Organometallics 1988, 7, 88–98

Electron-Rich Hydrocarbon–Metal Complexes: Synthesis and Electrochemical and NMR Studies of (η^4-Trimethylenemethane)- and (η^4-*o*-Xylylene)iron Complexes and Their One-Electron Oxidation, Paramagnetic Derivatives. X-ray Structure of the 17-Electron (η^4-Trimethylenemethane)tris(trimethylphosphine)iron(1+) Cation

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Received May 4, 1987

$Fe(\eta^4\text{-TMM})L_3$ complexes **3** (TMM is trimethylenemethane; L = PMe_3 (**a**), L = PMe_2Ph (**b**), L_3 = $MeC(CH_2PMe_2)_3$ (**c**)) were prepared directly from $FeCl_2$, via addition of $CH_2{=}C(CH_2Cl)_2$ to $FeCl_2L_2/L$ and magnesium in tetrahydrofuran (THF). NMR studies of **3** indicate that the presence of phosphine ligands L favors an electron transfer from the iron toward the methylene carbons of the TMM ligand. $Fe(\eta^4\text{-}o\text{-xylylene})L_3$ complexes **6a**, **6b**, and **6c** were prepared either by addition of *o*-$(ClMgCH_2)_2C_6H_4$ to $FeCl_2(PMe_3)_2$ (**1a**)/PMe_3, $FeCl_2(PMe_2Ph)_2$ (**1b**)/PMe_2Ph, and $FeCl_2(P(OMe)_3$ (**1c**) or by addition of *o*-$(ClCH_2)_2C_6H_4$ to a mixture of **1a**/PMe_3 or **1b**/PMe_2Ph and magnesium. Complexes **6a** and **6b** were also obtained from the reaction of *o*-$(BrMgCH_2)C_6H_4CH_3$ with **1a**/PMe_3 and **1b**/PMe_2Ph, via a process relevant to δ(C–H) activation, whereas the same reaction performed with **1c** led to the C–C bond formation product *o,o'*-$CH_3C_6H_4CH_2CH_2C_6H_4CH_3$. NMR studies of complexes **6** demonstrated that both exocyclic C=C double bonds of the *o*-xylylene ligand are bonded to the iron atom. **3b** reacted with FSO_3Me, to give **3b**$^+$, which was easily reduced into **3b** by hydride, and with $NOBF_4$, to give $Fe(NO)_2(PMe_2Ph)_2$ via **3b**$^+$. The 17-electron paramagnetic complexes **3a**$^+$($CF_3SO_3^-$) and **3b**$^+$($CF_3SO_3^-$) were isolated from the reaction of $Ag(CF_3SO_3^-)$ with **3a** and **3b**. The structure of **3a**$^+$($CF_3SO_3^-$) was determined at 128 K by an X-ray diffraction study [monoclinic, $P2_1/c$; a = 12.313 (2) Å; b = 11.016 (2) Å; c = 17.064 (3) Å; β = 103.1 (2)°; V = 2254.7 (6) Å^3; Z = 4; R = 0.026; R_w = 0.024] and showed a piano-stool geometry for the cation **3a**$^+$ with an umbrella shape of the η^4-TMM ligand. The paramagnetic ^1H NMR shifts (δ) were measured for **3a**$^+$ (−213.5), **3b**$^+$ (−215.1), and **6a**$^+$ (−50.1, −11.3, −4.8), the lesser distortion in the planarity of the hydrocarbon ligand in **6a**$^+$ than in **3**$^+$ being related to a smaller observed shift in **6a**$^+$ than in **3**$^+$. Electrochemical studies established the electron-rich nature of both complexes **3** and **6**: cyclic voltammetry showed a first *reversible* oxidation at low potential [$E_{1/2}$ (V vs ECS) = −0.450 (**3a**), −0.365 (**3b**), −0.655 (**3c**), −0.610 (**6a**), −0.510 (**6b**), −0.100 (**6c**)] followed by an irreversible oxidation. The first oxidation is a one-electron process (coulometry), takes place more easily with electron donor phosphorus ligands, and occurs at lower potential for **6** than for **3**.

Introduction

Electron-rich, hydrocarbon-metal complexes have become a topic of current interest because they provide unusual properties and allow novel chemical transformations to occur. Such complexes have led to the general observation that M–H–C_α intramolecular two-electron interactions[2] play an important role in the stabilization of coordinatively unsaturated species. Some examples of stabilization via a M–H–C_β intramolecular bond have also been described.[3] Moreover, evidence has been given for M–H–C three-electron intramolecular agostic interactions in stable paramagnetic systems.[4,5] Oxidative additions of an alkane C–H bond to a coordinatively unsaturated metal center is well-documented[6] and essentially takes place when the metal site is low-valent and is bonded to electron-donating ligands or belongs to the third row. It is noteworthy that recently novel fluxional processes,[7] radical-promoted reactions leading to stabilized 17-electron species,[4,8,9] and unusual rearrangements, such as olefin-hydride to alkylidene[10] or metal to carbon 1,2-hydride

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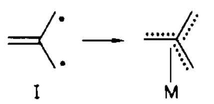
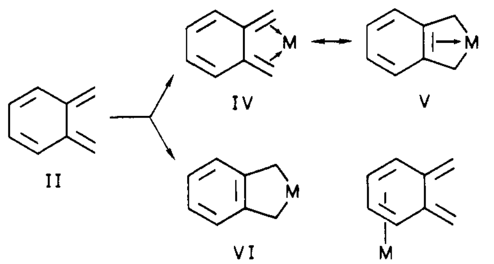
migrations,[11,12] have been observed in complexes that are rather easy to oxidize and that contain hydrocarbon ligands alone or with additional very basic ligands.

Most of the above phenomena involve complexes containing stable hydrocarbon–metal moieties, such as cyclopentadienyl–, pentadienyl–, allyl–, or arene–metal moieties. Their unusual properties have directed our interest toward the fixation of unstable hydrocarbon ligands to an electron-rich metal center: the trimethylenemethane (I) and the *o*-xylylene (II) ligands. The trimethylenemethane (TMM) fragment can play the role of a cross-conjugated dianion[13] or can be generated[14] or trapped[15] as a four-electron biradical system (I). Although TMM–metal carbonyl complexes or type III, including the most representative and the first reported example Fe(TMM)-$(CO)_3$,[15] have been described,[16] no electron-rich metal–trimethylenemethane complexes have been characterized as such, besides those mentioned in our preliminary report.[17] However, such complexes are likely to be formed as unstable TMM–palladium–phosphine intermediates in carbon–carbon bond formation reactions.[18]



I III



II IV V VI VII

o-Xylylene, also called *o*-quinodimethane, is an unstable molecule which has only been observed very recently.[19] It has been found to be very useful when generated under mild conditions for cycloaddition reactions[20,21] and offers, as a ligand, a variety of coordination patterns. *o*-Xylylene, as trimethylenemethane, can formally behave as a four-electron biradical ligand as in canonical form of type V but also as a diene ligand as in complexes of type IV. Thus, examples of complexes (IV ↔ V) with *o*-xylylene coordinated to $Fe(CO)_3$,[22] $Co(C_5H_5)$,[21,23] or $Ru(PR_3)_3$[24] have been reported. *o*-Xylylene can also be involved in intracyclic diene–metal complexes of type VII[25] and type VI. (η^2-*o*-Xylylene metal complexes, in group 4, 5, and 6 metal or platinum(II)[26] and in bimetallic[21] systems, have also been described.

We now wish to report (i) a simple one-pot reaction leading directly from $FeCl_2$ to the electron-rich iron complexes of trimethylenemethane and *o*-xylylene and their characterization, (ii) the facile and reversible oxidation to 17-electron iron complexes and related electrochemical and paramagnetic NMR studies, and (iii) the X-ray diffraction structural determination of the stable 17-electron Fe-$(TMM)(PMe_3)_3{}^+$ cation at 128 K.

Experimental Section

All reactions were carried out under an argon atmosphere by using Schlenk techniques. NMR spectra were recorded on a Bruker WP 80 FT (^1H, ^{31}P, ^{13}C) and a Bruker AM 300 WB FT (^{13}C) spectrometer. The mass spectra were obtained with a Varian MAT 311 mass spectrometer at the Centre de Mesures Physiques de l'Ouest, University of Rennes. Elemental analyses were performed by the CNRS, Villeurbanne, France.

Materials. Solvents were dried by refluxing them over appropriate drying agents and stored under an inert atmosphere. Tetrahydrofuran (THF) and diethyl ether were distilled over sodium benzophenone ketyl, pentane and hexane were distilled over calcium hydride, dichloromethane was distilled over phosphorus pentoxide, and acetonitrile was distilled over phosphorus pentoxide first and then over calcium hydride.

Paramagnetic NMR Studies. The paramagnetic NMR spectra were obtained from samples freshly prepared at −40 °C. The pure $\mathbf{3a}^+(CF_3SO_3^-)$ salt was dissolved in CD_3CN, while the less stable corresponding salts of $\mathbf{3b}^+(NO_3^-)$ and $\mathbf{6a}^+(NO_3^-)$ were prepared in a 10 mm diameter NMR tube, equipped with ground-glass joint and stopper, just before the measurement by reacting **3b** or **6a** in CD_3CN with a slight excess of silver nitrate. A Bruker CXP 200 spectrometer with BVT 1000 temperature controller was used; the instrumental parameters were similar to those given earlier.[27] The experimental shifts were measured relative to the solvent signals ($\delta(^1H)$ 1.95; $\delta(^{13}C)$ 0.2, CD_3CN) and calculated relative to the signals of **3a**, **3b**, and **6a** to give paramagnetic shifts. For **6a** a mean reference shift of $\delta(^1H)$ 3.7 was taken. Frequency shifts to high frequency are negative.

Electrochemical Studies. *Cyclic voltammetric* measurements were obtained with a conventional three-electrode system. The working electrode was a platinum or vitreous carbon electrode. A Tacussel UAP-4 or PAR Model 362 potentiostat and a Kipp and Zonen BD 90X-Y recorder were used for cyclic voltammetric

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Table I. Crystal Data, Intensity Collection, Reduction, and Refinement for $(\eta^4\text{-}C_4H_6)Fe(PMe_3)_3^+(CF_3SO_3^-)$

formula	$C_{14}H_{33}F_3FeO_3P_3S$
mol wt	487.3
cryst system	monoclinic
space group	$P2_1/c$
a, Å	12.313 (2)
b, Å	11.016 (2)
c, Å	17.064 (3)
β, deg	103.1 (2)
V, Å^3	2254.7 (6)
Z	4
ρ_{calcd}, g cm^{-3}	1.44
$F(000)$	1020
μ(Mo Kα), cm^{-1}	10.01 (no absorptn correctn)
T, K	128 ± 1
cryst size, mm	0.15 × 0.20 × 0.20
radiatn, Å	λ(Mo Kα) = 0.71069
max 2θ, deg	50
scan	$\omega/2\theta = 1$
t_{max} (for one measure), s	60
stds (every 3600 s)	511, 431, 060
variance of stds	0.5% (no appreciable decay)
reflcns measd	4323
reflcns obsd ($I \geqslant 3\sigma(I)$)	3177
R_{INT}(from merging equivalent reflections)	0.015
R(isotropic)	0.080
R(anisotropic)	0.049
final R (included hydrogens)	0.026
R_w	0.024
w	$1/\sigma(F_o)^2 = \|\sigma^2(I) + (0.04F_o^2)^2\|^{-1/2}$
max residuals, e Å^{-3}	0.27

Table II. Positional Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å^2
Fe	0.80278 (2)	0.23169 (3)	0.26322 (2)	1.609 (6)
S	0.75606 (5)	−0.27475 (6)	0.52280 (3)	2.29 (1)
P(1)	0.62345 (5)	0.22904 (6)	0.19182 (3)	1.93 (1)
P(2)	0.79090 (5)	0.06756 (6)	0.34090 (4)	2.08 (1)
P(3)	0.79275 (5)	0.37799 (6)	0.35565 (4)	2.04 (1)
F(1)	0.5842 (1)	−0.3096 (2)	0.5864 (1)	5.13 (4)
F(2)	0.6051 (2)	−0.1261 (2)	0.5529 (1)	5.59 (5)
F(3)	0.7121 (2)	−0.2013 (2)	0.65846 (9)	5.57 (5)
O(1)	0.7969 (2)	−0.3879 (2)	0.5588 (1)	3.99 (5)
O(2)	0.8357 (2)	−0.1789 (2)	0.5332 (1)	4.45 (5)
O(3)	0.6852 (2)	−0.2824 (2)	0.4436 (1)	3.56 (4)
C(1)	0.5998 (2)	0.1330 (3)	0.1028 (2)	3.19 (6)
C(2)	0.5699 (2)	0.3746 (3)	0.1491 (2)	3.07 (6)
C(3)	0.5102 (2)	0.1811 (3)	0.2373 (2)	2.86 (6)
C(4)	0.7115 (2)	0.0755 (3)	0.4189 (2)	3.10 (6)
C(5)	0.7338 (2)	−0.0696 (3)	0.2877 (2)	3.15 (6)
C(6)	0.9242 (2)	0.0123 (3)	0.3982 (2)	3.62 (6)
C(7)	0.6631 (2)	0.4020 (3)	0.3879 (2)	2.78 (5)
C(8)	0.8925 (2)	0.3647 (3)	0.4523 (2)	3.26 (6)
C(9)	0.8193 (2)	0.5313 (3)	0.3248 (2)	3.44 (6)
C(10)	0.9223 (2)	0.2387 (3)	0.2071 (1)	2.61 (5)
C(11)	0.9774 (2)	0.2683 (3)	0.2870 (2)	2.77 (5)
C(12)	0.8847 (2)	0.1170 (3)	0.1953 (2)	2.94 (5)
C(13)	0.8453 (2)	0.3274 (3)	0.1670 (2)	3.08 (6)
C(14)	0.6608 (2)	−0.2251 (3)	0.5830 (2)	3.06 (6)
H(1A)	0.648 (2)	0.161 (3)	0.070 (2)	4*
H(1B)	0.621 (2)	0.051 (3)	0.117 (2)	4*
H(1C)	0.524 (2)	0.135 (3)	0.078 (2)	4*
H(2A)	0.572 (2)	0.433 (3)	0.191 (2)	4*
H(2B)	0.492 (2)	0.367 (3)	0.121 (2)	4*
H(2C)	0.612 (2)	0.401 (3)	0.115 (2)	4*
H(3A)	0.509 (2)	0.232 (3)	0.283 (2)	4*
H(3B)	0.442 (2)	0.187 (3)	0.202 (2)	4*
H(3C)	0.520 (2)	0.103 (3)	0.258 (2)	4*
H(4A)	0.712 (2)	0.004 (3)	0.444 (2)	4*
H(4B)	0.738 (2)	0.135 (3)	0.455 (2)	4*
H(4C)	0.633 (2)	0.098 (3)	0.397 (2)	4*
H(5A)	0.737 (2)	−0.133 (3)	0.325 (2)	4*
H(5B)	0.780 (2)	−0.086 (3)	0.251 (2)	4*
H(5C)	0.662 (2)	−0.058 (3)	0.261 (2)	4*
H(6A)	0.958 (2)	0.076 (3)	0.426 (2)	4*
H(6B)	0.970 (2)	−0.011 (3)	0.360 (2)	4*
H(6C)	0.912 (2)	−0.052 (3)	0.430 (2)	4*
H(7A)	0.641 (2)	0.330 (3)	0.410 (2)	4*
H(7B)	0.669 (2)	0.463 (3)	0.425 (2)	4*
H(7C)	0.608 (2)	0.422 (3)	0.345 (2)	4*
H(8A)	0.962 (2)	0.367 (3)	0.443 (2)	4*
H(8B)	0.881 (2)	0.287 (3)	0.478 (2)	4*
H(8C)	0.879 (2)	0.430 (3)	0.486 (2)	4*
H(9A)	0.808 (2)	0.588 (3)	0.362 (2)	4*
H(9B)	0.768 (2)	0.550 (3)	0.277 (2)	4*
H(9C)	0.892 (2)	0.533 (3)	0.313 (2)	4*
H(11A)	1.017 (2)	0.206 (3)	0.315 (2)	4*
H(11B)	0.995 (2)	0.352 (3)	0.300 (2)	4*
H(12A)	0.932 (2)	0.053 (3)	0.224 (2)	4*
H(12B)	0.839 (2)	0.092 (3)	0.146 (2)	4*
H(13A)	0.862 (2)	0.410 (3)	0.178 (2)	4*
H(13B)	0.801 (2)	0.309 (3)	0.114 (2)	4*

[a] Parameters with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

experiments. All the measurements were carried out at 25 °C under a nitrogen atmosphere with a solution of the complex [(1.4–1.5) × 10^{-3} M] in 0.1 M Bu_4NPF_6/CH_3CN. All the potentials are referred to a saturated calomel electrode. *Coulometry* experiments were performed with a Tacussel PRT-20-2 potentiostat and a Tacussel IG-5 integrator by using a cell[28] equipped with a vitreous carbon electrode (diameter, 4 cm) as the working electrode, a platinum electrode (diameter, 4 cm) as the auxiliary electrode, and a saturated calomel electrode (SCE). Rotating-disk experiments were performed in the same cell by using a platinum rotating–disk electrode (RDE) as the working electrode.

Crystallographic Analysis of 3a$^+$($CF_3SO_3^-$). Single crystals of **3a**$^+$ were grown from ether/dichloromethane solutions at 195 K. Since crystals slowly decomposed at room temperature, the data were collected at 128 K with an Enraf-Nonius CAD-4 diffractometer. The structure was solved by a combination of Multan and Patterson and several Fourier difference map(s). All the hydrogen atoms were found with one Fourier difference map (between 0.67 and 0.43 e Å^{-3}). The least-squares refinement (x, y, z and β_{ij} for non-hydrogen atoms and x, y, z for hydrogen atoms) converged to R = 0.024. Details of the crystal data, experimental conditions, and solution and refinement are given in Table I. Table II contains the atomic positions and Table III a selection of bond lengths and angles.

Synthesis of $FeCl_2(PR_3)_n$ (1). $FeCl_2(PMe_3)_2$[29] (**1a**) and $FeCl_2(P(OMe)_3)_3$[30] (**1c**) were prepared according to literature procedures. $FeCl_2(PMe_2Ph)_2$ (**1b**) was obtained by using an adapted procedure of that reported for **1a**.[29] In a Schlenk tube under argon atmosphere containing a suspension of 3 mmol (0.37 g) of anhydrous $FeCl_2$ in 20 mL of THF was introduced 7 mmol (0.97 g) of PMe_2Ph. The red solution turned brown when refluxed for 1 h and was then filtered on a frit. The THF was removed under vacuum and replaced by 50 mL of pentane. The solution was filtered on a silica-gel column (10 cm) and then cooled at −20 °C. Light brown crystals were thus obtained (0.85 g, 70%). Anal. Calcd for $C_{16}H_{22}Cl_2P_2Fe$: C, 47.64; H, 5.45; P, 15.38; Cl, 17.61. Found: C, 47.21; H, 5.45; P, 14.82; Cl, 17.38. In the ^1H NMR spectrum no signal was observed in the diamagnetic shift range.

Synthesis of $Fe(\eta^4\text{-}C_4H_6)(PMe_3)_3$ (3a). (a) Reduction with Magnesium. To 0.64 g (5 mmol) of anhydrous iron(II) chloride in 30 mL of THF was added an excess of PMe_3 (1.52 g, 20 mmol). The pale green solution was refluxed for 1 h and then filtered. Magnesium (0.48 g, 20 mmol) and 0.75 g of methallyl dichloride (**2**) (6 mmol) were successively added to the solution at room temperature. An exothermic reaction took place, and the green solution progressively turned dark orange. The solution was stirred for 2 h, and then 2 mL of dioxan was added to precipitate the magnesium dichloride. After filtration on a frit, the solvent was removed under vacuum and the residue extracted with ether.

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[28] Jacob, G.; Moinet, C. *Bull. Soc. Chim. Fr.* **1983**, *1*, 291.

[29] Rathke, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1975**, *97*, 3272.

[30] Harris, T. V.; Rathke, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 6966.

Table III. Selected Bond Lengths and Angles of 3a$^+$

Bond Distances, Å			
Fe–P(1)	2.268 (1)	P(2)–C(4)	1.822 (3)
Fe–P(2)	2.266 (1)	P(2)–C(5)	1.820 (3)
Fe–P(3)	2.280 (2)	P(2)–C(6)	1.815 (3)
Fe–C(10)	1.930 (2)	P(3)–C(7)	1.820 (3)
Fe–C(11)	2.134 (2)	P(3)–C(8)	1.823 (3)
Fe–C(12)	2.118 (3)	P(3)–C(9)	1.821 (3)
Fe–C(13)	2.115 (3)	F(1)–C(14)	1.335 (3)
S–O(1)	1.429 (2)	F(2)–C(14)	1.328 (3)
S–O(2)	1.424 (2)	F(3)–C(14)	1.326 (3)
S–O(3)	1.436 (2)	C(10)–C(11)	1.418 (4)
S–C(14)	1.810 (3)	C(10)–C(12)	1.417 (4)
P(1)–C(1)	1.820 (3)	C(10)–C(13)	1.425 (4)
P(1)–C(2)	1.822 (3)	C(11)–C(12)	2.392 (4)
P(1)–C(3)	1.820 (3)	C(12)–C(13)	2.395 (4)
Bond Angles, deg			
P(1)–Fe–P(2)	96.90 (3)	C(11)–Fe–C(12)	68.5 (1)
P(1)–Fe–P(3)	100.53 (3)	C(11)–Fe–C(13)	68.8 (1)
P(1)–Fe–C(10)	119.51 (8)	C(12)–Fe–C(13)	68.9 (1)
P(1)–Fe–C(11)	157.10 (8)	O(1)–S–O(2)	115.3 (1)
P(1)–Fe–C(12)	102.98 (8)	O(1)–S–O(3)	115.7 (1)
P(1)–Fe–C(13)	88.33 (8)	O(1)–S–C(14)	103.3 (1)
P(2)–Fe–P(3)	97.91 (2)	O(2)–S–O(3)	114.5 (1)
P(2)–Fe–C(10)	118.64 (8)	O(2)–S–C(14)	102.8 (1)
P(2)–Fe–C(11)	103.57 (9)	C(8)–P(3)–C(9)	102.0 (2)
P(2)–Fe–C(12)	86.89 (9)	O(3)–S–C(14)	102.6 (1)
P(2)–Fe–C(13)	155.81 (9)	F(1)–C(14)–F(3)	106.4 (2)
P(3)–Fe–C(10)	118.86 (8)	F(2)–C(14)–F(3)	107.7 (2)
P(3)–Fe–C(11)	86.82 (8)	Fe–P(1)–C(1)	114.1 (1)
P(3)–Fe–C(12)	155.25 (8)	Fe–P(1)–C(2)	115.1 (1)
P(3)–Fe–C(13)	104.34 (9)	Fe–P(1)–C(3)	121.4 (1)
C(10)–Fe–C(11)	40.4 (1)	C(1)–P(1)–C(2)	101.7 (2)
C(10)–Fe–C(12)	40.7 (1)	C(1)–P(1)–C(3)	101.2 (2)
C(10)–Fe–C(13)	40.9 (1)	C(2)–P(1)–C(3)	100.5 (1)

The solution was filtered on a short silica gel column (5 cm) and eluted with ether. The orange band was collected and the solvent slowly evaporated under vacuum to give an orange powder of **3a** (0.71 g, 71%).

(b) Reduction with Na/Hg. A solution of $FeCl_2(PMe_3)_2/PMe_3$, prepared from 0.37 g of iron(II) chloride (3 mmol) and 1 g of PMe_3 (13 mmol) in 40 mL of THF, was transferred with a cannula into a Schlenk flask containing 20 mmol of 1% sodium amalgam (0.46 g, 20 mmol) and 5 mL of THF. The green solution immediately turned dark orange. After the reaction mixture was stirred for a few minutes, 0.050 g of methallyl dichloride (**2**) (4 mmol) was added and the solution was stirred for 2 h. The solution was decanted and filtered through a cannula to remove insoluble material and amalgam. The solvent was removed under vacuum and the residue extracted with ether. After filtration on a frit, the solvent was removed under vacuum and the residue extracted with pentane. The solvent was slowly evaporated under vacuum to give an orange powder of **3a** (0.70 g, 70%). ^1H NMR (C_6D_6, 80 MHz, 305 K): δ 1.04 (d, $^2J_{PH} = 5.8$ Hz, PMe_3); 0.79 (d, $^3J_{PH} = 10.9$ Hz, CH_2). $^{31}P\{^1H\}$ NMR (C_6D_6, 32.38 MHz, 309 K): δ 26.84 (s, PMe_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.47 MHz, 310 K): δ 106.4 (s, CCH_2); 42.7 (s, CCH_2); 24.0 (m, PMe_3). MS: *m/e* (M)$^+$, calcd 338.114, found 338.113; 262 $(M - PMe_3)^+$; 208 $(M - PMe_3 - C_4H_6)^+$; 186 $(M - 2PMe_3)^+$. Anal. Calcd for $C_{13}C_{33}FeP_3$: C, 46.15; H, 9.76. Found: C, 46.87; H, 9.76.

Synthesis of Fe(η^4-C_4H_6)(PMe_2Ph)$_3$ (3b). (a) Reduction with Mg. Analogous to the preparation of **3a**, 1.2 g of **3b** (46%) was obtained from 0.64 g of iron(II) chloride (5 mmol), 2.20 g of PMe_2Ph (16 mmol), 0.48 g of magnesium (20 mmol), and 0.75 g of methallyl dichloride (6 mmol) in 30 mL of THF. Complex **3b** was crystallized from ether at −20 °C.

(b) Reduction with Na/Hg. Analogous to the preparation of **3a**, 0.63 g of **3b** (40%) was obtained from 0.37 g of iron(II) chloride (3 mmol), 1.38 g of PMe_2Ph, 1% sodium amalgam (0.46 g Na, 20 mmol), and 0.60 g of methallyl dichloride (4 mmol) in 30 mL of THF. ^1H NMR (C_6D_6, 80 MHz, 305 K): δ 7.05 (m, C_6H_5); 1.40 (d, $^2J_{PH} = 5$ Hz, PMe_2); 0.75 (d, $^3J_{P-H} = 10.5$ Hz, CH_2). $^{31}P\{^1H\}$ NMR (C_6D_6, 32.38 MHz, 309 K): δ 34.71 (s, PMe_2Ph). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.47 MHz, 309 K): δ 147.60, 130.2, 127.2 (C_6H_5); 107.22 (s, CCH_2); 45.25 (s, CCH_2); 23.4 (m, PMe_2). MS: *m/e* (M)$^+$, calcd 524.162, found 524.163; 386 $(M - PMe_2Ph)^+$; 332 $(M - PMe_2Ph - C_4H_6)^+$; 248 $(M - 2\,PMe_2Ph)^+$. Anal. Calcd for $C_{28}H_{39}FeP_3$: C, 64.12; H, 7.44; P, 17.74. Found: C, 63.73; H, 7.44; P, 17.42.

Synthesis of Fe(η^4-C_4H_6)(Me_2PCH_2)$_3$CMe (3c). MeC(CH_2PMe_2)$_3$ (c). The preparation of $MeC(CH_2PMe_2)_3$ was adapted from that of $Me_2P(CH_2)_3PMe_2$.[31] To a solution of sodium dimethylphosphide, prepared from tetramethyldiphosphine (8 g, 65 mmol) and sodium (3 g, 130 mmol) in 300 mL of liquid ammonia at −78 °C, was slowly added a solution of $CH_3C(CH_2Cl)_3$ (7.5 g, 43 mmol) in 50 mL of ether. A deep orange color appeared at the beginning of the addition and disappeared at the end. The ammonia was evaporated by letting the mixture warm to room temperature. Ether (200 mL) was added, the solution was filtered on a frit, and the ether was distilled at room temperature. Distillation of the crude oil at 145 °C at 0.2 Torr gave a 50% yield (5 g) of $MeC(CH_2PMe_2)_3$. ^1H NMR (C_6D_6, 80 MHz, 308 K): δ 1.72 (d, CH_2, $^2J_{PH} = 3.5$ Hz; 1.16 (s, CH_3)); 0.97 (d, PMe_2, $^2J_{PH} = 3.5$ Hz). ^{31}P NMR (C_6D_6, 32.28 MHz, 310 K): δ 62.7 (s, PMe_2).

Complex 3c. In a Schlenk tube containing a suspension of anhydrous $FeCl_2$ (0.37 g, 3 mmol) in 20 mL of THF, 3 mmol (0.76 g) of $MeC(CH_2PMe_2)_3$ was added at room temperature, and a violet precipitate formed immediately. After 10 min of stirring, magnesium (0.24 g, 10 mmol) and methallyl dichloride (**2**) (0.50 g, 4 mmol) were added successively. A slightly exothermic reaction took place, and the violet suspension turned progresssively into an orange solution. After evaporation of the solvent, extraction with 50 mL of ether, filtration, and concentration to 2 mL, the solution was purified by filtration on a short silica-gel column (5 cm). The yellow fraction led to an orange oil, which on cooling to −40 °C afforded 0.22 g (20%) of yellow crystals of **3c** that are extremely air-sensitive and turned green in the presence of air. **3c** was oxidized with $AgCF_3SO_3$ to yield a green salt, which gave a cyclic voltammogram similar to that of **3a**$^+$ and **3b**$^+$. Further characterization of **3c** was not possible due to its air sensitivity; its nature was assumed on the basis of the involved reaction and of the electrochemical study analogous to those of **3a** and **3b**.

Synthesis of Fe(*o*-xylylene)(PMe_3)$_3$ (6a). From (*o*-BrMgCH$_2$)$C_6H_4CH_3$ (5). A solution of the Grignard compound **5** in 10 mL of THF, prepared from 0.94 mL of (*o*-BrCH$_2$)$C_6H_4CH_3$ (7 mmol) and 0.36 of magnesium (15 mmol), was transferred with a cannula into a Schlenk flask containing a solution of $FeCl_2(PMe_3)_2/PMe_3$ in 20 mL of THF at 0 °C, prepared from 0.37 g of iron(II) chloride (3 mmol) and 0.76 g of PMe_3 (10 mmol). The solution immediately turned dark red: it was stirred for 2 h and the solvent was removed under vacuum. The residue was extracted with pentane and then filtered on a frit. The filtrate was concentrated to 20 mL and afforded on cooling at −40 °C 0.60 g (51%) of red crystals of **6a**. ^1H NMR (toluene-d_8, 300 MHz, 297 K): δ 7.50 (m, 2 H); 7.10 (m, 2 H); 1.40 (m, $^3J_{PH} = 5.2$ Hz, 2 H, H_s); 1.30 (d, $^2J_{PH} = 6.7$ Hz, 9 H, PMe_3); 0.87 (d, $^2J_{PH} = 2.3$ Hz, *18* H, 2PMe_3); −1.29 (m, $^3J_{PH} = 3.8$ Hz, 2 H, H_a). $^{31}P\{^1H\}$ NMR (C_6D_6, 32.38 MHz, 310 K): δ 33.0 (t, $J_{pp} = 6$ H, PMe_3); 19.8 (d, $J_{pp} = 6$ Hz, 2PMe_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.47 MHz, 310 K): δ 135.2 (s, C_4); 123.8 (s, C_3); 97.4 (s, C_2); 29.4 (d, $J_{PC} = 16$ Hz, C_1); 24.3 (d, $^2J_{PC} = 21$ Hz, PMe_3); 22.9 (t, $^1J_{PC} = 19.7$ Hz, PMe_3). MS: *m/e* (M$^+$), calcd 388.130, found 388.128; 312 $(M - PMe_3)^+$; 236 $(M-2PMe_3)^+$; 208 $(M - PMe_3 - C_8H_8)^+$.

Synthesis of Fe(*o*-xylylene)(PMe_2Ph)$_3$ (6b). (a) From (*o*-BrMgCH$_2$)$C_6H_4CH_3$ (5). Analogous to the preparation of **6a**, 0.7 g (40%) of red crystals of **6b** was obtained from **5** (7 mmol), 0.37 g of iron(II) chloride (3 mmol), and 1.38 g of PMe_2Ph (10 mmol) in 30 mL of THF at 0 °C.

(b) From *o*-(ClMgCH$_2$)$_2C_6H_4$ (4b). A solution of *o*-($ClCH_2$)$_2C_6H_4$ (**4a**) (4 mmol, 0.70 g) in 10 mL of THF was added dropwise in a Schlenk flask containing 0.48 g of magnesium (20 mmol) in 30 mL of THF at 0 °C. The mixture was stirred for 3 h and the solution was then transferred with a cannula into a Schlenk flask containing a solution of $FeCl_2(PMe_2Ph)_2/PMe_2Ph$ in 20 mL of THF at 0 °C ($FeCl_2$, 3 mmol (0.37 g); PMe_2Ph, 10 mmol (1.38 g)). The solution turned immediately dark red; it was stirred for 2 h and the solvent was removed under vacuum. The residue was extracted with ether. The solvent was removed, and

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[31] Kordosky, G.; Cook, B. R.; Cloyd, J., Jr.; Meek, D. W. *Inorg. Synth.* **1973**, *14*, 14.

the red oil was dissolved in pentane, which afforded, on cooling at 0 °C, 0.6 g (37%) of red crystals of **6b**.

(c) From *o*-$(ClCH_2)_2C_6H_4$ and Magnesium. In a Schlenk tube containing 3 mmol of $FeCl_2(PMe_2Ph)_2/PMe_2Ph$ in 30 mL of THF (prepared from 0.37 g (2 mmol) of $FeCl_2$ and 1.38 g (10 mmol) of PMe_2Ph) and an excess of magnesium (20 mmol, 0.48 g) at room temperature were added dropwise 4 mmol (0.7 g) of *o*-$(ClCH_2)_2C_6H_4$ (**4a**) in 10 mL of THF. The solution turned red progressively. After addition, the mixture was stirred at room temperature for 3 h and the solution was filtered before removal under vacuum of the solvent. Extraction with ether and crystallization in pentane afforded 0.65 g (38%) of **6b**. ^1H NMR (toluene-d_8) 300 MHz, 297 K): δ 7.5 (m, 2 H); 7.3 (m, 2 H); 1.71 (d, $^2J_{PH}$ = 5 Hz, 6 H, PMe_2); 1.31 (m, $^3J_{PH}$ = 4.7 Hz, 2 H, H_s); 1.22 (d, $^2J_{PH}$ = 2.3 Hz, 6 H, PMe_2); 1.06 (d, $^2J_{PH}$ = 2.3 Hz, 6 H, PMe_2); −1.49 (m, $^2J_{PH}$ = 2.5 Hz, 2 H, H_a). $^{31}P\{^1H\}$ (C_6D_6, 32.38 MHz, 309 K): δ 42.4 (s, PMe_2Ph); 26.2 (s, $2PMe_2Ph$). **6b** decomposed in the source of the mass spectrometer.

Synthesis of Fe(*o*-xylylene)$(P(OMe)_3)_3$ (6d). A solution of the Grignard compound **4**, in 10 mL of THF, was prepared from (*o*-$ClCH_2)_2C_6H_4$ (4 mmol, 0.70 g) and magnesium (20 mmol, 0.48 g). It was transferred with a cannula into a Schlenk flask containing a suspension of 1.49 g of $FeCl_2(P(OMe_3)_3$ (**1d**) (3 mmol) in 10 mL of THF at 0 °C. The color turned immediately dark yellow. The solution was stirred for 2 h at room temperature, and the solvent was removed under vacuum. The residue was extracted with ether, filtered on a frit, chromatographed on a short-gel column (10 cm), and eluted with ether. The yellow band was collected, and after removal of ether under vacuum the yellow residue was dissolved in pentane. On cooling to −25 °C, 45% (1.20 g) of yellow crystals of **6d** were obtained. ^1H NMR (C_6D_6, 80 MHz, 310 K): δ 7.6 (m, 2 H); 7.2 (m, 2 H); 3.31 (m, 27 H, $P(OMe)_3$); 2.13 (m, 2 H, H_s); −0.32 (m, 2 H, H_a). $^{31}P\{^1H\}$ NMR (C_6D_6, 32.38 MHz, 310 K): δ 192 (s, $P(OMe)_3$); 176 (s, 2 $P(OMe)_3$). MS: *m/e* (M^+), calcd 532.084, found 532.085; 428 (M − C_8H_8)$^+$, 408 (M − $P(OMe_3)^+$. Anal. Calcd for $C_{17}H_{35}FeO_9P_3$: C, 38.34; H, 6.57; P, 17.47. Found: C, 38.36; H, 6.49; P, 17.98.

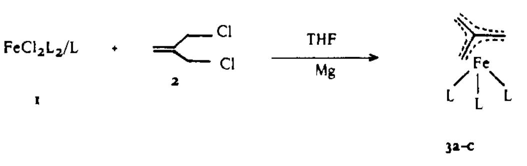
Synthesis of Bis(*o*-methylphenyl)-1,2-ethane (7). A solution of the Grignard reagent **5** in 10 mL of THF, prepared from 0.94 mL of *o*-$BrCH_2C_6H_4CH_3$ (7 mmol) and 0.36 g of magnesium (15 mmol), was transferred with a cannula into an Schlenk flask containing a suspension of $FeCl_2(P(OMe)_3)_3$[30] (**1d**) (3 mmol) in 10 mL of THF at 0 °C. The color turned immediately red and then progressively brown with formation of a black precipitate. The solution was stirred overnight at room temperature, and the solvent was removed under vacuum. The residue was dissolved in pentane, which afforded on cooling white crystals of **7** (80%). ^1H NMR (C_6D_6, 300.13 MHz, 297 K) δ 7.05 (m, 8 H, $-C_6H_4-$); 2.72 (s, 4 H, CH_2CH_2); 2.07 (s, 6 H, CH_3). MS: *m/e* (M^+), calcd 210.141, found 210.142.

Fe(η^3-methyl-2-allyl)$(PMe_2Ph)_3(OCOCF_3)$ (8b). The reaction was performed in a ^1H NMR tube. An excess of trifluoroacetic acid was added to a solution of **3b** in 0.6 mL of CD_3COCD_3. The orange solution turned immediately colorless. The reaction was quantitative as indicated by NMR. ^1H NMR (CD_3COCD_3, 80 MHz, 310 K): δ 7.8 (m, C_6H_5, 15 H); 4.59 (m, 2 H, H_s); 2.38 (d, $^2J_{PH}$ = 13.7 Hz, PMe_2, 18 H); 1.65 (m, 5 H, CH_3 + $2H_a$), irradiation at δ 4.59 gives a singlet at δ 1.65 (5 H) and irradiation at δ 1.65 gives a singlet at δ 4.59 (2 H), showing the existence of a coupling between H_s and H_a. $^{31}P\{^1H\}$ NMR (CD_3COCD_3, 32.38 MHz, 310 K): δ 33.61 (s, PMe_2Ph).

Synthesis of Fe(η^4-C_4H_6)$(PMe_3)_3{}^+$ $(CF_3SO_3)^-$. To a solution of 0.68 g of **3a** (2 mmol) in 30 mL of CH_2Cl_2 was added 0.51 g of silver triflate (2 mmol). The orange solution immediately turned green with formation of a black precipitate. The solution was stirred for 1 h and then carefully filtered on a frit. The filtrate was concentrated to 10 mL and added dropwise to 300 mL of ether. The green precipitate was filtered, washed several times with ether, and dried under vacuum. An 80% yield (0.78 g) of $\mathbf{3a}^+(CF_3SO_3^-)$ was thus obtained. Because of its instability, this radical species did not allow elemental analyses and had to be stored at −20 °C.

Synthesis of Fe(η^4-C_4H_6)$(PMe_2Ph)_3{}^+(CF_3SO_3)^-$. To a solution of 0.524 g of **3b** (1 mmol) in 20 mL of CH_2Cl_2 at −78 °C was added 0.26 g of silver triflate (1 mmol). The orange solution immediately turned green with formation of a black precipitate. The solution was stirred for 1 h, then decanted, and filtered with a cannula. The filtrate was concentrated to 5 mL at −78 °C and added slowly to 300 mL of ether at −78 °C. The green precipitate was filtered, washed with ether, and dried under vacuum. In an inert atmosphere at low temperature a 70% yield (0.47 g) of $\mathbf{3b}^+(CF_3SO_3^-)$ was obtained. Because of its instability, this radical species did not allow elemental analyses and had to be stored at −20 °C.

Scheme I



a : L=PMe_3
b : L=PMe_2Ph
c : $L_3=CH_3C(CH_2PMe_2)_3$

Synthesis of $Fe(NO)_2(PMe_2Ph)_2$ (9b). To a solution of **3b** (0.5 mmol) in 10 mL of CH_2Cl_2 at room temperature was added 0.117 g of $NOBF_4$ (1 mmol). The orange solution turned immediately green and, after 10 min of stirring, dark orange. The solvent was evaporated, and the residue was chromatographed on a silica-gel column by using a mixture of hexane/ether (1/1) as eluent. The red fraction gave, on cooling at −20 °C, 0.07 g of red crystals of **9b** (35%). IR (Nujol): ν(NO) 1720, 1670 cm^{-1}. ^1H NMR (CD_2Cl_2, 80 MHz, 307 K): δ 7.34 (m, C_6H_5); 1.48 (d, $^2J_{PH}$ = 7.3 Hz, PMe_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 32.38 MHz, 310 K): δ 25.69 (s, PMe_2Ph). MS: *m/e* (M^+), calcd 392.050, found 392.050; 362 (M − NO)$^+$; 332 (M − 2NO)$^+$; 224 (M − PMe_2Ph − NO)$^+$.

Results and Discussion

Synthesis and Characterization of Fe(TMM)$(PR_3)_3$ Complexes (3). The precursors $FeCl_2L_2$ (**1a**[29] and **1b**) were prepared without isolation by addition of a large excess (4 equiv) of the corresponding alkylphosphine (L) to anhydrous iron(II) chloride in THF, followed by boiling under reflux for 1 h. To the resulting solution, containing the system $FeCl_2L_2/L$, was added an excess of magnesium at room temperature. Then the addition of 1 equiv of 3-chloro-2-(chloromethyl)prop-1-ene (methallyl dichloride) (**2**) resulted in a rapid color change from green to orange-brown. Purification on a silica-gel column led to the isolation of complexes **3a** and **3b** as orange, air-sensitive solids in 70% and 46% yields, respectively (Scheme I). Reaction of the tridentate phosphine $MeC(CH_2PMe_2)_3$ (**c**) with $FeCl_2$ in THF, followed by the successive additions of magnesium and the precursor **2**, afforded an extremely air-sensitive complex in 20% yield that could not be fully characterized. Its structure was assumed to be **3c** on the basis of the reaction involved and the electrochemical behavior, which is similar to that of **3a**,**b**. Attempts failed to produce the analogous complex **3** containing the less basic triphenylphosphine or trimethyl phosphite ligand. By direct addition of the Grignard derivative of **2** to a THF solution of $FeCl_2(PMe_2Ph)_2/PMe_2Ph$, complex **3b** was obtained in lower yield (10%). This low yield can be explained by the difficulty of preparing such a Grignard reagent, owing to its tendency to form a carbon–carbon bond in THF.[32] Thus, the formation of complex **3** may be explained by the in situ formation of the Grignard derivative **B** that can be trapped by $FeCl_2L_2$ (**1**) to give, by two successive transmetalation reactions, Fe(TMM)L_3 complexes (**3**). The reaction of the mono-Grignard compound **A** with $FeCl_2L_2$ is an alternative route to the intermediate **D**, via **C** (Scheme II).

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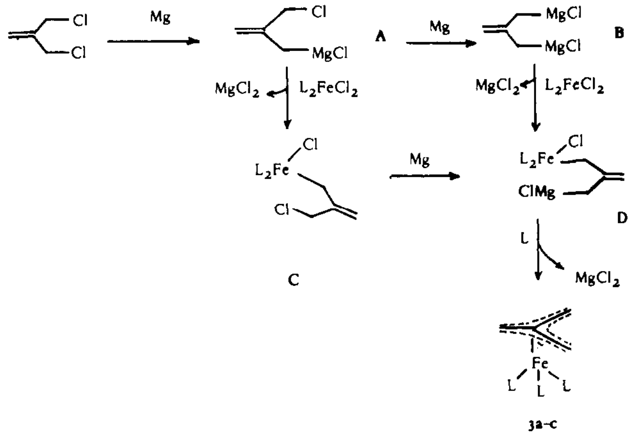
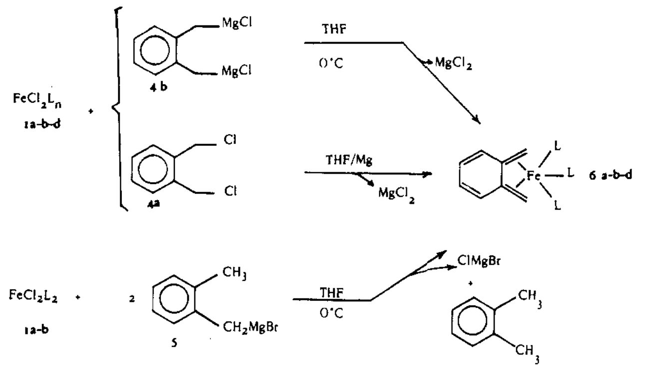
[32] Seetz, J. W. F. L.; Hartog, F. A.; Böhm, H. P.; Blomberg, C.; Akkerman, O. S.; Bickelhaupt, F. *Tetrahedron Lett.* **1982**, *23*, 1497.

Scheme II



Scheme III



n=2, a:L=PMe_3, b:L=PMe_2Ph ; n=3, d:L=$P(OMe)_3$

Sodium amalgam reduction of $FeCl_2L_n$ in the presence of an excess of phosphine or phosphite ligand has been studied by Muetterties et al.[30] Therefore, the sodium amalgam reduction of $FeCl_2L_2$ (**1a**,**b**) in the presence of 1 equiv of phosphines **a**,**b**, followed by addition of **2**, has been investigated. At room temperature the Fe(TMM)L_3 complexes **3a** and **3b** were thus produced in 68% and 40% yields, respectively. These yields in **3** are similar to those obtained by using the magnesium route, but in the latter the ease of the separation of magnesium, with respect to amalgam, offers the most convenient route to **3** in a one-pot reaction starting directly from $FeCl_2$. Recently we also found that the reaction of lithium or potassium methyl-2-propyl derivatives with **1a** or **1b** afforded complex **3a** or **3b** but in the presence of Fe(Me-2-allyl)$_2$(PR_3)$_2$ derivatives.[9]

The derivatives **3a**,**b** were characterized on the basis of their elemental analyses and ^1H, ^{31}P, and ^{13}C NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum at 36 °C of **3a**,**b** shows a single line, consistent with spectroscopic equivalence of the three phosphine ligands. The high symmetry of these derivatives is confirmed by the ^1H NMR spectrum at 36 °C, which shows only two doublets, one for the phosphine methyl resonance [**3a**, δ 1.04 ($^2J_{PH}$ = 5.8 Hz); **3b**; δ 1.40 ($^2J_{PH}$ = 5 Hz)] and the other for the three equivalent methylene hydrogen atoms of the TMM ligand [**3a**, δ 0.79 ($^3J_{PH}$ = 10.9 Hz); **3b**, δ 0.75 (J_{PH} = 10.5 Hz)].[33] The $^{13}C\{^1H\}$ NMR spectrum at 36 °C give only three lines due to the central and the three equivalent methylene carbon atoms of the TMM ligand, and the equivalent phosphine methyl carbon nuclei respectively [**3a**, δ 106.4, 42.7, 26.8; **3b**, δ 107.2, 45.02, 34.7.]. The methylene proton and the TMM carbon signal shifts of **3a**,**b** can be compared with the corresponding resonances of the Fe(TMM)$(CO)_3$ complex[15] [δ (CCl_4): ^1H NMR 2.0 (CH_2); ^{13}C NMR 105 (central carbon), 53 (CH_2)]. This comparison shows that the replacement of the three carbonyls by three alkylphosphines leads to a shielding of the proton and carbon resonances of the methylene groups. On the other hand, the resonance of the TMM central carbon does not change appreciably. This observation is consistent with a greater electron transfer toward the methylene carbon than toward the central carbon, which is related to the increase of electron density at the metal center by coordination of the phosphine ligands to the iron.

Synthesis and Characterization of Fe(*o*-xylylene)L_3 Complexes (6). The *o*-xylylene moiety is formally capable of coordination to a metal center as a four-electron ligand in the canonical form IV ↔ V or in complexes VII or as a two electron ligand as in derivatives of type VI. The Fe(*o*-xylylene)$(CO)_3$ complex of type IV has already been obtained in low yield,[34] and the Fe(butadiene)$(PMe_3)_3$ complex,[30] with a structure analogous to that of IV, has been prepared by reduction of $FeCl_2(PMe_3)_2$ in the presence of butadiene and an excess of trimethylphosphine. On the other hand, the formally iron(II) derivative Fe(*o*-xylylene)$(PR_3)_3$, of type V, would be analogous to Fe(TMM)$(PR_3)_3$ complexes (**3**). Therefore, we attempted to produce Fe(*o*-xylylene)$(PR_3)_3$ derivatives by reduction of $FeCl_2(PR_3)_n$ (**1**) in the presence of potential precursors of the *o*-xylylene ligand: *o*-$(ClCH_2)_2C_6H_4$ (**4a**), *o*-$(ClMgCH_2)_2C_6H_4$ (**4b**), and *o*-$(ClMgCH_2)C_6H_4CH_3$ (**5**). The Grignard reagent **4b** has already been used by Lappert et al.[26a] to produce *o*-xylylene group 4 metal complexes $Cp_2M(\eta^2$-*o*-xylylene) of structure VI.

A similar approach was used for the coordination of the *o*-xylylene ligand to the electron-rich FeL_3 moiety. When a THF solution of $FeCl_2(PMe_2Ph)_2/PMe_2Ph$ or $FeCl_2(P(OMe_3)_3$ was treated at 0 °C with 1 equiv of the Grignard compound **4b**, the color immediately turned red, producing the very air-sensitive complexes **6b** and **6d**, which were isolated in 34% and 45% yields, respectively (Scheme III). The same compounds were more easily obtained in comparable yield by direct addition of **4a** to the mixture of $FeCl_2(PMe_2Ph)_2/PMe_2Ph$ and magnesium, or of $FeCl_2(P(OMe)_3)_3$ and magnesium, in THF. Very likely, the mechanisms of the formation of **6b** or **6d** and Fe(TMM)L_3 are comparable: two successive transmetalation reactions of the in situ formed Grignard intermediate **4b** lead to the iron complexes **6**.

The reaction of the Grignard derivative **5** with $FeCl_2(PR_3)_2/PR_3$ systems was then investigated as a possible way of access either to electron-rich $(\eta^3$-$CH_2C_6H_4CH_3)$iron[9,35] or (*o*-xylylene)iron complexes. One equivalent of **5** reacted at 0 °C with the system **1a**/**a** in THF to afford 10% yield of the red complex Fe(*o*-xylylene)$(PMe)_3)_3$ (**6a**). When 2 equiv of **5** were used, **6a** was isolated in a 51% yield. Similarly, 2 equiv of **5** with $FeCl_2(PMe_2Ph)_2/PMe_2Ph$ gave 40% of **6b**. In these reactions the in situ formation of *o*-xylene was established by gas chromatography analysis.

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[33] The signal due to the TMM methylene protons of **3a** shows some intensity between the two external lines of the doublet. This is typical of an apparent coupling with two different phosphorus nuclei of the methylene protons ($|^3J_{PH} + {^3J_{P'H}}|$).

[34] Fe(*o*-xylylene)$(CO)_3$ was obtained in 6% yield by treatment of *o*-$(ClCH_2)_2C_6H_4$ with $Fe_2(CO)_9$[22a] and in 35% yield from *o*-$(BrCH_2)_2C_6H_4$ and $Na_2Fe(CO)_4$.[22b]

[35] Carmona, E.; Martin, J. M.; Palma, P.; Paneque, M.; Poveda, M. L. *Organometallics* **1985**, *4*, 2053. The reaction of **5** with $NiCl_2(PMe_3)_2$ afforded $NiCl(\eta^1$-$CH_2C_6H_4CH_3)(PMe_3)_2$ and $NiCl(\eta^3$-$CH_2C_6H_4CH_3)(PMe_3)$.

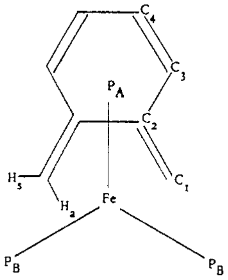
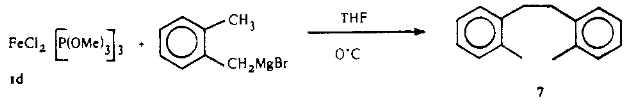


Figure 1. Numbering of atoms and representation of complexes **6**.

Scheme IV



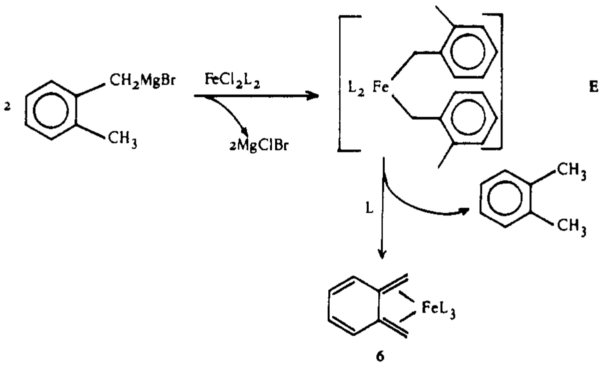
Attempts to prepare Fe(*o*-xylylene)(P(OMe)$_3$)$_3$ (**6d**) under similar conditions developed in a different way: addition of 2 equiv of the Grignard derivative **5** to FeCl$_2$(P(OMe)$_3$)$_3$ in THF at 0 °C led to a red solution, which progressively faded at room temperature. Extraction of the reaction products with pentane did not afford **6d**. Instead a white solid was isolated and identified as the organic compound **7**, resulting formally from a carbon–carbon coupling reaction of the precursor **5** (Scheme IV).

The Fe(η^2,η^2-*o*-xylylene)(PR$_3$)$_3$ structure of type IV for complexes **6a,b** was established on the basis of ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy. The ^{31}P{^{1}H} NMR spectra show, as for the corresponding Ru(η^4-*o*-xylylene)(PR$_3$)$_3$ complexes,[24a] two signals with an intensity ratio of 1:2, which are consistent with the presence of two types of phosphorus nuclei P$_A$ and P$_B$, with a symmetry plane containing P$_A$ (Figure 1).[36] Likewise, the ^{1}H NMR spectrum of **6a** shows two signals with the ratio 1:2 for the methyl groups of the phosphorus ligands.

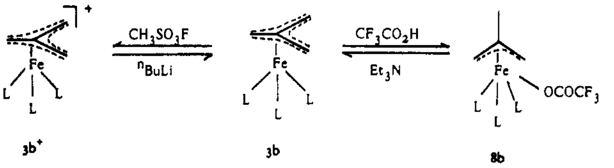
The methylene groups of the exocyclic diene of **6a,b** appears equivalent, in contrast with the methylene groups of Fe(η^3-CH$_2$C(CH$_3$)CH$_2$)$_2$(PR$_3$)$_2$.[9] Each group gives two different multiplet signals, one at very high field assigned to the anti protons (Ha) [δ, −1.29 (**6a**); δ, −1.49 (**6b**)] and one at lower field assigned to the syn protons (Hs) [δ, 1.40 (**6a**); δ, 1.31 (**6b**)]. Decoupling experiments on **6a** indicated that signals at δ 1.40 and −1.29 correspond to protons that are coupled to each other, thus indicating their location on the same carbon, rather than in relative 1,4-positions.

The ^{13}C{^{1}H} NMR spectra of **6a** confirm the η^4-coordination of the hydrocarbon ligand. In addition to the methylphosphine carbon doublets, which are in the ratio 1:2, two lines appear in the aromatic region at δ 135.2 (C$_4$) and 123.8 (C$_3$) and one line at δ 92.4 and one doublet at δ 29.4 are shown corresponding respectively to a quaternary carbon (C$_2$) and to a metal bonded exocyclic carbon (C$_1$). These chemical shifts are comparable to those observed for Co(η^2,η^2-*o*-xylylene)(C$_5$H$_5$)[23] and Ru(η^2,η^2-*o*-xylylene)(PR$_3$)$_3$.[24a] On the other hand, the signal shift of carbon C$_2$ in the Pt(η^2-*o*-xylylene)(PEt$_3$)$_2$ complex[26b] has been observed at lower field (δ 157.5) in the aromatic region and this confirms the loss of aromaticity for the *o*-xylylene ligand in **6**. The C$_1$ carbon atom resonance occurs at much higher field than for the intracyclic (η^4-*o*-xylylene)metal complexes M(C$_6$Me$_4$(CH$_2$)$_2$)(C$_6$Me$_6$): δ 88.0 (M = Fe)[25a] and 89.04 (M = Ru);[25b] it is the only one to show a ^{13}C–^{31}P coupling, suggesting a stronger interaction between the iron center and the exocyclic carbons C$_1$ than with the intracyclic C$_2$ carbons.

Scheme V



Scheme VI



The formation of complexes Fe(η^2,η^2-*o*-xylylene)(PR$_3$)$_3$ (**6a,b**) from **5** involves a formal δ(C–H) abstraction of the (*o*-methylbenzyl)iron moiety, which corresponds to a δ(C–H) activation process, for **5** itself in THF does not undergo formation of *o*-xylene. An analogous phenomenon has been observed during the reaction of the same Grignard reagent **5** with RuCl$_2$L$_4$ (L = PMe$_2$Ph, PMePh$_2$, PEt$_3$),[24a] which led to the formation of Ru(η^2,η^2-*o*-xylylene)L$_3$ complexes, whereas **5** reacted differently with NiCl$_2$(PEt$_3$)$_2$[35] but with PtCl$_2$(PEt$_3$)$_2$ afforded Pt(η^1-CH$_2$C$_6$H$_4$CH$_3$)$_2$(PEt$_3$)$_2$, which on heating was transformed into Pt(η^2-*o*-xylylene)(PEt$_3$)$_2$.[26b] The formation of **6** from **1** is not disfavored by the necessity of phosphine elimination as in the case of the analogous ruthenium (0) complex.[37]

Scheme V can account for the formation of complexes **6**: two transmetalation reactions of the 2 mol equiv of **5** to **1a** and **1b** are expected to lead to the 14-electron intermediate E. This coordinatively unsatured iron center bonded to basic phosphines should favor either a δ(C–H–Fe) two-electron agostic interaction or a δ(C–H) oxidative addition.[6] Elimination of *o*-xylene and addition of phosphine would then lead to complex **6**. An alternative pathway may involve addition of phosphine prior to oxidative addition of the C–H bond to the resulting 16-electron iron intermediate, as has been shown for Os(H)(η^1-CH$_2$C(CH$_3$)$_3$)(PMe$_3$)$_4$[6e] before neopentane elimination. However, it has been shown that Pt(η^1-CH$_2$C$_6$H$_4$CH$_3$)$_2$(PEt$_3$)$_2$ on heating also led to *o*-xylene elimination via C–H activation[26a] and that Pt(η^1-CH$_2$C(CH$_3$)$_3$)$_2$(PR$_3$)$_2$[38] involves initially a 14-electron intermediate, via phosphine dissociation, and lead to γ(C–H) intramolecular oxidative addition prior to neopentane elimination. Scheme V also supports the transformation of **1d** and **5** into **7** instead of the expected analogous complex **6d**. In that case, the presence of three phosphite ligands in **1d** would give a 16-electron intermediate of type E with a less electron-rich

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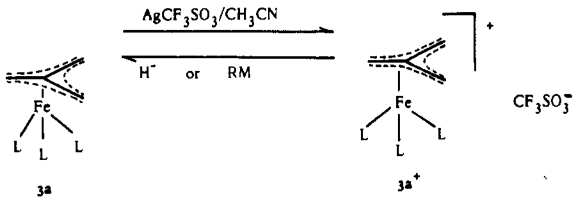
[36] The spectrum of **6a** only showed a coupling between P$_A$ and P$_B$, although with a low $^2J_{P_AP_B}$ value of 6 Hz. No such coupling was observed in **6b**, Fe(η^4-butadiene)(PMe$_3$)$_3$,[30] or Ru(*o*-xylylene)(PR$_3$)$_3$.[24a]

[37] Ru(η^2,η^2-*o*-xylylene)(PMe$_3$)$_3$ could not be obtained from the Grignard reagent **5** but was obtained by treatment of RuCl$_2$(PMe$_3$)$_4$ with *o*-CH$_3$C$_6$H$_4$CH$_2$Li·Me$_2$NCH$_2$CH$_2$NMe$_2$, likely because of the stability of the RuPMe$_3$ bond.[24a]

[38] Foley, P.; Di Cosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* 1980, *102*, 6713.

Scheme VII



center than from **1a** and **1b**. Thus, the δ(C–H) oxidative addition is expected to be disfavored vs reductive elimination with carbon–carbon bond formation.

Chemical Properties of Fe(TMM)L$_3$ and Fe(*o*-xylylene)L$_3$ Complexes (3 and 6). Protonation of 3. The protonation of the Fe(TMM)L$_3$ complex **3b** has been monitored by NMR spectroscopy. Reaction of complex **3b** with trifluoroacetic acid at room temperature in acetone-d_6 led instantaneously to a fading of the solution with quantitative formation of the corresponding methyl-2-allyl complex **8b** (Scheme VI). In the ^{1}H NMR spectrum, beside the doublet for the methyl groups of PMe$_2$Ph at δ 2.38, two new signals were observed: at δ 4.59 corresponding to the resonance of the syn protons (H$_s$) and at δ 1.65 resulting from the superposition of the anti protons (H$_a$) and allyl methyl proton resonances as shown by selective decoupling experiments.

Unlike Fe(η^3-methyl-2-allyl)(CO)$_3$Cl,[15] which reversibly eliminates HCl on heating in cyclohexane, complex **8b** was inert in refluxing THF, acetonitrile, or toluene. However, **8b** was easily deprotonated by triethylamine and afforded **3b** in 75% yield.

Reactivity of 3 toward FSO$_3$CH$_3$. Addition of FSO$_3$CH$_3$ to complex **3b** was carried out in an attempt to alkylate the TMM ligand. At −78 °C in ether it led immediately to the formation of a green precipitate stable at low temperature. Addition of 1 equiv of *n*-BuLi, in an attempt to deprotonate the green cation, actually gave back quantitatively the starting complex **3b**. The green complex was characterized as a salt of the 17-electron complex TMMFeL$_3^+$ (**3b**$^+$) (vide supra). Its formation suggested that "magic methyl" played the role of an oxidant and that functionalization of the TMM ligand could not be achieved with strong oxidative reagents (Scheme VI).

Oxidation of Fe(TMM)L$_3$ Complexes (3). Addition of 1 equiv of silver triflate to a CH$_3$CN solution of **3a** led immediately to a color change from orange to green, with formation of the paramagnetic 17-electron complex (TMM)Fe(PMe$_3$)$_3^+$CF$_3$SO$_3^-$, **3a**$^+$ (CF$_3$SO$_3^-$), isolated as a green crystalline powder in 80% yield (Scheme VII). Oxidation of complex **3b** with silver triflate at room temperature in acetone or acetonitrile gave quantitatively the **3b**$^+$ cation which slowly decomposed at room temperature to give a noncharacterized yellow compound, whereas it was found to be indefinively stable at −50 °C. The stability of **3b**$^+$ was also found to be solvent dependent: oxidation of **3b** in CH$_2$Cl$_2$ gave **3b**$^+$, which decomposed at room temperature within a few minutes. The products **3a**$^+$ and **3b**$^+$ were characterized by paramagnetic ^{1}H NMR and by X-ray structure analysis of **3a**$^+$.

The reactivity of cations **3a**$^+$ and **3b**$^+$ toward nucleophiles differed radically from that of Mo(TMM)(CO)$_2$(C$_5$Me$_5$)$^+$,[16d] which afforded the (η^3-allyl)metal derivatives via nucleophilic addition to the methylene carbons. Nucleophiles such as H$^-$ (NaH, NaBH$_4$) and R$^-$ (CH$_3$MgI, (PhCH$_2$)$_2$Cd, NaCH(CO$_2$Et)$_2$) reacted with **3a**$^+$ in THF to give quantitatively the starting complex **3a**. These reactions were consistent with an electron transfer from the nucleophile to the oxidized species **3**$^+$.

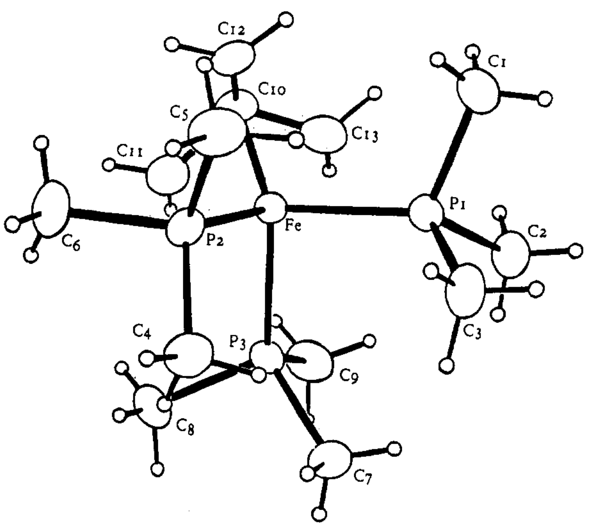
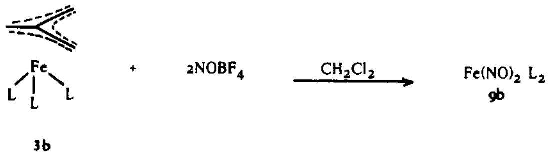


Figure 2. ORTEP drawing of Fe(η^4C$_4$H$_6$)(PMe$_3$)$_3^+$, in **3a**$^+$(CF$_3$SO$_3^-$).

Scheme VIII



Reactivity of 3b toward NOBF$_4$. It is well-known that the nitrosonium ion can function as a ligand or as a one-electron oxidant.[39] When 1 equiv of NOBF$_4$ was added at room temperature to a CH$_2$Cl$_2$ solution of **3b**, a color change immediately occurred from orange to green and then progressed to red. Addition to another equivalent of NOBF$_4$ led to the complete disappearance of **3b** with formation of the diamagnetic red complex Fe(NO)$_2$(PMe$_2$Ph)$_2$ (**9b**) in 35% yield (Scheme VIII). This complex, which showed two NO stretching vibrations at 1720 and 1670 cm^{-1} in the infrared spectrum, could also be obtained by addition of NOBF$_4$ to Fe(η^3-allyl)$_2$(PR$_3$)$_2$ derivatives.[9]

The possibility that the transient green species could be the oxidized complex **3b**$^+$ was confirmed by a rotating-disk voltammetry experiment. When 1 equiv of NOBF$_4$ was added to an acetonitrile solution of **3b** (containing 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte), the voltammogram showed a reduction wave at −0.36 V vs SCE corresponding to the oxidized species **3b**$^+$ (vide supra). A few minutes later, a new oxidation wave appeared at +0.13 V. By addition of a second equivalent of NOBF$_4$, the reduction wave of **3b**$^+$ disappeared with, at the same time, an increase of the anodic intensity of the wave at +0.13 V. This new wave was found to be due to the oxidation of the dinitrosyl complex **9b**. Therefore, although the overall mechanism is not elucidated, this study establishes that the formation of **9b** from **3b** occurs via an initial one-electron transfer from **1b** to the nitrosonium cation.

X-ray Crystallographic Studies of 3a$^+$(CF$_3$SO$_3^-$). An ORTEP drawing of the cation **3a**$^+$ with hydrogen atoms is shown in Figure 2. Atomic coordinates for the nonhydrogen atoms are listed in Table II, while selected bond distances and angles are given in Table III. The molecular structure, determined at 128 K, of the organometallic

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[39] (a) Connelly, N. G.; Kelly, R. L. *J. Organomet. Chem.* **1976**, *102*, C16. (b) Connelly, N. G.; Demidowicz, Z.; Kelly, R. J. *J. Chem. Soc., Dalton. Trans.* **1975**, 2335.

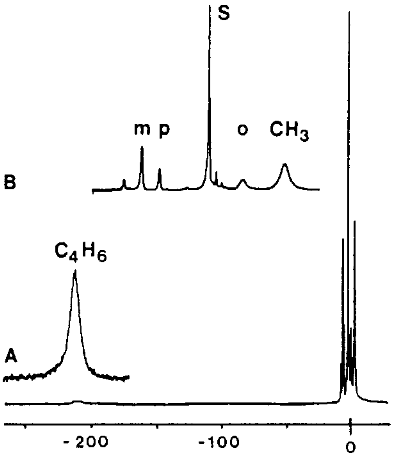

Figure 3. A 200 MHz ^1H NMR spectrum of $Fe(\eta^4\text{-}C_4H_6)(PMe_2Ph)_3{}^+NO_3{}^-$ (**3b**$^+$) in CD_3CN at 237.8 K. The scale (in ppm) is linked arbitrarily to TMS since experimental spectra do not give uniform paramagnetic shifts: (A) vertical scale × 25; (B) region around 0 ppm expanded (S = solvent).

moiety **3a**$^+$ presents a rare example of a piano-stool paramagnetic 17-electron complex. The η^4-C_4H_6 ligand adopts an umbrella shape for which the central C(10) atom is bent away from the iron center, with regard to the C(11),C(12),C(13) plane. This conformation was also found in other structurally solved metal–TMM complexes such as Fe(TMM-Ph)$(CO)_3$,[40] Fe(TMM)$(CO)_3$,[41] Cr(TMM)$(CO)_3(PPh_3)$,[16b] Mo(TMM)$(CO)_2(C_5Me_5)(BF_4)$,[16d] of Ir(TMM)Cl(CO)(PPh_3).[16c] Structural comparison can be made between **3a**$^+$ and Fe(TMM)$(CO)_3$ whose structure was determined by electron diffraction:[41] the bond distances in cation **3a**$^+$ for C(central–C(outer) (average 1.420 Å), C(central)–Fe (1.930 (2) Å), and C(outer)–Fe (average 2.122 Å) are similar to the corresponding bond lengths in Fe(TMM)$(CO)_3$ of 1.437 (2), 1.938 (5), and 2.123 (5) Å,[41] respectively. Likewise, the Fe–C(central)–C(outer) [**3a**$^+$ (average 76.9°; Fe(TMM)$(CO)_3$ (76.4 (2)°)] and C(outer)–C(central)–C(outer) angles [**3a**$^+$ (average 115.10°); Fe(TMM)$(CO)_3$ (114.6 (2)°)] are nearly identical in both structures. This comparison leads to the conclusion that the neutral "$Fe(CO)_3$" and the charged "$Fe(PMe)_3{}^+$" fragments have approximately the same electronic effects on the Fe(TMM) moiety, even if the positive charge and the radical nature induce a different reactivity of **3a**$^+$ as compared to Fe(TMM)$(CO)_3$.

The structure shows a distorted staggered conformation of the $Fe(PMe_3)_3$ unit with respect to the TMM ligand, with a larger torsion angle of 45.3° for the P(1)–Fe–C(10)–C(13) angle and with a larger P(1)–Fe–P(3) angle (100.53 (3)°) than the other two (97.91 (2)° and 96.90 (3)°). However, the careful search for a possible stabilizing interaction in **3a**$^+$ does not allow for the detection of any Fe···H–C three-center, three-electron agostic interaction.[4] Nevertheless, Figure 2 shows that the 33 C–H bonds of **3a**$^+$ are spread around the cation making almost a regular sphere. This may constitute a steric protection of the iron center and explain the relative stability of **3a**$^+$ with respect to **3b**$^+$.

^{1}H NMR Spectra of 3$^+$ and 6$^+$. The 17-electron oxidation products of the trimethylenemethane and *o*-xylylene complexes may be studied by NMR spectroscopy. Representative examples are **3a**$^+$, **3b**$^+$, and **6a**$^+$, and the ^{1}H NMR spectrum of **6b**$^+$ is shown in Figure 3.

Table IV. Paramagnetic ^{1}H NMR Shifts ($\delta^{para}(^1H)$)

		proton position	
compd	temp, K	η^4-ligand	phosphine
3a$^+$	235.0	−213.5	3.7
3b$^+$	237.8	−215.1	4.4 (CH_3) 7.3 (ortho) 0.8 (meta) 3.2 (para)
6a$^+$	237.8	−50.1 −11.3 −4.8	1

The resonances of the phosphine and TMM appear in rather different shift ranges. While the TMM signal has a large paramagnetic shift, the signals of interest in the diamagnetic shift range are easily identified, beside some diamagnetic impurities, since they move on changing the temperature. The assignment is based on the relative signal areas while ortho and meta protons are distinguished by the signal width: the meta and para protons are less susceptible to dipolar relaxation than the ortho protons. The latter should have a signal that is broadened similarly as the PCH_3 signal. In fact, this is observed in Figure 3.

We can obtain the ^{1}H NMR spectrum of **6a**$^+$ only in the presence of the precursor **6a**. The fact that we see different sets of signals means that the interconversion of **6a** and **6a**$^+$ is slow. On the other hand, this does not allow us to identify the PMe_3 signals of **6a**$^+$. They are buried under the corresponding signals of **6a**, and we estimate their paramagnetic shifts to be smaller than 1 ppm. For the *o*-xylylene ligand three signals appear with intensity ratios of roughly 1/2/1 in the order of decreasing frequency. One is tempted to believe that the spin density at the ligand nuclei determines the signal shifts so that the protons linked to the cycle fall together. However, because of a lack of ESR information[42] nothing precise is known about the dipolar shift contribution, and hence a detailed signal assignment is too speculative at present. The ^{1}H NMR data are collected in Table IV.

Temperature-dependent studies on **3a**$^+$ show that the Curie law is followed rather closely. The deviation is not uniform; it is best discernible by the reduced paramagnetic shifts $\vartheta = \delta^{\,para}T/298$ in Table V.

For the interpretation of the data two approaches may be put forward. Considering first a planar TMM, the orbital interaction diagram for **3a** and **3b** should be similar to that of (TMM)Fe$(CO)_3$.[43a] In particular, no inversion of the highest three orbitals is expected since PR_3 is a better σ donor and a weaker π acceptor than CO. Hence, in **3a**$^+$ and **3b**$^+$ the unpaired electron is expected to be in degenerate orbitals with a considerable ligand π-orbital content. This in turn should lead to direct π delocalization of the electron spin density and to a *low*-frequency signal shift similar to what is known for cobaltocenes or nickelocenes.[44] By contrast, the experimental shifts are to *high* frequency. Such a shift sign could be due to a dipolar shift. However, a crude estimate that follows the ferricinium ion[45] yields dipolar shifts which should not exceed −10 to −15 ppm. Contact shifts $\delta_{235}{}^{con}$ −200 must therefore be present. The shift to high frequency can be related to the fact that the TMM in **3a**$^+$ is not planar (cf. Table III). For

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Table V. Temperature Dependence of the ^{1}H Shifts^a of $[(\eta^4\text{-}C_4H_6)Fe(PMe_3)_3]^+NO_3^-$

	CH$_2$			CH$_3$		
temp, K	$\delta^{\rm exptl}$	$\delta^{\rm para}$	ϑ	$\delta^{\rm exptl}$	$\delta^{\rm para}$	ϑ
295.3	-170.1	-171.3	-169.7	2.4	1.6	1.6
286.7	-174.9	-176.1	-169.4	3.2	2.4	2.3
278.1	-180.0	-181.2	-169.1	3.7	2.9	2.7
269.5	-185.7	-186.9	-169.0	4.1	3.3	3.0
260.8	-191.8	-193.0	-168.9	4.4	3.6	3.2
252.7	-197.9	-199.1	-168.5	4.9	4.1	3.5
243.6	-204.9	-206.1	-168.5	5.2	4.4	3.6
235.0	-212.3	-213.5	-168.4	5.5	4.7	3.7

[a] Experimental shift, $\delta^{\rm exptl}$, measured relative to the signal of the residual protons in the solvent CD_3CN. Paramagnetic shift, $\delta^{\rm para}$, calculated relative to the corresponding signals of the diamagnetic precursor. Reduced shift, $\vartheta = \delta^{\rm para}T/298$.

Table VI. Cyclic Voltammetric Data of 3 and 6^a

	1st wave		2nd wave^b
complex	$E_{1/2}$, V	ΔE_p, mV	E_{p_a}, V
3a	-0.450	60	+0.50
3b	-0.365	70	+0.70
3c	-0.655	70	+0.15
(TMM)Fe(CO)$_3$	+2.0^c		
6a	-0.610	60	+0.50
6b	-0.510	60	+0.70
6d	-0.100	60	+0.65

[a] At a platinum electrode in CH_3CN solutions containing 0.1 M Bu_4NPF_6 and 0.5×10^{-3} complex. Scan rate 100 mV·s^{-1}. Potentials are reported relative to SCE. [b] Irreversible wave. [c] Irreversible peak potential.

an umbrella-shaped TMM σ-type e′ ligand, orbitals are mixed into the spin-containing molecular orbital[43a] and direct σ delocalization should lead to negative $\delta^{\rm con}$ as observed.

A second approach is to allow for orbital relaxation on passing from **3** to **3**$^+$. Actually, Böhm and Gleiter[43b] have shown that the highest occupied molecular orbital of $[(TMM)Fe(CO)_3]^+$ is essentially metal in character, which is in nice agreement with photoelectron results. In this case we expect π polarization to create unpaired spin density on the ligand and to lead to negative $\delta^{\rm con}$. The shifts could be enhanced by the above-mentioned σ-delocalization.

Paramagnetic ^{13}C NMR should rule out one interpretation because the first leads to negative $\delta^{\rm con}(^{13}C)$ of the TMM signals while the second leads to positive shifts. Unfortunately, for **3a**$^+$ the signal-to-noise ratio allowed detection of only one signal with an experimental shift of -91.2 ppm. We tentatively assign this signal to the phosphine ligands which, according to ^{1}H NMR, are little affected by the unpaired spin.

A similar reasoning applies for **6a**$^+$. The fact that the $\delta^{\rm para}$ is much smaller than those for **3a**$^+$ and **3b**$^+$ agrees well with *o*-xylylene being a less distorted ligand than TMM. Actually, from Ru(*o*-xylylene)$(PMe_2Ph)_3$[24a] it may be derived that the π ligand of **6a**$^+$ has a carbon skeleton that is essentially planar so that the π delocalization should be greatly reduced. Yet the $\delta^{\rm para}(^1H)$ are negative. Whether this is due to π polarization cannot be decided at present because nothing is known about the orbital relaxation of **6a**/**6a**$^+$.

Electrochemical Studies of Complexes 3 and 6. The cyclic voltammetry of Fe(TMM)L_3 (**3**) and Fe(*o*-xylylene)L_3 (**6**) was studied in acetonitrile. The cyclic voltammogram of **3b** (0.1 M Bu_4NPF_6/CH_3CN) is shown in Figure 4. The electrochemical oxidation potentials for the complexes **3** and **6** are listed in Table VI. Fe(TMM)L_3 complexes **3** showed a *reversible* oxidation wave between -0.65 and -0.20 V vs SCE. This very low potential and the reversibility, therefore the stability of **3**$^+$, demonstrate the electron-rich character of the formally iron(II) complexes of **3**. An additional *irreversible* oxidation was observed between +0.15 and +0.70 V. Successive scans, farther than this second wave, resulted in a poisoning of the electrode (Figure 3). This is attributed to the decomposition of the complexes and oxidation of related phosphines. The same phenomenon was observed during oxidation of PMe_2Ph, for instance, at the same potential.

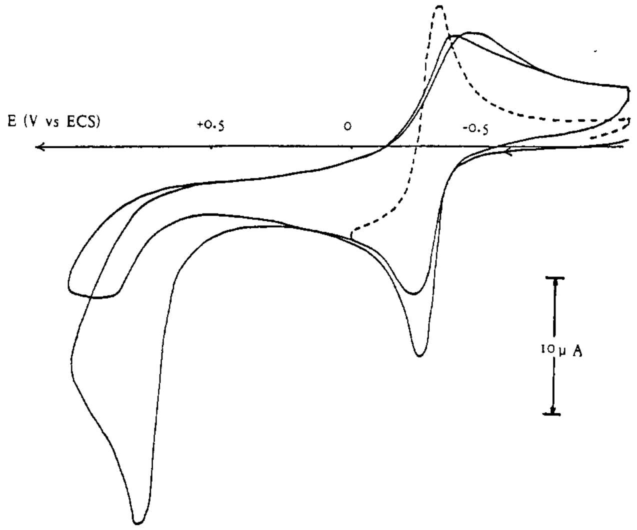

Figure 4. Cyclic voltammogram of Fe$(\eta^4\text{-}C_4H_6)(PMe_2Ph)_3$ (**3b**) in 0.1 M tetrabutylammonium hexafluorophosphate/CH_3CN medium at 100 mV·s^{-1}.

Oxidation of complex **3b** was also studied by voltammetry, by using a rotating disk electrode: addition of 1 equiv of an oxidant ($AgCF_3SO_3$ or $Cp_2Fe^+PF_6^-$) to a CH_3CN solution of **3b** led immediately to the disappearance of the *oxidation* wave and to the formation of the corresponding reduction wave of **3b**$^+$.

The one-electron character of the first oxidation was confirmed by controlled potential coulometry at a vitreous carbon electrode of **3b** at 0 V vs SCE in CH_3CN which gave a value of 1 F. Controlled potential coulometry of **3b** at +0.9 V showed that the second oxidation is an approximately 4-F oxidation. This is consistent with the decomposition of complex **3** with dissociation of the three phosphines at such a potential.

The first oxidation potential for the **3**/**3**$^+$ couples strongly depends on the nature of the phosphine ligands L. $E^{1/2}$ is lowered as the electron-donor capability of L is increased and follows the sequence $PMePh_2 < PMe_3 < MeC(CH_2PMe_2)_3$ (Table VI). Moreover, this electrochemical study shows the striking effect of these phosphorus groups in **3** as compared to the carbonyl TMM complex: we found Fe$(\eta^4\text{-}C_4H_6)(CO)_3$ to be oxidized *irreversibly* and at much more positive potential (E_p = +2 V vs SCE) than complexes **3**. This correlates with the important difference in chemical reactivity between $Fe(TMM)L_3$ complexes ($L = PR_3$ (**3**) and L = CO): a one-electron transfer easily occurs from **3** on attempts of alkylation and the resulting 17-electron intermediate is stabilized by the basic phosphines L, whereas $Fe(TMM)(CO)_3$ is the site of electrophilic substitutions,[15] but its one-electron abstraction is difficult to perform and immediately undergoes decomposition, presumably via initial cleavage of an Fe–CO bond. This illustrates the deciding role of the nature of the ligands to modulate the behavior of complexes within the same family.

Cyclic voltammetry of **6a–c** showed a *reversible* one-electron oxidation at negative potential corresponding to the formation of $Fe(o\text{-xylylene})L_3^+$ (**6**$^+$), and an *irreversible* wave between 0.50 and 0.70 V was observed (Table VI). The latter oxidation can be attributed to the **6**$^+$/**6**$^{2+}$ couple which may decompose with phosphine dissociation. The ease of the first oxidation of **6** confirms their electron-rich character. The lowering of the corresponding potential follows the expected increase in electron-donor ability of phosphorus derivatives L according to the sequence $P(OMe)_3 < PMe_2Ph < PMe_3$. Of special interest is the comparison of the first oxidation potentials for **3** and **6** and for the same ligand L. It shows a greater reducing power for **6** vs **3** of more than 0.2 V. This is consistent with a lower oxidation state of the iron center in **6** than in **3**. It confirms the nature of an (η^4-diene)Fe^0 complex of type IV for derivatives **6**.

Conclusion

Our results present an easy access to electron-rich (η^4-hydrocarbon)iron complexes via $FeCl_2(PR_3)_n$ intermediates, magnesium, and halogenated substrates. This method avoids the preliminary preparation of unstable Grignard reagents and should offer a potential for organometallic syntheses. The nature and the number of ancillary PR_3 groups play a determining role for the reactivity of $FeCl_2(PR_3)$ with $o\text{-BrMgCH}_2C_6H_4CH_3$, which leads to either a C–H activation or a C–C coupling reaction. The studied $Fe(\eta^4\text{-TMM})L_3$ and $Fe(\eta^4\text{-}o\text{-xylylene})L_3$ complexes show at the same time a high tendency to give an electron transfer and an unexpected stability of the resulting paramagnetic species. These two characteristics, which are indicative of the electron-rich nature of the complexes, appear to be modulated by the electron-donor capability of the phosphorus groups and also by the type of interaction between the hydrocarbon ligand and the metal.

Acknowledgment. We are grateful to C. Mountassir and Dr. S. Sinbandhit for helpful assistance and discussions.

Registry No. **1a**, 55853-16-2; **1b**, 95911-92-5; **1d**, 55059-43-3; **2**, 1871-57-4; **3a**, 95911-86-7; **3a**$^+(CF_3SO_3^-)$, 95911-88-9; **3a**$^+(NO_3^-)$, 111409-19-9; **3b**, 95911-83-4; **3b**$^+(CF_3SO_3^-)$, 95911-85-6; **3c**, 111409-15-5; **3c**$^+(CF_3SO_3^-)$, 111409-17-7; **4a**, 612-12-4; **5**, 56812-61-4; **6a**, 111409-13-3; **6a**$^+$, 111409-14-4; **6b**, 95911-91-4; **6d**, 95911-89-0; **7**, 952-80-7; **8b**, 111409-18-8; **9b**, 110074-88-9; $MeC(CH_2PMe_2)_3$, 77609-83-7; $CH_3C(CH_2Cl)_3$, 1067-09-0.

Supplementary Material Available: Tables of bond lengths, bond angles, and anisotropic temperature factors and an ORTEP of the structure including the anion (Figure S1) for **3a**$^+(CF_3SO_3^-)$ (4 pages); a listing of calculated and observed structure factors (10 pages). Ordering information is given on any current masthead page.

Metallacyclobutadiene versus Metallatetrahedrane Structures for $Cl_3MoC_3H_3$ Complexes

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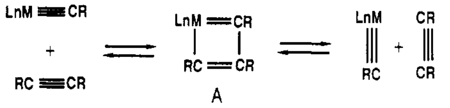
Received May 13, 1987

The bonding and energetics in the $Cl_3MoC_3H_3$ metallacyclobutadiene are contrasted with those in the metallatetrahedrane. The complexes are found to be within 20 kcal/mol of one another, with the metallatetrahedrane being the lower in energy. The Mo–C bonds are essentially covalent in both structures, and the metallacyclobutadiene possesses resonance stabilization. Charge distribution in the carbon fragments reveals no cyclopropenium character in the C_3H_3 ring of the metallatetrahedrane. Bonding, energetics, and charge distributions are all discussed with an emphasis on structure and reactivity.

I. Introduction

Metallacyclobutadienes A are believed to play the same role in acetylene metathesis[1] (eq 1) as metallacyclobutanes B play in olefin metathesis[2] (eq 2). Strong evidence for the role of A in acetylene metathesis is provided by the isolation and crystal structures of the following complexes: **1**, $W[C(CMe_3)(CMe)_2]Cl_3$;[3] **2**, $W(C_3Et_3)[O\text{-}2,6\text{-}C_6H_3(i\text{-}Pr)_2]_3$;[4] **3**, $W(C_3Et_3)[OCH(CF_3)_2]_3$.[5] Unfortunately, not all



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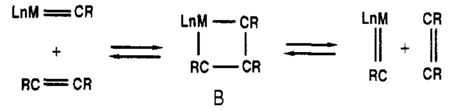

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