Novel Cationic Vinylidene Complexes of Iron(II) Containing $Fe(\eta\text{-}C_5H_5)L_2$ as Metal Auxiliary (L_2 = Bis(diphenylphosphino)methane (dppm) and Bis(dimethylphosphino)methane (dmpm)). Crystal Structure of $[Fe\{=C=C(Me)Ph\}(\eta\text{-}C_5H_5)(dppm)]I$

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Received July 31, 1991

Electrophilic additions of $HBF_4{\cdot}Et_2O$ and $MeOSO_2CF_3$ to the neutral σ-alkynyl complexes $Fe(C{\equiv}CR^1)(\eta\text{-}C_5H_5)L_2$ yield the cationic vinylidene complexes $[Fe\{=C=C(R^1)R^2\}(\eta\text{-}C_5H_5)L_2]^+$ (L_2 = bis(diphenylphosphino)methane (dppm), R^2 = H, R^1 = Ph, CO_2Me, CO_2Et, ${}^tBu$, CH_2OCH_3; L_2 = dppm, R^2 = Me, R^1 = Ph, ${}^tBu$, CO_2Me, CH_2OCH_3; L_2 = bis(dimethylphosphino)methane (dmpm), R^2 = Me, R^1 = CH_2OCH_3, ${}^tBu$), which have been isolated as tetrafluoroborate or triflate salts in good yields. The reaction of $Fe(C{\equiv}CSiMe_3)(\eta\text{-}C_5H_5)(dppm)$ with $HBF_4{\cdot}Et_2O$ leads to the cleavage of the C-Si bond to give the unsubstituted vinylidene complex $[Fe(=C=CH_2)(\eta\text{-}C_5H_5)(dppm)][BF_4]$. Methylation of the ethynyl complex $Fe(C{\equiv}CH)(\eta\text{-}C_5H_5)(dppm)$ leads to an equilibrium mixture of the corresponding vinylidene complex $[Fe\{=C=C(R^1)R^2\}(\eta\text{-}C_5H_5)(dppm)]^+$ (R^1 = H, R^2 = Me) and the symmetrical analogues ($R^1 = R^2$ = H; $R^1 = R^2$ = Me), which are formed by methyl-proton exchange processes. Iodine reacts with $Fe(C{\equiv}CR^1)(\eta\text{-}C_5H_5)(dppm)$ (R^1 = Ph, ${}^tBu$), acting as a source of the electrophilic cation I^+, to give the iodovinylidene complexes $[Fe\{=C=C(I)R^1\}(\eta\text{-}C_5H_5)(dppm)]I$ (R^1 = Ph, ${}^tBu$). ${}^1H$, ${}^{31}P\{{}^1H\}$, and ${}^{13}C$ NMR data are discussed. Variable-temperature ${}^{31}P\{{}^1H\}$ NMR studies on dppm complexes reveal that the vinylidene unit can readily rotate at the Fe=C bond; barriers for rotation have been evaluated to be 7.2-9.8 kcal mol^{-1}, indicating that there is little steric influence between the relatively bulky phosphine and the vinylidene groups. The structure of $[Fe\{=C=C(Me)Ph\}(\eta\text{-}C_5H_5)(dppm)]I$ (**2a′**) has been determined by an X-ray diffraction study. It crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$ in a unit cell of dimensions a = 19.722 (8) Å, b = 15.186 (6) Å, c = 11.547 (4) Å, and β = 102.62 (1)°. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares on the basis of 4304 observed reflections to R and R_w values of 0.0329 and 0.0436, respectively. In the structure of the cationic complex the Fe atom is almost linearly bonded (Fe-C(1)-C(2) = 173.7 (3)°) to a substituted vinylidene ligand through a short Fe-C(1) bond (1.748 (4) Å), in agreement with a formal double bond. The coordination around the Fe atom is completed by a η^5-bonded cyclopentadienyl group and by two P atoms from a chelating dppm molecule. The orientation of the vinylidene plane is nearly orthogonal to the pseudo mirror plane of the $Fe(\eta\text{-}C_5H_5)(P\text{-}P)$ moiety, in accordance with theoretical predictions and with the negligible steric influence observed in solution.

Introduction

Half-sandwich moieties of the type $(\eta^5\text{-}C_5H_5)MLL'$ (M = Fe, Ru; L, L′ = CO, phosphines, phosphites) are among the most versatile systems of organotransition-metal chemistry.[1-5] These derivatives have been extensively used in both theoretical and experimental studies, including bonding calculations,[4a,b] conformational analyses,[4c-f] kinetics and mechanisms,[5] and synthetic applications.[1e,2d,3] Recent remarkable developments[6] (M = Fe)

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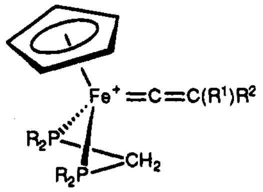
have focused on their use in novel synthetic organic methodology as metal auxiliaries for C_1 and C_2 template ligands, involving highly regio-[6a–c] and stereoselective[6d–f] transformations.

Cyclopentadienyliron derivatives are typical metal auxiliaries in recent metal carbene chemistry.[7] An important class of these well-known complexes is that containing unsaturated carbene groups (cumulenylidenes)[8] and, in particular, vinylidene units ($=C=C(R^1)R^2$), which have recently received special attention mainly due to their use in a number of stoichiometric organic syntheses.[9] Nucleophilic addition dominates the reactivity of vinylidene complexes, and many nucleophiles can be added regioselectively to the extremely electrophilic α-carbon.[10] Thus, heterocarbene complexes are obtained[10a,b,f,g] by reactions with alcohols, thiols, and amines, whereas additions of nucleophiles such as phosphines and hydride or cyanide anions lead to vinyl derivatives.[10c–e]

The synthetic potential of the vinylidene complexes is further evident through the possibility of influencing the reactivity of the bound organic moiety by changing the ancillary ligands (or the metal) in the organometallic auxiliary. Bruce and co-workers[11] have carried out studies on the general reaction of alcohols with ruthenium vinylidene complexes and determined that the attack on the α-carbon depends on a combination of electronic factors and the steric constraints imposed by phosphine ligands and the vinylidene substituents. In general, carbonyl ligands, due to their smaller size relative to that of phosphines and their electron-withdrawing character, increase the electrophilicity of the vinylidene α-carbon and hence the reactivity. In contrast, the presence in the complexes of relatively bulky phosphine ligands or disubstituted vinylidene groups results generally in slower reactions.[11b,12] The information is rather limited for iron vinylidene complexes, but the reactivity seems to be similar. Thus, whereas the $[Fe\{=C=C(R)Me\}(\eta\text{-}C_5H_5)(dppe)]^+$ (dppe = bis(diphenylphosphino)ethane; R = H, Me) complexes do not react with methanol,[13,14] the unsubstituted complex $[Fe(=C=CH_2)(\eta\text{-}C_5H_5)(CO)(PPh_3)]^+$ yields, by the reaction with different alcohols, alkoxycarbene derivatives $[Fe\{=C(OR')CH_3\}(\eta\text{-}C_5H_5)(CO)(PPh_3)]^+$ (R′ = Me, Et, ^iPr, $CH_2CH=CH_2$).[10a]

Consequently, it is now apparent that the reactivity of the vinylidene group may be controlled by changing the ancillary ligands and/or the substituents at the β-carbon. Hence, the syntheses of new vinylidene complexes would enable us to explore the potential variation in reactivity even if the types of reactions do not change. In this context we believed it of interest to use small-bite diphosphines, such as bis(diphenylphosphino)methane (dppm), for which the smaller steric requirements relative to those of dppe or a bis(monodentate phosphine) system could favor the reactivity of the vinylidene group. Herein we describe the synthesis and the chemical and structural characterization of an extensive series of novel cationic mono-, di-, and unsubstituted vinylidene complexes $[Fe]^+=C=C(R^1)R^2$, isolated as the tetrafluoroborate or triflate salts, where [Fe] denotes metal auxiliaries of the types $Fe(\eta\text{-}C_5H_5)(dppm)$ (complexes **1a–f**, **2a–d**, **3a**,**b**) and $Fe(\eta\text{-}C_5H_5)(dmpm)$ (dmpm = bis(dimethylphosphino)methane; complexes **4a**,**b**).



$[Fe]^+=C=C(R^1)R^2$; R = Ph (dppm), Me (dmpm)

dppm: R^2 = H, R^1 = H (**1a**), Ph (**1b**), CO_2Me (**1c**), CO_2Et (**1d**), ^tBu (**1e**), CH_2OCH_3 (**1f**); R^2 = Me, R^1 = Ph (**2a**), ^tBu (**2b**), CO_2Me (**2c**), CH_2OCH_3 (**2d**); R^2 = I, R^1 = Ph (**3a**), ^tBu (**3b**)
dmpm: R^2 = Me, R^1 = CH_2OCH_3 (**4a**), ^tBu (**4b**)

Only a small number of analogous complexes with bidentate phosphines have been described. These include $Ph_2P(CH_2)_2PPh_2$ (dppe) ($R^1 = R^2$ = H, Me; R^1 = H, R^2 = Me;[13a,b] $R^1 = C_7H_7$, R^2 = Ph;[13c] R^1 = Ph, R^2 = Me, Et, $PhCH_2$;[15] R^1 = Me, $R^2 = CS_2Me$;[16] R^1 = H, R^2 = Ph[17]) and the chiral phosphines $Ph_2P(CHR)_2PPh_2$ ((*S*,*S*)-chiraphos (R = CH_3), R^1 = H, $R^2 = C_6H_5$, CH_3; *trans*-cypenphos (R = $-(CH_2)_3-$), R^1 = H, $R^2 = C_6H_5$, Me, $^tC_4H_9$[17]). In addition, the pentamethylcyclopentadienyl derivative $[Fe\{=C=C(H)Ph\}(\eta\text{-}C_5Me_5)(dppe)]^+$[18] and a dinuclear complex,[19] namely $[(\eta\text{-}C_5H_5)(dppe)Fe=C=C(Me)C(Me)=C=Fe(dppe)(\eta\text{-}C_5H_5)]^{2+}$, are also known.

We have carried out dynamic studies using variable-temperature ^{31}P NMR spectroscopy, showing that the vinylidene group can rotate about the iron atom. The energy barrier, which has been estimated from the coalescence temperatures, reveals that the rotation is seldom affected by the presence of the relatively space-demanding dppm ligand. The structure of iodide complex **2a′** has been

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(12) In contrast to the stability of $[Ru\{=C=C(H)Ph\}(\eta\text{-}C_5H_5)(PPh_3)_2]^+$ in refluxing ethanol,[11b] it reacts with allyl alcohols to give a catalyzed condensation of acetylenes and allyl alcohols: Trost, B. M.; Dyker, G.; Kulawiec, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 7809.

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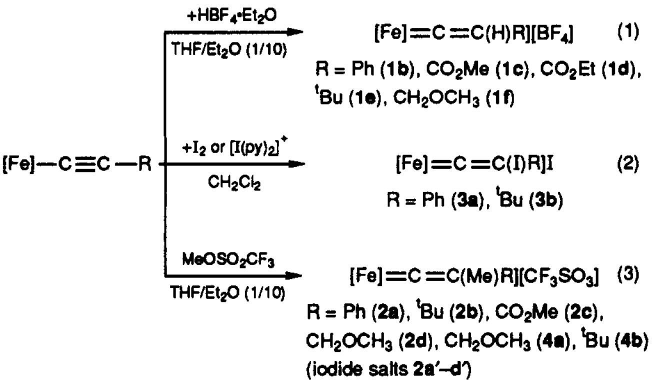
Scheme I



[Fe] = Fe(η-C_5H_5)(dppm) (**1b–f**; **2a–d**; **3a,b**); Fe(η-C_5H_5)(dmpm) (**4a,b**)

determined by X-ray diffraction and, as far as we know, is the first example of a mononuclear vinylideneiron(II) complex. The structure of a related (heteroalkylidene)iron derivative, namely [Fe{=C=C(Me)(CS_2Me)}(η-C_5H_5)(dppe)]I, is also known.[16] We also describe new (σ-alkynyl)cyclopentadienyliron(II) complexes [Fe(C≡CR)(η-C_5H_5)(L-L)] (L-L = dppm, R = CO_2Et, CH_2OCH_3; L-L = dmpm, R = CH_2OCH_3, ᵗBu), which have been used in this work as precursors for the synthesis of the vinylidene complexes. This extends the previously reported series of alkynyl complexes synthesized in our laboratory.[20]

Results and Discussion

The main synthetic procedures described for the preparation of vinylidene complexes $[M]^+$=C=C(R^1)R^2, where [M] has the same meaning as [Fe] with a metal M replacing the Fe atom, are (a) reactions of terminal alkynes with [M]—X complexes (in the presence of an abstractor of the halide anion X^-) which proceed through the rearrangement of the alkynes, giving the vinylidene unit, (b) reactions of σ-alkynyl complexes [M]—C≡CR, by electrophilic additions to the β-carbon of the alkynyl group, and (c) formal dehydrations of acyl derivatives. The first method is limited to the synthesis of monosubstituted vinylidene complexes (R^1 or R^2 = H) and the last two, although potentially more general, require the availability of alkynyl or acyl complexes.

Since our attempts[20] to prepare the halide derivative FeCl(η-C_5H_5)(dppm) produced instead [FeCl(CO)(η-C_5H_5)(dppm-*P*)] or $[Fe(CO)(\eta\text{-}C_5H_5)(dppm)]^+$, we have taken advantage of our previously reported σ-alkynyl complexes [Fe(C≡CR)(η-C_5H_5)(dppm)],[20] along with [Fe(C≡CR)(η-C_5H_5)(dppm)] (R = CO_2Et, CH_2OCH_3) and Fe(C≡CR)(η-C_5H_5)(dmpm) (R = CH_2OCH_3, ᵗBu) (see Experimental Section) to use them, according to method b, as precursors of the novel vinylidene complexes. The syntheses of the compounds are summarized in Scheme I.

Treatment of a solution of Fe(C≡CR)(η-C_5H_5)(dppm) (R = Ph, CO_2Me, CO_2Et, ᵗBu, CH_2OCH_3) and Fe(C≡CCH_2OCH_3)(η-C_5H_5)(dmpm) in a mixture of tetrahydrofuran/diethyl ether (ca. 1/10) at −20 °C with an excess of $HBF_4·Et_2O$ leads to the formation of the monosubstituted vinylidene cationic complexes **1b–f** as insoluble solids in the reaction mixture. The complexes are isolated as tetrafluoroborate salts (eq 1).

However, for R = $SiMe_3$, the protonation leads to the cleavage of the C–Si bond even when a stoichiometric amount of the acid is used, giving instead the unsubstituted vinylidene complex (**1a**; eq 4).

$$[Fe(C{\equiv}CSiMe_3)(\eta\text{-}C_5H_5)(dppm)] + 2HBF_4{\cdot}Et_2O \rightarrow [Fe({=}C{=}CH_2)(\eta\text{-}C_5H_5)(dppm)][BF_4] + Me_3SiBF_4 \quad (4)$$

The treatment of Fe(C≡CR)(η-C_5H_5)(dppm) (R = Ph, ᵗBu, CO_2Me, CH_2OCH_3) and Fe(C≡CCH_2OCH_3)(η-C_5H_5)(dmpm) with $MeOSO_2CF_3$, under the same conditions, gives the analogous methyl-substituted vinylidene derivatives **2a–d** and **4a,b** (eq 3) isolated as the triflate salts. The reactions with methyl iodide lead to lower yields (ca. 60%). The ethynyl complex [Fe(C≡CH)(η-C_5H_5)(dppm)] also undergoes a rapid methylation, but the reaction gives a mixture of the unsubstituted vinylidene complex **1a** and probably $[Fe({=}C{=}CMe_2)(\eta\text{-}C_5H_5)(dppm)]^+$, as shown by ^1H NMR spectroscopy. In fact, the spectrum shows other methyl resonances, pointing to the existence of methyl and proton exchange equilibria (Scheme II).

Scheme II

$$\begin{aligned}2[Fe]{-}C{\equiv}CH &\xrightleftharpoons{Me^+} [Fe]^+{=}C{=}C(H)Me + \\ [Fe]{-}C{\equiv}CH &\rightleftharpoons [Fe]^+{=}C{=}CH_2 + \\ [Fe]{-}C{\equiv}CMe &\xrightleftharpoons{Me^+} 2[Fe]^+{=}C{=}CMe_2\end{aligned}$$

$$[Fe] = Fe(\eta\text{-}C_5H_5)(dppm)$$

Similar behavior has been reported for the analogous ethynyl complex Fe(C≡CH)(η-C_5H_5)(dppe).[13]

By using iodine or $[I(py)_2][BF_4]$[21] as electrophiles, iodovinylidene cationic complexes **3a,b** can be similarly obtained (eq 2). However, the reaction with bromine yields nonseparable mixtures of the corresponding bromo derivatives and paramagnetic oxidized species.

All vinylidene cationic complexes are stable in the solid state and in the absence of air. They are soluble in chlorinated solvents and THF but unsoluble in diethyl ether and hexane. The complex **1a**, however, is less stable and decomposes gradually in chlorinated solvents and in the solid state at room temperature. The formulation proposed for these complexes is based on analytical data, conductance measurements, and NMR (^1H, $^{31}P\{^1H\}$, ^{13}C) spectroscopy. Tables I–III collect analytical and spectroscopic data for the new compounds. In addition, the structure of the complex **2a′** has been determined by X-ray diffraction methods.

Conductance values in acetone show that these complexes are 1:1 electrolytes, and the IR spectra (KBr) exhibit the expected absorptions of the counteranions BF_4^- and $CF_3SO_3^-$ as well as those characteristic for the bidentate phosphines and the substituents of the vinylidene group. New absorption bands which appear in the range of 1400–1600 cm^{-1} can be tentatively assigned to ν(C=C) of the vinylidene group, but they are in general overlapped by those of the phosphine, and consequently, the correct assignment is uncertain.

NMR Studies. Proton and ^{13}C NMR spectra in CD_2Cl_2 at room temperature exhibit aromatic, cyclopentadienyl, methylene (CH_2P_2), methyl (Me_2P), and R signals in accordance with the proposed structures (Tables II and III). In general, resonances are shifted to lower field with respect to the corresponding signals for the σ-alkynyl precursors,[20] reflecting the positive charge of the vinylidene complexes: e.g. $\delta(C_5H_5)$, ^1H NMR 5.15–5.5 ppm (vs 4.4–4.5 ppm), ^{13}C NMR 85.5–88.6 ppm (vs 74.8–76.8 ppm). A

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Table I. Analytical and Physical Data for the Vinylidene Complexes

complex^d	anal., %^{a} C	anal., %^{a} H	color	Δ_M^{b}	yield, %
[Fe{=C=C(H)H}(η-C$_5$H$_5$)(dppm)][BF$_4$] (**1a**)	62.3 (62.2)	4.5 (4.7)	yellow-brown	105	85
[Fe{=C=C(H)Ph}(η-C$_5$H$_5$)(dppm)][BF$_4$] (**1b**)	64.9 (65.7)	4.7 (4.8)	orange	139	82
[Fe{=C=C(H)(CO$_2$Me)}(η-C$_5$H$_5$)(dppm)][BF$_4$] (**1c**)	59.8 (60.4)	4.7 (4.6)	orange-yellow	152	65
[Fe{=C=C(H)(CO$_2$Et)}(η-C$_5$H$_5$)(dppm)][BF$_4$] (**1d**)	61.1 (62.2)	4.6 (4.9)	yellow-brown	140	60
[Fe{=C=C(H)^{t}Bu}(η-C$_5$H$_5$)(dppm)][BF$_4$] (**1e**)	63.7 (64.1)	5.5 (5.5)	red-orange	144	85
[Fe{=C=C(H)(CH$_2$OCH$_3$)}(η-C$_5$H$_5$)(dppm)][BF$_4$] (**1f**)	59.9 (61.7)	4.6 (5.0)	yellow-brown	116	70
[Fe{=C=C(Me)Ph}(η-C$_5$H$_5$)(dppm)]I (**2a**)	62.2 (62.3)	4.5 (4.6)	pink	130	80
[Fe{=C=C(Me)^{t}Bu}(η-C$_5$H$_5$)(dppm)][Tf] (**2b**)	60.0 (60.8)	5.3 (5.2)	pink-orange	155	70
[Fe{=C=C(Me)(CO$_2$Me)}(η-C$_5$H$_5$)(dppm)][Tf] (**2c**)	56.4 (57.5)	4.3 (4.4)	yellow-orange	111	75
[Fe{=C=C(Me)(CH$_2$OCH$_3$)}(η-C$_5$H$_5$)(dppm)][Tf] (**2d**)	58.4 (58.6)	4.8 (4.7)	yellow-orange	138	73
[Fe{=C=C(I)Ph}(η-C$_5$H$_5$)(dppm)]I (**3a**)	50.0 (49.6)^c	3.6 (3.6)^c	yellow-green	118	60
[Fe{=C=C(I)^{t}Bu}(η-C$_5$H$_5$)(dppm)]I (**3b**)	52.0 (51.5)	4.4 (4.3)	yellow	120	65
[Fe{=C=C(Me)(CH$_2$OCH$_3$)}(η-C$_5$H$_5$)(dmpm)][Tf] (**4a**)	39.7 (39.2)	5.3 (5.5)	yellow	102	78
[Fe{=C=C(Me)^{t}Bu}(η-C$_5$H$_5$)(dmpm)][Tf] (**4b**)	43.5 (43.0)	6.4 (6.2)	pink	104	80

[a] Calculated values are given in parentheses. [b] Ω^{-1} cm^2 mol^{-1} (in acetone solutions at 20 °C). [c] Solvated with 1 CH$_2$Cl$_2$. [d] Abbreviations: Tf = SO$_3$CF$_3$.

Table II. ^{1}H and ^{31}P{^{1}H} NMR Data (ppm) for the Complexes^a

complex	^{31}P 295 K	^{31}P *b*	^{1}H Cp	^{1}H =C(R^1)(R^2)	others
1a	27.60 s		5.15 s	3.98 m (=CH$_2$)	4.56 m, 4.90 m (PCH$_a$H$_b$) 7.25–7.50 m (PPh$_2$)
1b	25.12 s	32.3 d^c 21.2 d	5.35 s	5.63 t (=CH; $^4J_{P-H}$ = 3.1) 6.38 m, 6.89 m (=CPh)	4.65 t (PCH$_2$; $^2J_{P-H}$ = 11.3) 7.20–7.60 m (Ph$_2$P)
1c	23.35 s	28.6 d^d 21.4 d	5.38 s	4.95 m (=CH) 3.25 s (=CCO$_2$Me)	4.55 m, 4.83 m (PCH$_a$H$_b$) 7.30–7.50 (PPh$_2$)
1d	22.53 s	28.2 d 22.1 d	5.33 s	4.88 m (=CH), 1.06 m, 3.75 m (=CCO$_2$Et)	4.50 m, 5.10 m (PCH$_a$H$_b$) 7.20–7.80 m (PPh$_2$)
1e	26.45 s	33.8 d^c 26.9 d	5.23 s	4.25 m (=CH) 0.59 s (=C^{t}Bu)	4.46 m, 4.71 m (PCH$_a$H$_b$) 7.26–7.50 m (PPh$_2$)
1f	27.16 s		5.21 s	4.4 m (=CH), 2.95 s (OCH$_3$) 3.25 m (=CCH$_2$O)	4.65 m (PCH$_a$CH$_b$) 7.20–7.80 m (PPh$_2$)
2a	25.29 s	28.9 d^c 22.6 d	5.24 s	1.24 s (=CMe) 6.54 m, 6.85 m (=CPh)	4.46 m, 4.78 m (PCH$_a$H$_b$) 7.15–7.50 m (PPh$_2$)
2b	26.32 s	28.8 d 27.6 d	5.24 s	0.93 s (=CMe) 0.69 s (=C^{t}Bu)	4.37 m, 4.84 m (PCH$_a$H$_b$) 7.20–7.40 m (PPh$_2$)
2c	24.49 s	27.6 d 25.6 d	5.43 s	1.12 s (=CMe) 3.09 s (=CCO$_2$Me)	4.46 m, 5.20 m (PCH$_a$H$_b$) 7.30–7.50 m (PPh$_2$)
2d		26.43 s	5.31 s	1.00 s (=CMe), 3.14 s (=CCH$_2$O) 2.90 s (OCH$_3$)	4.61 m (PCH$_2$) 7.20–7.50 m (PPh$_2$)
3a		26.44 s	5.43 s	6.52 m, 6.90 m (=CPh)	4.62 m, 5.15 m (PCH$_a$H$_b$) 6.80–7.80 m (PPh$_2$)
3b		27.50 s	5.24 s	0.53 s (=C^{t}Bu)	4.51 m, 5.02 m (PCH$_a$H$_b$) 7.30–7.40 m (PPh$_2$)
4a		11.49 s	4.95 s	4.16 s (=CCH$_2$O), 3.34 s (OCH$_3$), (=CMe)^d	3.65 m, 3.40 m (PCH$_a$H$_b$) 1.90, 1.60 m (P(CH$_3$)$_2$)
4b		9.92 s	4.88 s	1.17 s (=C^{t}Bu), (=CMe)^d	3.75 m, 3.25 m (PCH$_a$H$_b$) 1.86 m, 1.60 m (P(CH$_3$)$_2$)

[a] *J* in Hz. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; Cp, C$_5$H$_5$. Spectra recorded in CD$_2$Cl$_2$. [b] **1b**, 190 K (J_{P-P} = 130); **1c**, 175 K (J_{P-P} = 127); **1d**, 161 K (unresolved signals); **1e**, 180 K (J_{P-P} = 127); **2a**, 190 K (J_{P-P} = 130); **2b**, 180 K (unresolved signals); **2c**, 175 K (unresolved signals). [c] T_c (coalescence temperature, K) and $\Delta G^\ddagger$ (kcal mol^{-1}): **1b**, T_c = 215, $\Delta G^\ddagger$ = 9.8; **1c**, T_c = 171, $\Delta G^\ddagger$ = 7.6; **1e**, T_c = 176, $\Delta G^\ddagger$ = 7.2; **2a**, T_c = 196, $\Delta G^\ddagger$ = 8.4. [d] Overlapped by the P(CH$_3$)$_2$ signals.

similar shifting is observed in the proton spectra for the methylene dppm resonances (δ 4.5–5.1 ppm vs 3.85–4.4 ppm), which appear, as in the alkynyl precursors, as one or two unresolved multiplets, showing the ABX$_2$ spin system consistent with the chemical inequivalence of the CH$_a$H$_b$P$_2$ protons in the chelated coordination of the phosphines.

Significantly, ^{13}C NMR spectra (Table III) are more informative, since they show the expected downfield signal for the extremely deshielded α-carbon of the vinylidene group. The resonances appear as triplets (due to coupling with the effectively equivalent phosphorus atoms in the diphosphines) in the range δ 357–367 ppm ($^2J_{P-C}$ = 30–32 Hz). These values can be compared with those reported for the analogous iron complexes [Fe(=C=C(R^1)R^2)(η-C$_5$H$_5$)(dppe)]$^+$ (R^1 = R^2 = CH$_3$, δ 363.3 ppm; R^1 = R^2 = H, δ 358.3 ppm (t, $^2J_{P-C}$ = 33.3 Hz)[13]) and [Fe(=C=CH$_2$)(η-C$_5$H$_5$)(CO)(PPh$_3$)]$^+$ (δ 372.4 ($^2J_{P-C}$ = 29.3 Hz)[10c]). These data seem to indicate that the electronic influence of the auxiliary ligands with different basicities, i.e. dppe, dppm, dmpm, and CO–PPh$_3$, on the positive charge of the vinylidene α-carbon is rather small.

^{31}P{^{1}H} NMR spectra at room temperature show a single resonance (Table II; δ 22.5–27.6 and 11.4 ppm, for dppm

Table III. **^{13}C NMR Data (ppm) for the Complexes**[a]

complex	Cp	Fe=C$_\alpha$	J_{C-P}	=C$_\beta$	others
1a[b]	87.1	356.9 m		108.2 s	41.1 t (CH$_2$P; J_{C-P} = 27), 129–132 m (PPh$_2$)
1b	87.4	367.0 t	32	*c*	40.7 t (CH$_2$P; J_{C-P} = 27), 126–132 m (PPh$_2$)
1c	88.6	358.6 t	32	121.5 s	40.95 t (CH$_2$P; J_{C-P} = 27), 51.8 s (OMe), 164.9 s (C=O), 129–132 m (PPh$_2$)
1d	88.5	359.5 t	32	121.2 s	14.2 s (Me), 41.2 t (CH$_2$P; J_{C-P} = 27), 60.6 s (OCH$_2$), 129–132 m (PPh$_2$), 164.5 s (C=O)
1e	86.6	361.1 t	31	136.5 s	31.7 s (CH$_3$), 32.4 s (CMe$_3$), 40.2 t (CH$_2$P, J_{C-P} = 25), 129–134 m (PPh$_2$)
2a	86.5	367.0 t	32	136.0 s	10 s (CH$_3$), 39.7 t (CH$_2$P, J_{C-P} = 27), 125–132 m (PPh$_2$)
2b	85.5	365.5 t	30	143.1 s	6.3 s (CH$_3$), 29.6 s (Me, ^{t}Bu), 33.3 s (CMe$_3$), 38.7 t (CH$_2$P, J_{C-P} = 26), 128–134 m (PPh$_2$)
2c	87.5	359.4 t	32	135.4 s	7.2 s (CH$_3$), 40.4 t (CH$_2$P, J_{C-P} = 27), 51.1 s (OCH$_3$), 128–133 m (PPh$_2$), 168.1 s (C=O)
2d	86.1	358.7 t	32	134.8 s	7.4 s (CH$_3$), 56.7 s (OCH$_3$), 66.4 s (OCH$_2$), 39.5 t (CH$_2$P, J_{C-P} = 26.5), 128.9–133.1 m (PPh$_2$)
3b	87.3	361.4 t	31.5	136.7 s	31.9 s (Me, ^{t}Bu), 32.4 s (CMe$_3$), 41.9 m (CH$_2$P), 129–134 m (PPh$_2$)
4a	86.4	355.4 t	32.5	128.5 s	10.6 s (CH$_3$), 21.3 m (PCH$_3$), 20.0 m (PCH$_3$), 43.1 t (CH$_2$P, J_{C-P} = 25.1), 58.0 s (OCH$_3$), 69.9 s (OCH$_2$)
4b	86.3	*c*		141.6 s	9.8 s (CH$_3$), 20.4 m (PCH$_3$), 20.9 m (PCH$_3$), 30.5 s (Me, ^{t}Bu), 32.8 s (CMe$_3$), 44.1 t (CH$_2$P, J_{C-P} = 25)

[a] Spectra recorded in CD$_2$Cl$_2$. *J* in Hz. Abbreviations: s, singlet; t, triplet; m, multiplet. **1f**: decomposition during the measurement. [b] In THF/C$_6$D$_6$. [c] Not observed.

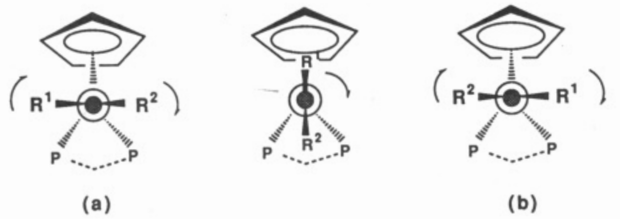

Figure 1. Newman projections along the vinylidene α-carbon to iron bond. The diagrams show the vertical and horizontal orientations of the substituents on the vinylidene β-carbon, giving rise to different rotamers.

and dmpm complexes, respectively), revealing that the two phosphorus atoms in each complex are chemically equivalent. Interestingly, the resonances appear at fields higher than those shown by the precursor alkynyl complexes (δ 43–45 ppm),[20] although the contrary shifting effect should be expected, in accordance with the higher electronic deshielding owing to the cationic character of the complexes. Apparently, the paramagnetic effect, of opposite sign,[22] seems to provide the major contribution to the actual phosphorus resonance in these complexes. The values of the chelation shift Δ_R (in the range −33.5 to −38.6 (Table II)) given by $\delta_{chel} - \delta_{coord}$ (δ_{coord} = 61.14 ppm in [Fe(η-C$_5$H$_5$)(dppm)(dppm-*P*)]$^+$)[23] are comparable to those found in similar complexes containing the strained four-membered metal–dppm ring.[20,24]

The chemical equivalence of the phosphorus atoms in the complexes [Fe(=C=C(R^1)R^2)(η-C$_5$H$_5$)(dppm)]$^+$, having unsymmetrical substitution at the β-carbon, can only arise from a rapid rotation of the vinylidene group around the Fe=C bond on the NMR time scale, since different rotamers (Figure 1) should give rise to diastereotopic phosphorus atoms.

Theoretical studies of the bonding in these types of pseudooctahedral metal auxiliaries indicate[4b] that the preferred orientation of the vinylidene unit is that perpendicular to the pseudo mirror plane of the Fe(η-C$_5$H$_5$)(P-P) moiety (orientations a and b of =C(R^1)R^2 in Figure 1). The rotation is, however, stereoelectronically favorable with energy values (calculated for the model complex [Fe(=C=CH$_2$)(η-C$_5$H$_5$)(PH$_3$)$_2$]$^+$) differing for the vertical and horizontal conformations by less than 2 kcal mol^{-1}.

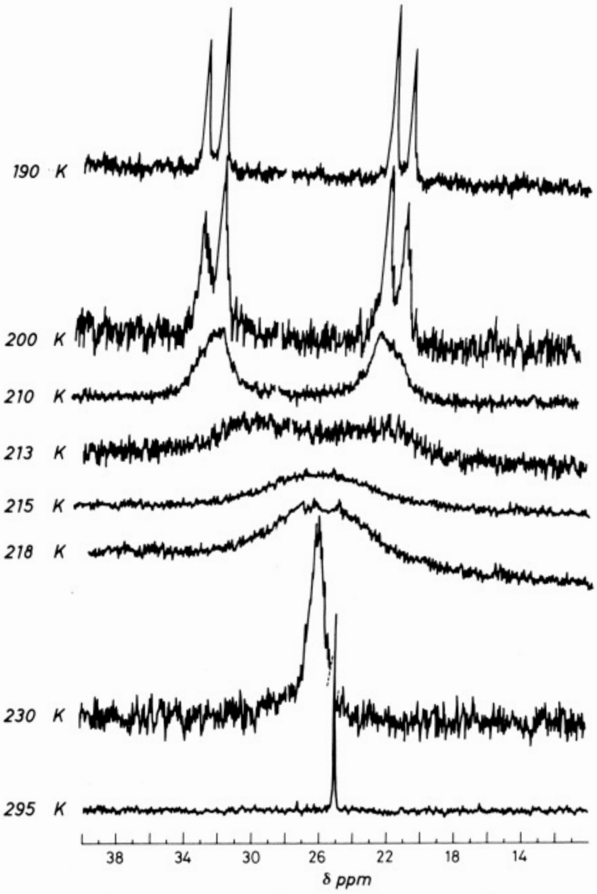

Figure 2. Variable-temperature ^{31}P{^{1}H} NMR spectra of the complex [Fe{=C=C(H)Ph}(η-C$_5$H$_5$)(dppm)][BF$_4$] (**1b**) (temperatures indicated on the left), showing the dependence of the rotation of the vinylidene unit with the temperature. The spectrum at 190 K shows the AB spin system arising from the inequivalence of the phosphorus atoms in the horizontal orientation (see Figure 1).

We have carried out variable-temperature ^{31}P NMR studies on a number of dppm complexes which allow us to extend the scarce information available on the dynamic behavior of the iron vinylidene complexes (Table II and Figure 2). Thus, the singlet resonance observable in the

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(22) (a) Mason, J., Ed. *Multinuclear NMR*; Plenum Press: New York, 1987. (b) Becker, E. D. *High Resolution NMR, Theory and Chemical Applications*, 2nd ed.; Academic Press: New York, 1980.

(23) Ruiz, J.; Garland, M. T.; Román, E.; Astruc, D. *J. Organomet. Chem.* **1989**, *377*, 309.

(24) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

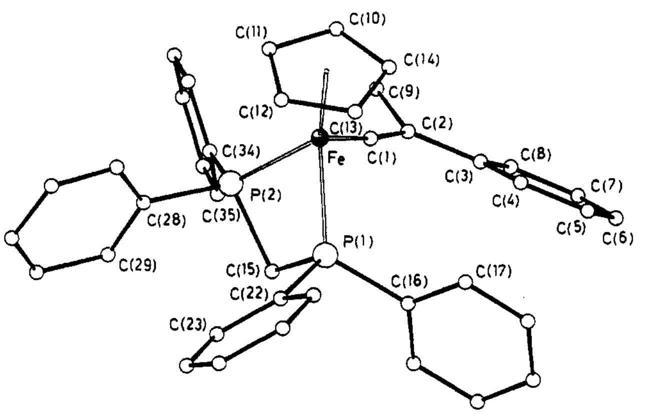

Figure 3. Perspective view of the structure of the cationic complex [Fe{=C=C(Me)Ph}(η-C_5H_5)(dppm)]$^+$ (**2a′**) with the atom-numbering scheme.

Table IV. Important Interatomic Distances (Å) and Angles (deg) for Complex 2a[a]

Fe–P(1)	2.212 (1)	P(1)–C(15)	1.829 (4)
Fe–P(2)	2.206 (1)	P(1)–C(16)	1.805 (4)
Fe–C(1)	1.748 (4)	P(1)–C(22)	1.821 (4)
Fe–C(10)	2.116 (4)	P(2)–C(15)	1.836 (3)
Fe–C(11)	2.105 (4)	P(2)–C(28)	1.835 (4)
Fe–C(12)	2.105 (5)	P(2)–C(34)	1.806 (4)
Fe–C(13)	2.106 (5)	C(1)–C(2)	1.319 (6)
Fe–C(14)	2.109 (5)	C(2)–C(3)	1.491 (6)
Fe–CE	1.736 (4)	C(2)–C(9)	1.515 (6)
P(1)–Fe–P(2)	72.5 (1)	Fe–P(2)–C(15)	93.8 (1)
P(1)–Fe–C(1)	92.2 (1)	Fe–P(2)–C(28)	122.6 (1)
P(1)–Fe–CE	131.4 (2)	Fe–P(2)–C(34)	121.4 (1)
P(2)–Fe–C(1)	88.0 (1)	Fe–C(1)–C(2)	173.7 (3)
P(2)–Fe–CE	133.8 (2)	C(1)–C(2)–C(3)	123.4 (4)
C(1)–Fe–CE	122.8 (2)	C(1)–C(2)–C(9)	118.6 (4)
Fe–P(1)–C(15)	93.8 (1)	C(3)–C(2)–C(9)	118.0 (4)
Fe–P(1)–C(16)	122.6 (1)	P(1)–C(15)–P(2)	91.0 (2)
Fe–P(1)–C(22)	119.2 (1)		

[a] CE is the centroid of the cyclopentadienyl ring.

spectra at room temperature gives rise to the two doublets of an AB system at low temperatures, the coalescence temperature being in the range 161–215 K, indicating rapid rotation even at these low temperatures. In fact, for the complexes **1d**, **2b**, and **2c** the two doublets are not completely resolved before reaching the freezing temperature of the solution. The estimated[25] energy barriers $\Delta G^{\ddagger}$ for rotation are in the range 7.2–9.8 kcal mol^{-1}, which are similar to those found for [Fe(C=CMe$_2$)(η-C_5H_5)(CO)(PPh$_3$)]$^+$ (8–9 kcal mol^{-1}),[10c] [Fe{C=C(H)Ph}(η-C_5H_5)(dppe)]$^+$ (9.4 kcal mol^{-1}),[17a] and a number of analogous ruthenium derivatives, e.g. [Ru{C=C(H)Ph}(η-C_5H_5)(dppe)]$^+$ (9.1 kcal mol^{-1}).[17b]

Description of the Crystal Structure of [Fe{=C=C(Me)Ph}(η-C_5H_5)(dppm)]I (2a′). In the crystals [Fe{=C=C(Me)Ph}(η-C_5H_5)(dppm)]$^+$ cations and I$^-$ anions, separated by normal contacts, are present. A view of the cationic complex is shown in Figure 3 together with the atom-numbering scheme. Selected bond distances and angles are given in Table IV. The cyclopentadienyl ring is bound to the Fe atom in a symmetric η^5 fashion (with Fe–C distances ranging from 2.105 (4) to 2.116 (4) Å, whereas the distance between the metal and the centroid of the ring, Fe–CE, is 1.736 (4) Å). The methyl-phenyl-substituted vinylidene ligand is bound to the Fe through the C(1) atom (Fe–C(1) = 1.748 (4) Å) in an almost linear manner (Fe–C(1)–C(2) = 173.7 (3)°). The coordination around the Fe atom is completed by two P atoms from a chelating dppm molecule (Fe–P(1) 2.212 (1) Å and Fe–P(2) = 2.206 (1) Å). The complex is an octahedral type if the cyclopentadienyl ring is considered as occupying three coordination sites. If the centroid of the cyclopentadienyl ring (CE) is taken into account, the coordination around the Fe atom can be described as a three-legged piano stool, where the P(1), P(2), and the C(1) atoms are the legs: the values of the interleg angles are 72.5 (1), 88.0 (1), and 92.2 (1)°, whereas those of the angles between the centroid CE and the legs are 122.8 (2), 131.4 (2), and 133.8 (2)°.

In the methylphenylvinylidene ligand the value of the C(1)–C(2) bond distance (1.319 (6) Å), as well as that of the already cited Fe–C(1) bond, is in agreement with a formal double bond. The angles at C(2) range from 118.0 (4) to 123.4 (4)°, consistent with a sp^2 hybridization of this atom. The vinylidene ligand is practically planar, the Fe, C(1), C(2), C(3), and C(9) atoms deviating from the mean plane passing through them by 0.002 (1), −0.071 (4), −0.019 (4), 0.031 (4), and 0.032 (5) Å, respectively.

The most significant structural parameters of **2a′** are comparable to those found in the only other mononuclear, structurally characterized iron vinylidene complex, [Fe{C=C(Me)(CS$_2$Me)}(η-C_5H_5)(dppe)]$^+$, in which the Fe–C and C–C bond distances are 1.74 (2) and 1.31 (2) Å and the Fe–C–C bond angle is 176 (1)°.[16] The Fe–P bond distances, involving the dppe ligand, were slightly longer than in **2a′** (2.217 (4) and 2.231 (4) Å); the dppe P–Fe–P bite angle (86.2 (1)°) is much larger than the dppm angle (72.5 (1)° in **2a′**). In the dinuclear cationic complex [(dppe)(η-C_5H_5)Fe=C=C(Me)C(Me)=C=Fe(η-C_5H_5)(dppe)]$^{2+}$, in which a divinylidene ligand bridges two iron atoms, the Fe–C and C–C bond distances are 1.746 (9), 1.766 (9) and 1.32 (1), and 1.33 (1) Å.[19]

The mean vinylidene plane in **2a′** is nearly orthogonal to the pseudo mirror plane of the Fe(η-C_5H_5)(P-P) moiety, defined by the Fe atom, the C(1) atom, and the centroid of the cyclopentadienyl ring, the dihedral angle being 88.0 (2)°, as expected by theoretical studies.[4b] In contrast, the dihedral angle in the complex [Fe{C=C(Me)(CS$_2$Me)}(η-C_5H_5)(dppe)]$^+$[16] is 130.3°, which probably reveals the steric and/or electronic influence of the dithiocarbomethoxy substituent along with the more space-demanding size of the dppe ligand. In [(dppe)(η-C_5H_5)Fe=C=C(Me)C(Me)=C=Fe(η-C_5H_5)(dppe)]$^{2+}$ the two dihedral angles involving the divinylidene ligand are 90.0 and 117.2°, the larger value being probably due to steric crowding.[19]

Finally it is interesting to compare the structure of the cationic complex **2a′** with that of the neutral complex [Fe(C≡CPh)(dppm)(η-C_5H_5)], in which the ethynyl ligand, almost linearly bonded to the Fe atom, substitutes the vinylidene ligand. In this complex the Fe–P bond distances (2.165 (2) and 2.169 (2) Å) are shorter than in **2a′**, because of the cationic charge on **2a′**, and the P–Fe–P dppm bite angle (74.6 (2)°) is slightly larger than in **2a′**.[20]

Concluding Remarks

New cyclopentadienyliron(II) vinylidene complexes [Fe{=C=C(R^1)R^2}(η-C_5H_5)(L-L)]$^+$ (L-L = dppm, dmpm) have been obtained by systematic electrophilic additions to alkynyl complexes. Variable-temperature ^{31}P{^{1}H} NMR studies reveal that the vinylidene unit can readily rotate on the Fe=C bond, showing low energy barriers (7.2–9.8 kcal mol^{-1}). This seems to indicate the negligible influence of the substituent size of the vinylidene group, which can rotate without any apparent hindrance even in the presence of the relatively space-demanding phenyl groups of the dppm ligand. The X-ray structure of **2a′** confirms the

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(25) Estimated from the coalescence temperature using the Eyring equation: Günter, H. *NMR Spectroscopy*; Wiley: New York, 1980.

theoretical prediction, showing that the orientation of the vinylidene unit is nearly orthogonal to the pseudo mirror plane of the $Fe(\eta\text{-}C_5H_5)(P\text{-}P)$ moiety.

This method of synthesis provides the possibility of preparing a series of vinylideneiron complexes with a wide range of substituents where modulation of the electronic and steric properties can be properly selected. In addition, the novel metal auxiliary containing the chelating phosphine dppm shows a narrow P–Fe–P "bite" angle (72.5 (1)°) which results in, relative to the case for the known systems with similar ancillary phosphine ligands, a particular case with small steric demand. In conclusion, these metal auxiliaries, with electrophilicity lower than that of the analogous carbonyl complexes, provide appropriately versatile systems to explore vinylidene reactivity. Studies on the chemical behavior of these vinylidene complexes are in progress.

Experimental Section

The reactions were carried out under dry nitrogen using Schlenk techniques. All solvents were dried by standard methods and distilled under nitrogen before use. The σ-alkynyl complexes $Fe(C{\equiv}CR)(\eta\text{-}C_5H_5)(dppm)$ (R = Ph, $SiMe_3$, CO_2Me, ${}^tBu$) were prepared as described in ref 20. $MeOSO_2CF_3$, $HBF_4{\cdot}Et_2O$, and alkynes $HC{\equiv}CCO_2Et$ and $HC{\equiv}CH_2OCH_3$ were used as received from Aldrich Chemical Co. Bis(dimethylphosphino)methane (dmpm) was purchased from Strem.

Photolysis reactions were performed with external irradiation using an UV lamp (400 W, Applied Photophysics). Infrared spectra were recorded on a Perkin-Elmer 1720-X FT spectrometer, and electron impact mass spectra were obtained using a Hewlett-Packard 58971 instrument. The C and H analyses were carried out with a Perkin-Elmer 240-B microanalyzer. NMR spectra were recorded on a Bruker AC300 instrument at 300 MHz (^1H), 121.5 MHz (^{31}P), or 75.4 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standards.

Analytical data, colors, yields, and conductivity data for all the new vinylidene complexes are collected in Table I. ^1H, ^{13}C, and $^{31}P\{^1H\}$ NMR spectral data are collected in Tables II and III.

Preparation of $[Fe\{{=}C{=}C(H)R\}(\eta\text{-}C_5H_5)(dppm)][BF_4]$ (R = Ph (1b), CO_2Me (1c), CO_2Et (1d), ${}^tBu$ (1e), CH_2OCH_3 (1f)). General Procedure. A solution (100 mL) of the corresponding alkynyl complex $Fe(C{\equiv}CR)(\eta\text{-}C_5H_5)(dppm)$ (1 mmol) in a mixture of THF/Et_2O (1/10), at room temperature, was treated dropwise with strong stirring with a dilute solution of $HBF_4{\cdot}Et_2O$ in diethyl ether (ca. 7%). Immediately, an insoluble solid precipitated but the addition was continued until no further solid was formed (ca. 2 mL). The solution was decanted and the solid washed with diethyl ether (3 × 20 mL) and vacuum-dried. IR (KBr), cm^{-1}): $\nu(BF_4)$ 1085–1050 (s, br); **1c** $\nu(CO_2)$ 1696 s, 1615 m; **1d**, $\nu(CO_2)$ 1693 s, 1614 m.

Preparation of $[Fe\{{=}C{=}C(H)H\}(\eta\text{-}C_5H_5)(dppm)][BF_4]$ (1a). To a solution of $Fe(C{\equiv}CSiMe_3)(\eta\text{-}C_5H_5)(dppm)$ (0.6 g, 1 mmol) in a mixture (100 mL) of THF/diethyl ether (1/10) was added dropwise a dilute solution of $HBF_4{\cdot}Et_2O$ in diethyl ether (ca. 7%). The initial red color immediately disappeared to give an insoluble solid which completely precipitated by the addition of an excess of the acid solution (ca. 6 mL). The mother liquors were decanted, and the solid was washed with diethyl ether (5 × 25 mL) to give **1a** as yellow-brown microcrystals.

Preparation of $[Fe\{{=}C{=}C(Me)R\}(\eta\text{-}C_5H_5)(dppm)][OSO_2CF_3]$ (R = Ph (2a), ${}^tBu$ (2b), CO_2Me (2c), CH_2OCH_3 (2d)). General Procedure. To a solution of $Fe(C{\equiv}CR)(\eta\text{-}C_5H_5)(dppm)$ (1 mmol) in a mixture (100 mL) of THF/diethyl ether (1/10) was added dropwise 2.5 mL of a dilute solution (5%) of $MeOSO_2CF_3$. By workup as described above for the complexes **1b–f**, the triflate salts **2a–d** were similarly obtained as microcrystalline powders. IR (KBr, cm^{-1}): $\nu(CF_3SO_3)$ 1260–1270 s, br, 1225 s, 1152–1158 s; **2c**, $\nu(CO_2)$ 1695 s, 1631 m.

Preparation of $[Fe\{{=}C{=}C(Me)R\}(\eta\text{-}C_5H_5)(dppm)]I$ (2a′–d′). The iodide salts were prepared as described above for the triflate salts **2a–d** by using a solution containing an excess of MeI in diethyl ether. The compounds were identified by comparison of their ^1H and ^{31}P NMR spectra with those of **2a–d**.

Reaction of $Fe(C{\equiv}CH)(\eta\text{-}C_5H_5)(dppm)$ with $MeOSO_2CF_3$. To a solution of $Fe(C{\equiv}CH)(\eta\text{-}C_5H_5)(dppm)$ (0.53 g, 1 mmol) in a mixture (100 mL) of THF/diethyl ether (1/10) was added dropwise a dilute solution of $MeOSO_2CF_3$. A precipitate immediately formed and was recovered by decantation. The solid was identified by ^1H NMR spectroscopy as a mixture mainly of **1a** and $[Fe({=}C{=}CMe_2)(\eta\text{-}C_5H_5)(dppm)]^+$.

Preparation of $[Fe\{{=}C{=}C(I)R\}(\eta\text{-}C_5H_5)(dppm)]I$ (R = Ph (3a), ${}^tBu$ (3b)). A solution of the corresponding alkynyl complex $Fe(C{\equiv}CR)(\eta\text{-}C_5H_5)(dppm)$ (2 mmol) in dichloromethane (15 mL) was treated with I_2 (0.51 g, 2 mmol) and stirred for 15 min. The solution became deep green (R = Ph) or purple (R = ${}^tBu$). After filtration, the addition of diethyl ether to the concentrated solution gave the desired product **3a,b** as crystalline insoluble solids. Analytically pure samples were obtained by recrystallization from dichloromethane/hexane.

Preparation of $[Fe\{{=}C{=}C(Me)(R)\}(\eta\text{-}C_5H_5)(dmpm)][OSO_2CF_3]$ (R = CH_2OCH_3 (4a), ${}^tBu$ (4b)). General Procedure. A solution of $Fe(C{\equiv}CR)(\eta\text{-}C_5H_5)(dmpm)$ (see below; 1 mmol) in a mixture (100 mL) of THF/diethyl ether (1/10) was treated with $MeOSO_2CF_3$, under conditions similar to those described above. By workup as for **2a–d**, the desired complexes **4a,b** were isolated as insoluble solids. IR (KBr, cm^{-1}): $\nu(CF_3SO_3)$ 1260–1263 s, br, 1225 m, 1156–1158 s.

Synthesis of Novel σ-Alkynyl Complexes $Fe(C{\equiv}CR)(\eta\text{-}C_5H_5)L_2$. The complexes were obtained according to procedures that we have previously described.[20]

(a) L = CO; R = CO_2Et, CH_2OCH_3. To a solution of $FeBr(CO)_2(\eta\text{-}C_5H_5)$[26] (1 g, 3.9 mmol) in 35 mL of THF was added 4 mmol of $LiC{\equiv}CR$ (prepared in situ by treating the corresponding alkyne with Li^nBu, 1.6 M in 15 mL of THF at −20 °C). After it was warmed to room temperature, the solution was evaporated. The resulting solid residue was extracted with diethyl ether (3 × 25 mL) and purified by filtration through an Alox IV plug. The filtrate was concentrated and cooled at −20 °C to give orange crystals of the products. R = CO_2Et: yield 65%. Anal. Calcd for $C_{12}H_{10}O_4Fe$: C, 52.59; H, 3.68. Found: C, 50.31; H, 3.87. IR (THF, cm^{-1}): $\nu(CO)$ 2043 vs, 2000 vs; $\nu(C{\equiv}C)$ 2107 m; $\nu(CO_2)$ 1686 m. Mass spectrum (*m/e*): 121 [M − 2CO − C_2CO_2Et]; 218 [M − 2CO]; M^+ (parent ion) 274. ^1H NMR ($CDCl_3$; δ, ppm): 1.3 (t, CH_3, $^3J_{H-H}$ = 7 Hz), 3.8 (q, CH_2, $^3J_{H-H}$ = 7 Hz), 5.1 (s, Cp). R = CH_2OCH_3: yield 80%. Anal. Calcd for $C_{11}H_{10}O_3Fe$: C, 53.70; H, 4.10. Found: C, 54.10; H, 4.25. IR (THF, cm^{-1}): $\nu(CO)$ 2037 vs, 1988 vs; $\nu(C{\equiv}C)$ 2122 w. Mass spectrum (*m/e*): 121 [M − 2CO − C_2OCH_3]; 190 [M − 2CO]; 218 [M − CO]; M^+ (parent ion) 246. ^1H NMR (C_6D_6; δ, ppm): 3.35 (s, OCH_3), 4.12 (s, CH_2O), 5.0 (s, Cp).

(b) L_2 = dppm; R = CO_2Et, CH_2OCH_3. A mixture of $Fe(C{\equiv}CR)(\eta\text{-}C_5H_5)(CO)_2$ (1 mmol) and dppm (0.384 g, 1 mmol) in 40 mL of THF at −20 °C was irradiated with an UV lamp (400 W, Applied Photophysics). The reaction was monitored by IR spectroscopy in the $\nu(CO)$ region, and the irradiation was discontinued when the carbonyl absorptions had completely disappeared (the reaction times are indicated below). The resulting solution was evaporated to dryness to give a solid residue which was dissolved in CH_2Cl_2 (5 mL) and transferred to an Alox IV *n*-hexane chromatography column. Elution with *n*-hexane/dichloromethane (3/1) gave an orange-red band which was collected, reduced in volume, and cooled to −20 °C to give the desired product as a crystalline solid. Reaction time, yield (%), color, and IR bands (THF; $\nu(C{\equiv}C)$, cm^{-1}) are as follows. R = CO_2Et: 20 h; 65; red; 2045 w. Anal. Calcd for $C_{35}H_{32}O_2P_2Fe$: C, 69.78; H, 5.35. Found: C, 68.72; H, 5.92. Mass spectrum (*m/e*): M^+ (parent ion) 602. R = CH_2OCH_3: 10 h; 95; brick red; 2094 m. Anal. Calcd for $C_{34}H_{32}OP_2Fe$: C, 71.09; H, 5.61. Found: C, 70.89; H, 5.40. Mass spectrum (*m/e*): 121 [M − dppm − $C_2CH_2OCH_3$]; M^+ (parent ion) 574. $^{31}P\{^1H\}$ NMR: R = CO_2Et ($CDCl_3$), δ 43.10 s ppm; R = CH_2OCH_3 (C_6D_6), δ 45.27 s ppm. ^1H NMR: R = CO_2Et ($CDCl_3$), δ 1.02 (t, CH_3 $^3J_{H-H}$ = 7.0 Hz), 3.81 (q, CH_2, $^3J_{H-H}$ = 7 Hz), 4.15 (m, PCH_a), 4.27 (m, PCH_b), 4.50 (s, Cp), 7.15–7.6 (m, PPh_2) ppm; R = CH_2OCH_3 (C_6D_6), δ 2.98 (s, OCH_3), 3.95 (m, CH_2P), 4.10 (s, CH_2O), 4.43 (s, Cp), 6.8–7.8 (m, C_6H_5). $^{13}C\{^1H\}$

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Table V. Summary of Crystallographic Data for Complex 2a

formula	$C_{39}H_{35}FeIP_2$
mol wt	748.40
cryst syst	monoclinic
space group	$P2_1/n$
radiation (λ, Å)	niobium-filtered Mo Kα (0.71073)
a, Å	19.722 (8)
b, Å	15.186 (6)
c, Å	11.547 (4)
β, deg	102.62 (1)
V, Å^3	3375 (2)
Z	4
D_{calcd}, g cm^{-3}	1.473
F(000)	1512
cryst size, mm	0.15 × 0.21 × 0.25
μ(Mo Kα), cm^{-1}	14.70
diffractometer	Siemens AED
2θ range, deg	6–54
rflns measd	±*h*,*k*,*l*
no. of unique total data	7650
no. of unique obsd data ($I > 2\sigma(I)$)	4304
R	0.0329
R_w	0.0436

NMR: R = CO_2Et ($CDCl_3$), δ 14.5 (s, CH_3), 43.8 (t, $^2J_{C-P}$ = 21 Hz, CH_2P), 59.6 (s, OCH_2), 77.2 (s, Cp), 113.9 (s, $\equiv C_\beta$), 127–138 (m, PPh_2), 150.4 (t, J_{C-P} = 37 Hz, C_α), 151.2 (s, CO) ppm; R = CH_2OCH_3 (C_6D_6), δ 44.7 (t, $^2J_{C-P}$ = 20 Hz), 55.6 (s, CH_3), 63.1 (s, OCH_2), 76.6 (s, Cp), 116.2 (s, $\equiv C_\beta$), 113.7 (m, C_α), 127.7–140.0 (m, C_6H_5).

(c) L_2 = dmpm; R = CH_2OCH_3, ^{t}Bu. These complexes were obtained as described above for L_2 = dppm. Reaction time, yield (%), color, and IR bands (THF; ν(C≡C), cm^{-1}), are as follows. R = CH_2OCH_3: 1 h; 90; red; 2073 (w). Anal. Calcd for $C_{14}H_{24}OP_2Fe$: C, 51.56; H, 7.42. Found: C, 52.05; H, 7.30. R = ^{t}Bu: 5 h; 60; red-orange; 2068 (w). Anal. Calcd for $C_{16}H_{28}P_2Fe$: C, 56.82; H, 8.34. Found: C, 57.25; H, 7.98. $^{31}P\{^1H\}$ NMR (C_6D_6): R = CH_2OCH_3, δ 22.62 s ppm; R = ^{t}Bu, δ 22.49 s ppm. ^1H NMR (C_6D_6): R = CH_2OCH_3, δ 1.07 (m, PCH_3), 1.45 (m, PCH_3), 2.30 (m, PCH_a), 2.74 (m, PCH_b), 3.51 (s, OCH_3), 4.13 (t, $^3J_{P-H}$ = 1.5 Hz, Cp), 4.65 (m, CH_2O); R = ^{t}Bu, δ 1.12 (m, PCH_3), 1.49 (m, PCH_3), 1.53 (m, $C(CH_3)_3$), 2.35 (m, PCH_a), 2.80 (m, PCH_b), 4.11 (s, Cp).

X-ray Crystal Structure Determination of [Fe{=C=C(Me)Ph(η-C_5H_5)(dppm)]I (2a′). The crystallographic data are summarized in Table V. Unit cell parameters were determined from the θ values of 30 carefully centered reflections, having 10.9 < θ < 17.6°. Data were collected at room temperature, the individual profiles having been analyzed by the method of Lehmann and Larsen.[27] Intensities were corrected for Lorentz and polarization effects; no absorption correction was applied. Only the observed reflections were used in the structure solution and refinement.

The structure was solved by Patterson (SHELX-86)[28] and Fourier methods and refined by full-matrix least squares (SHELX-76),[28] first with isotropic and then with anisotropic thermal parameters in the last cycles for all non-hydrogen atoms. All hydrogen atoms were clearly located in the final Δ*F* map and refined isotropically. The final cycles of refinement were carried out on the basis of 529 variables; after the last cycles, no parameters (except those of the hydrogen atoms) shifted by more than 1.0 esd. The largest remaining peak (close to the Fe atom) in the final difference map was equivalent to about 0.6 e/Å^3. In the final cycles of refinement a weighting scheme, $w = K/[\sigma^2(F_o) + gF_o^2]$, was used; at convergence the *K* and *g* values were 0.737 and 0.0037, respectively. The atomic scattering factors, corrected for the real and imaginary parts of anomalous dispersion, were taken from ref 29.

Table VI. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^3) with Esd's in Parentheses for the Non-Hydrogen Atoms of Complex 2a

	x/*a*	*y*/*b*	*z*/*c*	U_{eq}[a]
I	2279 (1)	2200 (1)	4881 (1)	51.6 (1)
Fe	1882 (1)	3602 (1)	−783 (1)	32.3 (2)
P(1)	2218 (1)	3788 (1)	1158 (1)	32.6 (3)
P(2)	1459 (1)	2495 (1)	78 (1)	31.3 (3)
C(1)	2601 (2)	2940 (3)	−829 (3)	36.8 (13)
C(2)	3113 (2)	2427 (3)	−988 (3)	38.2 (13)
C(3)	3862 (2)	2658 (3)	−572 (4)	43.3 (14)
C(4)	4065 (3)	3512 (4)	−279 (5)	60.6 (20)
C(5)	4760 (3)	3726 (4)	116 (6)	80.1 (26)
C(6)	5264 (3)	3091 (5)	209 (5)	82.1 (30)
C(7)	5074 (3)	2253 (5)	−116 (5)	76.9 (24)
C(8)	4383 (3)	2024 (4)	−514 (4)	61.0 (21)
C(9)	2935 (3)	1571 (3)	−1658 (4)	55.0 (18)
C(10)	1658 (3)	3828 (3)	−2636 (4)	56.2 (18)
C(11)	1042 (2)	3844 (3)	−2219 (4)	49.9 (16)
C(12)	1096 (3)	4536 (3)	−1382 (4)	49.6 (17)
C(13)	1744 (3)	4937 (3)	−1269 (4)	52.8 (17)
C(14)	2089 (3)	4505 (4)	−2050 (4)	59.3 (19)
C(15)	2090 (2)	2630 (3)	1492 (3)	35.1 (12)
C(16)	3090 (2)	4113 (3)	1867 (3)	36.9 (13)
C(17)	3378 (2)	4845 (3)	1441 (4)	47.3 (14)
C(18)	4036 (3)	5121 (3)	2020 (5)	58.5 (20)
C(19)	4396 (2)	4682 (4)	2986 (5)	62.8 (20)
C(20)	4120 (3)	3961 (4)	3423 (5)	65.6 (21)
C(21)	3457 (2)	3667 (3)	2859 (4)	48.4 (16)
C(22)	1686 (2)	4453 (3)	1927 (3)	36.6 (14)
C(23)	1254 (3)	4105 (3)	2596 (5)	64.3 (21)
C(24)	870 (4)	4661 (5)	3152 (6)	95.2 (33)
C(25)	917 (3)	5541 (4)	3071 (5)	73.5 (24)
C(26)	1342 (3)	5899 (3)	2414 (5)	59.4 (19)
C(27)	1726 (2)	5359 (3)	1831 (4)	46.9 (16)
C(28)	612 (2)	2546 (3)	488 (3)	34.5 (13)
C(29)	507 (2)	2016 (3)	1402 (4)	56.4 (19)
C(30)	−111 (3)	2038 (4)	1775 (4)	62.0 (19)
C(31)	−630 (2)	2578 (3)	1228 (4)	53.2 (17)
C(32)	−540 (3)	3098 (4)	316 (5)	63.0 (21)
C(33)	76 (2)	3078 (3)	−66 (4)	50.6 (16)
C(34)	1503 (2)	1376 (3)	−428 (4)	36.8 (14)
C(35)	1903 (3)	738 (3)	274 (4)	52.2 (17)
C(36)	1939 (3)	−109 (3)	−172 (5)	64.8 (21)
C(37)	1592 (3)	−316 (3)	−1293 (6)	67.4 (24)
C(38)	1194 (3)	306 (4)	−1988 (5)	66.3 (20)
C(39)	1148 (2)	1149 (3)	−1563 (4)	53.4 (17)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

All calculations were carried out on the Cray X-MP/12 computer of the "Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale" (CINECA, Casalecchio Bologna) and on the Gould Powernode 6040 computer of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma, Italy.

The final atomic coordinates for the non-hydrogen atoms are given in Table VI. The atomic coordinates and isotropic thermal parameters of the hydrogen atoms are given in Table S1 and the anisotropic thermal parameters for the non-hydrogen atoms in Table S2 (supplementary material).

Acknowledgment. We thank the Dirección General de Investigación Científica y Técnica of Spain for financial support (Proyect PB 87-912) and the Ministerio de Educación y Ciencia for a scholarship grant (to E.L.). We are also grateful to Dr. Pablo Bernad (Universidad de Oviedo) for running mass spectra.

Registry No. 1a, 134148-26-8; **1b**, 138813-65-7; **1c**, 138813-67-9; **1d**, 138813-69-1; **1e**, 138813-71-5; **1f**, 138813-73-7; **2b**, 138813-75-9; **2c**, 138813-77-1; **2d**, 138813-79-3; **3a**, 138813-80-6; **3b**, 138813-81-7; **4a**, 138834-34-1; **4b**, 138834-36-3; [Fe{=C=C(Me)Ph}(η-C_5H_5)(dppm)][I], 138813-82-8; Fe(C≡CCO_2Et)$(CO)_2$(η-C_5H_5),

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130666-28-3; $Fe(C{\equiv}CCH_2OCH_3)(CO)_2(\eta\text{-}C_5H_5)$, 138813-83-9; $Fe(C{\equiv}CCO_2Et)(dppm)(\eta\text{-}C_5H_5)$, 138813-84-0; $Fe(C{\equiv}CCH_2OCH_3)(dppm)(\eta\text{-}C_5H_5)$, 138813-85-1; $Fe(C{\equiv}CCH_2OCH_3)(dmpm)(\eta\text{-}C_5H_5)$, 138834-37-4; $Fe(C{\equiv}C^tBu)(dmpm)(\eta\text{-}C_5H_5)$, 138834-38-5; $Fe(C{\equiv}CH)(dppm)(\eta\text{-}C_5H_5)$, 134148-19-9; $Fe(C{\equiv}CPh)(dppm)(\eta\text{-}C_5H_5)$, 134148-20-2; $Fe(C{\equiv}CCO_2Me)(dppm)(\eta\text{-}C_5H_5)$, 134148-17-7; $Fe(C{\equiv}C^tBu)(dppm)(\eta\text{-}C_5H_5)$, 134148-18-8; $Fe(C{\equiv}CSiMe_3)(dppm)(\eta\text{-}C_5H_5)$, 134148-16-6; $[Fe\{{=}C{=}C(Me)Ph\}(\eta\text{-}C_5H_5)(dppm)][Tf]$, 138813-87-3.

Supplementary Material Available: Hydrogen atom coordinates and isotropic thermal parameters (Table S1) and anisotropic thermal parameters for the non-hydrogen atoms (Table S2) (2 pages); a listing of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

Bismuth(III) Chloride–Aluminum-Promoted Alkylations of Immonium Cations to Amines in Aqueous Media: Unstabilized Carbanion Equivalents for Use in the Presence of Water

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Received October 22, 1991

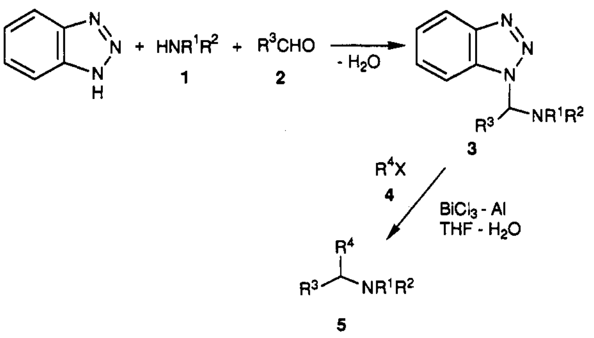
In the presence of bismuth(III) chloride–metallic aluminum, allyl, propargyl, benzyl, and methyl halides react with a large range of 1-(aminoalkyl)benzotriazoles at room temperature in THF–water to give the corresponding homoalkylated amines in high yields. 1-(Amidoalkyl)benzotriazoles derived from benzaldehyde are also successfully converted under these conditions into N-substituted amides.

Introduction

The Barbier reaction has recently received interest as a one-step alternative to the Grignard reaction, owing to the development of several modifications which expand its synthetic potential. The use of metals alternative to magnesium, such as lithium,[1] zinc,[2] bismuth,[3] and lead,[4] has been investigated and ultrasound irradiation has been found to improve yields.[5] Generally, intermolecular Barbier reactions are between allyl or benzyl halides and aldehydes or ketones, but the use of other alkyl halides has been reported.[2] Recently, electroreductive Barbier-type allylations of carbonyl compounds have been achieved in metal-redox systems such as Sn(IV)/Sn(0)[6] and Bi(III)/Bi(0).[7] Torii and co-workers have achieved the Barbier allylation of imines using either a $TiCl_4$/Al bimetal system[8a] or alternatively an electroreductive allylation procedure employing a combination of a Pb(II)/Pb(0) redox system and an aluminum anode.[8b]

One of the more intriguing developments concerns the allylation of carbonyl compounds in the presence of water utilizing organometallics derived from allyl halides and zinc or tin. Such carbon–carbon bond-forming processes involving unstabilized carbanions in aqueous solution are extremely rare. Allylations of aldehydes were carried out in a variety of two-phase solvent systems. For example, organozinc allylations were performed using aqueous ammonium chloride with either solvent THF[9] or a solid (C-18 silica gel)[10] as coorganic phase, whereas those of tin were carried out in water–ether or water–THF mixtures and required promotion by sonication,[9a,b] traces of acid,[11] or aluminum metal.[11] It is likely that the aluminum has two functions; it both generates Sn(0) by reduction of Sn(II) and Sn(IV) from tin(II) chloride and activates the oxidative addition of allyl bromide to the tin.[12,13] Recent developments in aqueous alkylations include organotin alkylations

Scheme I



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