Fourteen-Electron Organoiron Species: Synthesis and Characterization of High-Spin Iron(II) Alkyls and the Crystal Structure of the Benzyl Derivative $Fe(CH_2C_6H_4CH_3)_2$(dippe)

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The four-coordinate iron phosphine complex $FeBr_2$(dippe) (dippe = 1,2-bis(diisopropylphosphino)ethane) can be alkylated with Grignard or dialkylmagnesium reagents to give the unusual 14-electron iron(II) alkyls FeR_2(dippe) (R = CH_2SiMe_3, CH_2CMe_3, CH_2CMe_2Ph, CH_2Ph, $CH_2C_6H_4Me$). With bulky alkyl groups or with proper control of stoichiometry, the monoalkyl species $Fe(C_6H_2Me_3)Br$(dippe) and $Fe(CH_2CMe_3)Br$(dippe) may be obtained. All of these four-coordinate alkyls possess magnetic moments characteristic of high-spin species ($\mu = 4.9\ \mu_B$) and exhibit large contact shifts in their ^1H NMR spectra. An X-ray crystal structure of the *p*-methylbenzyl complex $Fe(CH_2C_6H_4Me)_2$(dippe) reveals a distorted tetrahedral geometry, with C–Fe–C and P–Fe–P angles of 111.8 (2)° and 83.33 (7)°. The Fe–C distances of 2.120 (6) Å show little change from low-spin iron(II) species, while the Fe–P distances of 2.462 (2) Å are greatly lengthened. Despite the low electron count, there are no Fe···H···C interactions or Fe···C contacts to benzylic positions in the *p*-methylbenzyl groups, and this fact may be accounted for on electronic grounds, although steric effects may also play a part. Specifically, the lack of empty d orbitals in these high-spin alkyls inhibits "agostic" interactions, despite the low electron counts. This behavior is consistent with the observation that the iron alkyls are incapable of olefin insertion processes that would lead to Ziegler–Natta catalytic activity. X-ray crystallographic data for $Fe(CH_2C_6H_4Me)_2$(dippe) at 25 °C: monoclinic, space group $C2/c$, $a = 8.957$ (2) Å, $b = 15.620$ (5) Å, $c = 22.510$ (8) Å, $\beta = 98.20$ (2)°, $V = 3117$ (2) Å^3, $Z = 4$, $R = 5.2\%$, and $R_w = 5.8\%$ for 1234 data and 151 variables.

Introduction

The synthesis and chemistry of coordinately unsaturated transition metal complexes represent a major focus of our research. While the vast majority of organo-transition-metal complexes are diamagnetic and obey the 18-electron rule, paramagnetic and coordinately unsaturated organometallic species have received relatively little attention, despite their importance in at least one industrial process, Ziegler–Natta catalysis.[1,2] Indeed, it is interesting to speculate how the presence of unpaired electrons in Ziegler–Natta catalysts such as Ti^{III} alkyls might facilitate the insertion of olefins into metal–carbon bonds.[3]

For the transition-metal iron, few organometallic complexes are known that possess unpaired electrons. The most common are the ferrocinium salts and their substituted derivatives,[4-8] closely related π-arene species such as $Fe(C_6Me_6)_2$ and $[Fe(C_6Me_6)_2{}^+]$,[9,10] the porphyrin complexes Fe(tpp)R,[11,12] and some analogous tetraaza macrocycle complexes Fe(L)R.[13,14] In addition, the paramagnetic bipyridine complexes $[FeR_2(bpy)_2{}^+]$ can be prepared by electrochemical oxidation from their Fe^{II} analogues and have been shown to undergo facile decomposition at 30 °C.[15] All these species are low-spin and possess electron counts of 15 or higher. The only high-spin organoiron species that have been reported are the Schiff base complex $Fe^{III}(CH_2Ph)$(salen),[16] and some recent Fe^{III} porphyrins with pseudohalogen substituents such as C_6F_5.[12]

We now describe the synthesis and characterization of a unique series of new organoiron complexes that are high spin (four unpaired electrons per iron center) and that have electron counts of 14. These unusual complexes are obtained through the use of bulky phosphine ligands that severely limit the coordination number and ensure coordinative unsaturation at the metal center.

Results

Synthesis of FeR_2(dippe) Complexes. Ferrous halides react with 1,2-bis(diisopropylphosphino)ethane (dippe) to give the tetrahedral, high-spin adducts FeX_2(dippe) (X = Cl, Br, I).[17] These species may be alkylated with Grignard or dialkylmagnesium reagents to give unique 14-electron organoiron(II) complexes **1**–**5**. Physical properties for these new organometallic species are given in Table I.

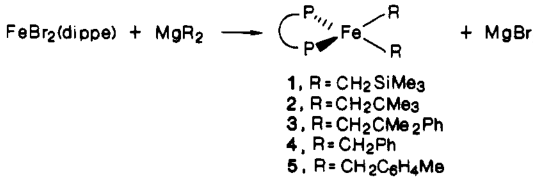

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Table I. Physical and Microanalytical Data for the New Iron Complexes

compd	color	mp, °C	calcd C	calcd H	found C	found H
$Fe(CH_2SiMe_3)_2(dippe)$	yellow	104 dec	53.6	11.1	53.8	11.2
$Fe(CH_2CMe_3)_2(dippe)$	yellow	128 dec	61.6	11.8	61.2	11.5
$Fe(CH_2CMe_2Ph)_2(dippe)$	yellow-orange	115 dec	68.5	10.4	67.7	10.0
$Fe(CH_2Ph)_2(dippe)$	red-orange	137 dec	67.2	9.3	66.0	9.0
$Fe(CH_2C_6H_4Me)_2(dippe)$	red	120 dec	68.2	9.5	66.8	9.4
$Fe(C_6H_2Me_3)Br(dippe)$	yellow	150 dec	53.4	8.4	53.4	8.3[a]
$Fe(CH_2CMe_3)Br(dippe)$	orange	125–128	48.6	9.2	48.4	9.9[b]

[a] Br: calcd, 15.5; found, 15.7. [b] Br: calcd, 17.0; found, 16.5.

Table II. ^1H NMR Data for the Paramagnetic Iron Compounds[a]

compd	P*CH*Me$_2$	P*CH$_2$*	PCH*Me$_2$*	alkyl resonances
$Fe(CH_2SiMe_3)_2(dippe)$	98.6 (910)	64.3 (580)	11.0 (600) 1.2 (670)	9.3 (400), Si*Me$_3$*
$Fe(CH_2CMe_3)_2(dippe)$	86.9 (780)	67.9 (500)	9.4 (500) 2.5 (470)	23.2 (500), C*Me$_3$*
$Fe(CH_2Ph)_2(dippe)$	91.9 (610)	65.9 (740)	11.0 (470) 2.0 (500)	35.3 (85), *m-H* −57.5 (500), *o-H* −74.7 (100), *p-H*
$Fe(CH_2C_6H_4Me)_2(dippe)$	93.1 (810)	67.0 (560)	11.1 (500) 1.6 (500)	83.2 (70), *p-Me* 35.7 (110), *m-H* −58.3 (810), *o-H*
$Fe(CH_2CMe_3)Br(dippe)$	161.7 (730) 102.5 (485)	51.6 (540) 29.6 (560)	12.2 (600) 8.7 (490) 3.1 (545) −4.8 (440)	35.0 (590), C*Me$_3$*

[a] C_6D_6 at 25 °C. Figures in parentheses are full widths at half-maximum. Chemical shifts in ppm.

These hydrocarbon-soluble complexes range in color from bright yellow to red and are air- and moisture-sensitive. Magnetic susceptibility measurements in toluene at room temperature by Evans' method indicate that these organometallic species adopt high-spin d^6 electronic configurations, with $\mu_{eff} = 4.9\ \mu_B$, corresponding to four unpaired electrons. The high-spin nature of the FeR_2(dippe) complexes is strong evidence for a tetrahedral geometry, since the square-planar species *trans*-$Fe(C_6Cl_5)_2(PEt_2Ph)_2$ is known to be low spin in the solid state.[18]

The ^1H NMR spectra of the new iron alkyl complexes (Table II) show phosphine resonances[19] at ca. δ 90 (P*CH*Me$_2$) and 65 (P*CH$_2$*) and two peaks in the δ 0–10 region for the diastereotopic methyl groups of the isopropyl substituents. The alkyl ligand resonances also vary over a large range. In general, the protons on the α-carbon atoms are not observable, evidently due to the large contact shifts resulting from their proximity to the paramagnetic center. The ^1H NMR spectrum of the *p*-methylbenzyl complex **5** is representative and is shown in Figure 1. The resonances at δ 83.2 (*p*-Me), 35.7 (*m*-H), and δ −58.3 (*o*-H) may be assigned to the aromatic ring substituents. These large shifts, particularly of the para methyl group, indicate significant delocalization of spin density into the benzyl π-system. All the NMR data are consistent with a tetrahedral disposition of ligands about the iron center.

Attempts to obtain ^{13}C and ^{31}P NMR spectra for these compounds were unsuccessful due to the paramagnetism, and all are EPR silent in frozen toluene glasses at −196 °C and in solution at room temperature.

Structure of $Fe(CH_2C_6H_4Me)_2(dippe)$ (5). Single crystals of the *p*-methylbenzyl complex **5** were obtained by cooling saturated toluene solutions to −20 °C; this

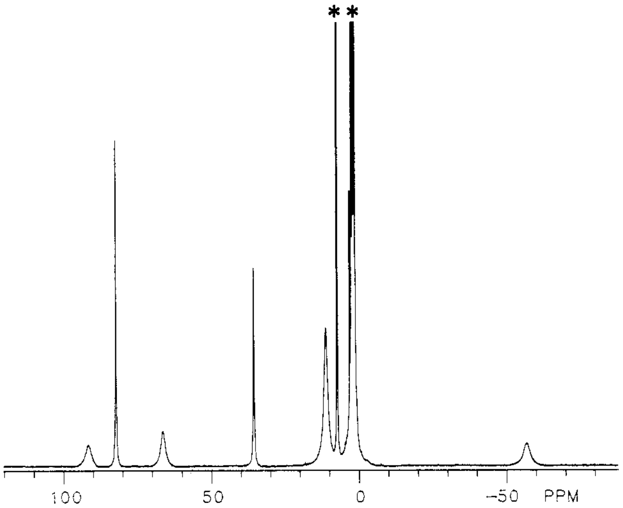

Figure 1. ^1H NMR spectrum of $Fe(CH_2C_6H_4Me)_2(dippe)$ in C_6D_6 at 25 °C. Assignments given in Table II. Asterisks indicate off-scale peaks due to solvent and trace amounts of free dippe. A base line corrected spectrum is shown.

Table III. Crystal Data at 25 °C

space group: *C*2/*c*	$V = 3117\ (2)\ Å^3$
$a = 8.957\ (2)\ Å$	$Z = 4$
$b = 15.620\ (5)\ Å$	mol wt = 528.52
$c = 22.510\ (8)\ Å$	$d_{calcd} = 1.126\ g\ cm^{-3}$
$\beta = 98.20\ (2)°$	$\mu_{calcd} = 5.98\ cm^{-1}$
$\alpha = \gamma = 90°$	size = 0.12 × 0.28 × 0.35 mm

diffractometer: Enraf-Nonius CAD-4
radiation: Mo K$\bar{\alpha}$, $\bar{\lambda} = 0.71073$ Å
monochromator: graphite crystal, $2\theta = 12°$
scan range, type: $2.0 \leq 2\theta \leq 53.0°$, ω/θ
scan speed, width: 3–16° min^{-1}, $\Delta\omega = 1.50(1.00 + 0.35 \tan \theta)°$
rflctns: 3647, 3327 unique, 1234 with $I > 2.58\sigma(I)$
internal consistency: $R_i = 2.0\%$

$R = 5.2\%$	variables = 151
$R_w = 5.8\%$	*p* factor = 0.03

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[19] Assignments of ^1H NMR resonances due to the phosphine ligands were made by comparisons with the corresponding FeX_2(dippe) halo complexes. The P*CH*Me$_2$ methine and P*CH$_2$* methylene resonances were distinguished by selectively deuteriating the methine positions and noting the disappearance of the peak at ca. δ 90.[17]

Table IV. Final Atomic Coordinates for $Fe(CH_2C_6H_4Me)_2(dippe)$

	x/a	y/b	z/c
Fe	0.0000	0.03613 (8)	0.2500
P1	0.0601 (2)	0.1539 (1)	0.32215 (8)
C1	−0.1921 (6)	−0.0400 (4)	0.2580 (3)
C2	−0.2610 (8)	−0.0629 (4)	0.1942 (4)
C3	−0.4041 (8)	−0.0350 (5)	0.1688 (4)
C4	−0.4708 (9)	−0.0556 (5)	0.1113 (4)
C5	−0.397 (1)	−0.1042 (5)	0.0742 (4)
C6	−0.256 (1)	−0.1328 (5)	0.0972 (5)
C7	−0.1881 (9)	−0.1134 (5)	0.1549 (4)
C8	−0.468 (1)	−0.1266 (6)	0.0117 (4)
C9	−0.0070 (7)	0.2534 (4)	0.2832 (3)
C10	0.2588 (7)	0.1768 (4)	0.3512 (3)
C11	0.3524 (8)	0.1871 (5)	0.2997 (3)
C12	0.2844 (9)	0.2535 (5)	0.3938 (3)
C13	−0.0333 (9)	0.1540 (5)	0.3900 (3)
C14	−0.2035 (9)	0.1389 (6)	0.3731 (4)
C15	0.035 (1)	0.0859 (6)	0.4336 (4)
H1a	−0.2621	−0.0088	0.2776
H1b	−0.1632	−0.0906	0.2801
H3	−0.4584	0.0004	0.1926
H4	−0.5696	−0.0356	0.0973
H6	−0.2022	−0.1669	0.0724
H7	−0.0901	−0.1350	0.1686
H8a	−0.5652	−0.1015	0.0035
H8b	−0.4763	−0.1871	0.0079
H8c	−0.4063	−0.1055	−0.0162
H9a	0.0505	0.2998	0.3017
H9b	−0.1102	0.2611	0.2874
H10	0.2916	0.1280	0.3747
H11a	0.3363	0.1393	0.2735
H11b	0.4563	0.1906	0.3157
H11c	0.3229	0.2380	0.2781
H12a	0.2261	0.2467	0.4256
H12b	0.2548	0.3045	0.3723
H12c	0.3882	0.2570	0.4099
H13	−0.0180	0.2081	0.4090
H14a	−0.2445	0.1820	0.3458
H14b	−0.2509	0.1413	0.4082
H14c	−0.2205	0.0843	0.3548
H15a	0.1405	0.0960	0.4436
H15b	0.0194	0.0311	0.4156
H15c	−0.0110	0.0881	0.4690

compound was chosen for study since the unsubstituted benzyl derivative was unsuited for crystallographic studies. Crystal data are given in Table III, while final atomic coordinates and anisotropic thermal parameters are given with estimated standard deviations in Tables IV and V. Bond lengths and angles are presented with estimated standard deviations in Table VI.

The structural analysis shows that crystals of 5 are composed of discrete monomers of $Fe(CH_2C_6H_4Me)_2(dippe)$; a perspective view of the molecule is shown in Figure 2. The molecule possesses crystallographically imposed C_2 symmetry, where the C_2 axis bisects the C–Fe–C and P–Fe–P angles. The iron center adopts a distorted tetrahedral geometry, with a C–Fe–C angle of 111.8° and a P–Fe–P angle of 83.3°; these values reflect the steric bulk of the alkyl substituents and the chelating nature of the phosphine. The C–Fe–C and P–Fe–P planes are nearly perpendicular (dihedral angle of 85°), as required for a tetrahedral ligand array. The Fe–C bond lengths of 2.120 (6) Å are not significantly different from the 2.07–2.10 Å range reported[20-23] for Fe–C distances involving sp^3 alkyl ligands attached to diamagnetic iron(II) carbonyl complexes. In contrast, the Fe–P bonds of 2.462 (2) Å are intermediate between the 2.24–2.30-Å distances reported for octahedral low-spin iron(II) species, and the 2.53–2.71-Å distances found in octahedral high-spin complexes.[24,25] Undoubtedly, these variations in the Fe–P distances reflect the four- vs. six-coordinate metal centers and the signficantly decreased π-back-bonding to the phosphine ligands in high-spin compounds.

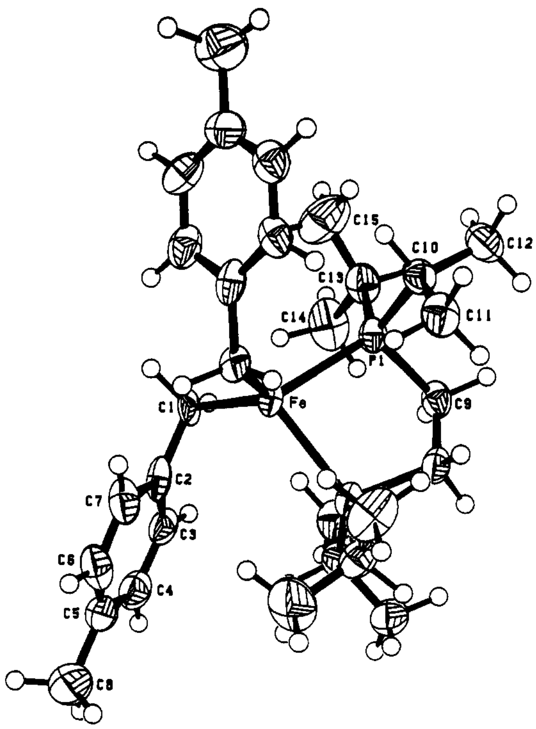

Figure 2. ORTEP diagram of $Fe(CH_2C_6H_4Me)_2(dippe)$. Thermal ellipsoids are drawn at the 35% probability level.

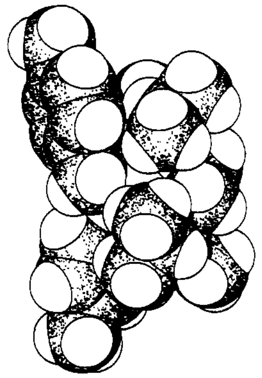

Figure 3. Space-filling SCHAKAL diagram of $Fe(CH_2C_6H_4Me)_2(dippe)$, showing contact of the aromatic ring with the isopropyl groups of the dippe ligand.

Other structural features of interest in $Fe(CH_2C_6H_4Me)_2(dippe)$ and in benzyl complexes in general are the M–C_α–C_{ipso} angles and the M···C_{ipso} and M···C_{ortho} contacts. The literature contains many examples of benzyl complexes with small M–C–C angles and short M···C contacts indicative of π-interactions of the benzyl unit with a coordinately unsaturated metal center.[26-36] In some

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Table V. Anisotropic Thermal Parameters for $Fe(CH_2C_6H_4Me)_2(dippe)$

	$U(11)$ or U_{iso}, Å	$U(22)$	$U(33)$	$U(23)$	$U(13)$	$U(12)$
Fe	0.0445 (8)	0.0336 (7)	0.067 (1)	0.000	0.0158 (7)	0.000
P1	0.052 (1)	0.042 (1)	0.067 (1)	−0.0051 (9)	0.0143 (10)	0.0022 (9)
C1	0.042 (4)	0.038 (3)	0.089 (5)	−0.001 (4)	−0.011 (4)	−0.019 (3)
C2	0.051 (5)	0.037 (4)	0.118 (7)	0.006 (4)	0.032 (5)	−0.010 (3)
C3	0.063 (5)	0.049 (4)	0.098 (6)	0.009 (5)	0.023 (4)	−0.007 (4)
C4	0.080 (6)	0.068 (6)	0.086 (6)	0.013 (5)	0.002 (5)	−0.015 (5)
C5	0.106 (8)	0.069 (6)	0.070 (6)	0.009 (5)	0.009 (6)	−0.032 (5)
C6	0.092 (7)	0.071 (6)	0.097 (7)	−0.022 (5)	0.027 (6)	−0.026 (5)
C7	0.062 (5)	0.056 (5)	0.127 (8)	−0.010 (5)	0.007 (5)	−0.007 (4)
C8	0.17 (1)	0.122 (8)	0.082 (7)	0.013 (6)	0.015 (7)	−0.045 (8)
C9	0.057 (5)	0.045 (4)	0.082 (5)	−0.008 (3)	0.002 (4)	0.006 (4)
C10	0.058 (5)	0.058 (4)	0.076 (5)	−0.003 (4)	−0.004 (4)	0.000 (4)
C11	0.052 (5)	0.082 (6)	0.117 (7)	0.003 (5)	0.009 (5)	−0.002 (4)
C12	0.089 (6)	0.081 (6)	0.096 (6)	−0.017 (5)	−0.019 (5)	−0.002 (5)
C13	0.091 (6)	0.073 (5)	0.073 (5)	−0.014 (4)	0.033 (5)	−0.007 (5)
C14	0.098 (7)	0.117 (7)	0.121 (7)	−0.025 (6)	0.071 (6)	−0.024 (6)
C15	0.19 (1)	0.133 (9)	0.102 (7)	0.034 (7)	0.069 (7)	0.024 (8)
H	0.111 (6)					

Table VI. Selected Bond Distances (Å) and Angles (deg) in $Fe(CH_2C_6H_4Me)_2(dippe)$

	Bond Distances		
Fe–C1	2.120 (6)	C2–C7	1.41 (1)
Fe–P1	2.462 (2)	C6–C7	1.39 (1)
Fe···C2	2.932 (7)	C5–C8	1.50 (1)
C1–C2	1.52 (1)	P1–C9	1.844 (6)
C2–C3	1.40 (1)	P1–C10	1.842 (7)
C3–C4	1.38 (1)	P1–C13	1.842 (8)
C4–C5	1.37 (1)	C9–C9′	1.518 (9)
C5–C6	1.37 (1)		
	Bond Angles		
C1–Fe–C1′	111.8 (2)	C2–C3–C4	124.0 (7)
P1–Fe–P1′	83.33 (7)	C3–C4–C5	121.3 (8)
P1–Fe–C1	117.8 (2)	C4–C5–C6	116.7 (8)
P1–Fe–C1′	111.8 (2)	C4–C5–C8	121.7 (9)
Fe–C1–C2	106.0 (4)	C6–C5–C8	121.6 (9)
C1–C2–C3	122.6 (6)	C5–C6–C7	122.7 (8)
C1–C2–C7	124.0 (6)	C2–C7–C6	121.9 (8)
C3–C2–C7	113.4 (7)		

cases, M–C–C angles of as little as 88° and M···C contacts of 2.6 Å to the ipso carbon have been observed. Despite the coordinative unsaturation of the iron *p*-methylbenzyl complex, the Fe–C–C angle of 106° and the Fe···C_{ipso} contact of 2.93 Å indicate that no extensive π-interactions are present, much as in the tin complex $Sn(CH_2Ph)_4$, where the Sn–C–C angles are 110–114°.[29] A space-filling SCHAKAL diagram of $Fe(CH_2C_6H_4Me)_2(dippe)$ (Figure 3) reveals a moderately crowded coordination sphere about the iron center that evidently prevents the *p*-methylbenzyl ligands from more closely approaching the metal. In particular, the π-systems of the benzyl groups contact the van der Waals surface of the isopropyl hydrogen atoms of the phosphine. The C···H distances of 2.8–3.0 Å are consistent with the 2.9-Å distance expected from the sum of the van der Waals radius of a hydrogen atom and the half-thickness of an aromatic ring.[37]

Coordinately unsaturated complexes are known in some instances to possess "agostic" M···H–C interactions to α-protons on alkyl substituents.[38] Unfortunately, the hydrogen atoms in $Fe(CH_2C_6H_4Me)_2(dippe)$ could not be located with certainty, since the peaks in the difference Fourier maps were poorly defined and the hydrogen atom positions could not be refined successfully. However, there is spectroscopic evidence that no M···H–C contacts are present, since the IR spectra of $Fe(CH_2C_6H_4Me)_2(dippe)$ and the other $FeR_2(dippe)$ alkyls do not show any low-energy ν_{C-H} absorptions in the 2350–2700 cm^{-1} region characteristic of "agostic" interactions.[38] Furthermore, there are theoretical grounds for expecting that these four-coordinate Fe^{II} alkyls should not exhibit M···H–C contacts (see below).

Overall, the structure of $Fe(CH_2C_6H_4Me)_2(dippe)$ may be compared with that of the manganese alkyl $Mn(CH_2CMe_2Ph)_2(PMe_3)_2$, which is also tetrahedral and high spin.[39] The Mn–C distance of 2.149 (6) Å in this molecule is only 0.03 Å longer than in the present iron complex, and this difference may be accounted for completely by the 0.03-Å difference in the ionic radii of Mn and Fe. In contrast, the Mn–P distance of 2.633 (4) Å is some 0.17 Å longer than in the iron alkyl. This much larger difference is unlikely to arise from weaker π-back-bonding to the phosphine ligand in a d^5 vs. a d^6 metal complex; instead the difference probably reflects weaker σ-bonding to the less basic PMe_3 group vs. the more basic bidentate dippe ligand.

Synthesis of FeRX(dippe) Complexes. Iron monoalkyl species are undoubtedly intermediates in the pathway leading to the $FeR_2(dippe)$ complexes, and these intermediates can in fact be isolated either with use of very bulky groups or by proper control of stoichiometry. With the bulky mesityl (2,4,6-trimethylphenyl) ligand, only the monoaryl derivative $Fe(C_6H_2Me_3)Br(dippe)$ can be obtained even with excess alkylating agent. By contrast, isolation of the mononeopentyl complex depends on strict control of stoichiometry; addition of only 0.5 equiv of

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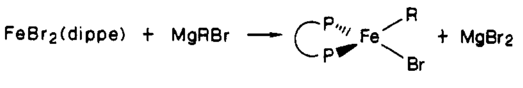
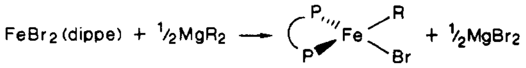


6, R = $C_6H_2Me_3$



7, R = CH_2CMe_3

dineopentylmagnesium to FeBr$_2$(dippe) gives Fe(CH$_2$CMe$_3$)Br(dippe).

The FeRBr(dippe) complexes are yellow to orange, air-sensitive species that are high spin like their dialkyl analogues. The ^{1}H NMR spectrum of the mesityl derivative was not obtainable due to its insolubility; however, the ^{1}H NMR spectrum of the neopentyl complex reflects a lowering of symmetry from C_{2v} in the dialkyls to C_s symmetry, showing two backbone CH$_2$ resonances, two isopropyl CH resonances, and four isopropyl CH$_3$ resonances. Infrared data again suggest that no "agostic" interactions are present in these molecules.

Discussion

Organometallic compounds are only very rarely high spin—they are most commonly low spin and diamagnetic when possible. This is a natural consequence of the strong field nature of typical organometallic ligands such as carbon monoxide, the cyclopentadienyl anion, organic isocyanides, and alkyl groups. For example, iron(II) alkyls with sterically small phosphine ligands such as PMe$_3$ or dmpe [1,2-bis(dimethylphosphino)ethane] are invariably six-coordinate and diamagnetic,[40,41] although a five-coordinate alkyl, FeMe$_2$(PPh$_3$)$_3$, has been reported.[42] In contrast, the present 14-electron organoiron(II) complexes are tetrahedral, and the small crystal field splittings characteristic of tetrahedral geometries favor high-spin electronic configurations. Indeed, only two low-spin tetrahedral complexes of the first-row transition elements are known: Fe(nor)$_4$ and Co(nor)$_4$ (nor = 1-norbornyl).[43]

The X-ray structure of the benzyl derivative Fe(CH$_2$C$_6$H$_4$Me)$_2$(dippe) shows that no "agostic" interactions involving the aromatic π-system or the α-hydrogen atoms are present. Two factors militate against such interactions. First, the high-spin configuration means that no empty d orbitals are present to participate in a three-center two-electron bond with a filled C–H bonding orbital. Second, extended Hückel calculations have suggested that "agostic" interactions are not possible in tetrahedral geometries, irrespective of the electron configuration.[44] The experimental observation that no M···H–C contacts are present in the 14-electron FeR$_2$(dippe) complexes is of considerable importance, since it emphasizes that the conventional gauges of unsaturation about a transition metal, the coordination number, and the electron count are not necessarily correlated with structure and reactivity. The electronic configuration and the presence or absence of suitable empty orbitals must be considered as well.

It has been proposed that the presence of three-center M···H–C interactions is a prerequisite for facile olefin insertion into metal–carbon bonds.[38,45,46] Although a 1:1 correlation between "agostic" interactions and Ziegler–Natta activity has not been definitely established, the 14-electron FeR$_2$(dippe) complexes do not react with ethylene at 25 °C and 10 atm and thus lend support to this proposal. In this context, it is interesting to note that the 18-electron FeR$_2$(bpy)$_2$ compounds are also unreactive toward ethylene, although activated olefins such as acrylonitrile and methyl methacrylate are rapidly polymerized.[47,48]

We are continuing to explore the chemistry of the FeR$_2$(dippe) species; reactions of these high-spin organoiron complexes with carbon monoxide and hydrogen will be reported separately.

Experimental Section

All operations were carried out under vacuum or under argon. Solvents were distilled under nitrogen from sodium (toluene) or sodium benzophenone (pentane, diethyl ether, tetrahydrofuran) immediately before use. 1,2-Bis(diisopropylphosphino)ethane was prepared via a literature route.[49] Dialkylmagnesium[50] and Grignard reagents were prepared from the alkyl halides and used as stock solutions in diethyl ether or tetrahydrofuran. The halo complexes FeX$_2$(dippe) were prepared as described elsewhere.[17]

Microanalyses were performed by Mr. Josef Nemeth of the University of Illinois Microanalytical Laboratory. The IR spectra were recorded on a Perkin-Elmer 599B as Nujol mulls. The ^{1}H NMR data were recorded on a Perkin-Elmer R24-B instrument at 60 MHz or on a General Electric QE-300 at 300 MHz. Chemical shifts are uncorrected for the paramagnetic shift of the solvent. The X-band EPR experiments were performed on a Varian E-9 instrument using frozen toluene solutions at −196 °C. Magnetic moments were determined by a modification of Evans' method.[51] Melting points were determined on a Thomas-Hoover Unimelt apparatus in closed capillaries under argon.

1. **Bis[(trimethylsilyl)methyl][1,2-bis(diisopropylphosphino)ethane]iron(II).** To a cold (−78 °C) suspension of FeBr$_2$(dippe) (1.0 g, 2.1 mmol) in diethyl ether (30 mL) was added bis[(trimethylsilyl)methyl]magnesium (3.0 mL of a 0.79 M solution in diethyl ether, 2.4 mmol). The solution turned bright yellow immediately. After being stirred 20 min, the reaction was warmed to room temperature and the ether removed in vacuo. The residue was extracted with pentane (50 mL), and the filtered solution was concentrated to ca. 15 mL. Cooling to −20 °C resulted in formation of large yellow prisms. Additional crops were obtained from the supernatant. Yield: 0.60 g (58%). Magnetic moment (Evans' method, toluene, 25 °C): 4.9 μ_B. IR (cm^{-1}): 2715 w, 1412 w, 1408 w, 1363 s, 1298 w, 1275 w, 1243 s, 1230 s, 1151 m, 1090 m, 1070 sh, 1022 s, 915 sh, 860 s, 810 s, 785 sh, 737 s, 712 s, 668 s, 649 s, 600 w, 467 s, 431 m.

2. **Dineopentyl[1,2-bis(diisopropylphosphino)ethane]iron(II).** To a cold (−78 °C) suspension of FeBr$_2$(dippe) (0.40 g, 0.84 mmol) in diethyl ether (25 mL) was added dineopentylmagnesium (7.0 mL of a 0.15 M solution in diethyl ether, 1.0 mmol). The solution turned bright yellow immediately. After being stirred for 20 min, the reaction mixture was warmed to room temperature, the ether was removed in vacuo, and the residue was extracted with pentane (60 mL). The filtered solution was concentrated to ca. 40 mL and cooled to −20 °C to yield yellow needles. A second crop was obtained from the supernatant. Yield: 0.28 g (72%). IR (cm^{-1}): 2800 w, 2740 w, 1415 w, 1410 w, 1382 s, 1349 s, 1297 w, 1258 w, 1240 sh, 1227 s, 1201 m, 1152 w, 1090

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m, 1037 m, 1020 m, 990 w, 980 w, 917 m, 895 w, 877 s, 840 m, 775 m, 734 m, 715 w, 673 s, 649 s, 598 w, 575 w, 544 m, 455 w, 438 w.

3. **Bis(2-methyl-2-phenylpropyl)[1,2-bis(diisopropylphosphino)ethane]iron(II).** To a cold (0 °C) suspension of $FeBr_2$(dippe) (0.70 g, 1.5 mmol) in diethyl ether (30 mL) was added bis(2-methyl-2-phenylpropyl)magnesium (6.0 mL of a 0.29 M solution in diethyl ether, 1.7 mmol). The solution turned yellow-orange as the solid dissolved. After being stirred for 20 min, the reaction was warmed to room temperature and the ether removed in vacuo. The residue was extracted with toluene (30 mL), and the filtered solution was concentrated to ca. 20 mL. Cooling to −20 °C resulted in formation of yellow-orange prisms that turned opaque on drying. Additional crops were obtained from the supernatant. Yield: 0.41 g (49%). Magnetic moment (Evans' method, toluene, 25 °C): 4.7 μ_B. IR (cm^{-1}): 3070 m, 3040 m, 3000 w, 2790 m, 2728 m, 1950 w, 1932 w, 1868 w, 1850 w, 1785 w, 1725 w, 1655 w, 1595 s, 1572 m, 1523 w, 1488 s, 1420 sh, 1403 m, 1370 s, 1365 s, 1352 sh, 1287 m, 1255 m, 1230 s, 1185 m, 1170 m, 1150 m, 1100 m, 1090 m, 1025 s, 979 w, 953 w, 918 m, 890 m, 877 s, 840 m, 827 w, 785 s, 757 s, 701 m, 688 s, 672 s, 650 s, 584 m, 565 s, 455 s, 430 m, 395 w.

4. **Dibenzyl[1,2-bis(diisopropylphosphino)ethane]iron(II).** To a suspension of $FeBr_2$ (0.72 g, 3.3 mmol) in toluene (30 mL) was added dippe (0.9 mL, 3.3 mmol). After the solid dissolved, benzylmagnesium chloride (5.5 mL of a 1.38 M solution in diethyl ether, 7.6 mmol) was added. The solution turned red immediately and a red-orange solid formed. After being stirred for 2 h, the solution was filtered and the remaining solid was extracted in toluene (100 mL). The combined extracts were cooled to −20 °C to yield red-orange plates. Additional crops were obtained from the supernatant. The combined crops were recrystallized from toluene. Yield: 1.07 g (65%). IR (cm^{-1}): 3050 w, 3000 sh, 1925 w, 1589 s, 1565 sh, 1535 w, 1465 s, 1402 s, 1360 sh, 1323 w, 1295 m, 1260 w, 1237 m, 1201 s, 1171 s, 1152 w, 1148 w, 1090 w, 1040 sh, 1022 m, 995 w, 965 sh, 950 sh, 937 s, 879 m, 860 sh, 839 m, 825 w, 815 w, 785 s, 731 s, 689 s, 652 s, 600 w, 549 s, 521 m, 458 w, 420 s.

5. **Bis(*p*-methylbenzyl)[1,2-bis(diisopropylphosphino)ethane]iron(II).** To a suspension of $FeBr_2$ (1.64 g, 7.6 mmol) in toluene (50 mL) was added dippe (2.2 mL, 7.7 mmol). After the solid dissolved, (*p*-methylbenzyl)magnesium chloride (30 mL of 0.61 M solution in ether, 18.3 mmol) was added. The solution turned deep red immediately, and a red-orange crystalline solid formed. After being stirred for 1 h, the solution was filtered and the remaining solid was extracted in toluene (100 mL). The combined extracts were cooled to −20 °C to yield red plates. Additional crops were obtained from the supernatant. The combined crops were recrystallized from toluene. Yield: 2.65 g (66%). IR (cm^{-1}): 3040 w, 3005 sh, 2700 w, 1860 w, 1620 w, 1596 s, 1492 s, 1396 m, 1358 sh, 1300 w, 1288 w, 1275 w, 1255 w, 1229 m, 1212 w, 1200 sh, 1191 s, 1167 s, 1145 w, 1110 w, 1085 w, 1030 m, 1020 m, 1004 m, 949 s, 985 sh, 910 m, 870 m, 841 w, 815 w, 790 s, 723 s, 698 sh, 673 m, 647 s, 538 s, 518 m, 473 m, 426 s.

6. **Mesitylbromo[1,2-bis(diisopropylphosphino)ethane]iron(II).** To a cold (−78 °C) solution of $FeBr_2$(dippe) (0.72 g, 1.5 mmol) in tetrahydrofuran (30 mL) was added mesitylmagnesium bromide (3.5 mL of a 0.45 M solution in tetrahydrofuran, 1.5 mmol). After being stirred for 1 h at −78 °C, the yellow solution was warmed to 0 °C. The THF was removed in vacuo and the solid residue extracted with toluene (70 mL). The yellow-orange solution was filtered and concentrated to ca. 50 mL. Cooling to −20 °C resulted in the formation of yellow crystals. Further crops were obtained from the supernatant. Yield: 0.31 g (40%). IR (cm^{-1}): 2720 w, 1588 m, 1525 w, 1408 m, 1360 m, 1290 w, 1275 w, 1233 s, 1209 w, 1152 m, 1100 w, 1090 sh, 1071 w, 1023 s, 957 w, 922 w, 880 m, 841 s, 793 w, 715 w, 700 w, 680 m, 663 s, 655 s, 609 m, 578 w, 548 w, 535 w, 475 w, 420 w, 315 w.

7. **Neopentylbromo[1,2-bis(diisopropylphosphino)ethane]iron(II).** To a cold (−78 °C) suspension of $FeBr_2$(dippe) (1.0 g, 2.1 mmol) in diethyl ether (30 mL) was added dineopentylmagnesium (4.4 mL of a 0.24 M solution in ether, 1.06 mmol). The solution turned yellow as the $FeBr_2$(dippe) dissolved. After being stirred for 1 h, the reaction solution was warmed to 25 °C, stirred for 12 h, and the ether was removed in vacuo. The residue was extracted with pentane (150 mL), and the extract was filtered and concentrated to ca. 120 mL. Cooling to −20 °C resulted in the formation of orange prisms. A second crop was obtained from the supernatant. Yield: 0.60 g (62%). IR (cm^{-1}): 2723 w, 1422 m, 1391 s, 1363 s, 1298 w, 1263 w, 1245 s, 1238 s, 1221 w, 1168 w, 1116 w, 1093 w, 1056 m, 1038 m, 938 m, 893 m, 872, 814 m, 752 w, 728 w, 683 s, 674 s, 643 w, 626 w, 588 w, 551 m, 483 w, 471 w.

Crystallographic Studies. Single crystals of the *p*-methylbenzyl complex $Fe(CH_2C_6H_4Me)_2$(dippe), grown from toluene, were sealed in thin-walled capillaries under argon. Preliminary photographs yielded rough cell dimensions, and a suitable crystal was transferred to the diffractometer. Standard peak search and automatic indexing procedures followed by least-squares refinement using 25 reflections yielded the cell dimensions given in Table III.

Data were collected in one quadrant of reciprocal space ($-h,+k,\pm l$) by using measurement parameters listed in Table III. Systematic absences for hkl, $h + k \neq 2n$, and $h0l$, $l \neq 2n$ were consistent with space groups Cc or $C2/c$; the average values of the normalized structure factors suggested the centric choice $C2/c$, which was confirmed by successful refinement. The measured intensities were reduced to structure factor amplitudes and their estimated standard deviations by correction for background, scan speed, and Lorentz and polarization effects. While corrections for crystal decay were unnecessary, absorption corrections were applied, the maximum and minimum transmission factors being 0.934 and 0.858, respectively. Systematically absent reflections were eliminated, and symmetry-equivalent reflections were averaged to yield the set of unique data. Only those data with $I > 2.58\sigma(I)$ were used in the least-squares refinement.

The structure was solved by Patterson and weighted difference Fourier methods. The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, where $w = 1.59/(\sigma(R_o)^2 + (pF_o)^2)$. The analytical approximations to the scattering factors were used, and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion. The iron atom was constrained to lie on the 2-fold axis. In the final cycle of least squares, all non-hydrogen atoms were independently refined with anisotropic thermal coefficients, and a group isotropic thermal parameter was varied for the hydrogen atoms that were fixed in "idealized" positions, C–H = 0.95 Å. (Hydrogen atoms H1a and H1b had been located in the difference Fourier maps but were fixed in calculated positions due to the paucity of data. Attempted refinement of their positions did not converge in nine least-squares cycles.) Successful convergence was indicated by the maximum shift/error of 0.06 for the last cycle. Final refinement parameters are given in Table III. The final difference Fourier map had no significant features. There were no apparent systematic errors among the final observed and calculated structure factors.

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Registry No. **1**, 106905-31-1; **2**, 106905-32-2; **3**, 106905-33-3; **4**, 106905-34-4; **5**, 106928-93-2; **6**, 106905-35-5; **7**, 106905-36-6; $FeBr_2$(dippe), 106905-37-7; $FeBr_2$, 7789-46-0; bis[(trimethylsilyl)methyl]magnesium, 51329-17-0; dineopentylmagnesium, 19978-31-5; bis(2-methyl-2-phenylpropyl)magnesium, 62218-17-1; benzyl chloride, 100-44-7; *p*-methylbenzyl chloride, 104-82-5; mesityl bromide, 576-83-0.

Supplementary Material Available: Tables of final observed and calculated structure factors for $Fe(CH_2C_6H_4CH_3)_2$(dippe) (6 pages). Ordering information is given on any current masthead page.