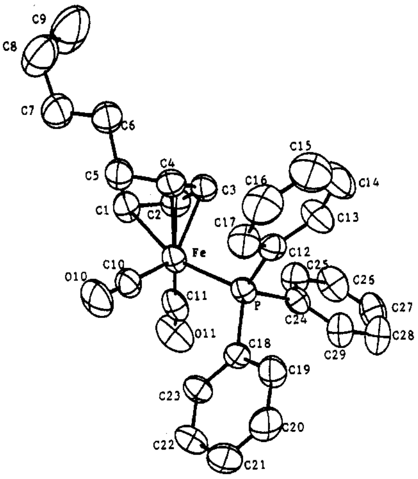


Figure 1. Molecular plot of $(\eta^4\text{-}BuC_5H_5)Fe(CO)_2(PPh_3)$ (**1Bu**). Selected bond lengths: Fe–P 2.211(1); Fe–C(10) 1.796(5); Fe–C(11) 1.752(6); O(10)–C(10) 1.129(5); O(11)–C(11) 1.158(7) Å. Selected bond angles: P–Fe–C(10) 98.35(13); P–Fe–C(11) 92.06(15); Fe–C(10)–O(10) 178.9(4); Fe–C(11)–O(11) 178.4(4)°. Selected interplanar angle: [C1, C2, C3, C4]–[C1, C4, C5] 34.9(4)°.

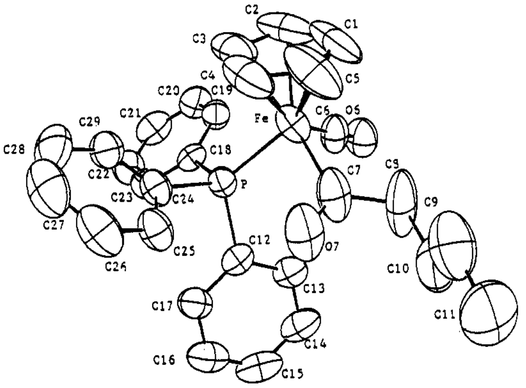


Figure 2. Molecular plot of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)C(O)Bu$ (**2Bu**). Selected structural parameters: Fe–P 2.198(2), Fe–C(6) 1.723(9), Fe–C(7) 1.992(8), O(6)–C(6) 1.158(10), O(7)–C(7) 1.221(10), C(7)–C(8) 1.503(12) Å; P–Fe–C(6) 95.9(3), P–Fe–C(7) 91.3(3), C(6)–Fe–C(7) 92.1(4), Fe–C(6)–O(6) 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)°.

X-ray Structures. A molecular plot of **1Bu** is shown in Figure 1. The original $\eta^5\text{-}C_5H_5$ bonding in $(\eta^5\text{-}C_5H_5)$-

---

[8] (a) Treichel, P. M.; Shubkin, R. L. *Inorg. Chem.* **1967**, *6*, 1328. (b) Green, M. L. H.; Whiteley, R. N. *J. Chem. Soc. A* **1971**, 1943.

[9] Bashiardes, G.; Collingwood, S. P.; Davies, S. G.; Preton, S. C. *J. Organomet. Chem.* **1989**, *364*, C29.

[10] Akita, M.; Mitani, O.; Sayama, M.; Moro-oka, Y. *Organometallics* **1991**, *10*, 1394.

[11] Baird, G. J.; Bandy, J. A.; Davies, S. G.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1983**, 1202.

[12] Nesmeyanov, A. N.; Chapovsky, Yu. A.; Polovyanyuk, I. V.; Makarova, L. G. *J. Organomet. Chem.* **1967**, *7*, 329.

$Fe(CO)_2X$ changes to η^4-BuC_5H_5 bonding in **1Bu**. C1, C2, C3, and C_4 are coplanar within 0.001 Å. The plane of C_5, C_6, 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 $(\eta^4$-$RC_5H_5)Fe(CO)_2(PPh_3)$ structures for comparison are **1Ph**[13] and $(\eta^4$-*exo*-$PhCH_2C_5H_5)Fe(CO)_2(PPh_3)$,[14] the latter being obtained from a photolytic reaction of $(\eta^5$-$C_5H_5)Fe(CO)_2CH_2Ph$ with PPh_3.[15] The corresponding angles are 34.1° in **1Ph** and 34.7° and 32.9° in the two independent molecules of $(\eta^4$-*exo*-$PhCH_2C_5H_5)Fe(CO)_2(PPh_3)$. 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 $(\eta^4$-*exo*-$PhCH_2C_5H_5)Fe(CO)_2(PPh_3)$. On the basis of the structural parameters of **1Bu**, **1Ph**, and $(\eta^4$-*exo*-$PhCH_2C_5H_5)Fe(CO)_2(PPh_3)$, the minimum energy conformation of $(\eta^4$-$RC_5H_5)Fe(CO)_2(PPh_3)$ may reasonably be described as a pseudo-square-pyramid with one of the CO ligands at the apical position, PPh_3 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 PPh_3. 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 $(\eta^5$-$C_5H_5)Fe(CO)(PPh_3)C(O)Me$,[16] −168°. The coordination sphere around Fe atom conforms to a piano stool with the bonding geometry characteristic to a pseudo-octahedron, the η^5-C_5H_5 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 $(\eta^5$-$C_5H_5)Fe(CO)(PR'_3)$(acyl) as retrieved from the Cambridge Structural Database[18] 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 $(\eta^5$-$C_5H_5)Fe(CO)_2X$ is expected to receive RLi at the coordinated CO site rather than the Fe center or the η^5-C_5H_5 ligand initially.[19] If followed by the Fe–X bond cleavage, the immediately product $(\eta^5$-$C_5H_5)Fe(CO)C(O)R$—or its alkyl migrated, 18-e$^-$ equivalent, $(\eta^5$-$C_5H_5)Fe(CO)_2R$—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 $(\eta^5$-$C_5H_5)Fe$ skeleton is resistive to modification in bonding such that an anionic alkyl usually deprotonates, not adds to, a η^5-C_5H_5 ring. One example is the reaction of *n*-BuLi and $(\eta^5$-$C_5H_5)_2Fe$, the product being $(\eta^5$-$C_5H_4Li)Fe(\eta^5$-$C_5H_5)$[21] or, in the presence of TMEDA, $(\eta^5$-$C_5H_4Li)_2Fe$.[22] The carbonyl systems $(\eta^5$-$C_5H_5)Fe(CO)_2R$ giving evidence to the activity of $(\eta^5$-$C_5H_5)$-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 η^5-C_5H_5 in $(\eta^5$-$C_5H_5)Fe(CO)_2X$ changes to the nonaromatic cyclopentadiene in **1R**. The catalytic property of **3** has been reported in the replacement reaction of CO or I^- of $(\eta^5$-$C_5H_5)Fe(CO)_2I$ with ligands, e.g., PPh_3, *t*-BuNC.[24] Shown in Scheme 1, complex **3** catalyzes the formation of cation $[(\eta^5$-$C_5H_5)Fe(CO)_2(PPh_3)]^+$ from $(\eta^5$-$C_5H_5)Fe(CO)_2X$ and PPh_3. In this catalytic cycle, complex **3** is considered a better electrophile toward PPh_3 than $(\eta^5$-$C_5H_5)Fe(CO)_2X$ and the resulting $(\eta^5$-$C_5H_5)Fe(CO)_2^-$ is considered a better nucleophile toward $(\eta^5$-$C_5H_5)Fe(CO)_2X$ than PPh_3. The radical mechanism is not ruled out, however. The cation $[(\eta^5$-$C_5H_5)Fe(CO)_2(PPh_3)]^+$ is much more electrophilic toward R^- than the neutral complex $(\eta^5$-$C_5H_5)Fe(CO)_2X$. The cationic complexes $(\eta^5$-$C_5H_5)FeL_3^+$, where L_3 = $(CO)_3$, $(CO)_2(PPh_3)$, or $[P(OPh)_3]_3$, have been reported to undergo the nucleophilic addition on η^5-C_5H_5 ring with PhLi or $NaBH_4$ to give η^4-cyclopentadiene complexes.[8]

The IR spectrum of an equimolar mixture of $(\eta^5$-$C_5H_5)Fe(CO)_2I$ and PPh_3 in THF at −78 °C (Figure 3b) is identical with that of only $(\eta^5$-$C_5H_5)(Fe(CO)_2I$ (ν_{CO} 2035, 1988 cm^{-1} in THF, Figure 3a), that is, there is no detectable concentration of the cation $[(\eta^5$-$C_5H_5)Fe(CO)_2(PPh_3)]^+$ (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 $(\eta^5$-$C_5H_5)Fe(CO)_2I/PPh_3$, 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 $[(\eta^5$-$C_5H_5)Fe(CO)_2(PPh_3)]^+$, 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 $(\eta^5$-$C_5H_5)Fe(CO)_2I$, PPh_3, and 0.05 mol % of **3** in THF has been found to

---

[13] (a) Luh, L.-S.; Liu, L.-K. *Bull. Inst. Chem. Academia Sinica* **1994**, *41*, 39. (b) The structure of CpFe(CO)(PPh$_3$)C(O)Ph was also reported earlier in a different space group: Semion, V. A.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1969**, *10*, 664.

[14] Sim, G. A.; Woodhouse, D. I.; Knox, G. R. *J. Chem. Soc., Dalton Trans.* **1979**, 629.

[15] Blaha, J. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 2694.

[16] X-ray of CpFe(CO)(PPh$_3$)C(O)Me. (a) Davies, S. G.; Dordor-Hedgecock, I. M.; Warner, P.; Jones, R. H. *J. Organomet. Chem.* **1985**, *285*, 213. (b) Brown, S. L.; Davies, S. G.; Warner, P.; Jones, R. H. *J. Chem. Soc., Chem. Commun.* **1985**, 1446. (c) Davies, S. G.; Dordor-Hedgecock, I. M.; Sutton, K. H.; Walker, J. C.; Bourne, C.; Jones, R. H.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1986**, 607. (d) Bernal, I.; Brunner, H.; Muschiol, M. *Inorg. Chim. Acta* **1988**, *142*, 235. (e) Marsh, R. E. *Inorg. Chim. Acta* **1989**, *157*, 1. (f) Liu, H. Y.; Koh, L. L.; Eriks, K.; Giering, W. P.; Prock, A. *Acta Crystallogr.* **1990**, *C46*, 51.

[17] Seeman, J. I.; Davies, S. G. *J. Am. Chem. Soc.* **1985**, *107*, 6522 and references within.

[18] *Cambridge Structural Database* and the associated software *Cambridge Structural Database System*. Version 4. Cambridge Crystallographic Data Centre: Cambridge, 1991.

[19] Wong, A.; Pawlick, R. V.; Thomas, C. G.; Leon, D. R.; Liu, L.-K. *Organometallics* **1991**, *10*, 530.

[20] Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds. *Comprehensive Organometallic Chemistry. The Synthesis, Reactions, and Structures of Organometallic Compounds*, Volume 4; Pergamon: Oxford, 1982; pp 331–613.

[21] Okuhara, K. *J. Org. Chem.* **1976**, *41*, 1487.

[22] Bishop, J. J.; Davison, A.; Katcher, M. L.; Lichtenberg, D. W.; Merrill, R. E.; Smart, J. C. *J. Organomet. Chem.* **1971**, *27*, 241.

[23] (a) Berryhill, S. R.; Clevenger, G. L.; Burdurlu, F. Y. *Organometallics* **1985**, *4*, 1509. (b) Pannell, K. H.; Cervantes, J.; Hernandez, C.; Cassias, J.; Vincenti, S. *Organometallics*, **1986**, *5*, 1056. (c) Cervantes, J.; Vincenti, S. P.; Kapoor, R. N.; Pannell, K. H. *Organometallics* **1989**, *8*, 744.

[24] (a) Coville, N. J.; Albers, M. O.; Ashworth, T. V.; Singleton, E. *J. Chem. Soc., Chem. Commun.* **1981**, *408*. (b) Coville, N. J.; Darling, E. A.; Hearn, A. W.; Johnston, P. *J. Organomet. Chem.* **1987**, 328, 375.

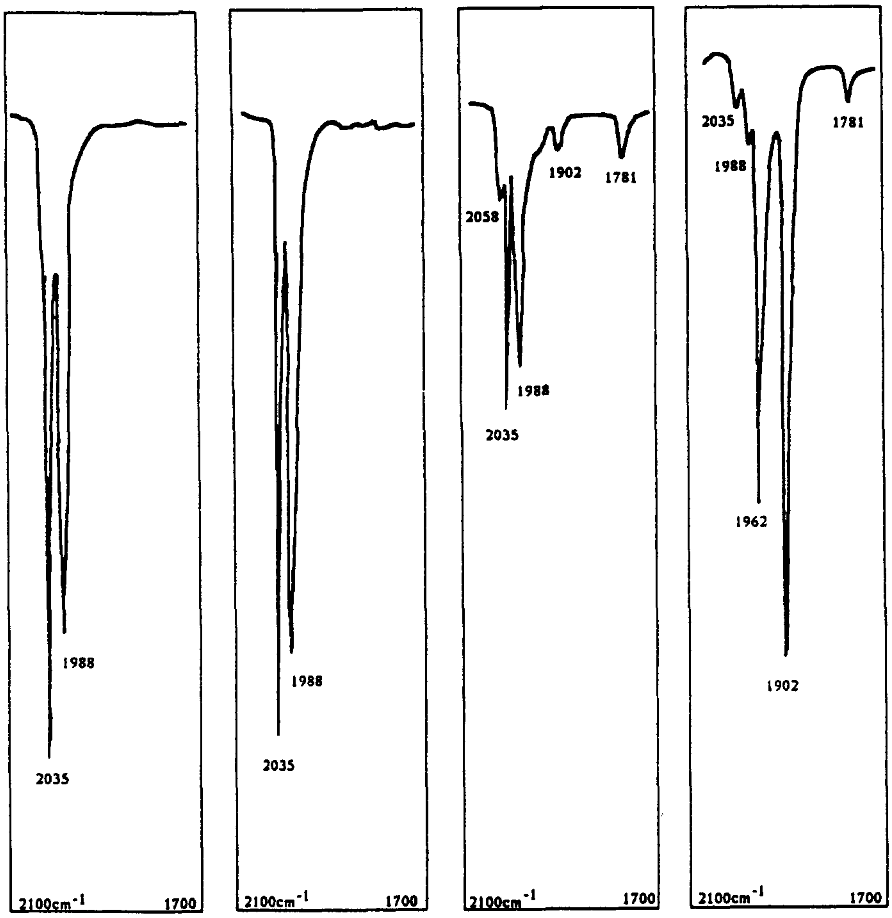
Table 2. Summary of the Relevant Bond Angles and Torsion Angles of Compounds with the Common Fragment $(\eta^5\text{-}C_5H_5)Fe(CO)(PR'_3)C(O)R$. The Atomic Numbering Scheme Used is That of 2Bu

	bond angle, deg			torsion angle, deg	
compound	$\angle PFeC_6$	$\angle PFeC_7$	$\angle C_6FeC_7$	$PFeC_7O_2$	$C_6FeC_7O_2$
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] BAPYEW = 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*,*SR*)-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*)-carbonylcrotonyl(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*)-carbonylcrotonyl(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-phenylethenyl)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)(triphenylphosphine)((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)methyltetracarbonylirontungsten: 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)(methyldiphenylphosphine)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-(benzyloxy)-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 $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)]^+I^-$ (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 $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)]^+I^-$ 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**.

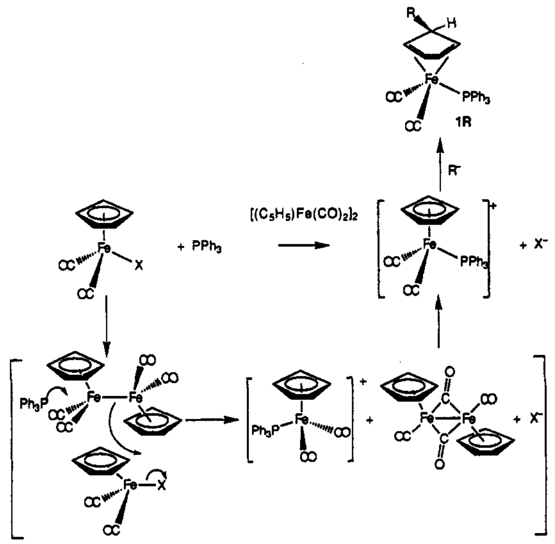
In varying the halides, the product ratios of **1R**/**2R** have been found to decrease drastically (I > Br > Cl) as revealed in Table 1. Since the bond energy of Fe–I is the smallest (in complexes FeX_2, 279, 340, and 400 KJ/mol for Fe–I, Fe–Br, and Fe–Cl, respectively),[26] the catalytic process to shift $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ to the cation $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)]^+$ is the easiest one among three halides $(\eta^5\text{-}C_5H_5)Fe(CO)_2X$. The possibility of the R^- attack at CO of the cation $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PPh_3)]^+$ to produce **2R** is likely of less importance, judged from the $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ results. The initial R^- attack at a CO site of $(\eta^5\text{-}C_5H_5)Fe(CO)_2X$, followed by PPh_3 ligation with simultaneous Fe–X bond dissociation, would also produce **2R**. For $(\eta^5$-



(a) (b) (c) (d)

Figure 3. IR monitoring for the reaction of 1:1 (η^5-C_5H_5)Fe(CO)$_2$I/PPh$_3$ with *n*-BuLi. (a) IR spectrum of (η^5-C_5H_5)Fe(CO)$_2$I in THF at −78 °C. (b) IR spectrum of an equimolar mixture of (η^5-C_5H_5)Fe(CO)$_2$I and PPh$_3$ in THF at −78 °C. (c) Adding a few drops of *n*-BuLi to (b). (d) Adding 1 molar equiv of *n*-BuLi to (b).

Scheme 1



C_5H_5)Fe(CO)$_2$Cl, with its higher barrier in steps involving Fe–Cl bond dissociation, the rate of 3-catalyzed reaction is lowered, making the associative ligand substitution of Cl$^-$ in the intermediate (η^5-C_5H_5)Fe(CO)C(O)R·Cl$^-$ by PPh$_3$ competitive, giving an additional, important route to the increased production of **2R**. The PPh$_3$ ligand in the cation [(η^5-C_5H_5)Fe(CO)$_2$(PPh$_3$)]$^+$ directs the incoming nucleophile R$^-$ to the η^5-C_5H_5 site. Without PPh$_3$, [(η^5-C_5H_5)Fe(CO)$_2$(THF)]$^+$ simply reacts with a nucleophilic alkyl R$^-$ to give (η^5-C_5H_5)Fe(CO)$_2$R in enhanced yields.[1e]

Preparation of [(η^5-C_5H_5)Fe(CO)C(O)Me](μ,η^1,η^1-dppf)[(η^4-*exo*-MeC$_5$H$_5$)Fe(CO)$_2$]. The unidentate complex (η^5-C_5H_5)Fe(CO)(η^1-dppf)C(O)Me has been produced in reluxing 1:2 (η^5-C_5H_5)Fe(CO)$_2$Me and dppf [dppf = (η^5-C_5H_4PPh$_2$)$_2$Fe]. A small amount of the bridging product [(η^5-C_5H_5)Fe(CO)C(O)Me]$_2$(μ,η^1,η^1-dppf) is also obtained. Contrasted to the dppf-assisted methyl migration reaction, those of PPh$_2$(CH)$_n$PPh$_2$ (n = 2–4) have been found to easily yield complexes derived from double assistance instead, i.e., the bridging products [(η^5-C_5H_5)Fe(CO)C(O)Me]$_2$[μ,η^1,η^1-PPh$_2$(CH)$_n$PPh$_2$] being major.[27] The 1:1 (η^5-C_5H_5)Fe(CO)(η^1-dppf)C(O)Me and (η^5-C_5H_5)Fe(CO)$_2$I are allowed to slowly react with dropping MeLi at −78 °C to create the novel complex [(η^5-C_5H_5)Fe(CO)C(O)Me](μ,η^1,η^1-dppf)[(η^4-*exo*-MeC$_5$H$_5$)Fe(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 (η^5-C_5H_5)Fe(CO)C(O)Me linked to dppf; on the other hand,

---

(25) (a) Zakrezewski, J. *J. Organomet. Chem.* **1991**, *412*, C23. (b) Alway, D. G.; Barnett, K. W. In *Inorganic and Organometallic Photochemistry* (Adv. Chem. Ser. 168); Wrighton, M. S., Ed.; American Chemical Society: Washington, DC, 1978; pp 115–131. (c) Pandey, V. N. *Inorg. Chim. Acta* **1977**, *22*, L39 and references within.

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

(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 ^{1}H NMR shifts at δ 4.92, 2.52, and 2.11 (integration 2:1:2) are indicative for the presence of a $(\eta^4\text{-RC}_5\text{H}_5)\text{Fe(CO)}_2(\text{PR}_3)$ fragment in 5 as well, in good comparison with $(\eta^4\text{-MeC}_5\text{H}_5)\text{Fe(CO)}_2(\text{PPh}_3)$ 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 (^{1}H, integration 2:1:2). Thus, a dppf linking two isomeric, methylated $[(\text{C}_5\text{H}_5)\text{Fe(CO)}_2]$ units has been obtained, one end in the form of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)C(O)Me}$ and the other end in the form of $(\eta^4\text{-MeC}_5\text{H}_5)\text{Fe(CO)}_2$.

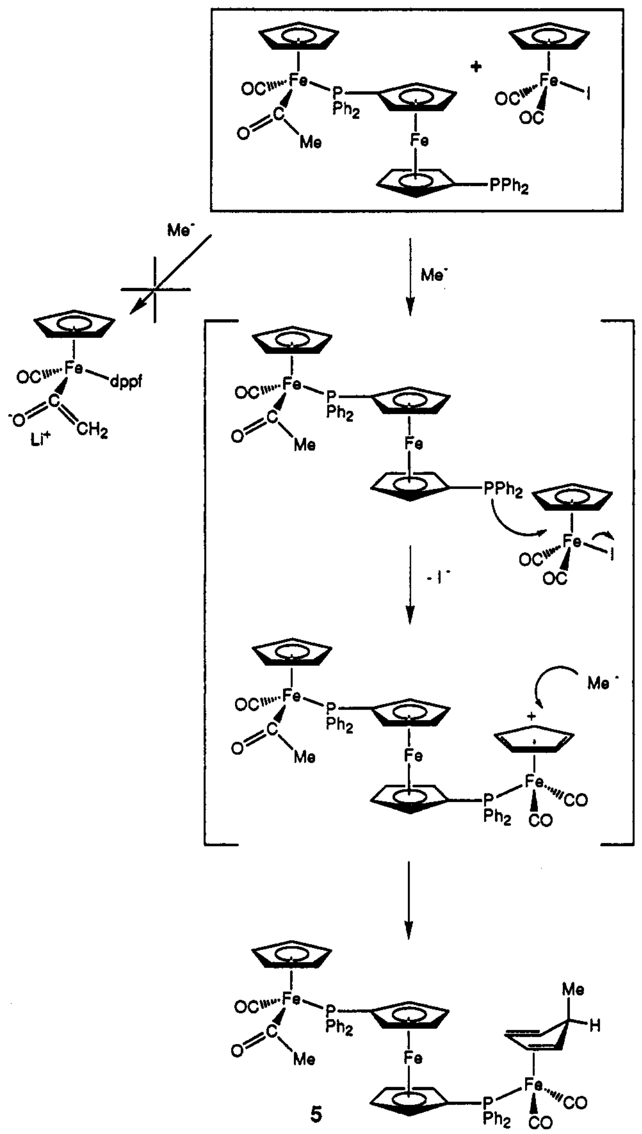
The elaboration of the acyl Me group in $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)(PPh}_3)\text{C(O)Me}$ is well known.[5] With a similar chirality center on the half sandwich Fe, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}(\eta^1\text{-dppf)C(O)Me}$ has been expected to proceed with a deprotonation by MeLi to give the anionic intermediate $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}(\eta^1\text{-dppf)C(O)CH}_2^-$ to be trapped by the electrophile $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{I}$. On the basis of the results, the deprotonation pathway has been judged to be less important than the three-component reaction. Treating $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}(\eta^1\text{-dppf)C(O)Me}$ sequentially with MeLi and then $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{I}$ 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 PPh$_2$ group of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}(\eta^1\text{-dppf)C(O)Me}$ coordinates to $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{I}$ to first form a cationic intermediate that is attacked by Me$^-$ immediately, the methylation on η^5-C$_5$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$_2$Cl$_2$ using CaF$_2$ optics on a Perkin-Elmer 882 spectrophotometer. The ^{1}H 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}P{^{1}H} NMR spectra were obtained on Bruker MSL200/AC200/AC300 spectrometers using 85% H$_3$PO$_4$ as an external standard. The halides $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{X}$ (X = Cl, Br, I) and $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{Me}$ 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 $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{X}$ and PPh$_3$ with MeLi. $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{X}$ (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$_2$Cl$_2$ 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 $(\eta^4\text{-MeC}_5\text{H}_5)\text{Fe(CO)}_2(\text{PPh}_3)$ (**1Me**), the orange $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)(PPh}_3)\text{C(O)Me}$ (**2Me**,[5] the purple **3**, and a trace amount of greenish **4**. The product distribution and the respective yields are listed in Table 1.

Scheme 2



1Me: mp 131–133 °C; IR (CH$_2$Cl$_2$) ν_{CO} 1964 (s), 1904 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.33 (d, J = 6 Hz, 3H, Me), 2.41 (b, 2H, —CH═C*H*CHMe—), 2.72 (b, 1H, —CH═CHC*H*Me—), 5.03 (b, 2H, —C*H*═CHCHMe—), 7.32–7.42 (m, 15H, Ph); ^{13}C NMR (CDCl$_3$) δ 28.2 (s, Me), 50.8 (s, —CH═CH*C*HMe—), 57.6 (s, —CH═*C*HCHMe—), 82.0 (s, —*C*H═CHCHMe—), 128.0–136.7 (m, Ph), 219.8 (d, $^{2}J_{\text{P-C}}$ = 10.1 Hz, CO); ^{31}P{^{1}H} NMR (CDCl$_3$) δ 73.2(s); MS (*m/z*) M$^+$ 454 (parent ion). Anal. Calcd for C$_{26}$H$_{23}$FeO$_2$P: C, 68.74; H, 5.10. Found: C, 69.04; H, 5.19.

Reaction of 1:1 $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{X}$ and PPh$_3$ with *n*-BuLi. $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{X}$ (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$_2$Cl$_2$ 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 $(\eta^4\text{-BuC}_5\text{H}_5)\text{Fe(CO)}_2(\text{PPh}_3)$ (**1Bu**), the orange $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)(PPh}_3)\text{C(O)Bu}$ (**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$_2$Cl$_2$/*n*-hexane by a slow evaporation method.

---

(28) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, 1981.

(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.

1Bu: mp 123–124 °C; IR (CH_2Cl_2) ν_{CO} 1962 (s), 1902 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.73–1.11 (m, 9H, Bu), 2.46 (b, 2H, —CH=C*H*CHBu—), 2.61 (b, 1H, —CH=CHC*H*Bu—), 5.06 (b, 2H, —C*H*=CHCHBu—), 7.36–7.44 (m, 15H, Ph); ^{13}C NMR ($CDCl_3$) δ 14.0 (s, $CH_2CH_2CH_2$*Me*), 22.7 (s, CH_2CH_2*C*H_2Me), 28.3 (s, CH_2*C*H_2CH_2Me), 42.9 (d, *J* = 5 Hz, *C*$H_2CH_2CH_2$Me), 56.0 (s, —CH=*C*HCHBu—), 56.5 (s, —CH=CH*C*HBu—), 82.3 (s, —*C*H=CHCHBu—), 128.0–136.7 (m, Ph), 219.8 (d, $^2J_{P-C}$ = 10.1 Hz, CO); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 73.32 (s); MS (*m/z*) M$^+$ 496 (parent ion). Anal. Calcd for $C_{29}H_{29}FeO_2P$: C, 70.17; H, 5.89. Found: C, 70.16; H, 5.81.

2Bu: mp 126–127 °C; IR (CH_2Cl_2) ν_{CO} 1912 (s), 1602 (m) cm^{-1}; ^{31}P{^{1}H} NMR ($CDCl_3$) δ 76.24 (s); MS (*m/z*) M$^+$ 496 (parent ion). Anal. Calcd for $C_{29}H_{29}FeO_2P$: C, 70.17; H, 5.89. Found: C, 70.19; H, 5.86.

Reaction of 1:1 (η^5-C_5H_5)Fe(CO)$_2$I and PPh_3 and 0.05 Equiv of 3. Under a N_2 atmosphere, (η^5-C_5H_5)Fe(CO)$_2$I (1.52 g, 5 mmol), PPh_3 (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 [(η^5-C_5H_5)Fe(CO)$_2$(PPh_3)]$^+$I$^-$ were colleced (*ca.* 2 g, 70% yields): IR (CH_2Cl_2) ν_{CO} 2058 (s), 2013 (s) cm^{-1} (lit. 2045, 2005 cm^{-1} in $CHCl_3$); 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 (η^5-C_5H_5)Fe(CO)(PPh_3)I under prolonged stirring.

Reaction of 1:1 (η^5-C_5H_5)Fe(CO)$_2$X and PPh_3 with *s*-BuLi. (η^5-C_5H_5)Fe(CO)$_2$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. *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 $MgSO_4$, 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. Purification by column chromatography eluting with 1:10 EtOAc/*n*-hexane gave, according to the order of appearance, four products: the yellow (η^4-*s*-BuC_5H_5)Fe(CO)$_2$(PPh_3) (**1s-Bu**), the orange (η^5-C_5H_5)Fe(CO)(PPh_3C(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.

1*s*-Bu: mp 125–126 °C; IR (CH_2Cl_2) ν_{CO} 1969 (s), 1909 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.48–1.26 (m, 9H, *s*-Bu), 2.36 (b, 1H, —CH=CHC*H*s-Bu—), 2.51 (b, 2H, —CH=C*H*CH*s*-Bu), 5.03 (b, 2H, —C*H*=CHCH*s*-Bu—), 7.30–7.44 (m, 15H, Ph); ^{13}C NMR ($CDCl_3$) δ 11.3 (s, CHMeCH_2*Me*), 15.2 (s, CH*Me*CH_2), 25.6 (s, CHMeCH_2Me), 46.2 (d, *J* = 5 Hz, *C*HMeCH_2Me), 54.6 (s, —CH=*C*HCH*s*-Bu—), 62.4(s, —CH=CH*C*H*s*-Bu—), 82.5 (s, —*C*H=CHCH*s*-Bu—), 128.0–136.8 (m, Ph), 219.7 (d, $^2J_{P-C}$ = 10.1 Hz, CO); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 73.21 (s); MS (*m/z*) M$^+$ 516 (parent ion). Anal. Calcd for $C_{31}H_{25}FeO_2P$: C, 72.11; H, 4.88. Found: C, 72.01; H, 4.70.

Reaction of 1:1 (η^5-C_5H_5)Fe(CO)$_2$X and PPh_3 with PhLi. (η^5-C_5H_5)Fe(CO)$_2$X (X = Cl, Br, or I, respectively, 5 mmol) and PPh_3 (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 $MgSO_4$, 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. Purification by column chromatography eluting with 1:20 EtOAc/*n*-hexane gave, according to the order of appearance, four products: the yellow (η^4-PhC_5H_5)Fe(CO)$_2$(PPh_3) (**1Ph**), the orange (η^5-C_5H_5)Fe(CO)(PPh_3)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.

Table 3. Crystal Data and Structure Refinement Details for (η^4-*exo*-BuC_5H_5)Fe(CO)$_2$(PPh_3) (1Bu) and (η^5-C_5H_5)Fe(CO)(PPh_3)C(O)Bu (2Bu)

	1Bu	2Bu
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
cell dimensions		
a, Å	8.870(3)	15.277(3)
b, Å	11.333(2)	9.851(2)
c, 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)
reflns 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	$C_{29}H_{29}FeO_2P$	$C_{29}H_{29}FeO_2P$
formula weight	496.37	496.37
F(000)	519.93	1039.86
Z	2	4
D_{calc}, g/cm^3	1.281	1.315
μ, mm^{-1}	0.67	0.68
radiation	Mo Kα	Mo Kα
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
h,*k*,*l* ranges	$-9 < h < 9$ $0 < k < 12$ $-14 < l < 14$	$-10 < h < 10$ $0 < k < 10$ $0 < l < 17$
no. reflns measd	3618	2845
no. unique reflns	3358	2703
no. observations	2774[$I_o < 2.5\sigma(I_o)$]	1732[$I_o < 2.5\sigma(I_o)$]
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
R^a	0.040	0.048
$R_w{}^b$	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.

1Ph: mp 179–180 °C (lit.[8a] mp 172 °C); IR (CH_2Cl_2) ν_{CO} 1969 (s), 1909 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.63 (b, 2H), 3.88 (b, 1H), 5.18 (b, 2H), 6.91–7.42 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 55.2 (s, —CH=*C*HCHPh—), 59.7 (s, —CH=CH*C*HPh—), 82.5 (s, —*C*H=CHCHPh—), 128.0–147.7 (m, Ph), 219.4 (d, $^2J_{P-C}$ = 15.1 Hz, CO); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 73.21 (s); MS (*m/z*) M$^+$ 516 (parent ion). Anal. Calcd for $C_{31}H_{25}FeO_2P$: C, 72.11; H, 4.88. Found: C, 72.01; H, 4.70.

2PH: mp 170–171 °C (lit.[12] mp 164 °C); IR (CH_2Cl_2) ν_{CO} 1919 (s), 1558 (m) cm^{-1}; ^{31}P{^{1}H} NMR ($CDCl_3$) δ 75.42 (s); IR (CH_2Cl_2) ν_{CO} 1919 (s), 1558 (m) cm^{-1}; MS (*m/z*) M$^+$ 516 (parent ion). Anal. Calcd for $C_{31}H_{25}FeO_2P$: C, 72.11; H, 4.88. Found: C, 71.98; H, 5.10.

Preparation of (η^5-C_5H_5)Fe(CO)(η^1-dppf)C(O)Me. (η^5-C_5H_5)Fe(CO)$_2$Me (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 (SiO_2, 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)

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)

complex (η^5-C_5H_5)Fe(CO)(η^1-dppf)C(O)Me (0.49 g, 40%) and the byproduct [(η^5-C_5H_5)Fe(CO)C(O)Me]$_2$(μ,η^1,η^1-dppf) (6.19 mg, 0.4%).

(η^5-C_5H_5)Fe(CO)(η^1-dppf)C(O)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 $C_{42}H_{36}O_2Fe_2P_2$: C, 67.59; H, 4.86. Found: C, 67.18; H, 4.88.

[(η^5-C_5H_5)Fe(CO)C(O)Me]$_2$(μ,η^1,η^1-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 $C_{50}H_{44}O_4Fe_3P_2$: C, 64.0; H, 4.73. Found: C, 63.84; H, 4.93.

Preparation of [(η^5-C_5H_5)Fe(CO)C(O)Me](μ,η^1,η^1-dppf)-[(η^4-*exo*-MeC_5H_5)Fe(CO)$_2$]. (η^5-C_5H_5)Fe(CO)(η^1-dppf)C(O)Me (1.493 g, 2 mmol) and (η^5-C_5H_5)Fe(CO)$_2$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 [(η^5-C_5H_5)Fe(CO)C(O)Me](μ,η^1,η^1-dppf)[(η^4-*exo*-MeC_5H_5)Fe(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}; ^{1}H NMR ($CDCl_3$) δ 0.26 (b, 3H, *Me*), 2.11 (b, 2H, —CH=C*H*CHMe—), 2.44 (b, 3H, C(O)*Me*), 2.56 (b, 1H, —CH=CHC*H*Me—), 3.83 (b, 8H, $C_5\mathit{H}_4$), 4.21 (b, 5H, $C_5\mathit{H}_5$), 4.92 (b, 2H, —C*H*=CHCHMe), 7.30 (b, 20H, Ph); ^{13}C NMR ($CDCl_3$) δ 28.0 (s, *Me*), 50.7 (s, —CH=CH*C*HMe—), 51.9 (s, C(O)*Me*), 57.7 (s, —CH=*C*HCHMe—), 72.8–81.5 (m, C_5H_4), 82.2 (s, —*C*H=CHCHMe—), 85.2 (s, C_5H_5), 127.6–133.6 (m, Ph), 220.1 (d, $^2J_{P-C}$ = 15.1 Hz, CO), 275.7 (s, —*C*(O)Me); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 71.26 (s), 67.24 (s); MS (*m*/*z*) M$^+$ 938 (parent ion). Anal. Calcd for $C_{50}H_{44}Fe_3O_4P_2$: 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 Kα radiation; 25 high-angle reflections were used in a least-squares fit to obtain accurate cell constants. Diffraction intensities were collected up to $2\theta < 45°$ 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 $I_o > 2.5\sigma(I_o)$ 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 methods[30] and refined by a full-matrix least-squares routine[31] 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.

---

(30) Main, P. In *Crystallographic Computing* 3: *Data Collection, Structure Determination, Proteins and Databases*; Sheldrick, G. M., Krueger, C., Goddard, R., Eds.; Charendon Press: Oxford, 1985; pp 206–215.

(31) (a) Gabe, E. J.; Le Page, Y.; White, P. S.; Lee, F. L. *Acta Cystallogr.* 1987, *A43*, S294. (b) Gabe, E. J.; Le Page, Y.; Lee, F. L. In *Crystallographic Computing* 3: *Data Collection, Structure Determination, Proteins and Databases*; Sheldrick, G. M., Krueger, C., Goddard, R., Eds.; Charendon Press: Oxford, 1985, pp 167–174.

(32) Ibers, J. A.; Hamilton, W. C. *International Tables for X-ray Crystallography*, Vol. 4; Kynoch: Birmingham (Current distributor D. Reidel, Dordrecht), 1974; Tables 2.2A, 2.3.1D.

Acknowledgment. The partial financial support from the National Science Council, R.O.C., is acknowledged. We thank Mr. Y.-S. Wen for assistance with single-crystal X-ray diffraction data collection. We also thank Ms. M.-M. Chen for detection of $^{31}P\{^1H\}$ NMR spectra using a MSL200 spectrometer.

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.

OM940200H