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New Molybdenum and Iron Phosphoranides. Mechanism and Stereochemistry of the Rearrangement and Migration of a Phosphorus-Bound Allylic Group into an Iron-Bound Vinylic Group

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The series of phenylphosphoranides of Mo, W, Ru, and Fe (4) has been successfully extended to their benzyl, vinyl, and allyl analogues 12 and 13, showing that the nature of the substituent at phosphorus in the bicyclic aminophosphoranes 7 is not of prime importance in the isolation of metal phosphoranides. The iron allylphosphoranides **13b,c**, and only these, are thermally converted into the vinyliron complexes **14b,c**. These transformations occur stereoselectively, since **14b,c** are formed, respectively, in a trans and cis configuration at the double bond. Chemical labeling of the allyl group in **13c** allowed us to show that this conversion proceeds through insertion of iron into an allyl C–H bond, followed by a 1,3-proton shift to the terminal olefinic carbon atom, with concomitant P–C bond cleavage. This reactivity pattern differs both from the previously found phenyl group migration between phosphorus and iron, which implies only P–C bond rupture (1,2-sigmatropic shift mechanism), and from an ortho-metalation reaction, which implies only insertion of a metal into a C–H bond. In the present case, the anionic phosphoranide ligand in 13 is likely to increase the charge density on iron and hence its basicity, which allows this unexpected new phenomenon to take place.

Introduction

Our current studies on the interplay between transition metals and phosphorus-based ligands, with the specific aim of developing new metal-induced phosphorus chemistry, led us to the first series of transition-metal phosphoranides 4[1,2] and 5[3] (Scheme I). The chelated adducts 2 of the tautomeric phosphane form of 1 provided a relay to facilitate the abstraction of the proton initially located on phosphorus in 1. This intramolecular–intraligand approach proved effective in the synthesis of the phosphoranides 4 and was also successfully extended to cyclamphosphoranides.[4] When applied to the iron analogue 2, this approach led however to an unexpected reversible migration of the phenyl group between phosphorus and iron (2 ⇄ 6), but it could be shown that the reaction 2 → 6 proceeds via the expected iron phosphoranide adduct 4.[2,5] This reversible migration process exemplifies a metal-induced interconversion between a phosphorane and a phosphane derivative, i.e., between a hypervalent and a trivalent species via, formally, the reductive elimination or oxidative addition of benzene onto phosphorus. Also noteworthy is the fact that it is the same carbon atom of the phenyl group which is alternately bonded to the phosphorus and to the iron atom.

The questions thus arose as to what the extent of this reactivity pattern is, and more specifically as to which substituents at phosphorus permit the observation of such a behavior, and also whether advantage could be taken of it as a means of forming metal–carbon bonds.

We investigated the behavior of bicyclic phosphoranes similar to 1, but with other substituents than a phenyl group at phosphorus, toward η^5-CpMo(CO)$_3$Cl and η^5-CpFe(CO)$_2$Br. As reported in a preliminary communication,[7] a migration reaction was also observed in the case of the allylphosphorane **7b**, but it was the (σ-vinyl)iron compound **14b** that was obtained instead of the (σ-allyl) iron derivative **15b**, which would have been anticipated if the same reaction as with the phenyl group had taken place.

We wish now to report the isolation of the phosphoranides 12 and 13, to present a closer, detailed analysis of the reaction sequences involved, and to discuss the mechanism of the *P*-allyl to *Fe*-vinyl conversion.

Results and Discussion

Synthesis of the Chelated Cationic Adducts 10 and 11 (Scheme II). Molybdenum Derivatives. The coordination behavior of the bicyclic phosphoranes **7a,b** or **7d** toward η^5-CpMo(CO)$_3$Cl is comparable to that of the previously reported phenylphosphorane 1.[8] It results in the substitution of one carbonyl group and coordination of the tautomeric open form of 7 through phosphorus. This is attested by the IR spectra of the resulting compounds 8 which exhibit, in all cases investigated, two ν(CO) absorptions and a ν(NH) frequency at 3340 cm^{-1}, characteristic of the noncoordinated nitrogen site.[8]

The chelated cationic complexes **10** were obtained, as described for **2** (M = Mo) by a Cl$^-$/BPh$_4^-$ anion exchange. Under these conditions, the coordination of the nitrogen atom is assisted and adducts **10a,b** or **10d** precipitate. The ca. 100 cm^{-1} shift toward lower frequencies measured for the ν(NH) of **10** with respect to that of **8** reflects this coordination of the nitrogen site. The ^{31}P and ^{1}H NMR spectra show, respectively, one singlet for the coordinated phosphorus and one singlet for the protons of the cyclopentadienyl ligand. These data are very close to those

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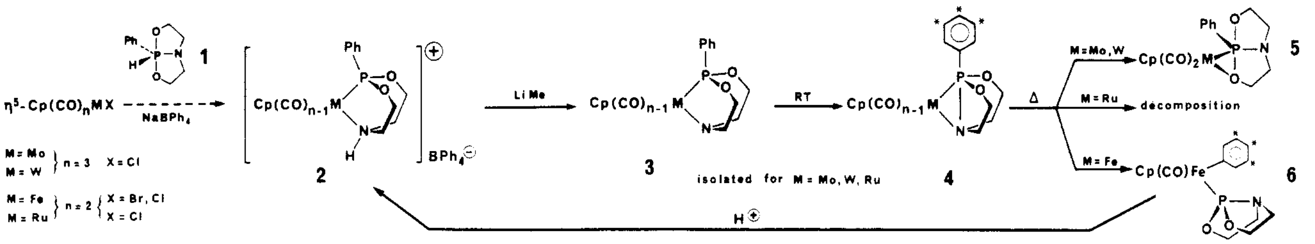
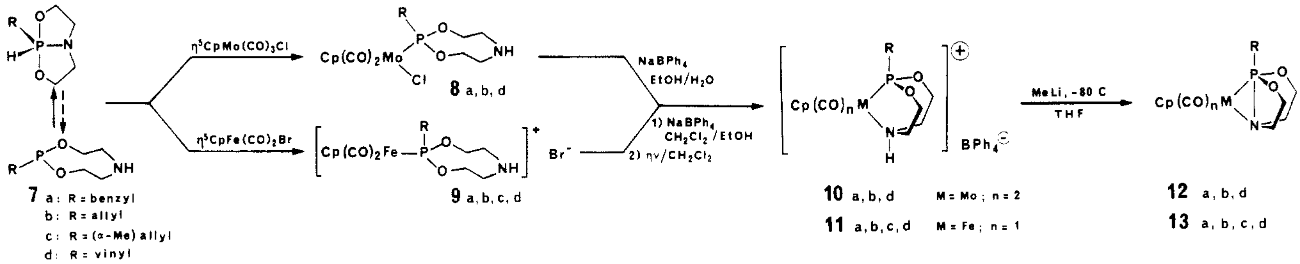
Scheme I. Access to the Mo, W, Ru, and Fe Phenylphosphoranides 4 and 5. Reversible Phenyl Migration between Phosphorus and Iron: 2 → 6



Scheme II. Part A: Access to the Mo and Fe R-Phosphoranides 12 and 13. Part B: Conversion of the Fe Allylic Phosphoranides 13b,c into the Fe Vinylic Adducts 14b,c



PART B

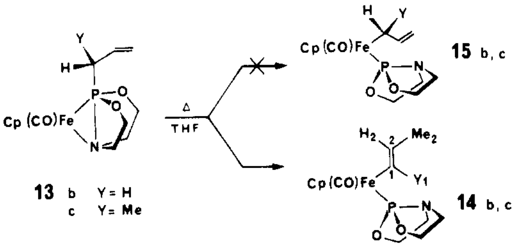


Table I. Principal Spectroscopic Data for Compounds 10–13

	Mo derivatives					Fe derivatives			
	$\nu(CO)^a$	$\nu(NH)^b$	$\delta(^{31}P\{^1H\})^b$	$\delta(^1H(Cp))^g$		$\nu(CO)^a$	$\nu(NH)^b$	$\delta(^{31}P\{^1H\})^b$	$\delta(^1H(Cp))$ ($J_{H,P}$, Hz)^g
2[8]	1965–1885	3220	198^c	5.72^c	**2**[2]	1960	3240	209^c	$4.85 (1.2)^c$
10a	1970–1885	3220	210^c	5.31^c	**11a**	1965	3230	222^c	$4.76 (1.5)^c$
10b	1975–1895	3240	209^c	5.67^c	**11b**	1965	3220	222^d $222 + 204^e$	$4.36 (1.3)^d$ $4.53 (1.3) + 4.73 (1.2)^e$
10c					**11c**	1960	3230	$224 + 223.8^d$ $225 + 224.5^c$	$4.83 (1.2) + 4.84 (1.0)^{c,d}$
10d	1970–1895	3240	199^c	5.75^c	**11d**	1960	3220	209^d $210 + 191^c$	$4.42 (1.3)^d$ $4.72 (1.3) + 4.78 (1.5)^e$
4[1]	1945–1850	...	44^a		**4**[2]	1910	...	73^a	
12a	1940–1850	...	52^a		**13a**	1910	...	82^a	
12b	1940–1850	...	49^a		**13b**	1910	...	80^a	
12c					**13c**	1910	...	$83.4 + 83.3^a$	
12d	1940–1850	...	43^a		**13d**	1910	...	74^a	
$\Delta\nu$(CO)(10–12)	20–45				$\Delta\nu$(11–13)	50–55			
$\Delta\delta$(2–4)			154					135	
$\Delta\delta$(10–12)			156–160		$\Delta\delta$(11–13)			134–140	

[a] In THF. [b] KBr disks. [c] In CH_3CN for $\delta(^{31}P)$, in CD_3CN for $\delta(^1H)$. [d] In CH_2Cl_2 for $\delta(^{31}P)$; in CD_2Cl_2 for $\delta(^1H)$. [e] In CH_3CN/CH_2Cl_2 for $\delta(^{31}P)$; in CD_3CN/CD_2Cl_2 for $\delta(^1H)$. [f] All $\delta(^{31}P\{^1H\})$ resonances are singlets. [g] Singlets for Mo compounds; doublets for Fe compounds.

measured for **2** (Table I), whose structure has been confirmed by X-ray analysis in the case of its PF_6^- salt.[9]

Iron Derivatives. We have previously reported that the action of **1** on η^5-CpFe(CO)$_2$Br leads directly to a mixture of the halogen-substituted cationic derivative analogous to **9**[2] (main product) and of the carbonyl- and halogen-displaced derivative **2** (M = Fe; Br^- in place of BPh_4^-). It was also shown that coordination on nitrogen, leading to **2**, could be forced, starting from the analogue of **9**, by expulsion of CO under UV irradiation, provided the bromide anion has been previously replaced by BPh_4^-.[2]

The action of ligands **7** on η^5-CpFe(CO)$_2$Br in THF led to the halogen-substituted compounds **9** in 85–95% yields. The IR spectra of **9** exhibit two ν(CO)absorptions and a ν(NH) frequency at 3340–3380 cm^{-1} characteristic of the noncoordinated nitrogen atom.[8] The carbonyl- and bromine-substituted complexes analogous to **11** are also formed, but in very low yield. The chelated monocarbonyl cationic derivatives **11** were prepared by photolysis of a CH_2Cl_2 solution of **9** (40–70% yields) after the bromide anion had been replaced by BPh_4^-. The IR data collected on the compounds isolated, with one ν(CO) absorption and a ν(NH) stretch at 3220–3240 cm^{-1} (Table I) characteristic of coordinated nitrogen, agree with the proposed structure **11**. Both P and N coordination in **11a,b,d** are preserved

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(9) Wachter, J.; Mentzen, B. F.; Riess, J. G., unpublished results.

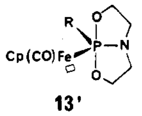
in CD_2Cl_2 solution where the ^{31}P NMR spectra exhibit respectively one singlet for the coordinated phosphorus and one doublet for the cyclopentadienyl protons. Similar patterns are observed in CD_3CN solution for **11a** only. In contrast, the ^{31}P and ^1H NMR spectra recorded on CD_3CN or CD_2Cl_2/CD_3CN solutions of **11b** or **11d** show two singlets for the coordinated phosphorus and two doublets for the cyclopentadienyl protons (Table I). This probably means that **11b,d** coexist in solution with **11′b,d**, respectively, where the ligand is monodentate through phosphorus and where nitrogen has been replaced by an acetonitrile molecule. The fact that only one species is detected in CH_2Cl_2 excludes coordination of the double bond of the *P*-allyl or *P*-vinyl group to iron.

A different situation is found in the case of **11c**, where the ^{31}P spectra measured in CH_3CN and CH_2Cl_2 solutions are very similar, whereas in the ^1H NMR spectrum the doublet observed for the cyclopentadienyl protons in CD_2Cl_2 solutions is split into two very close doublets in CD_3CN solutions. This excludes a substitution of the coordinated nitrogen by an acetonitrile molecule as for **11b,d**, which would result in very different chemical shifts in both ^{31}P and ^1H NMR. Furthermore, the ^1H NMR spectra of **11c**, in CD_2Cl_2 or CD_3CN, show two well-separated doublets of doublets, the first located at 1.36 ppm ($^3J_{H,CH_3}$ = 7 Hz, $^3J_{H,P}$ = 17.5 Hz) and the other at 1.32 ppm ($^3J_{H,CH_3}$ = 7 Hz, $^3J_{H,P}$ = 20 Hz), assigned to two different methyl groups. These data are consistent with the presence in **11c** of two asymmetric centers. The existence of two diastereoisomeric pairs of enantiomers for **11c** is also apparent in the ^{13}C NMR spectra recorded in CD_2Cl_2 or CD_3CN solutions for the signals of the $CH{=}CH_2$ moiety: the diastereotopic CH carbon atoms appear as a singlet located at 133.1 pm and as a doublet at 132.7 ppm ($J_{C,P}$ = 6 Hz) and the diastereotopic CH_2 carbon atoms as two doublets centered at 120 and 119.3 ppm ($J_{C,P}$ = 15 Hz for both). The diastereoisomers have indiscernible chemical shifts for the Cp, P–C, and CH_3 carbon atoms.

The above results show that the nature of the substituent R at phosphorus in the phosphoranes **7** has little or no influence on their coordination chemistry with η^5-$CpMo(CO)_3Cl$[8] while their reactivity toward η^5-$CpFe(CO)_2Br$ and the lability of the derivatives obtained depend strongly on R. The ease of displacement of a carbonyl group by P-coordination diminishes on going from phenyl- to benzyl-, allyl-, and vinylphosphoranes. These differences may be accounted for by the fact that phosphorus is more nucleophilic and basic in character in **7** than in **1**, thus favoring halogen displacement. The cationic derivatives **11** are also sensitive to modifications of the substituents at phosphorus, the coordinated nitrogen atom being partially replaced by a donating solvent molecule in **11b,d** and more strongly bonded to iron in **11a,c** and **2**.

Synthesis of the Metal Phosphoranides 12 and 13. Subsequent displacement of the proton from phosphorus, in **1**, to nitrogen in the chelated adducts **2**, through coordination of the tautomeric phosphane form of **1**, and further reaction with a base, proved effective in the synthesis of the Mo, W,[1,3] Fe, and Ru[2] phenylphosphoranides **4** and **5**. The question was then to know to what extent the nature of the substituents at phosphorus influence this reactivity pattern.

We found that in THF at −80 °C the cationic derivatives **10** and **11** are quantitatively converted into the phosphoranides **12** and **13**, respectively, by the action of CH_3Li. The molybdenum complexes **12** were isolated in nearly quantitative yields, whereas the iron analogues **13** decompose during workup, precluding their complete characterization. They are, however, stable in solution at temperatures below 0 °C. The neutral phosphoranides **12** and **13** exhibit CO absorptions shifted to lower frequencies with respect to the cationic derivatives **10** and **11**, by 20–55 cm^{-1}, respectively, as expected from the increase in charge density at the metal (Table I). Concomitantly, the low-field ^{31}P resonances of **10** and **11** are replaced by an upfield signal for **12** and **13**. In the case of **13c**, the two close ^{31}P resonances measured are consistent with the diastereotopic character of the phosphorus atom. This variation in chemical shifts is considerable (Δδ = 156–160 ppm for Mo and 134–140 ppm for Fe; Table I) and is comparable in magnitude to those which accompany the formation of the Mo, W, and Fe phenylphosphoranides **4** from their corresponding cationic adducts **2** (Δδ = 154, 142, and 135 ppm, respectively[1-3]), indicating the formation of a phosphoranide adduct rather than that of an amidophosphane complex analogous to **3**. The formation of **3** has, indeed, been found to be accompanied by downfield Δδ's of −8, −13, and 0 ppm only in the *P*-phenyl Mo, W, and Ru series, the ^{31}P chemical shift thus remaining within the 160–220 ppm range characteristic of M(II)–phosphane adducts. Such amido–phosphane adducts have not been detected during the abstraction of the proton from **10** or **11** even at −100 °C; if they exist, these species are of very short lifetime. However, as previously discussed for the *P*-phenyl iron derivative **4**,[2] a 16-electron species where the phosphoranide ligand would be monodentate through P (as in **13′**) or a fast exchange, even at low temperature), between such a species and the $\overline{\mathrm{M{-}N{-}P}}$ phosphoranide adducts **13** and their isomeric $\overline{\mathrm{M{-}O{-}P}}$ analogues of **5** cannot be excluded for derivatives **13a–c** on the basis of the ^{31}P NMR data.



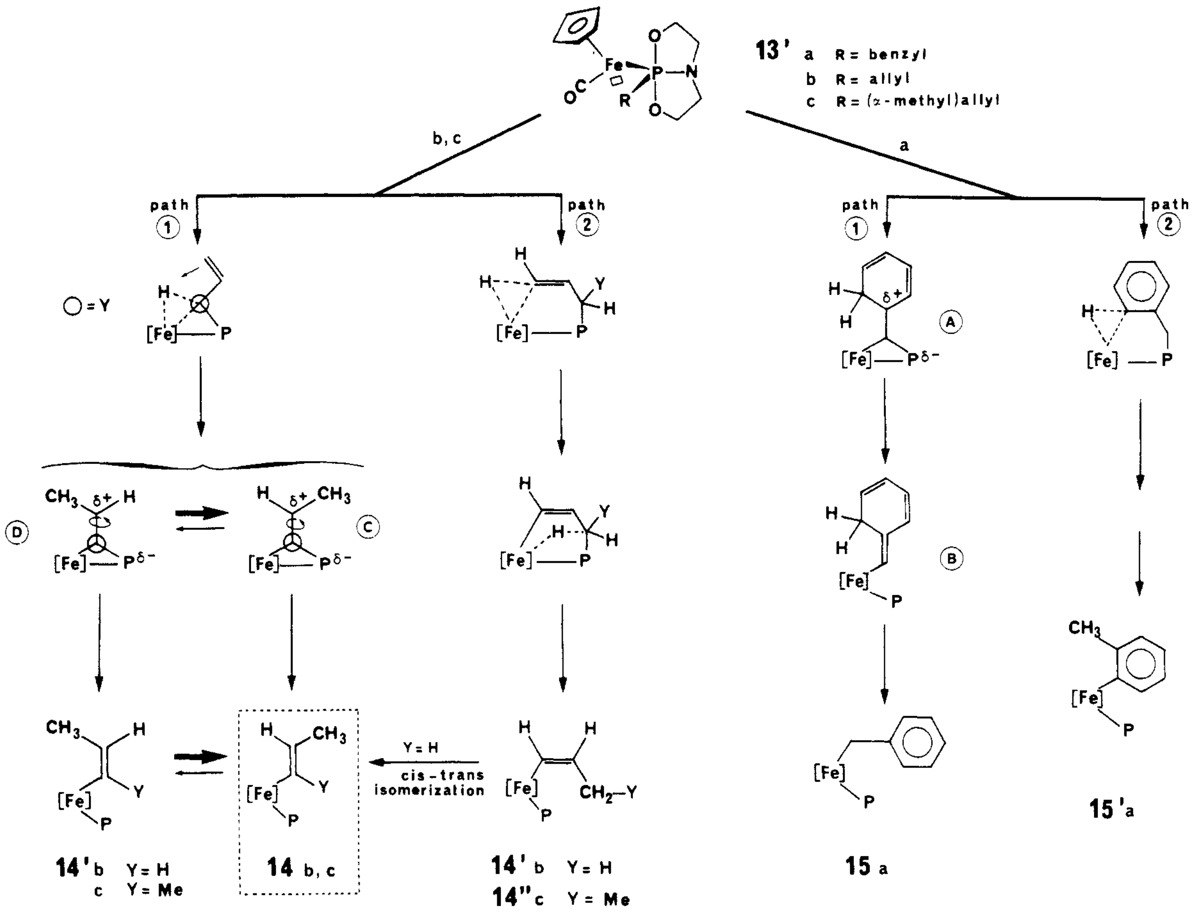
13′

The formation of the *P*-allyl, -benzyl, or -vinyl phosphoranides **12** and **13** shows that the presence of a phenyl group on phosphorus, which could have been expected to stabilize the phosphoranide ligand by charge delocalization, does not appear to be of prime importance. The stability of these derivatives appears to be essentially related to the nature of the metal. The bicyclic nature of the ligand plays a more determinant part in the isolation of metal phosphoranides, as shown by our unsuccessful attempts[6] to prepare the acyclic analogues of **12** or **13**. This illustrates the importance of the transannular relationship of N and P in the flexible ligands **1** and **7**.

Rearrangement and Migration of the *P*-Allyl Group. One important aspect of the phenyl group migration phenomenon[2,5] was the formation of M–C bonds. We have, therefore, investigated the ability of the phosphoranides **12** and **13** to transfer the phosphorus-bonded organic group to the metal.

Molybdenum Derivatives. Heating a THF solution of the molybdenum phosphoranides **12a–c** under reflux led to a complex mixture of compounds, as shown by the ^{31}P NMR spectra of the reaction solution. However, the presence of a ^{31}P resonance, among others, shifted upfield by 10–20 ppm with respect to those of **12a,b,d**, suggests formation of the isomeric $\overline{\mathrm{M{-}O{-}P}}$ phosphoranides analogous to **5**: such an isomerization (**4** → **5**) has already been shown in the Mo and W phenylphosphoranide series[1,2] to be accompanied by a similar variation in ^{31}P chemical shifts. No compound containing a Mo–R bond (R = benzyl, allyl, or vinyl) could be isolated by the usual

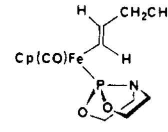
Scheme III. Mechanism of the Rearrangement and Migration of the P-Bound Allylic Group into the Fe-Bound Vinylic Group



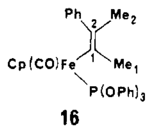
workup of the reaction mixture.

Iron Derivatives. The iron *P*-benzyl and *P*-vinyl phosphoranides **13a,d** are also transformed rapidly into several compounds when refluxed in THF, as attested by ^{31}P NMR. A ν(CO) absorption at 1930 cm^{-1} in the crude reaction mixture indicates (vide infra) that an analogue of **6** or of **14b** may have been formed. In contrast, a much cleaner reaction occurs when a THF solution of the allyl derivative **13b** is heated. The CO vibration at 1910 cm^{-1} of **13b** is then seen to disappear, while a new CO stretch develops progressively at 1930 cm^{-1}. At 60 °C the transformation is complete within 1 h. Adduct **14b** is isolated as a yellow powder in 40% yield by column chromatography (SiO_2/Et_2O) of the crude reaction product. Its structure is unambiguously established by its spectroscopic characteristics, which also exclude its being the initially expected (σ-allyl)iron derivative **15b**. The conversion of the phosphoranide ligand into the aminophosphane ligand as in **6**, for which it has been proven by an X-ray structure determination,[5] is established by the downfield ^{31}P chemical shift of 136 ppm from 80 ppm for **13b** to 216 ppm for **14b** and by the ^{13}C resonances of the NCH_2 and OCH_2 groups (two doublets at 54.6 and 54.4 ppm and two doublets at 69.3 and 69.1 ppm, respectively), these being very close to those found for **6**.

The rearrangement of the P-bonded allyl group into a Fe-bonded vinyl group is clearly attested by the ^1H and ^{13}C NMR data. The ^{13}C off-resonance spectrum of **14b** displays two vinylic carbons at 133 (C1) and 138 (C2) ppm, each coupled with one proton, while the third carbon at 24.8 ppm belongs to a methyl group (Me2), definitely establishing a $CH{=}CH{-}CH_3$ pattern. Both these chemical shifts and the coupling constants with phosphorus ($J_{C1P} = 38$, $J_{C2P} \approx 0$, and $J_{Me2P} = 5$ Hz) are also consistent with those published for the related compound **16** (δ (^{13}C) 136.5, 152.4, and 23.8 ppm; $J_{CP} = 37$, 0, and 3 Hz, respectively), whose structure has been confirmed by X-ray diffraction analysis.[10] The trans configuration at the double bond is asserted by the magnitude of the $J_{H_1H_2}$ coupling of 16 Hz.[11]



14''c



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Reaction Mechanism. The rearrangement of a P-bonded allyl group into a Fe-bonded vinylic group is particularly intriguing, especially since the 1,2-sigmatropic shift mechanism established for the phenyl migration[2] cannot operate here. Its mechanism will be discussed in view of the current interest in P–C bond cleavage by metal complexes. Allylphosphorus compounds are known to undergo base-catalyzed isomerization into their 1-propenylphosphorus analogues.[12] By analogy with the phenyl migration,[2] the process observed here could therefore consist either in a *P*-allyl to *P*-propenyl rearrangement in phosphoranide **13b**, followed by the 1,2-sigmatropic migration of the resulting vinylic group from P to Fe or in a 1,2 sigmatropic shift of the allyl group to give the (σ-allyl)iron species **15b** followed by a σ-allyl to

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Table II. Comparison of the ^{1}H and ^{13}C NMR Data of Compounds 14c, 17, and 18

		14c		17[17]		18[17]	
$\delta(^1H)$	H vinyl	5.35 (m)		5.8 (m)		6.4 (m)	
	Me_1	1.98 (s)		2.22 (s)		2.53 (s)	
	Me_2	1.64 (d)	$J_{H,Me_2} = 6.4$ Hz	1.95	$J_{H,Me_2} = 7$ Hz	2.11 (d)	$J_{H,Me_2} = 7$ Hz
$\delta(^{13}C)$	Me_1	17.2 (b s)	$J_{C,P} \leq 2$ Hz	17 (d)	$J_{C,P} = 2.4$ Hz	20.7 (s)	$J_{C,P} = 0$ Hz
	Me_2	30.8 (s)	$J_{C,P} < 1$ Hz	30.7 (s)	$J_{C,P} = 0$ Hz	40.9 (d)	$J_{C,P} = 3.7$ Hz
	C_1	141.4 (d)	$J_{C,P} = 47$ Hz	139.1 (d)	$J_{C,P} = 41.5$ Hz	142.7 (d)	$J_{C,P} = 34.6$ Hz
	C_2	131.9 (s)	$J_{C,P} < 1$ Hz	132.4 (d)	$J_{C,P} = 4.4$ Hz	120.4 (d)	$J_{C,P} = 5$ Hz

σ-vinyl isomerization at iron.[13] Both mechanisms involve a 1,2-sigmatropic shift of an organic group. If such a shift were operative, one would then expect the vinyl group of **13d**, and even more the benzyl group of **13a**, to migrate to iron, even more easily than the allyl group, to give derivatives **15a,d**; but this was not observed.

Two other mechanisms may account for the process reported here: they consist in the insertion of iron either into an allylic (Scheme III, pathway 1) or into a terminal olefinic (pathway 2) C–H bond, followed by a 1,3-proton shift to the terminal vinylic or allylic carbon atom, respectively, and P–C bond cleavage (concomitantly or not). These mechanisms find real support in the existence of three-membered M—P—C metallacycles,[14] which are similar to the intermediates C or D involved in path 1, and in the existence of the three-centered Fe···C···H interactions.[15]

It is known that insertion of a metal into C–H, C–C, or P–C bonds requires unsaturation at, and proximity to, the metal. The intermediate formation of the 16-electron species **13′** may therefore be involved. Pathway 2 (Scheme III) could be eliminated by using the *P*-(α-methyl)allyl derivative **13c** chemically labeled at the allylic carbon atom. If pathway 1 is operative, **13c** will lead to the 1,2-dimethylvinylic adduct **14c**, while pathway 2 would give the 1-butenyl complex **14″c**.

Derivative **13c** is converted after 10 h of reflux in THF into the *Fe*-vinylic species **14c**, which was isolated in 22% yield after chromatography on SiO_2 of the ether-soluble fraction of the crude reaction product; the product exhibits very similar NMR (in C_6D_6) and IR patterns before and after chromatography, indicating that isomerization had not taken place during the purification step. This fraction consists mainly in compound **14c**; no particular spectroscopic evidence was found for the formation of species such as **15c** or **14″c**. The conversion of the phosphoranide ligand into the aminophosphane ligand is indicated by a downfield ^{31}P chemical shift of 217 ppm and by the shifts of the ^{13}C resonances of the NCH_2 and OCH_2 groups (a broad singlet at 54.5 ppm and two doublets at 69.3 and 68.9 ppm, respectively), these data being very close to those found for **6** and **14b** (vide supra).

The rearrangement of the P-bonded α-methylallyl group into the Fe-bonded 1,2-dimethylvinylic group is unambiguously attested by the ^{1}H and ^{13}C NMR data. The off-resonance ^{13}C spectrum of **14c** displays a C–H vinylic carbon at 131.9 ppm ($J_{C,P} < 1$ Hz) and two carbons at 30.8 ($J_{C,P} < 1$ Hz) and 17.2 ppm ($J_{C,P} < 2$ Hz), each belonging to a methyl group; the Fe–C vinylic carbon appears as a doublet at 141.4 ppm ($J_{C,P} = 47$ Hz). The ^{1}H NMR spectra exhibit a complex multiplet at 5.35 ppm, which after a decoupling experiment could be assigned to the vinylic hydrogen atom, a singlet at 1.98 ppm (broad due to residual coupling), and a doublet at 1.64 ppm ($J_{CH_3,H} = 6.4$ Hz), each of the latter resonances corresponding to a methyl group; the coupling constant of 6.4 Hz is also in the range usually found for geminal CH_3–H couplings. These data establish a Fe—C(Me)=CHMe sequence and exclude the reaction product from being **14″c** and therefore the reaction mechanism from proceeding through the insertion of iron into the olefinic C—H bond (path 2).

Pathway 1 further accounts for the following experimental observations: first, the insertion or activation of the alllylic C–H bond is more difficult to achieve in the α-methylallyl derivative **13c** than in **13b**, presumably for steric reasons (**13b** is converted after 1 h of heating, whereas 10 h are required for **13c**). Secondly, such a mechanism also accounts for the stereoselectivity observed for these transformations (vide infra). Finally, it would, in the case of the benzyl derivative **13a**, lead to the benzyliron compound **15a** after rearomatization of B (Scheme III). However, the formation of the bridged Fe–P intermediate A would imply dearomatization of the phenyl ring, which here would constitute a high-energy barrier to the rearrangement and migration of the benzyl group. One should also note that, if the process had involved olefinic C–H bond insertion, which in the case of the benzyl group is similar to an ortho-metalation reaction, we should have expected the benzyl moiety to rearrange and migrate to iron even faster than the allyl group, to yield the stable *o*-tolyliron species **15′a** analogous to **6** (it is known that activation of C–H olefinic bonds is more difficult to achieve than that of C–H aromatic bonds).

Stereochemistry. The fact that only the trans isomer was isolated for **14b** (Fe and Me, trans) strongly suggested a cis configuration (Fe and H, cis) for **14c** and could thus be indicative of a stereoselective process. To confirm the cis configuration of **14c**, we undertook a NOE experiment, but this was unsuccessful, which is not uncommon with iron–alkenyl complexes.[16,17] However, the ^{1}H and ^{13}C NMR data of **14c** are much closer to those published for

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[13] (a) An H^+-catalyzed σ-allyl to σ-vinyl isomerization, as observed for Ir^{III}—CH_2—CMe=CH_2, but not for Ir^{III}—CH_2—CH=CH_2,[13b] which could have occurred here during the chromatographic purification of **14c** on SiO_2, is excluded, since the products before and after chromatography exhibit almost identical NMR (in $CDCl_3$ or C_6D_6 solution) and IR patterns. It is also unlikely that such an isomerization occurs during the mild thermolysis of **13b**, as catalytic traces of H^+ would be trapped by the excess of CH_3Li used. A base-catalyzed σ-allyl to σ-vinyl isomerization due to the 10% excess of CH_3Li used is also unlikely, since the same reaction occurs, and at a similar rate, with less than 1 equiv of the base. So far the only rearrangement reported for a (σ-allyl)iron derivative, e.g., η^5-CpFe(CO)(PPh$_3$)(η^1-allyl), is its thermal σ/π rearrangement, leading to the stable η^5-CpFe(CO)(η^3-allyl), which implies the dissociation of the phosphane adduct.[13c] Although an acid- or base-catalyzed σ-allyl to σ-vinyl cannot be definitively ruled out, the arguments against them add up to the stronger ones we have against the 1,2-sigmatropic shift that would also take part in these mechanistic paths. (b) Deeming, A. J.; Shaw, B. L.; Stainbauk, R. E. *J. Chem. Soc. A* **1971**, 334. (c) Aris, K. R.; Brown, J. M.; Taylor, K. A. *J. Chem. Soc., Dalton Trans.* **1974**, 2222.

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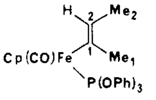
[17] Reger, D. L.; Belmore, K. A. *Organometallics* **1985**, *4*, 305.

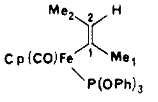
the very close iron–alkenyl analogue **17**, for which a cis configuration has been established, than to those of **18** which has the opposite configuration (see Table II).[17]

Let us now consider the mechanism of formation of compounds **14**, depicted in Scheme III. Insertion of iron into the allylic bond followed by the 1,3-proton shift could lead to the intermediate(s) C and/or D. The isolated materials **14** arise either directly from C and/or from the intermediary adduct **14′**, which has the opposite configuration, followed by a thermal or acid- (or base-) catalyzed cis/trans isomerization reaction.

A thermal cis/trans isomerization has been observed in similar derivatives only with η^5-CpFe(CO)[P(OPh$_3$)][η^1-(*Z*)-C(Me)=C(CO$_2$Me)Me],[16] activated to such by the ester group, and seems very unlikely here. A H$^+$-catalyzed isomerization, as observed for the very close iron alkenyl derivatives **17** and **18**, which occur only upon chromatography over alumina or in CHCl$_3$ solution, but not in benzene solution,[17] can also be excluded since very similar NMR spectra are measured for **14** in C$_6$D$_6$ solution before and after chromatography. The observed stereochemistry of **14** is thus most likely related to the relative thermodynamic stability of the intermediates C or D, C being the more stable one, probably for steric reasons.



17



18

Tentative Reverse Migration from Iron to Phosphorus. The fact that, under the action of HCl, the phenyl iron derivative **6** was converted quantitatively back to the starting phenylphosphane iron adduct **2** led us to explore this possibility with the vinylic iron analogues **14b,c**. However, no clean reaction was observed when similar conditions were applied, and we found no evidence for the formation of the expected vinylphosphane iron derivative analogous to **11d**.

Experimental Section

All reactions were carried out under dry oxygen-freed argon. All solvents were freshly distilled under argon from appropriate drying agents. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker WH-90 spectrometer. Chemical shifts are given in parts per million downfield from internal Me$_4$Si for the ^{1}H and ^{13}C shifts and from external H$_3$PO$_4$ for the ^{31}P shifts. Infrared spectra were obtained on a Perkin-Elmer 577 grating spectrophotometer. Elemental analyses were performed by the Service Central de Microanalyses of the CNRS, France.

Synthesis of the RP(NEt$_2$)$_2$ Derivatives. The synthesis of the R = vinyl derivative is detailed below; the same procedure was applied for the preparation of the other derivatives. To a solution of 29.6 g (107 mmol) of P(NEt$_2$)$_3$ in 50 mL of ether was added a solution of 7.4 g (54 mmol) of PCl$_3$ in 50 mL of ether dropwise under stirring at 0 °C. The mixture was then heated under reflux for 1 h, concentrated to 40 mL, and further heated to 60 °C for 1 h to complete the redistribution reaction. The oil was then redissolved in 100 mL of ether and cooled to −40 °C, and 14.9 g (170 mmol) of CH$_2$=CHMgCl in 100 mL of THF was added dropwise. The resulting solution was heated under reflux for 1 h. Filtration and evaporation of the solvent led to an oily residue from which CH$_2$=CHP(NEt$_2$)$_2$ was distilled under reduced pressure, yielding 28.1 g (139 mmol, 85%) of a colorless oil, bp 45–46 °C (0.02 mmHg). ^{31}P NMR (neat): δ 90. ^{1}H NMR (CDCl$_3$): δ 6.1–5.3 (m, 3 H, CH=CH$_2$), 2.95 (dq, 8 H, NCH$_2$, $^3J_{\mathrm{H,P}}$ = 8 Hz, $^3J_{\mathrm{H,H}}$ = 6.8 Hz), 1.0 (t, 12 H, CH$_3$). IR (film): ν(C=C) 1590 cm^{-1}.

The same procedure afforded C$_6$H$_5$CH$_2$P(NEt$_2$)$_2$ as a colorless oil in 70% yield; bp 67 °C (0.02 mmHg). ^{31}P NMR (neat): δ 90. ^{1}H NMR (CDCl$_3$): δ 7.34 (b s, 5 H, Ph), 3.18 (dq, 8 H, NCH$_2$, $^3J_{\mathrm{H,P}}$ = 9 Hz, $^3J_{\mathrm{H,H}}$ = 7.1 Hz), 3.11 (d, 2 H, PCH$_2$, $^2J_{\mathrm{H,P}}$ = 11 Hz), 1.17 (t, 12 H, NCH$_2$C*H*$_3$). IR (film): ν(C=C) 1600 cm^{-1}.

The CH$_2$=CHCH$_2$P(NEt$_2$)$_2$ derivative is obtained as a colorless oil in 70% yield; bp 59 °C (0.1 mmHg). ^{31}P NMR (neat): δ 86. IR (film): ν(C=C) 1640 cm^{-1}.

Synthesis of the Bicyclic Aminophosphoranes 7a–d. The synthesis of **7a** is described in detail; **7b–d** were prepared in a similar manner separately. Xylene instead of toluene was used as a solvent in the case of **7d**, since no reaction had occurred after 72 h in toluene.

7a. (Benzyl)P(NEt$_2$)$_2$ (1.86 g, 7 mmol) and diethanolamine (0.78 g, 7.4 mmol) were dissolved in toluene (150 mL). The solution was heated under reflux, and the NHEt$_2$ formed was distilled from the reaction solution and recuperated. The solvent was evaporated when the expected amount of amine had been obtained. The oily residue was then chromatographed on a short silica column by elution with toluene. After reevaporation of the solvent, the colorless oil was dissolved in 50 mL of pentane. **7a** crystallized from this solution when cooled to −40 °C and was isolated in 85% yield as white crystals melting at room temperature. ^{31}P NMR (neat): δ −38 (d, $^1J_{\mathrm{H,P}}$ = 670 Hz). IR (film): ν(PH) 2340, ν(C=C) 1600 cm^{-1}.

7b was obtained as a colorless oil in 93% yield from (allyl)P(NEt$_2$)$_2$ and diethanolamine. ^{31}P NMR (neat): δ −39 (d, $^1J_{\mathrm{H,P}}$ = 685 Hz. ^{1}H NMR (CDCl$_3$): δ 5.93 (m, 1 H, CH=), 5.15 (m, 2 H, CH$_2$=), 3.83 (m, OCH$_2$, 4 H), 2.95 (m, 4 H, NCH$_2$), 2.90 (d, 1 H, PH), 2.52 (m, 2 H, PCH$_2$). IR (film): ν(PH) 2340, ν(C=C) 1635 cm^{-1}.

7c was obtained as a colorless oil in 70% yield from (α-methylallyl)P(NEt$_2$)$_2$ and diethanolamine and was further purified by distillation; bp 40 °C (0.05 mmHg). ^{31}P NMR (neat): δ −30 (d, $^1J_{\mathrm{H,P}}$ = 685 Hz). ^{1}H NMR (CDCl$_3$): δ 6.61 (d, 1 H, PH), 5.85 (m, 1 H, CH=), 5.12 (m, 2 H, CH$_2$=), 3.85 (m, 4 H, OCH$_2$), 3.0 (m, 4 H, NCH$_2$), 2.59 (dq, 1 H, PCH, $^2J_{\mathrm{H,P}}$ = 25 Hz, $^3J_{\mathrm{CH,CH_3}}$ = 7 Hz), 1.23 (dd, 3 H, CH$_3$, $^3J_{\mathrm{H,P}}$ = 16 Hz, $^3J_{\mathrm{CH,CH_3}}$ = 7 Hz). IR (film): ν(PH) 2330, ν(C=C) 1630 cm^{-1}.

7d was obtained in 40% yield after 72 h of reflux in xylene from (vinyl)P(NEt$_2$)$_2$ and diethanolamine and was further purified by distillation; bp 43 °C (10^{-4} mmHg). ^{31}P NMR (neat): δ −53 (d, $^1J_{\mathrm{P,H}}$ = 700 Hz). IR (film): ν(PH) 2340, ν(C=C) 1605 cm^{-1}.

Synthesis of the Cationic Molybdenum Adducts 10a,b,d. The cationic molybdenum derivatives **8a,b,d** were prepared according to the procedure published for the preparation of **2a**[8] with some modifications. The preparation of **10a** is described; those of **10b,d** are identical.

10a. A 1-g (3.55-mmol) sample of η^5-CpMo(CO)$_3$Cl and 0.78 g (3.5 mmol) of **7a** were dissolved in 100 mL of ether. This solution was stirred at room temperature for 2 days. The orange precipitate was filtered, washed with ether, and dried, to give 1.5 g (3.2 mmol, 90%) of **8a**. IR (KBr, cm^{-1}): ν(CO) 1970, 1900, ν(NH) 3340. The latter compound was then dissolved in 50 mL of ethanol, and 2 g (6 mmol) of NaBPh$_4$ dissolved in 50 mL of a 5/1 mixture of ethanol/water was added. This solution was stirred for 1 day, and the orange-yellow precipitate was filtered, washed several times with water and then ether, and dried, to give 2.1 g (1.8 mmol, 88%) of **10a**. IR (KBr, cm^{-1}): ν(CO) 1940, 1885, ν(NH) 3220, ν(C=C) (BPh$_4^-$) 1580. ^{1}H NMR (CD$_3$CN): δ 5.31 (s, 5 H, Cp). ^{31}P NMR (CH$_3$CN): δ 210.3. Anal. Calcd for C$_{42}$H$_{41}$BMoNO$_4$P (M_r 761): C, 66.23; H, 5.39; N, 1.84; P, 4.07. Found: C, 65.90; H, 5.38; N, 1.83; P, 4.27.

10b. The same procedure applied to 5.45 g (12 mmol) of η^5-CpMo(CO)$_3$Cl and 2.04 g (12 mmol) of **7b** led to **8b** (4.6 g, 10.8 mmol, 90%; IR (KBr, cm^{-1}) ν(CO) 1960, 1875, ν(NH) 3340, ν(C=C) 1630), which was converted into **10b** (7.1 g, 10 mmol, 93%), as an orange-yellow powder. IR (KBr, cm^{-1}): ν(CO) 1975, 1895, ν(NH) 3240, ν(C=C) (allyl) 1640, ν(C=C) (BPh$_4^-$) 1580. ^{1}H NMR (CD$_3$CN): δ 5.67 (s, 5 H, Cp). ^{31}P NMR (CH$_3$CN): δ 209. Anal. Calcd for C$_{38}$H$_{39}$BMoNO$_4$P (M_r 711): C, 64.14; H, 5.49; N, 1.97; P, 4.36. Found: C, 63.60; H, 5.45; N, 1.97; P, 4.68.

10d. The same procedure applied to η^5-CpMo(CO)$_3$Cl (2.7 g, 9.65 mmol) and **7d** (1.46 g, 9.1 mmol) led to **8d** (3.9 g, 8.9 mmol, 95%; IR (KBr, cm^{-1}) ν(CO) 1965, 1880, ν(NH) 3340, ν(C=C) (vinyl) 1605) which was converted after the anion-exchange procedure into **10d** (6.3 g, 8.65 mmol, 97%), as a yellow-orange powder. IR (KBr, cm^{-1}): ν(CO) 1970, 1895, ν(NH) 3240, ν(C=C) (vinyl) 1605, ν(C=C) (BPh$_4^-$) 1580. ^{1}H NMR (CD$_3$CN): δ 5.75 (s, 5 H, Cp). ^{31}P NMR (CH$_3$CN): δ 199. Anal. Calcd for C$_{37}$H$_{37}$BMoNO$_4$P (M_r 697): C, 63.70; H, 5.31; N, 2.01; P, 4.45. Found:

C, 63.97; H, 5.33; N, 2.01; P, 4.71.

Synthesis of the Cationic Iron Adducts 11a,b,c,d. The synthesis of the iron derivatives **11** required first the preparation of complexes **9** which, after a Br$^-$ vs. BPh$_4^-$ anion exchange, were photochemically converted into the adducts **11**.[2] The experimental procedures for preparing **11a**,**b**,**d** or **c** are identical, and only that of complex **11a** is described.

11a. η^5-CpFe(CO)$_2$Br (2 g, 2.7 mmol) and **7a** (1.7 g, 7.5 mmol) were dissolved in 50 mL of THF. The solution was stirred for 2 days, and the cream-colored precipitate formed was then filtered off and washed with THF and ether, leading to **9a** (3.1 g, 6.5 mmol, 86%; IR (KBr, cm^{-1}) ν(CO) 2060, 2000, ν(NH) 3400). This latter derivative was dissolved in 100 mL of CH$_2$Cl$_2$, and 10 mmol of NaBPh$_4$ in 20 mL of ethanol was added. The resulting solution was stirred for 4 h, and the precipitate of NaBr was filtered. The organic layer was washed with water (3 × 50 mL), filtered, and irradiated for 8 h (HP lamp, 125 W) (this transformation was monitored by IR, and the irradiation was stopped as soon as the starting material had been consumed). The solution was concentrated to 10 mL, chromatographed on a 50 g silica column, and eluted with CH$_2$Cl$_2$. **11a** was eluted first as an orange-yellow band. Evaporation of the solvent and washing of the residue with ether led to **11a** (2.3 g, 3.3 mmol, 50%) as an orange powder. IR (KBr, cm^{-1}): ν(CO) 1965, ν(NH) 3230, ν(C═C) (BPh$_4^-$) 1580. ^{31}P NMR (CH$_3$CN): δ 222. ^{1}H NMR (CD$_3$CN): 4.76 (d, $^3J_{\mathrm{H,P}}$ = 1.5 Hz, 5 H, Cp). Anal. Calcd for C$_{41}$H$_{41}$BFeNO$_3$P (M_r 693): C, 71.00; H, 5.92; N, 2.09. Found: C, 70.90; H, 5.92; N, 2.09.

11b. The same procedure applied to 4.6 g (26 mmol) of **7b** and 6 g (22 mmol) of η^5-CpFe(CO)$_2$Br led first to **9b** (9 g, 21 mmol, 95%; IR (KBr, cm^{-1}) ν(CO) 2080, 2030, ν(NH) 3380), as a cream-colored powder and, after conversion, to 8 g (12.5 mmol, 60%) of **11b** as an orange powder. IR (KBr, cm^{-1}): ν(CO) 1965, ν(NH) 3220, ν(C═C) (allyl) 1635, ν(C═C) (BPh$_4^-$) 1580. ^{31}P NMR (CH$_2$Cl$_2$ or THF): δ 222. ^{31}P NMR (CH$_3$CN): δ 222 and 204 (**11′b**, see text). ^{1}H NMR (CD$_2$Cl$_2$): δ 4.36 (d, $J_{\mathrm{H,P}}$ = 1.3 Hz, 5 H, Cp). ^{1}H NMR (CD$_2$Cl$_2$/CD$_3$CN, 50/50): δ 4.53, 4.73 (d,d, $J_{\mathrm{H,P}}$ = 1.3, 1.2 Hz, 5 H, Cp, **11b** + **11′b**). ^{13}C NMR (CD$_2$Cl$_2$): δ 165 (4 lines due to $^1J_{\mathrm{C,B}}$ = 49 Hz, BC(Ph)), 137.0, 126.8 (s,s, o- or m-C(Ph)), 122.8 (s, p-C(Ph)), 81.8 (s, Cp), 65.9, 61.6 (s, d, $J_{\mathrm{P,C}}$ = 4.4 Hz, OC)*, 55.9, 49.5 (s, d, $J_{\mathrm{P,C}}$ = 8.8 Hz, NC)*, 43.9 (d, $J_{\mathrm{P,C}}$ = 41.2 Hz, PC). ^{13}C NMR (CD$_3$CN): identical plus a new singlet at 84 ppm (**11′b**) (Cp). The C═C and CO resonances were not located, and the assignment was further confirmed by a ^{13}C off-resonance NMR spectrum. Anal. Calcd for C$_{37}$H$_{39}$BFeNO$_3$P (M_r 643): C, 69.05; H, 6.07; N, 2.18; P, 4.82. Found: C, 69.02; H, 6.03; N, 2,18; P, 4.86.

11c. The same procedure applied to **7c** (4.26 g, 2.25 mmol) and η^5-CpFe(CO)$_2$Br (6.0 g, 2.3 mmol) led first to **9c** (9.5 g, 2.13 mmol, 95%; IR (KBr, cm^{-1}) ν(CO) 2060, 2010, ν(NH) 3380, ν(C═C) (allyl) 1630) as a cream-colored powder and, after Br$^-$ vs. BPh$_4^-$ exchange and UV irradiation, to 11.2 g (1.52 mmol, 68%) of **11c** as an orange powder. IR (KBr, cm^{-1}): ν(CO) 1960, ν(NH) 3230, ν(C═C) (allyl) 1630, ν(C═C) (BPh$_4^-$) 1580. ^{31}P NMR (CH$_3$CN): δ 225 and 224.5. ^{31}P NMR (CH$_2$Cl$_2$): δ 224 and 223.8. ^{1}H NMR (CD$_3$CN or CD$_2$Cl$_2$): δ 7.35–6.83 (m, 20 H, BPh), 6.18–5.71 (m, 1 H, CH═), 5.45–5.05 (m, 2 H, CH$_2$═), 4.84, 4.83 (d, d, $J_{\mathrm{H,P}}$ = 0.9, 1.2 Hz, 5 H, Cp), 4.29–3.71 (m, 4 H, OCH$_2$), 3.31–3.0 (m, 1 H, PCH), 2.58–2.13 (m, 4 H, NCH$_2$), 1.36 (dd, $J_{\mathrm{H,P}}$ = 17.5 Hz, $^3J_{\mathrm{H,CH_3}}$ = 7 Hz, CH$_3$), 1.32 (dd, $J_{\mathrm{H,P}}$ = 20 Hz, $^3J_{\mathrm{H,CH_3}}$ = 7 Hz, CH$_3$). ^{13}C NMR (CD$_2$Cl$_2$ or CD$_3$CN): δ 164.7 (4 lines due to $^1J_{\mathrm{C,B}}$ = 50 Hz, BC(Ph)), 136.5, 126.4 (s, s, o- or m-C(Ph)), 122.6 (s, p-C(Ph)), 133.1, 132.7 (s, d, $J_{\mathrm{C,P}}$ = 6 Hz, *C*H═CH$_2$), 120, 119.3 (d, d, $J_{\mathrm{C,P}}$ = 15 Hz, CH═*C*H$_2$), 83.2 (s, Cp), 67.8, 62.5 (s, d, $J_{\mathrm{C,P}}$ = 6 Hz, OC)*, 57.5, 50.0 (s, d, $J_{\mathrm{C,P}}$ = 10 Hz, NC)*, 48.1 (d, $J_{\mathrm{C,P}}$ = 41 Hz, PC), 13.5 (d, $J_{\mathrm{C,P}}$ = 25 Hz, CH$_3$). The CO resonance was not located. This assignment was further confirmed by a ^{13}C off-resonance NMR spectrum. Anal. Calcd for C$_{38}$H$_{41}$BFeNO$_3$P (M_r 657): C, 69.41; H, 6.24; N, 2.13. Found: C, 69.05; H, 6.30; N, 2.11.

11d. The same procedure applied to 1.43 g (8.9 mmol) of **7d** and 2.3 g (8.6 mmol) of η^5-CpFe(CO)$_2$Br led, in the first step, to **9c** (3.2 g, 7.7 mmol, 90%; IR (KBr, cm^{-1}) ν(CO) 2060, 2020, ν(NH) 3380; ^{31}P NMR (CH$_2$Cl$_2$) δ 181) and, after the second step, to 1.9 g (3.1 mmol, 40%) of **11d** as an orange powder. IR (KBr, cm^{-1}): ν(CO) 1960, ν(NH) 3220, ν(C═C) (vinyl) 1605, ν(C═C) (BPh$_4$)$^-$) 1580. ^{31}P NMR (CH$_2$Cl$_2$): δ 209. ^{31}P NMR (CH$_3$CN): δ 210 and 191 (**11d′**, see text). ^{1}H NMR (CD$_2$Cl$_2$): δ 4.42 (d, $J_{\mathrm{H,P}}$ = 1.3 Hz, Cp, 5 H). ^{1}H NMR (CD$_3$CN): δ 4.78, 4.72 (d, d, $J_{\mathrm{H,P}}$ = 1.5, 1.3 Hz, Cp, **11d′** + **11d**). ^{13}C NMR (CD$_2$Cl$_2$): δ 164.6 (4 lines, $^1J_{\mathrm{C,B}}$ = 50 Hz, BC(Ph)), 136.5, 126.5 (s, s, o- or m-C(Ph)), 122.6 (s, p-C(Ph)), 82.4 (s, Cp), 65.9, 61.5 (s, d, $J_{\mathrm{C,P}}$ = 4.4 Hz, OC)*, 56.3, 50.3 (s, d, $J_{\mathrm{C,P}}$ = 9 Hz, NC)*. The CO and vinylic resonances were not located. Anal. Calcd for C$_{36}$H$_{37}$BFeNO$_3$P (M_r 629): C, 68.68; H, 5.88; N, 2.23. Found: C, 68.64; H, 5.95; N, 2.23. [Similar changes in coupling constants for the inequivalent carbon atoms of each of the O–C and N–C methylene groups have already been reported for analogous derivatives in ref 9.]

Synthesis of the Molybdenum Phosphoranides 12a,b,d. **12a.** A 0.5-mL sample of a 1.6 M solution of CH$_3$Li in ether was added dropwise at −60 °C to a solution of 0.57 g (0.75 mmol) of **10a** in 10 mL of THF. The resulting solution turned from orange to yellow. The reaction mixture was allowed to warm to room temperature, and ether (40 mL) was added. A filtration system was then placed on the reaction vessel and the whole system cooled to −30 °C for 1 day. The precipitate of LiBPh$_4$ was then filtered at that temperature. Evaporation of the solvent and washing twice with pentane (30 mL) led to **12a** (0.31 g, 0.705 mmol, 94%) as a yellow powder. IR (KBr, cm^{-1}): 1945, 1935, 1860, 1835 (1940, 1850 in THF), ν(C═C) (Ph) 1600. ^{31}P NMR (THF): δ 52. Anal. Calcd for C$_{18}$H$_{20}$MoNO$_4$P (M_r 441): C, 49.98; H, 4.54; N, 3.17; P, 7.03. Found: C, 49.43; H, 4.64; N, 2.97; P, 7.05.

12b. The same procedure applied to 2.15 g (3 mmol) of **10b** and 3.2 mmol of LiMe led to 1.1 g (2.8 mmol, 93%) of the phosphoranide **12b** as a yellow powder. This derivative decomposes slowly at room temperature. IR (KBr, cm^{-1}): ν(CO) 1925, 1830 (1940, 1850 in THF), ν(C═C) 1630. ^{31}P NMR (THF): δ 49. A satisfactory analysis was not obtained, due to instability of the compound.

12d. The same procedure applied to 0.89 g (1.28 mmol) of **10d** and 1.4 mmol of CH$_3$Li led to 0.45 g (1.19 mmol, 93%) of the phosphoranide **12d** as a yellow powder. IR (KBr, cm^{-1}): ν(CO) 1930, 1820, ν(C═C) (vinyl) 1590. ^{31}P NMR (THF): δ 43. Anal. Calcd for C$_{13}$H$_{16}$MoNO$_4$P (M_r 377): C, 42.92; H, 4.70; N, 3.58; P, 7.92. Found: C, 43.05; H, 4.64; N, 3.38; P, 7.97.

Synthesis of the Iron Phosphoranides 13a–d. These derivatives are stable only in solution, at temperatures below 0 °C. At higher temperature they decompose slowly, except for **13b**,**c** (vide infra). Their isolation is accompanied by considerable decomposition. Thus they could be characterized only by ^{31}P NMR and IR spectroscopies. The spectra of the phosphoranides **13a–d** were recorded immediately after addition of CH$_3$Li (1.1 eq mmol) to a solution containing the corresponding cationic derivative **11** at −80 °C (for data see text).

Synthesis of the Iron η^1-Vinylic Derivatives 14b,c. **14b.** A solution (1.2 mL, 1.9 mmol) of CH$_3$Li (1.6 M) in ether was added dropwise to a solution of **11b** (1.1 g, 1.71 mmol) in 30 mL of THF cooled to −80 °C. The ν(CO) vibration of **11b** at 1960 cm^{-1} was replaced by that of **13b** at 1910 cm^{-1}. The solution was then heated under reflux of THF for 1 h. During this time the ν(CO) of the phosphoranide **13b** was seen to disappear and a new ν(CO) stretch developed at 1930 cm^{-1}. After completion of this transformation, the solvent was evaporated and ether (10 mL) was added. After filtration, the yellow solution was chromatographed on a short silica column by ether elution. **14b** eluted as a yellow band. This fraction was collected, and after evaporation of the solvent and washing with cold pentane, **14b** (0.22 g, 0.64 mmol, 40%) was isolated as a yellow powder. IR (KBr, cm^{-1}): ν(CO) 1930, ν(C═C) 1570. ^{31}P NMR (THF or CH$_2$Cl$_2$): δ 216. ^{1}H NMR (CD$_2$Cl$_2$ or C$_6$D$_6$): δ 6.5 (dm, $^4J_{\mathrm{H,Me}}$ = 1.2 Hz, $^3J_{\mathrm{CH,CH}}$ = 16 Hz, 1 H, FeCH), 5.5 (m, 1 H, CH═), 4.56 (d, $^3J_{\mathrm{H,P}}$ = 0.9 Hz, 5 H, Cp), 3.75 (m, 4 H, OCH$_2$), 3.25 (m, 4 H, NCH$_2$), 1.8 (dd, $^3J_{\mathrm{CH,me}}$ = 6 Hz, $J_{\mathrm{H,P}}$ = 1.2 Hz, 3 H, Me). ^{13}C NMR (CD$_2$Cl$_2$ or C$_6$D$_6$): δ 138 (s, CH(Me)), 133 (d, $^2J_{\mathrm{C,P}}$ = 38 Hz, FeC), 84 (s, Cp), 69.3, 69.1 (d,d, $J_{\mathrm{C,P}} \approx$ 4 Hz, OCH$_2$), 54.6, 54.5 (d,d, $J_{\mathrm{C,P}} \approx$ 4 Hz, NCH$_2$), 24.8 (d, $J_{\mathrm{C,P}}$ = 5 Hz, Me). This assignment was further confirmed by the ^{13}C off-resonance NMR spectra. The CO resonance was not located.

14c. The same experimental procedure applied to **11c** (1.56 g, 2.37 mmol) and CH$_3$Li (1.5 mL, 2.4 mmol) led after 10 h of reflux in THF and chromatography to **14c** (0.18 g, 0.53 mmol, 22%) as a yellow powder at low temperature, becoming oily at room temperature. IR (THF, cm^{-1}): ν(CO) 1930. ^{31}P NMR (CH$_2$Cl$_2$): δ 217. ^{1}H NMR (CDCl$_3$, CD$_2$Cl$_2$ or C$_6$D$_6$): δ 5.35 (m, 1 H, CH═),

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4.59 (s, Cp), 4.20–3.75 (m, 4 H, OCH_2), 3.70–2.85 (m, 4 H, NCH_2), 1.98 (b s, 3 H, $FeCCH_3$), 1.64 (b d, $^3J_{H\text{-}Me}$ = 6.4 Hz, 3 H, $=CHCH_3$). ^{13}C NMR ($CDCl_3$ or C_6D_6): δ 141.4 (d, $J_{C,P}$ = 47 Hz, FeC), 131.9 (s, $CH{=}C$), 84.0 (s, Cp), 69.3, 68.9 (d,d, $J_{C,P}$ = 4 Hz, OCH_2), 54.5 (b s, NCH_2), 30.8 (s, CH_3C), 17.2 (b s, $J_{C,P} \le 2$ Hz, CH_3CH). The CO resonance could not be located. This assignment was further confirmed by a ^{13}C off-resonance NMR spectrum.

Registry No. **7a** (bicyclic), 103794-48-5; **7a** (phosphine), 103794-53-2; **7b** (bicyclic), 103794-49-6; **7b** (phosphine), 103794-54-3; **7c** (bicyclic), 103794-50-9; **7c** (phosphine), 103794-55-4; **7d** (bicyclic), 103794-51-0; **7d** (phosphine), 103794-56-5; **8a**, 103794-41-8; **8b**, 103794-40-7; **8c**, 103816-39-3; **9a**, 103794-42-9; **9b**, 103794-43-0; **9c**, 103816-40-6; **9d**, 103794-44-1; **10a**, 103794-29-2; **10b**, 103794-39-4; **10d**, 103794-37-2; **11a**, 103794-35-0; **11b**, 89321-14-2; **11b′**, 103794-46-3; **11c**, 103794-31-6; **11d**, 103794-33-8; **11d′**, 103816-42-8; **12a**, 103816-33-7; **12b**, 103816-34-8; **12d**, 103816-38-2; **13a**, 103816-35-9; **13b**, 89321-12-0; **13c**, 103816-36-0; **13d**, 103816-37-1; **14b**, 89302-53-4; **14c**, 103794-47-4; $P(NEt_2)_3$, 2283-11-6; $CH_2{=}CHMgCl$, 3536-96-7; $CH_2{=}CHP(NEt_2)_2$, 89438-02-8; $C_6H_5CH_2P(NEt_2)_2$, 93633-48-8; $CH_2{=}CHCH_2P(NEt_2)_2$, 31480-07-6; (α-methylallyl)$P(NEt_2)_2$, 103794-52-1; η^5-$CpMo(CO)_3Cl$, 12128-23-3; η^5-$CpFe(CO)_2Br$, 12078-20-5; diethanolamine, 111-42-2.

Communications

Reaction of (Aminocarbene)iron Complexes with Alkynes. A Synthesis of 5-Aminofurans

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Summary: Alkynes react with ((dimethylamino)phenylmethylidene)tetracarbonyliron(0), compound **3**, with incorporation of CO to give 5-(dimethylamino)furans as the major products. Consistent with the mechanism proposed here and related to the mechanism proposed earlier for reactions of the corresponding (alkoxyalkylidene)iron complexes, the product distribution is CO-pressure-dependent, producing 6-(dimethylamino)-α-pyrones at the expense of furans under higher CO pressure. The regioselectivity in the addition of alkynes parallels that observed in the reactions of alkynes with (alkoxyalkylidene)chromium and -iron analogues. The 5-(dimethylamino)furans are relatively little studied; high reactivity toward oxygen and maleic anhydride is observed.

Chromium–carbene complexes such as **1** react with alkynes[1-4] and imines[5] in general processes to give potentially useful types of products,[1-3] although mechanistic features and the origin of selectivities are not well-defined. The iron analogues (e.g., **2**) react with alkynes to form 6-ethoxypyrones in a quite general way.[6] We now describe the reaction of alkynes with the corresponding amino derivatives **3**, leading generally to 2-aryl-5-aminofurans, in a process of preparative and mechanistic significance.[7]

Table I. Reaction of Alkynes with Aminocarbene Complex 3

entry	alkyne	solvt, atmosphere	products (% yield)
1	R_1, R_2 = Me	CH_2Cl_2, CO (55 psi)[c]	**6a** (47), **7a**/**8a** (13)
2	same	$ClCH_2CH_2Cl$, CO (650 psi)[d]	**6a** (20), **7a**/**8a** (47)
3	same	CH_2Cl_2, Ar (40 psi)[c]	**6a** (73), **9** (21)[b]
4	same	THF, Ar[e]	**6a** (62), **9** (4)[b]
5	R_1, R^2 = Et	$ClCH_2CH_2Cl$, Ar[e]	**6b** (74)[f]
6	same	THF, Ar[e]	**6b** (45)[f]
7	R_1, R_2 = CO_2Me	CH_2Cl_2, Ar (40 psi)[c]	**6c** (50)
8	same	$ClCH_2CH_2Cl$, Ar[e]	**6c** (35), **11c** (24)[b]
9	same	THF, Ar[e]	**6c** (16), **11** (13)[b]
10	R_1, R_2 = O-*t*-Bu	CH_2Cl_2, Ar (40 psi)[c]	**6d** (0), **13d** (5), **11d** (6)[b]
11	R_1 = Ph, R_2 = H	CH_2Cl_2, Ar (40 psi)[c]	**6e** (18)[g]
12	same	$ClCH_2CH_2Cl$, Ar[e]	**6e** (16), **13e** (30), **11e** (15)
13	same	THF, Ar[e]	**6e** (12), **10e** (13), **14e** (18), **11e** (13)
14	R_1 = *n*-C_3H_7, R_2 = H	$ClCH_2CH_2Cl$, Ar[e]	**6f** (64), **12f** (4)
15	R_1 = Me, R_2 = CO_2Me	$ClCH_2CH_2Cl$, Ar[e]	**6g** (73)

[a] Based on weighed samples purified by preparative layer chromatography or flash chromatography. [b] Based on alkyne at the start. [c] Glass pressure bottle. [d] Steel pressure vessel. [e] Conventional flask, under a small positive pressure of argon. [f] Based on oxidized product **20**. [g] Based on weight of adduct **21e** from addition of maleic anhydride.

Reaction of **2** with dimethylamine produced the known complex[9] **3** in 95% yield, mp 104–105 °C. A similar pro-

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