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Synthesis of Bis(methoxycarbene) and Bis(alkylidene) Ligands Bridging Two Iron Centers in the Cp*Fe(L1)(L2) Series. X-ray Crystal Structure of the Iron Alkylidene [Cp*Fe(dppe)(=C(H)Me)][PF$_6$]

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The carbene [Cp*Fe(dppe)(=C(OMe)Me)][CF$_3$SO$_3$] [**2b**, Cp* = η^5-C$_5$Me$_5$, dppe = ethylenebis(diphenylphosphine)] was prepared in 97% yield from [Cp*Fe(CO)$_2$(=C(OMe)Me)][CF$_3$SO$_3$] upon photochemical displacement of the carbonyl ligands, and the iron methoxycarbene [Cp*Fe(CO)(PMe$_3$)(=C(OMe)Me)][CF$_3$SO$_3$] (**2c**) was obtained (80%) upon alkylation of the acyl derivative Cp*Fe(PMe$_3$)(CO)(COCH$_3$) (**4**). The iron−methylidene [Cp*Fe(dppe)(=C(H)Me)][PF$_6$] (**6**) was synthesized (95%) by treatment of Cp*Fe(dppe)(CH(OMe)Me) (**5**) with an aqueous solution of hexafluorophosphate acid. The ethylidene **6** is very stable in solution as in the solid state, and no decomposition reaction was observed by NMR spectroscopy at 50 °C. The X-ray crystal structure of **6** was solved and refined. The Fe−C(37) bond distance (1.787 Å) reveals the double-bond character of the metal−carbon bond. Reaction of the iron carbene complexes **2a**−**c** and **6** with 2 equiv of potassium *tert*-butoxide in THF gave the corresponding vinyl derivatives **7a**−**d** in high yield (80−90%). CV analyses of the vinyl complexes **7a**−**d** display at 20 °C an oxidation wave at a platinum electrode with the $(i_p{}^a/i_p{}^c)$ current ratio less than unity. CV and ESR measurements established the stability of the 17-electron vinyl radical in CH$_2$Cl$_2$ at −80 °C. Warming to 20 °C of the 17-electron iron(III) complexes $[\mathbf{7a{-}d}]^{\bullet+}[\mathrm{PF}_6^-]$ in solid state allows the vinyl−vinyl coupling providing the new binuclear bis(carbene) complexes **8a**−**d** in 60−95% yield. The complex **8a** was isolated as a pure diastereoisomer, whereas **8b** was a mixture of the *meso* **8b(*RS*,*SR*)** and *dl* **8b(*RR*,*SS*)** isomers in the 2/1 ratio. The diastereoisomers were separated by CH$_2$Cl$_2$ extraction which only solubilizes the *dl* pair.

The bimetallic complexes without a metal−metal bond of general formula **I**, in which a hydrocarbon chain

$$\underset{\mathbf{I}}{L_nM(CH_2)_xML_n} \qquad \underset{\mathbf{II}}{L_nM{=}C(X)(CH_2)_{x-2}(X)C{=}ML_n}$$

spans two organometallic building blocks have been the subject of considerable interest.[1−11] In contrast, analogous complexes **II** which contain an organic bridging ligand with terminal carbene function coordinated to organometallic moieties have only been the subject of few reports.[12−20]

We had examined the reactivity of iron carbene complexes upon one electron reduction with the objective to make carbene−carbene ligand coupling, thus opening a route to new dimers. Meanwhile dimerization of many 19-electron metal-centered radicals by ligand−ligand coupling is often a kinetically favored reaction, we observed that the transient 19-electron metal carbene species does not follow this reaction pathway but reacts by loss of the carbene functionality.[21] Concomitantly, we had also an ongoing interest in the physical and chemical properties of the half-sandwich iron(III)

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17-electron complexes.[22] In particular we carried out works on the iron(III) ethynyl derivatives[23,24] which can form a butadiyndiyl carbon chain between the two Cp*Fe(dppe) units upon ligand−ligand coupling.[25,26] Other exemples of ligand−ligand coupling via a 17-electron transition metal radical involving various types of unsaturated hydrocarbons[27] such as *inter alia* cyclopentadienyl,[28] cyclooctatetraene,[29,30] vinylidene,[31] or dienyl are known as well.[32]

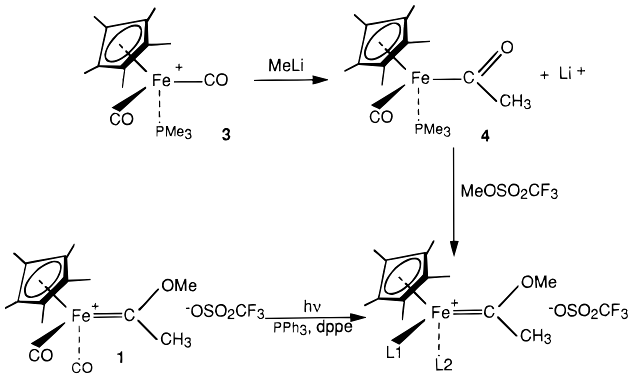
Following the same line, carbon−carbon bond coupling was also expected to occur between two 17-electron iron radical cations with a η^1-vinyl ether or vinyl ligand (eq 1) to give a convenient new entry to binuclear μ-bis(carbene) complexes.

$$2[L_nFeC(X)CH_2]^{\bullet+} \rightarrow [L_nFe{=}C(X)CH_2CH_2(X)C{=}FeL_n]^{2+} \quad (1)$$

$$L_nFe = Cp^*Fe(L1)(L2);\ X = OMe, H$$

In a previous communication we already reported the first exemple of such complexes of class **II**.[33] The stability of the related 17-electron intermediates is expected to be highly dependent on the nature of the ancillary ligands L1 and L2 coordinated to the metal, and as a consequence, the scope of the reaction could be limited. Examination of the relationship between the dimerization of these complexes and their thermal stability constitutes the first objective of this paper in which we also report the synthesis and the characterization of (i) the new methoxymethyl iron carbene complexes $[Cp^*Fe(L1)(L2)({=}C(OMe)Me)][CF_3SO_3]$ (**2a**, L1 = CO, L2 = PPh_3; **2b**, L1, L2 = dppe; **2c** = L1 = CO, L2 = PMe_3), (ii) the thermally stable mononuclear iron methylidene complex $[Cp^*Fe(dppe)({=}C(H)Me][CF_3SO_3]$ (**6**) and its X-ray crystal structure, (iii) the related mononuclear iron vinyl complexes $[Cp^*Fe(L1)(L2)(C(R)CH_2)]$ (**7a**, R = OMe, L1 = CO, L2 = PPh_3; **7b**, R = OMe, L1 = CO, L2 = PMe_3; **7c**, R = OMe, L1, L2 = dppe; **7d**, R = H, L1, L2 = dppe), and (iv) the binuclear μ-η^1:η^1-bis(carbene) complexes $[\{Cp^*Fe(L1)(L2)\}_2\mu\text{-}({=}C(R)CH_2CH_2C(R)C{=})][PF_6]_2$ (**8a**, R = OMe, L1 = CO, L2 = PPh_3; **8b**, R = OMe, L1 = CO, L2 = PMe_3; **8c**, R = OMe, L1, L2 = dppe; **8d**, R = H, L1, L2 = dppe). The diasteroselective coupling of the two vinyl radicals is also a complementary and important aspect when the vinyl ligand is coordinated to a stereogenic iron center as in **2a**−**b**.

Scheme 1



2a, L1 = CO, L2 = PPh_3
2b, L1 = CO, L2 = PMe_3
2c, L1, L2 = dppe

Results and Discussion

1. Synthesis of the Iron Methoxymethylcarbene $[Cp^*Fe(L1)(L2)({=}C(OMe)Me)][CF_3SO_3]$ (2a, L1 = CO, L2 = PPh_3; 2b, L1 = CO, L2 = PMe_3; 2c, L1, L2 = dppe) Complexes. We have previously shown that the alkoxycarbene complex $[Cp^*Fe(CO)_2({=}C(OMe)Me)][CF_3SO_3]$ (**1**) readily undergoes specific substitution of one or two carbonyl ligands, depending on the photochemical conditions, and compound **2a** was obtained following this route.[34] Following this procedure, the new carbene with the chelating dppe ligand $[Cp^*Fe(dppe)({=}C(OMe)Me)][CF_3SO_3]$ (**2c**) was prepared in 97% yield (see Experimental Section). Although the scope of this method is quite large and allows the preparation of various mono- and disubstituted iron methoxycarbene complexes, we found a limitation when making the monosubstitution of electrophilic carbene derivatives with the basic trimethylphosphine. Indeed, the carbene complex $[Cp^*Fe(CO)_2({=}C(OMe)Me)][CF_3SO_3]$ (**1**) reacts thermally with trimethylphosphine providing the phosphonium complex $[Cp^*Fe(CO)_2(C(PMe_3)(OMe)Me)][CF_3SO_3]$.[35] As a consequence, an alternative synthesis had to be used with this electron-rich phosphine, starting from the organometallic salt $[Cp^*Fe(CO)_2(PMe_3)][PF_6]$ (**3**)[33,36] (Scheme 1). Treatment of the complex **3** with 1.2 equiv of methyllithium afforded after hydrolysis the iron acyl $Cp^*Fe(PMe_3)(CO)(COCH_3)$ (**4**) isolated as a yellow powder in 78% yield and characterized by IR and ^1H, ^{13}C, and ^{31}P NMR spectroscopies (Table 1). The IR spectrum (CH_2Cl_2) of **4** displays the characteristic terminal carbonyl and the acyl stretching bands at 1891 and 1578 cm^{-1}, respectively. The carbonyl of the acyl moiety is observed on the ^{13}C NMR spectrum as a doublet at δ 288.3 (d, $^2J_{CP}$ = 27.9 Hz) whereas the carbonyl ligand resonates at δ 220.9 (d, $^2J_{CP}$ = 30.6 Hz). The compound **4** gave the tertiary methoxycarbene derivative $[Cp^*Fe(CO)(PMe_3)({=}C(OMe)Me)][CF_3SO_3]$ (**2b**) upon reaction with 1 equiv of methyl triflate in diethyl ether. The air-stable and analytically pure complex **2b** was isolated as orange yellow microcrystals in 80%

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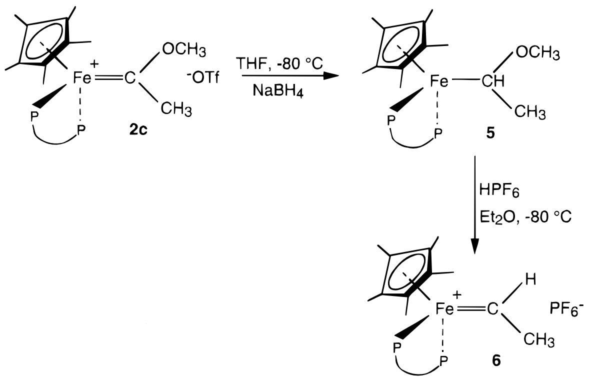
Scheme 2



yield. The resulting carbene complexes **2b**−**c** were characterized by IR and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies (Table 1). Their downfield ^{13}C resonance pattern is characteristic of the methoxycarbene fragment and similar to those found in other (alkoxyalkylcarbene)iron complexes of the Cp*Fe series.[34]

2. Synthesis of the Mononuclear Iron Ethylidene Complex [Cp*Fe(dppe)(=C(H)Me)][PF$_6$] (6). The complex **6** was prepared in a two-step procedure involving the formation and isolation of the (α-methoxyethyl)iron derivative Cp*Fe(dppe)(CH(OMe)-Me) (**5**). This complex was obtained from reduction of the iron carbene **2c**. The nucleophilic addition of the hydride at the carbene carbon atom was readily achieved with sodium borohydride in THF at −80 °C (Scheme 2). The resulting crude product is a mixture of (α-methoxyethyl)iron derivative Cp*Fe(dppe)(CH(OMe)-Me) (**5**) and the known iron hydride Cp*Fe(dppe)H[37] in the 95:5 spectroscopic ratio determined from the ^{1}H NMR spectrum. After several washings with pentane to remove the more soluble hydride byproduct, the complex **5** was obtained as an analytically pure red powder in 50% yield and was characterized as usual. On the ^{1}H NMR spectra, the hydrogen atom on the Cα is observed as a multiplet at δ 4.35 ppm due to the coupling with both phosphorus nuclei and the hydrogen atoms of the methyl group. The latter resonate as a doublet (δ 0.93, $^{3}J_{HH} = 5.4$ Hz). The ^{13}C NMR spectrum displays a characteristic doublet of triplet at δ 80.6 ($^{1}J_{CH} = 134$ Hz, $^{2}J_{CP} = 25$ Hz) for the carbon atom bound to the iron.

The iron−ethylidene complex **6** was prepared by treatment of a red solution of **5** in diethyl ether with an aqueous solution of hexafluorophosphoric acid. Immediately, a light beige precipitate formed and the solution turned colorless in 10 mn. After removal of the solvent, washing with diethyl ether, and recrystallization from a methylene chloride−diethyl ether mixture (50/50), the air-stable carbene complex [Cp*Fe(dppe)-(=C(H)Me)][PF$_6$] (**6**) was isolated in 95% yield. The complex **6** was characterized by ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy and the alkylidene moiety was clearly identified by the characteristic downfield resonances of Hα and Cα. The ^{1}H NMR spectrum ((CD_3)$_2$CO, 20 °C) exhibits a low-field signal at δ 15.8 due to the carbene proton; the other signals corresponding to the methyl groups of the carbene fragment and the Cp* ligand are located at δ 1.62 and 1.45, respectively. The ^{13}C resonance of the carbene carbon atom at δ 336.6 (dt, $^{1}J_{CH} = 132$ Hz, $^{2}J_{CP} = 30$ Hz) confirms the proposed structure. Note that the phosphorus atoms are equivalent and give a singlet at δ 103.3. The carbene complex **6** is very stable in solution or in the solid state, and no decomposition reaction was observed at 20 °C. A sample of the ethylidene complex **6** dissolved in $CD_3C(O)CD_3$ in a NMR tube was heated at 50 °C and monitored by ^{1}H and ^{31}P NMR. After 3 h, no visible decomposition took place.

Meanwhile the preparation of **6** represents the first case of synthesis and isolation achieved at room temperature for a first-row transition metal complex with an ethylidene ligand; its thermal stability is surprising. Thus, if the similar cationic methylene complex [CpFe-(CO)$_2$(=CH$_2$)]$^{+}$ [38] or the dimethylcarbene [CpFe(CO)$_2$-(=CMe$_2$)]$^{+}$ [39] were too unstable to be observed by ^{1}H NMR at low temperature, several ether iron methylene and alkylidene complexes were already spectroscopically characterized.[40,41] Brookhart has found that the iron ethylidene complex [CpFe(CO)(PPh$_3$)(=CHCH$_3$)]$^{+}$[O-SO$_2$CF$_3$]$^{-}$ possessed a half-live of $t_{1/2} \approx 3$ h at 25 °C and that the corresponding ethylene and other products were formed upon decomposition.[42,43] The highly electrophilic cationic phenylcarbene complexes [CpFe(CO)-(L)(=CHPh)]$^{+}$ were isolated and found to be very effective transfer agents for alkene cyclopropanation at low temperature.[44] Bodnar and Cutler found a bimolecular mechanism for the decomposition of the closely related ethylidene complexes [CpFe(CO)(L)(=CHMe)]$^{+}$ [45] giving bimolecular complexes. The neopentylidene iron derivative [CpFe(dppe)(=CHCMe$_3$)][BF$_4$] was the first secondary non-heteroatom-substituted alkylidene of the late transition metal to be isolated.[46] More recently, the synthesis of the thermally stable methylene complex [Cp*Fe(dppe)(=CH$_2$)][PF$_6$] was reported from our group.[47]

Similar reactivity trend have been also observed with rhenium alkylidene complexes. For exemple, Gladysz et al. have found that the alkylidene rhenium analogues [CpRe(NO)(PPh$_3$)(=CHR)]$^{+}$[PF$_6$$^{-}$] rearranged rather slowly.[48] As a general rule, the coordination of bulky and very electron-releasing ligand around the metal center strongly stabilizes the carbene ligand and inhibits its electrophilic properties at the α carbon atom. Thus, if the iron fragment [CpFe(CO)(PPh$_3$)]$^{+}$ is considered as a poorer π donor than the rhenium fragment [CpRe(NO)(PPh$_3$)]$^{+}$ as shown by a variety of other

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Table 1. Spectroscopic Characterization at 20 °C of the New Complexes

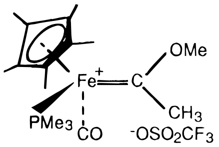
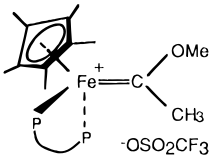
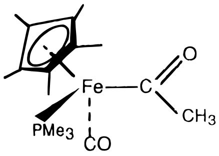
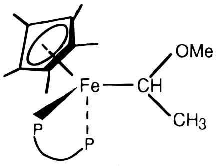
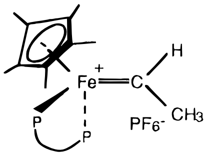
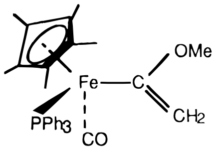
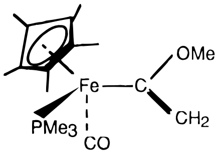
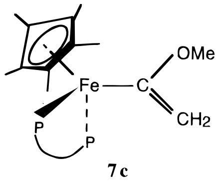
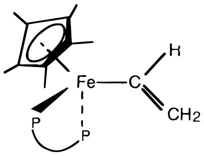
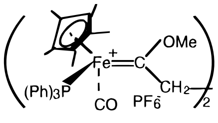
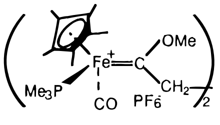
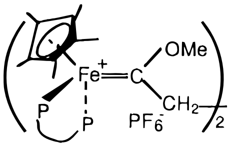
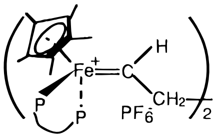
	IR: ν, cm^{-1}	^{1}H NMR: δ, ppm	^{13}C NMR: δ, ppm	^{31}P NMR: δ, ppm
 **2b**	1951 (s, ν_{CO})[a]	4.35 (s, 3 H, OMe), 2.83 (s, 3 H, Me), 1.68 (s, 15 H, C_5Me_5), 1.33 (d, 9 H, $^2J_{PH}$ = 9.9 Hz, P−Me$_3$)[a]	342.2 (d, $^2J_{CP}$ = 26.9 Hz, (=C(Me)(OMe)), 217.3 (d, $^2J_{CP}$ = 26.8 Hz, CO), 124.24 (q, $^1J_{CF}$ = 320 Hz, CF_3), 97.7 (s, C_5Me_5), 65.8 (s, OMe), 44.9 (d, $^3J_{CP}$ = 2.1 Hz, Me), 17.2 (d, $^1J_{CP}$ = 31.4 Hz, PMe_3), 9.8 (s, C_5Me_5)[a,f]	31.2 (s)[a]
 **2c**		7.40 (m, 20 H, Ph), 2.95, 2.74 (s, 2 H, PCH_2), 2.60 (s, 3 H, OMe), 2.15 (s, 3 H, Me), 1.38 (s, 15 H, C_5Me_5)[a]	318.5 (t, $^2J_{CP}$ = 28 Hz, (=C(Me)(OMe)), 138.0 (d, $^1J_{CP}$ = 33 Hz, C_{ipso}), 136.9 (d, $^1J_{CP}$ = 40 Hz, C'_{ipso}), 133.2, 132.6 (t, $^2J_{CP}$ = 4 Hz, C_{ortho}), 131.2, 131.0 (s, C_{meta}) 129.4, 129.1 (t, $^3J_{CP}$ = 4 Hz, C_{para}), 96.6 (s, C_5Me_5), 59.9 (q, $^1J_{CH}$ 147 Hz, OMe), 44.1 (q, $^1J_{CH}$ = 128 Hz, Me), 33.3 (t, $^1J_{CP}$ = 21 Hz, PCH_2), 11.2 (q, $^1J_{CH}$ = 127 Hz, C_5Me_5)[a]	111.9 (s)[a]
 **4**	1891 (s, ν_{CO}), 1578 (s, ν_{CO})	2.64 (s, 3 H, CO(Me)), 1.55 (s, 15 H, C_5Me_5), 0.99 (d, 9 H, $^2J_{PH}$ = 9.1 Hz, P−Me$_3$)[b]	288.3 (d, $^2J_{CP}$ = 27.9 Hz, CO(Me)), 220.9 (d, $^2J_{CP}$ = 30.6 Hz, CO), 93.0 (s, C_5Me_5), 51.7 (qd, $^3J_{CP}$ = 6.6 Hz, $^1J_{CH}$ = 125.6 Hz, CO(Me)), 17.2 (qd, $^1J_{CH}$ = 127.7 Hz, $^1J_{CP}$ = 26.6 Hz, P−Me$_3$), 9.9 (q, $^1J_{CH}$ = 126.9 Hz, C_5Me_5)[b]	38.1 (s)[b]
 **5**		7.40 (m, 20 H, Ph), 4.35 (m, 1 H, CH), 2.19 (s, 3 H, OMe), 1.80 (m, 4 H, PCH_2), 1.45 (s, 15 H, C_5Me_5), 0.93 (d, 3J_{HH} = 5.4 Hz, 3 H, Me)b	145.0−125.0 (m, Ph), 86.5 (s, C_5Me_5), 80.6 (td, $^1J_{CH}$ = 134.0 Hz, $^2J_{CP}$ = 25.2 Hz, CH), 55.5 (q, $^1J_{CH}$ = 138.0 Hz, OMe), 23.0 (q, $^1J_{CH}$ = 128.0 Hz, Me), 29.3 (t, $^1J_{CP}$ = 21.0 Hz, PCH_2), 11.3 (q, $^1J_{CH}$ = 127.0 Hz, C_5Me_5)[b]	113.2, 108.0 (s)[b]
 **6**		15.81 (m, 1 H, =CH), 7.40 (m, 20 H, Ph), 3.31 (m, 4 H, PCH_2), 1.62 (d, $^3J_{HH}$ = 8 Hz, 3 H, Me), 1.45 (s, 15 H, C_5Me_5)[c]	336.6 (dt, $^1J_{CH}$ = 132 Hz, $^2J_{CP}$ = 30 Hz, (=CH(Me)), 134.0 (m, Ph), 101.5 (s, C_5Me_5), 46.6 (q, $^1J_{CH}$ = 127.0 Hz, Me), 32.7 (t, $^1J_{CP}$ = 20 Hz, Ph_2PCH_2), 10.1 (q, $^1J_{CH}$ = 127.0 Hz, C_5Me_5)[c]	103.28 (s)[c]
 [g]**7a**	1902 (s, ν_{CO})	7.4−7.3 (m, 15 H, Ph), 4.08 (d, 1 H, $^4J_{PH}$ = 4 Hz, CH), 3.73 (b, 1 H, CH¢), 2.98 (s, 3 H, OMe), 1.46 (s, 15 H, C_5Me_5)[d]	223.8 (d, $^2J_{CP}$ = 28 Hz, CO), 198.2 (d, $^2J_{CP}$ = 28 Hz, C−Fe), 133.9−128.5 127−127.3 (Ph), 92.8 (s, C_5Me_5), 91.8 (s, CH_2); 55.8 (OMe), 9.5 (s, C_5Me_5)[d,e]	
 **7b**	1893 (s, ν_{CO})	4.73 (d, 1 H, $^4J_{PH}$ = 3 Hz, C−H); 4.28 (s, 1 H, =C−H¢); 3.42 (s, 3 H, OMe); 1.62 (s, 15 H, C_5Me_5); 1.06 (d, 9 H, $^2J_{PH}$ = 7.8 Hz, P−Me$_3$)[b]	222.0 (d, $^2J_{CP}$ = 31.0 Hz, CO); 199.9 (d, $^2J_{CP}$ = 33 Hz, (C−Fe); 92.2 (s, C_5Me_5); 91.6 (dd, $^1J_{CH}$ = 159.0 Hz, $^1J_{CH'}$ = 145.8 Hz, =CH_2); 55.8 (q, $^1J_{CH}$ = 142.0 Hz, OMe); 18.3 (qd, $^1J_{CH}$ = 127.7 Hz, $^1J_{CP}$ = 26.0 Hz, P−Me$_3$); 10.2 (q, $^1J_{CH}$ = 126.0 Hz, C_5Me_5)[b]	37.8 (s)[b]
 **7c**		7.40 (m, 20 H, Ph), 4.31 (s, 1 H, CH), 3.10 (s, 1 H, CH′), 2.60 (s, 3 H, OMe), 2.54−2.05 (m, 2 H, PCH_2), 1.34 (s, 15 H, C_5Me_5)[a]	201.2 (t, $^2J_{CP}$ = 32 Hz; C−Fe), 130 (m, Ph), 96.0 (dd, $^1J_{CH}$ = 157.0 Hz, $^1J_{CH'}$ = 145.0 Hz, CH_2), 87.9 (s, C_5Me_5), 56.8 (q, $^1J_{CH}$ = 140.3 Hz, OMe), 33.3 (t, $^1J_{CP}$ = 21 Hz, PCH_2), 11.2 (q, $^1J_{CH}$ = 126.0 Hz, C_5Me_5)[a]	108.59 (s)
 **7d**		7.93 (tdd, $^3J_{PH}$ = 1.6 Hz, $^3J_{HH}$ = 11.4 Hz, $^3J_{HH}$ = 18.6 Hz, 1 H, CH), 7.40 (m, 20 H, Ph); 6.58 (dd, $^3J_{HH}$ = 11.4 Hz, $^2J_{HH}$ = 2.6 Hz, 1 H, =C−H); 4.72 (dd, $^3J_{HH}$ = 18.6 Hz, $^2J_{HH}$ = 2.6 Hz, 1 H, C−H); 2.55 (m, 2 H, PCH_2); 1.84 (m, 2 H, PCH_2); 1.45 (s, 15 H, C_5Me_5)[a]	174.6 (dt, $^1J_{CH}$ = 124 Hz, $^2J_{CP}$ = 29 Hz, C−Fe); 131.5 (dd, $^1J_{CH}$ = 151 Hz, $^2J_{CH'}$ = 135 Hz, CH_2); 130.0 (m, Ph); 87.5 (s, C_5Me_5); 29.8 (tm, $^1J_{CH}$ = 124 Hz, PCH_2); 10.2 (q, $^1J_{CH}$ = 126.0 Hz, C_5Me_5)[a]	107.70 (s)[a]

Table 1 (Continued)

	IR: ν, cm^{-1}	^1H NMR: δ, ppm	^{13}C NMR: δ, ppm	^{31}P NMR: δ, ppm
 **8a(RS, SR)**	1945 (s, ν_{CO})	7.57 (m, 18H, *ortho*, *para*-Ph), 7.34 (m, 12H, meta-Ph), 4.51 (s, 6H, OCH_3), 2.08 (br, 4H, CH_2), 1.39 (s, 30H, C_5Me_5)[e]	339.0 (d, $^2J_{CP} = 25.6$ Hz, $Fe^+{=}C$); 220.0 (d, $^2J_{CP} = 24.5$ Hz, CO); 134.4 (dm, $^1J_{CH} = 163$ Hz, PPh_3); 132.8 (dm, $^1J_{CH} = 163$ Hz, PPh_3); 130.1 (dm, $^1J_{CH} = 164$ Hz, PPh_3); 101.1 (s, C_5Me_5); 67.6 (q, $^1J_{CH} = 150.7$ Hz, OCH_3); 47.3 (t, $^1J_{CH} = 131$ Hz, CH_2); 10.4 (q, $^1J_{CH} = 128.5$ Hz, $C_5(CH_3)_5$)[e]	59 (s, PPh_3) −143.5 (sept, PF_6^-)[e]
 **8b(RR, SS)**	1930 (s, ν_{CO})	4.48 (s, 6 H, OMe); 3.34, 3.04 (2m, 4 H, CH_2); 1.75 (s, 30 H, C_5Me_5); 1.42 (d, 18 H, $^2J_{PH} = 9.4$ Hz, $P{-}Me_3$)[e]	338.3 (d, $^2J_{CP} = 26.0$ Hz, (${=}C(CH_2)(OMe)$)); 218.6 (d, $^2J_{CP} = 28.0$ Hz, CO); 100.0 (s, C_5Me_5); 67.2 (s, OMe); 51.2 (t, $^3J_{CP} = 132$ Hz, CH_2); 17.9 (dq, $^1J_{CP} = 32.0$ Hz, PMe_3); 10.2 (q, $^1J_{CH} = 127.0$ Hz, C_5Me_5)[e]	30.88 (s, $PMe_3$$^{)}$ −143.40 (sept, PF_6)
 **8c**		7.40 (m, 40 H, Ph); 3.07, 2.81 (m, 2 H, PCH_2); 2.60 (s, 6H, OMe), 2.44 (b s, 4 H, CH_2); 1.41 (s, 30 H, C_5Me_5)[a]	316.8 (t, $^2J_{CP} = 22.0$ Hz, Fe=C); 133.0 (m, Ph); 97.2 (s, C_5Me_5); 62.6.7 (q, $^1J_{CH} = 151.0$ Hz, OMe); 48.7(t, $^1J_{CH} = 131.0$ Hz, CH_2) 32.6 (t, $^1J_{CP} = 20.7$ Hz, Ph_2PCH_2); 11.4 (q, $^1J_{CH} = 127.0$ Hz, C_5Me_5)[a]	107.2 (s, Ph_2PCH_2) −140.60 (sept, PF_6^-)[a]
 **8d**		15.09 (b, 2 H, =CH); 7.4 (m, 40 H, Ph); 3.03, 2.68 (m, 2 H, PCH_2); 1.75, 1.63 (s, 2 H, CH_2); 1.22 (s, 30 H, C_5Me_5)[a]	331.9 (t, $^2J_{CP} = 29.5$ Hz, Fe=CH); 133.0 (m, Ph); 102.0 (s, C_5Me_5); 57.7 (t, $^1J_{CH} = 127.0$ Hz, CH_2); 32.9 (t, $^1J_{CP} = 20.7$ Hz, Ph_2PCH_2); 10.1 (q, $^1J_{CH} = 128.0$ Hz, C_5Me_5)[a]	105.3 (s, Ph_2PCH_2) −140.60 (sept, PF_6^-)[a]

[a] CD_2Cl_2. [b] C_6D_6. [c] $CD_3C(O)CD_3$. [d] $CDCl_3$. [e] CD_3CN. [f] $^{13}C\{^1H\}$ spectrum. [g] Taken from ref 66.

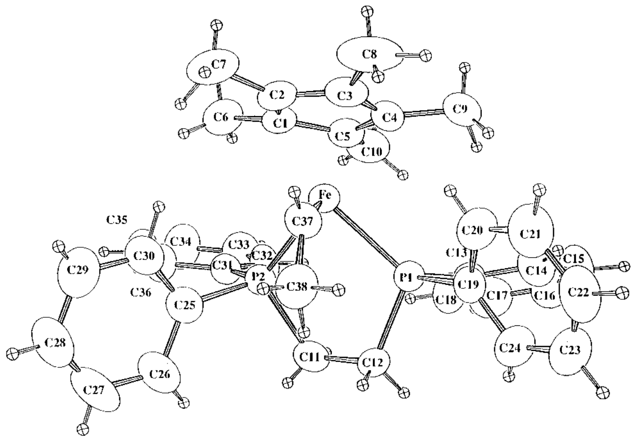


Figure 1. ORTEP representation of the ethylidene complex $[Cp^*Fe(dppe)({=}C(H)Me)][CF_3SO_3]$ (**6**).

Table 2. Experimental Crystallographic Data for 6

formula	$[C_{38}H_{43}P_2Fe][PF_6]{\cdot}C_4H_{10}O$
fw	836.65
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	14.133(2)
b, Å	14.147(9)
c, Å	21.869(9)
α, deg	
β, deg	108.36(3)
γ, deg	
V, $Å^3$	4446(3)
Z	4
d_{calcd}, Mg m^{-3}	1.339
cryst size, mm	0.20 × 0.20 × 0.30
$2\theta_{max}$, deg	50
hkl range	0−16; 0−16; +25 to −25
diffractometer	CAD4 Enraf Nonius
radiatn Mo Kα (λ), Å	0.710 69
monochromator	graphite cryst
T (K)	294
F(000)	1752
abs coeff (m), cm^{-1}	5.33
scan type	$\omega/2\theta = 1$
t_{max}, s	60
no. of reflns read	7941
no. of unique reflns	3685 [$I > 4\sigma(I)$]
R_{int} (from merging equiv reflns)	0.28
R(isotropic)	0.10
R(anisotropic)	0.085
Fourier diff	0.45−0.18
N(obs)/N(var)	3685/602
final R	0.063
R_w	0.060
S_w	2.6
max residual, e $Å^{-3}$; Δ/σ	0.58; 2.46

data,[5,49] an opposite situation is observed between the same rhenium fragment and the iron moiety $[CpFe(dppe)]^+$ as clearly shown from the comparison of the redox potentials of isostructural compounds in both series.[26,50]

3. X-ray Crystal Structure of the Iron Ethylidene $[Cp^*Fe(dppe)({=}C(H)Me)][PF_6]$ (6). Crystals of **6** were grown by slow diffusion of diethyl ether into a CH_2Cl_2 solution of this complex. The complex **6** crystallizes in the monoclinic space group $P2_1/c$, and the unit cell contains four molecules. The molecular structure of **6** is shown in Figure 1, and the X-ray data conditions are summarized in Table 2. Selected bond distances and angles are collected in Table 3. The metal center clearly adopts a pseudooctahedral geometry as invariably observed for these piano-stool complexes, with the Cp* ring occupying three coordination sites whereas the carbene carbon atom and the two phos-

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(49) Kowalczyk, J. J.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1991**, *10*, 1079.

(50) Seyler, J.; Weng, W.; Zhou, Y.; Gladysz, J. A. *Organometallics* **1993**, *12*, 3802−3804.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 6

Fe−P(1)	2.221(2)	Fe−C(37)	1.787(8)
Fe−P(2)	2.239(7)	C(37)−C(38)	1.49(1)
Fe−Cp*(centroide)	1.807(4)		
P(1)−Fe−P(2)	86.20(7)	P(2)−Fe−C(37)	91.4(2)
P(1)−Fe−C(37)	90.4(3)	C(38)−C(37)−H(37)	93.0(6)
Fe−C(37)−C(38)	141.3(6)		

phorus atoms occupy the three remaining sites. The Fe−P(1) and Fe−P(2) bond lengths and angle P(1)−Fe−P(2) compare well with the data determined for other mononuclear complexes in the Cp*Fe(dppe) series.[37,51,52] The carbene unit is essentially perpendicular to the plane of the Cp* plane (93°), and the hydrogen atom is directed toward the Cp* ligand. MO calculations have indicated that this upright orientation is favored in cyclopentadienylmetal carbene complexes of Mn(I) and Fe(II).[53] As no iron alkylidene has been structurally characterized to date, the Fe−C(37) bond distance (1.787 Å) reveals the strength of the metal−carbon bond. This bond is clearly shorter than those determined for the 17-electron radical cation [Cp*Fe(dppe)(CH$_2$OMe)][PF$_6$] (d(Fe−C) = 2.003 Å)[54] revealing the double-bond character of the iron−ethylidene bond. This Fe−C bond distance is also significantly shorter than the iron−carbon bond observed in the case of the (η^1-cycloheptatrienylidene) iron complex (1.979(3) Å).[55] Moreover the Fe−C(37)−C(38) and Fe−C(37)−H37 bond angles of 141.4 and 125.2°, respectively, confirms the sp^2 hybridization of the C(37) carbene carbon atom.

4. Synthesis of the Mononuclear Iron Vinyl Complexes [Cp*Fe(L1)(L2)(C(R)═CH$_2$)] (7a, R = OMe, L1 = CO, L2 = PPh$_3$; 7b, R = OMe, L1 = CO, L2 = PMe$_3$; 7c, R = OMe, L1, L2 = dppe; 7d, R = H, L1, L2 = dppe). The vinyl and vinyl ether complexes of electron-rich metals such as LnM{CH═C(OR′)R} have been the subject of several investigations.[39,45,56−62] In earlier papers, they were usually used as convenient precursors of carbene complexes and they have been prepared by following two routes: reaction of alkenyllithium or alkenylmagnesium halides with iron halides[63] or acylation of the sodium ferrate with α,β-unsaturated acid chlorides followed by a photochemical decarbonylation.[64] Here we followed the opposite strategy since the vinyl derivatives were readily prepared from the iron carbene precursors. Reaction of the iron carbene complexes **2a**−**c** and **6** with 2 equiv of potassium *tert*-butoxide in THF gave the corresponding vinyl derivatives **7a**−**d** isolated as yellow or red-orange powders in high yield (Scheme 3). The deprotonation selectively occured at the β carbon atom at 20 °C. Complexes **7a**−**d** were characterized by IR, ^{1}H, ^{13}C, and ^{31}P NMR (Table 1), and elemental analysis.[65,66] The ^{1}H NMR chemical shifts of the Cp* ligands and the IR $\nu_{C\equiv O}$ are characteristic of neutral complexes. The ^{1}H NMR spectrum of **7d** show the C$_\beta$ vinyl protons upfield of those of the C$_\alpha$ vinyl proton, as found with alkenes bearing electron-donating substituents.[67] The ^{13}C NMR spectra display the C$_\alpha$ resonance downfield of the C$_\beta$ resonance for all the vinyl iron complexes **7a**−**d**. However, for the vinyl ether complexes **7a**−**c**, C$_\alpha$ is found more upfield and the C$_\beta$ is observed more downfield than the corresponding resonances of the vinyl iron compound **7d**.

Scheme 3

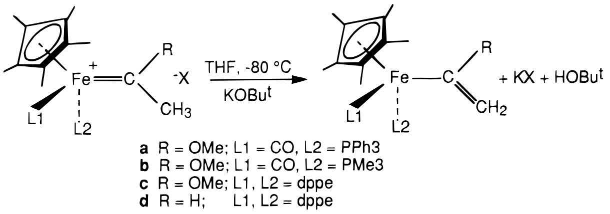

Table 4. Electrochemical Data for Compounds 7a−c in CH$_2$Cl$_2$ (0.1 M [^{n}Bu$_4$N][PF$_6$]; 20 °C, Pt Electrode, Sweep Rate 0.100 V s^{-1})

compd	E_p^a [a]	E_p^c [a]	i^c/i^a
7a	+0.25	+0.20	0.2
7b	+0.22	+0.15	0.4
7c	−0.33	−0.42	0.6
7d	−0.33	−0.40	0.8

[a] V *vs* SCE; ferrocene-ferrocenium couple was used as an internal calibrant for the potential measurements.

The initial scans in the cyclic voltammograms of the four complexes **7a-d** from −0.5 to +0.7 V (vs SCE) at a platinum electrode (CH$_2$Cl$_2$, 0.1 M tetrabutylammonium hexafluorophosphate, 20 °C) are all characterized by an anodic wave showing a well-defined current maximum and a cathodic wave on the reverse scan less intense at a 0.100 V·s^{-1} sweep rate. The (i_p^c/i_p^a) current ratio, less than unity, ranges from 0.2 for the less electron rich vinyl complex **2a** to 0.6 for the more electron rich compound **7c** (Table 4, eq 2). Such a behavior suggests

$$[L_nFeC(X)CH_2] \rightarrow [L_nFeC(X)CH_2H]^{\bullet +} + e^- \qquad (2)$$

$$L_nFe = Cp^*Fe(L1)(L2);\ X = OMe,\ H$$

that the electron transfer from these vinylmetals affords at the electrode the 17-electron radical cation (eq 2) which is neither thermodynamically stable nor kinetically inert toward the solvent. The formation of the iron carbene complexes resulting from the capture of a

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(51) Hamon, P.; Toupet, L.; Hamon, J.-R.; Lapinte, C. *Organometallics* **1996**, *15*, 10.

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(65) S. Nlate reported the first synthesis and characterization of complex **7a**.

(66) Nlate, S. Synthesis of Iron Complexes with Labile or Hemilabile Ligands, [Fe(C$_5$Me$_5$)(L)(L′)(═C(OMe)R)]$^+$: A New Route to Organoborane Complexes. Université de Rennes I, Rennes, France, 1993, pp 141.

(67) Bodner, G. S.; Smith, D. E.; Hatton, W. G.; Heah, P. C.; Georgiou, S.; Rheingold, A. L.; Geib, S. J.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7688−7703.

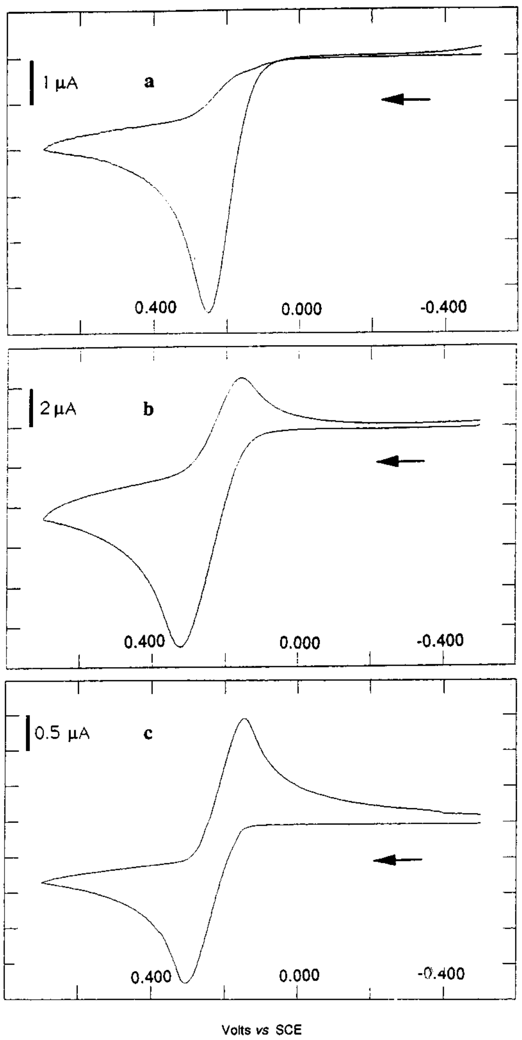

Figure 2. Cyclic voltammograms for iron vinyl complexes [Cp*Fe(CO)(PPh$_3$)(C(OMe)=CH$_2$)] (**7a**) in 0.1 M [^{n}-Bu$_4$N][PF$_6$]/CH$_2$Cl$_2$ (Pt electrode; V *vs* SCE; scan rate = 100 mV/s; **a**, 20 °C; **b**, −30 °C; **c**, −90 °C).

hydrogen atom of the solvent, observed when the oxidation is carried out on a preparative scale, supports the second assumption (*vide infra*).

The reversibility of the electron transfer process has been monitored by variable-temperature cyclic voltammetry for the iron vinyl Cp*Fe(CO)(PPh$_3$){C(OMe)CH$_2$} (**7a**) which has allowed observation of the less intense reversible reduction wave. As depicted in Figure 2, the (i_p^a/i_p^c) current ratio highly depends on the temperature, and the total reversibility of the redox process is observed at −75 °C ($i_p^a/i_p^c = 1$). As a consequence, the vinyl iron radical [**7a**$^{\bullet+}$] may be considered as thermally stable and possible to handle below −75 °C in methylene chloride.

The 17-electron radical cations **[7b$^{\bullet+}$]PF$_6$** and **[7c$^{\bullet+}$]PF$_6$** were generated in solution and characterized by ESR spectroscopy. Ferrocenium was added to a −80 °C solution of CH$_2$Cl$_2$/ClCH$_2$CH$_2$Cl (1:1) of the vinyl derivatives and the resulting suspension stirred for 5 min before being filtered in a quartz tube. The ESR spectrum recorded at 77 K exhibited three well-separated features corresponding to the three components of the **g** tensor. In the case of the complex **7b** the two high field features are split into doublets by hyperfine coupling with one ^{31}P nucleus. The resolution of the two high-field components into 1:2:1 triplets is observed in the spectrum of **7c**, in agreement with a hyperfine coupling with two equivalent ^{31}P nuclei. The stability of the radical cations was checked by warming the ESR samples at 193 K for 1 h. The new spectrum recorded at 77 K in the same conditions was strictly overlying with the first spectrum showing that the radical cations are stable at 193 K in solution. In contrast, warming the samples at 300 K for 1 min produced a dramatic and irreversible change in the ESR spectrum as well as a strong decrease in the intensity of the signal indicative of fast irreversible chemical reactions. The stability at −80 °C of 17-electron units having CO ligands is not trivial.[68] It has been shown that related alkyl electron-deficient iron(III) species are highly reactive entities which evolved toward metal acyl complexes at low temperature.[69,70]

The **g**-tensors and ^{31}P couplings (**7b**, $g_1 = 2.0123$, $A_1 = 17$ G, $g_2 = 2.0349$, $A_2 = 19$ G, $g_3 = 2.3130$; **7c**, $g_1 = 1.9922$, $A_1 = 17$ G, $g_2 = 2.0289$, $A_2 = 17$ G, $g_3 = 2.4056$) are very close to those observed for the isostructural ethynyl iron(III) [Cp*Fe(dppe)(C≡CR)][PF$_6$] (i.e. R = H, $g_1 = 1.977$, $g_2 = 2.034$, $g_3 = 2.457$),[23,26] and they establish the low-spin iron(III) character of the intermediate vinyl radical cation. Meanwhile the spin density is mainly located at the metal center, and the ligand−ligand coupling could be a possible reaction in the thermal evolution of these complexes because the π system of the vinyl group could participate in the delocalization of the spin density as also observed for the alkyne ligand in the case of the ethynyl radical [Cp*Fe(dppe)(C≡CR)][PF$_6$].[26]

5. Synthesis of the Iron *μ*-Bis(carbene) Complexes [{Cp*Fe(L1)(L2)}$_2$*μ*-(=C(R)CH$_2$CH$_2$C(R)=)][PF$_6$]$_2$ (8a, R = OMe, L1 = CO, L2 = PPh$_3$; 8b, R = OMe, L1 = CO, L2 = PMe$_3$; 8c, R = OMe, L1, L2 = dppe; 8d, R = H, L1, L2 = dppe). The cyclic voltammetry study and ESR spectroscopy having established that the 17-electron iron(III) vinyl complexes **7a**$^{\bullet+}$−**7d**$^{\bullet+}$ were stable enough in CH$_2$Cl$_2$ at −80 °C to be accumulated in solution, the synthesis of the bis(carbene) complexes by ligand−ligand coupling of two cationic iron vinyl units was considered to be viable. The addition of 0.95 equiv of [Cp$_2$Fe][PF$_6$] to a solution of **7a**−**d** at −80 °C and stirring for 6−10 h produced a slow color change of the solution from dark blue to brown indicating that the electron transfer was completed. At this step of the reaction, slow warming of the solution to room temperature (16 h) and removal of the solvent under vaccum allowed isolation of the corresponding mononuclear carbene species **2a**−**c** and **6**. This implies that the 17-electron vinyl radicals do not dimerize at −80 °C but that they probably capture an hydrogen atom from the solvent upon warming in solution (eq 3), as suggested previously.

$$2[L_nFeC(X)CH_2]^{\bullet+} + \text{“}H^{\bullet}\text{”} \rightarrow [L_nFe{=}C(X)CH_2H]^{+} \qquad (3)$$

$$(L_nFe = Cp^*Fe(L1)(L2);\ X = OMe,\ H)$$

Note that working under slightly different conditions dramatically changes the course of the reaction. After

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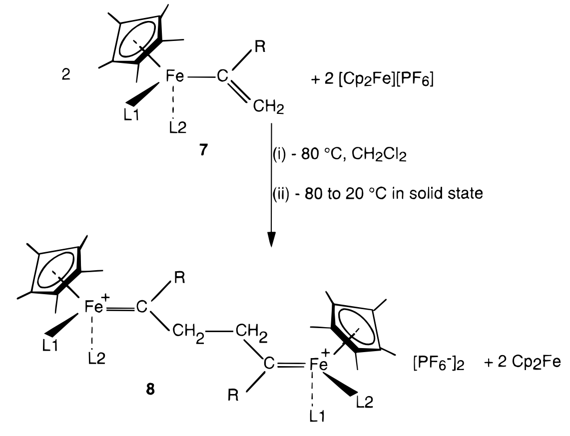
[68] Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217.

[69] Golovin, M. N.; Meirowitz, R.; Rahman, M. M.; Liu, H. Y.; Prock, A.; Giering, W. P. *Organometallics* **1987**, *6*, 2285−2289.

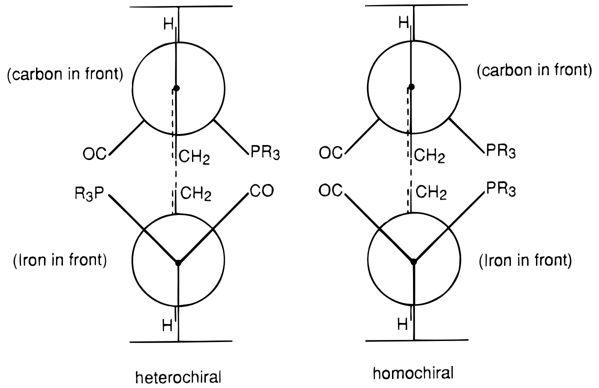
[70] Therien, M. J.; Trogler, W. *J. Am. Chem. Soc.* **1987**, *109*, 5127−5133.

Scheme 4



a R = OMe; L1 = CO, L2 = PPh3
b R = OMe; L1 = CO, L2 = PMe3
c R = OMe; L1, L2 = dppe
d R = H; L1, L2 = dppe

Scheme 5



all of the ferrocenium being consumed, precipitation of the vinyl radical at −80 °C by cold pentane addition to the CH_2Cl_2 solution, and removal of the liquid phase by filtration, an orange precipitate is produced which is dried *in vacuo* before being allowed to warm slowly at room temperature. Recrystallization of the crude product from a CH_2Cl_2−pentane mixture and drying *in vacuo* gave the air-stable orange compounds [{Cp*Fe(L1)(L2)}$_2\mu$-(=C(R)CH_2CH_2C(R)=)][PF_6]$_2$ (**8a**−**d**), isolated in 60−95% yield and identified as the binuclear carbene complexes (Scheme 4).

The pattern of reactivity of the 17-electron vinyl compounds confirms their stability at −80 °C and reveals that the ligand−ligand coupling occurs upon warming. The dimerization by carbon−carbon bond formation takes place in the same range of temperature as that for the hydrogen atom abstraction reaction from the solvent. As a consequence, the bis(carbene) complexes can be selectively obtained by dimerization of the iron(III) vinyl radical *in the solid state.* As shown from the CV data the half-life of the 17-electron iron(III) vinyl radical is highly dependent on the nature of the electron-releasing character of the ancillary ligands, but this effect should be rather considered as an indication of the reactivity of the radical cation toward the medium than a measurement of its intrinsic thermodynamic stability. Consequently, the outcome of the vinyl−vinyl coupling reaction does not very much depend on the electron density at the metal center, as was claimed,[18] but rather on the operating conditions.

The IR and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies summarized in Table 1 reveal only the presence of the bis(carbene) complexes **8a**−**d** and indicate that these species are free of monomeric impurities. The NMR data of the bis(carbene) complexes compare well with those reported Table 1 for the corresponding monomeric derivatives. The structure of the bis(carbene) linkage is evidenced by the methylene ^{13}C resonances appearing at δ 47.3−57.7 as a triplet with a $^1J_{CH}$ coupling constant ranging from 127 to 132 Hz in the ^{1}H-coupled ^{13}C NMR spectra. Characteristic downfield CHR resonance ^{13}C NMR (δ 331.9) and ^{1}H NMR (δ 15.08) are observed for the bis(alkylidene) compound **8d**. A CH_2Cl_2 solution of **8d** was kept at room temperature, and the stability of signals was monitored by ^{1}H and ^{31}P NMR spectroscopy. The resonances were very stable and no new resonance was observed, showing the thermal stability of this complex. In particular a 1,2 proton shift does not occur at 20 °C to yield the alkene rearrangment.

Considering the structures of **8a**,**b**, a mixture of two different diastereoisomers distinguishable by NMR could *a priori* form: one *meso* isomer (*RS*, *SR* configurations) and one *dl* pair (*RR*, *SS* configurations). After the reaction, only one stereoisomer is observed in the case of **8a**, whereas two diastereoisomers are obtained when the bulky triphenylphosphine is replaced by the trimethylphosphine. The ^{1}H NMR spectrum of the mixture of isomers shows only two distinct resonances by which they may be distinguished, and their integration indicates that the diastereoisomers are formed in a 1/2 ratio. This was confirmed by the ^{31}P NMR spectrum which displays one singlet for each isomers at δ 30.78 and 30.88. The two isomers were readily separated by washing the crude solid with CH_2Cl_2 which only solubilizes the minor isomer. The major isomer insoluble in CH_2Cl_2 was recrystallized from an acetonitrile−diethyl ether mixture. The meso *vs dl* geometry has been determined by X-ray crystallography of the complex [Cp*Fe(CO)(PMe_3)]$_2\mu$-{C(OMe)CH=CHC(OMe)}[PF_6]$_2$ derivatized from the major isomer of **8b**.[71] This compound possesses a crystallographic inversion center, and as a consequence, the major isomer shows the *meso* configuration labeled **8b(*RS*,*SR*)** and the structure of the minor isomer has been deduced to be the *dl* couple of enantiomers **8b(*RR*,*SS*)**. Most of the ^{1}H and ^{13}C resonances are identical for both diastereoisomers. The methoxymethyl groups are located at δ 4.58 and 4.48 by ^{1}H NMR for the isomers **8b(*RS*,*SR*)** and **8b(*RR*,*SS*)**, respectively. The methylene protons exhibit a double multiplet for both isomers, but the separation of the two resonances is small in **8b(*RS*,*SR*)** and quite large in **8b(*RR*,*SS*)**.

It has been widely shown that the chiral auxiliary [CpFe(CO)(PPh_3)] exerts a powerful stereocontrol in a variety of reactions involving coordinated ligands, and once again this is nicely confirmed by the high stereoselectivity of the C−C coupling reaction between the two vinyl radicals **[7a$^{•+}$]**[PF_6^-]. This remarkable degree of enantiomer recognition can be explained by the interactions in the transition state of the homochiral and heterochiral coupling (Scheme 5). An unfavorable steric interaction between the phosphine groups clearly exists in the homochiral transition state. In contrast, it could be predicted on the basis of the steric interaction in the

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[71] Mahias, V.; Lapinte, C. Work in progress.

transition state that the heterochiral coupling is favored. This fits very well with the experimental results.

In summary, we have synthesized and structurally characterized the first thermally stable iron ethylidene complex. We have also shown that 17-electron iron(III) vinyl radicals can be stabilized at low temperature and that they undergo oxidative coupling to produce diiron μ-bis(methoxycarbene) or μ-bis(ethylidene) complexes in good yields, all the resulting compounds being thermally stable. The coupling reaction is sensitive to steric effects of the ancillary ligands at the metal center, and both the *meso* and the *dl* couple of the bis(carbene) dimers were diastereoselectively produced and their separation readily achieved. These results open the route for the synthesis of new diiron(II) μ-bis(vinyl) complexes, and the study of their interesting redox properties which will be the subject of future reports from our group.

Experimental Section

General Data. Reagent grade tetrahydrofuran (THF), diethyl ether, and pentane were dried and distilled from sodium benzophenone ketyl prior to use. Pentamethylcyclopentadiene was prepared according to the published procedure,[72] and other chemicals were used as received. All the manipulations were carried out under argon atmosphere using Schlenk techniques or in a Jacomex 532 drybox filled with nitrogen. Routine NMR spectra were recorded using a Bruker AW 80 MHz. High-field NMR spectra experiments were performed on a multinuclear Bruker 300 MHz instrument. Chemical shifts are given in part per million relative to tetramethylsilane (TMS) for ^{1}H and ^{13}C NMR spectra and H_3PO_4 for ^{31}P NMR spectra. Cyclic voltammograms were recorded by using a PAR 263 instrument. X-Band ESR spectra were recorded on a Bruker ESP-300E spectrometer at 77 K in liquid nitrogen. Elemental analyses were performed at the Center for Microanalyses of the CNRS at Lyon-Solaise, France.

[Cp*Fe(PMe$_3$)(CO)(=C(OMe)(Me))][SO$_3$CF$_3$] (2b). To a suspension of Cp*Fe(PMe$_3$)(CO)(COMe) (**4**) (0.44 g, 1.3 mmol) in 20 mL of CH_2Cl_2 at −80 °C was added $CH_3SO_3CF_3$ (1.45 mmol, 160 μL). At room temperature, the solvent was concentrated *in vacuo* to 5 mL and 100 mL of diethyl ether was added to precipitate **2b** (0.52 g) as an orange powder (80% yield, 1.04 mmol). Anal. Calcd ($C_{18}H_{30}F_3FeO_5PS$): C, 43.04; H, 6.02. Found: C, 43.14; H, 6.05.

[Cp*Fe(dppe)(=C(OMe)(Me))][SO$_3$CF$_3$] (2c). dppe (1.1 mmol, 0.44 g) was added to a solution of the carbene complex **1** (1.1 mmol, 0.50 g) in CH_2Cl_2 (210 mL), and the mixture was photolyzed in a quartz vessel for 2 h. The solvent was removed *in vacuo* and the crude residue washed with diethyl ether (4 × 25 mL). After drying in vacuo, the complex **2c** is isolated as an orange powder in 97% yield (0.85 g, 1.07 mmol). Anal. Calcd ($C_{40}H_{45}F_3FeO_4P_2S$): C, 60.31; H, 5.69. Found: C, 60.33; H, 5.90.

Cp*Fe(PMe$_3$)(CO)(COMe) (4). To a suspension of [Cp*Fe(PMe$_3$) (CO)$_2$][PF$_6$] (1.38 g, 2.96 mmol) in 30 mL of THF at −80 °C was added 1.2 equiv of MeLi. The mixture was slowly allowed to warm to room temperature (16 h). The solvent was evaporated to dryness *in vacuo* and the residue was dissolved in toluene and hydrolyzed with a $H_2O/NaHCO_3$ solution. The solvent was removed *in vacuo*, and the crude residue was extracted with pentane. After evaporation of the solvent, the complex Cp*Fe(PMe$_3$)(CO)(COMe) was isolated with an overall yield of 50% (0.500 mg, 1.48 mmol). Anal. Calcd ($C_{16}H_{27}FeO_2P$): C, 56.82; H, 8.05. Found: C, 56.63; H, 7.92.

Cp*Fe(dppe){CH(OMe)Me} (5). To a −80 °C THF solution (20 mL) of **2b** (1.35 g, 1.7 mmol) is added 1.7 mmol (0.14 g) of $NaBH_4$. The mixture was allowed to warm to 20 °C under stirring (18 h). The solvent was removed *in vacuo*, and the solid residue was extracted with pentane. After removal of the solvent and drying in vacuo, the complex **5** was obtained as a red powder in 45% yield (0.50 g, 0.77 mmol). Anal. Calcd ($C_{39}H_{46}FeOP_2$): C, 72.22; H, 7.15. Found: C, 72.35; H, 7.23.

[Fe(η^5-C$_5$Me$_5$)(dppe)(CHMe)][PF$_6$] (6). To a solution of 0.10 g (0.155 mmol) of complex **5** in 40 mL of diethyl ether cooled to −80 °C was added 35 μL of hexafluorophosphoric acid (0.24 mmol). The mixture was allowed to warm to 20 °C, and a pale-orange precipitate was formed. After filtration and washing with 3 × 20 mL of diethyl ether, 0.11 g (0.144 mmol, 95%) of a pale-orange powder of the complex **6** was obtained. Anal. Calcd ($C_{38}H_{43}F_6FeP_3$): C, 59.86; H, 5.68. Found: C, 60.08; H, 5.72.

X-ray Crystallography for 6. Suitable crystals for single crystal X-ray diffraction studies were obtained from a dichloromethane−diethyl ether mixture at 20 °C. The data were measured on CAD-4 Enraf Nonius automated diffractometer. All the calculations were performed on a Digital MicroVax 3100 computer with the MOLEN package.[73] Crystal data collection and refinement parameters are collected in Table 2. The unit cell parameters were determined by least-squares fit of a set of 25 high-θ reflections. After Lorenz−polarization corrections, the structure was solved by direct methods, which revealed the Fe and the two P atoms. The remaining nonhydrogen atoms of the cation, the PF_6 anion, and the diethyl ether molecule were found after successive scale factor and Fourier differences. The PF_6 anion appeared as disordered between two positions (F(1)F(2)F(3) and F(4)F(5)F(6)). After isotropic ($R = 0.10$) and then anisotropic refinements ($R = 0.085$), all hydrogen atoms were found with a Fourier difference map (between 0.45 and 0.18 e Å^{-3}). The whole structure was refined by the full-matrix least-square techniques (use of F magnitudes; x, y, z and b_{ij} values for Fe, P, C, and O atoms, B_{iso} values for F atoms, x, y, z for H atoms of the cation and x, y, z fixed for H atoms of the solvent molecule; 602 variables and 3685 observations).

[Cp*Fe(L1)(L2)(C(R)=CH$_2$)] (7a, R = OMe, L1 = CO, L2 = PPh$_3$; 7b, R = OMe, L1 = CO, L2 = PMe$_3$; 7c, R = OMe, L1, L2 = dppe; 7d, R = H, L1, L2 = dppe). To a −80 °C THF solution of the appropriate carbene complex [**7a**, 2.138 g (3.1 mmol); **7b**, 0.440 g (0.87 mmol); **7c,** 1.635 g (2.05 mmol); **7d**, 0.356 g (0.47 mmol)] was added 2 equiv of potassium *tert*-butoxide (**7a**, 0.70 g; **7b**, 0.19 g; **7c**, 0.46 g; **7d** 0.11 g). After 30 min of stirring, the solution was allowed to warm and the solvent removed *in vacuo*. The solid residue was extracted with pentane (3 × 15 mL), and microcrystals were obtained by removal of the solvent *in vacuo* [**7a**, 89%, 1.48 g (2.75 mmol); **7b**, 85%, 0.26 g (0.74 mmol); **7c**, 80%, 1.06 g (1.64 mmol); **7d**, 85%, 0.25 g (0.40 mmol)]. Anal. Calcd for **7a** ($C_{32}H_{35}FeO_2P$): C, 71.38; H, 6.55. Found: C, 71.13; H, 6.81. Calcd for **7c** ($C_{39}H_{44}FeOP$): C, 72.45; H, 6.86. Found: C, 72.82; H, 7.00.

[{(η^5-C$_5$Me$_5$)Fe(CO)(PPh$_3$)}$_2$$\mu$-(=C(OMe)(CH$_2$)$_2$-C(OMe)=)][PF$_6$]$_2$ (8a). In a Schlenk tube was dissolved 547 mg (1.01 mmol) of complex **7a** in a minimum of degassed dichloromethane. The solution was cooled to −80 °C, and 0.319 g (0.95 equiv) of ferrocenium salt was added under argon. The mixture was stirred at −80 °C for 6 h and then precipitated with pentane cooled at −80 °C. After filtration at −80 °C of the resulting liquor, the residue was dried in vacuo and allowed to warm to room temperature overnight. The crude residue was washed with 2 × 20 mL of diethyl ether, 2 × 3 mL of CH_2Cl_2, and 2 x 2 mL of acetone. The complex **8a** was isolated as an orange-yellow powder of a pure diastereoisomer in 60% yield (0.41 g, 0.30 mmol). Anal. Calcd **(**$C_{64}H_{70}F_{12}Fe_2O_4P_4$): C, 56.24; H, 5.16. Found: C, 56.38; H, 5.14.

[{(η^5-C$_5$Me$_5$)Fe(CO)(PMe$_3$)}$_2$$\mu$-(=C(OMe)(CH$_2$)$_2$-C(OMe)=)][PF$_6$]$_2$ (8b). In a Schlenk tube was dissolved 0.40 g (1.13 mmol) of complex **7b** in a minimum of CH_2Cl_2. The

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(72) Kohl, F. X.; Jutzi, P. *J. Organomet. Chem.* **1983**, *243*, 119.

(73) Enraf-Nonius molecular structure determination package, MOLEN, Delft, The Netherlands, 1990.

solution was cooled to −80 °C, and 0.375 g (0.99 equiv) of ferrocenium hexafluorophosphate was added under argon. The mixture was stirred at −80 °C for 6 h and then precipitated with pentane at −80 °C. After filtration at −80 °C, the residue was dried under vacuum and allowed to warm to room temperature over 16 h. The crude residue was washed with 2 × 20 mL of diethyl ether and dried in vacuo. The complex **8b** was isolated as a brown-yellow powder composed of the (*RS*,*SR*) and *RR*,*SS*) diastereoisomers in the 2:1 ratio determined from the integration of the ^{1}H NMR spectrum. The diastereoisomer (*RR*,*SS*) was extracted with dichloromethane (0.185 g, 0.19 mmol, 33%) whereas the diastereoisomer (*RS*,*SR*), not soluble in that solvent, remained in the Schlenk tube as a yellow powder (0.37 g, 0.37 mmol, 66%). Anal. Calcd for $C_{34}H_{58}F_{12}Fe_2O_4P_4$: C, 41.07; H, 5.88. Found: C, 41.19; H, 6.03. FAB mass spectrum for $[M - PF_6]^+$ ($C_{34}H_{58}F_6Fe_2O_4P_3$): *m*/*z* 849.21; found, *m*/*z* 849.0.

[{(η^5-C$_5$Me$_5$)Fe(dppe)}$_2$$\mu$-(=C(OMe)(CH$_2$)$_2$C(OMe)=)][PF$_6$]$_2$ (8c). In a Schlenk tube was dissolved 1.43 g (2.22 mmol) of complex **7c** in a minimum of CH_2Cl_2. The solution was cooled to −80 °C, and 0.77 g (2.33 mmol) of ferrocenium hexafluorophosphate was added under argon. The mixture was stirred at −80 °C for 10 h and then precipitated with cooled pentane. After filtration at −80 °C, the residue was dried under vacuum and was allowed to warm to room temperature over 18 h. The crude residue was washed with 2 × 20 mL of diethyl ether and dried in vacuo. The complex **8c** was isolated as a brown powder in 83% yield (1.45 g, 0.92 mmol). Anal. Calcd for $C_{78}H_{88}F_{12}Fe_2O_2P_6$: C, 59.18; H, 5.60. Found: C, 59.05; H, 5.60.

[{(η^5-C$_5$Me$_5$)Fe(dppe)}$_2$$\mu$-(=CH(CH$_2$)$_2$CH=)][PF$_6$]$_2$ (8d). In a Schlenk tube was dissolved 0.245 g (0.39 mmol) of complex **7d** in a minimum of degassed dichloromethane. The solution was cooled to −80 °C, and 0.125 g (0.37 mmol) of the ferrocenium salt was added under argon. The mixture was stirred at −80 °C for 6 h and then precipitated with cooled pentane. After filtration at −80 °C, the residue was dried under vacuum and allowed to warm to room temperature overnight. The crude residue was washed with 2 × 20 mL of diethyl ether and dried under vacuum. The complex **8d** was isolated as a brown powder in 95% yield (0.27 g, 0.178 mmol). Anal. Calcd for $C_{76}H_{84}F_{12}Fe_2P_6$: C, 59.94; H, 5.56. Found: C, 59.71; H, 5.23.

Acknowledgment. We are grateful to Drs. S. Nlate for the first syntheses of complexes **2a** and **7a** and S. Sinbandhit (CRMPO, Rennes, France) and J. Maher (Bristol, U.K.) for NMR and ESR assistance.

Supporting Information Available: Complete tables of bond lengths and angles, atomic coordinates, and general temperature factor expressions for **6** (14 pages). Ordering information is given on any current masthead page.

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