General procedure for the azido-iodination of alkenes: A mixture of alkene (1 equiv) and resin **3a** was shaken at 300 rpm under light protection in absolute CH_2Cl_2 (2 mL mmol^{-1}; the number of equivalents of **3a** is given in Table 1) at room temperature. Completion of the reaction was monitored by TLC (cyclohexane/ethyl acetate between 80/1 and 8/1) and was terminated by filtration. The resin was washed with CH_2Cl_2 (3 × ; 20 mL per gram resin) and the combined organic washings and filtrate were concentrated under reduced pressure. In some cases, for example for the separation of stereo- and regioisomers, additional purification of the products by flash chromatography on silica gel was necessary.

The structures of all addition products were elucidated by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy, and mass spectrometry (EI or DCI). ^{1}H,^{13}C-COSY and the distortionless enhancement by polarization transfer (DEPT) spectral editing technique were used to determine the regiochemistry of the 1,2-addition products. The ^{13}C NMR shifts (in $CDCl_3$): $\delta = 58.0-64.7$ (CH_2-N_3), 62.6–74.9 (CH-N_3), 62.8–63.8 (C-N_3; **28**, **29**), 7.8–8.4 (CH_2-I), 25.1–35.2 (CH-I), 16.1 (C-I; **32**). Only the chemical ^{13}C NMR shifts for the secondary iodide-bound carbon atoms in **7**, **13**, and **14** show a pronounced downfield shift ($\delta = 39.7-49.1$) relative to all other examples. All new compounds gave either correct elementary analysis or were analyzed by high-resolution mass spectrometry in the CI-mode (reactant gas: isobutane).

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[1] Reviews: S. J. Shuttleworth, S. M. Allin, P. K. Sharma, *Synthesis* **1998**, 1217–1239; S. W. Kaldor, M. G. Siegel, *Curr. Opin. Chem. Biol.* **1997**, *1*, 101–106; J. S. Früchtel, G. Jung, *Angew. Chem.* **1996**, *108*, 19–46; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 17–42; P. Hodge, D. C. Sherringtom in *Polymer-Supported Reaction in Organic Synthesis*, Wiley, New York, **1990**; P. Laszlo in *Preparative Chemistry using Supported Reagents*, Academic, San Diego, **1987**.

[2] H. W. Gibson, F. C. Bailey, *J. Chem. Soc. Chem. Commun.* **1977**, 815–816; A. Nag, S. K. Sarkar, S. K. Palit, *Synth. Commun.* **1987**, *17*, 1007–1013.

[3] B. Hinzen, S. V. Ley, *J. Chem. Soc., Perkin Trans. 1*, **1997**, 1907–1908; B. Tamani, M. Hattam, D. Mohadjer, *Polymer,* **1991**, *32*, 2666–2670; B. Tamani, N. Goudarzian, *Eur. Polym. J.* **1992**, *28*(9), 1035–1038.

[4] R. J. Booth, J. C. Hodges, *J. Am. Chem. Soc.* **1997**, *119*, 4882–4886.

[5] N. Krause, M. Mackenstedt, *Tetrahedron Lett.* **1998**, *39*, 9649–9650.

[6] M. C. Desai, L. M. Stramiello, *Tetrahedron Lett.* **1993**, *34*, 7685–7688; M. Adamczyk, J. R. Fishpaugh, *Tetrahedron Lett.* **1996**, *37*, 4305–4308.

[7] M. Bernhard, W. T. Ford, *J. Org. Chem.* **1983**, *48*, 326–332; I. Hughes, *Tetrahedron Lett.* **1996**, *37*, 7595–7598

[8] Reviews: E. Block, A. L. Schwan in *Comprehensive Organic Synthesis, Vol. 4* (Eds.: B. M. Trost, I. Fleming, M. F. Semmelhack), Pergamon, Oxford, **1991**, pp. 329–362; J. Rodriguez, J.-P. Dulcère, *Synthesis* **1993**, 1177–1205.

[9] M. Tiecco, L. Testaferri, A. Temperini, L. Bagnoli, F. Marini, C. Santi, *Synth. Commun.* **1998**, *28*, 2167–2179, and references therein.

[10] G. A. Olah, X.-Y Li, Q. Wang, G. K. S. Prakash, *Synthesis* **1993**, 693–699; B. Zajc, M. Zupan, *Tetrahedron* **1989**, *45*, 7869–7878.

[11] A. Kirschning, C. Plumeier, L. Rose, *Chem. Commun.* **1998**, 33–34; A. Kirschning, A. Hashem, H. Monenschein, L. Rose, K.-U. Schöning, *J. Org. Chem.*, in press.

[12] F. W. Fowler, A. Hassner, L. A. Levy, *J. Am. Chem. Soc.* **1967**, *89*, 2077–2082; A. Hassner, *Acc. Chem. Res.* **1971**, *4*, 9–16; A. Hassner, F. W. Fowler, *J. Org. Chem.* **1968**, *33*, 2686–2691.

[13] G. O. Olah, Q. Wang, X,-Y. Li, G. K. S. Prakash, *Synlett* **1990**, 487–489.

[14] The structures of iodate(I) complexes **2** and **3a** are proposed with reference to the analogous tetraalkylammonium salts: G. Doleschall, G. Tóth, *Tetrahedron* **1980**, *36*, 1649–1665; C. Szántay, G. Blaskó, M. Bárcrczai-Beke, P. Péchy, G. Dörnei, *Tetrahedron Lett.* **1980**, *21*, 3509–3512.

[15] Polymer-bound iodate(I) complex **2** is also very useful for promoting iodoacetoxylation of alkenes: A. Kirschning, H. Monenschein, M. Jesberger, unpublished results.

[16] Most β-iodoazides described in Table 1 were conveniently prepared by means of automated parallel synthesis.

[17] In fact, in some cases we observed that aqueous work-up led to back reaction of the β-iodoazides to the starting alkenes, an obstacle which is completely avoided when employing our new polymer-bound reagent **3a**.

[18] K. B. Wiberg, A. J. Ashen, *J. Am. Chem. Soc.* **1968**, *90*, 63–74.

Olefin Cycloadditions of the Electrophilic Phosphinidene Complex $[i\mathrm{Pr_2N{-}P{=}Fe(CO)_4}]$**

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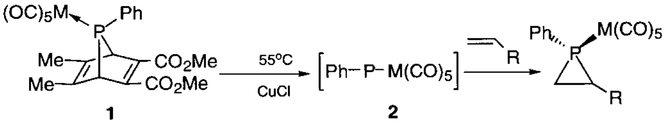
Electrophilic phosphinidene complexes are known to display carbene-like properties.[1] Through the pioneering work of Mathey et al.[2] in the early 1980s these transient species became accessible through thermal decomposition of phosphinidene precursor **1** (Scheme 1). Even today this is virtually the only route to $[RPM(CO)_5]$ (**2**) (M = W, Mo, Cr; R = Ph),[1a, 3] whereas the number of stable, isolable nucleophilic phosphinidene complexes continues to grow steadily.[4] Unfortunately, access to **2** is hampered by the limited thermal window for cheletropic elimination from **1** (100–130 °C or ca. 55 °C in the presence CuCl) and by the laborious synthesis of **1**. In view of the rich chemistry of electrophilic phosphinidenes we sought alternative synthetic pathways.



Scheme 1.

Our attention was drawn to the work of King et al. in the late 1980s,[5] in which dichlorophosphanes and Collman's salt were used to generate phosphorus–iron clusters such as **6** below 0 °C (Scheme 2). The formation of **6** was explained

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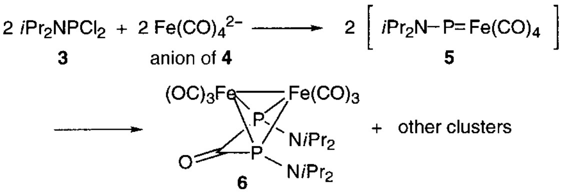
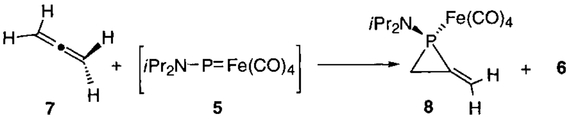


Scheme 2.

by the dimerization of the transient intermediate [iPr$_2$N–P=Fe(CO)$_4$] (**5**), which in our estimation is an electrophilic phosphinidene complex stabilized by an electron-donating amine group. To evaluate the proposed intermediacy of **5** we set out to trap this phosphinidene complex by cycloaddition to olefins.

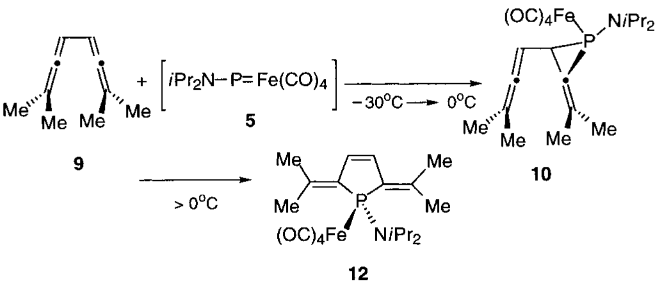
Warming a suspension of iPr$_2$NPCl$_2$ (**3**) and Na$_2$Fe(CO)$_4$ (**4**) in diethyl ether together with the trapping reagent styrene, stilbene, or 2,3-dimethyl-1,3-butadiene from −78 to −30 °C, where reaction between **3** and **4** starts, to room temperature resulted, however, mainly in the known carbonyl-bridged cluster **6**. Neither of the olefins yielded a phosphirane, although they are known to undergo cycloadditions at 55 °C with in situ generated [PhPW(CO)$_5$].[1a] Apparently, if indeed the [iPr$_2$N–P=Fe(CO)$_4$] phosphinidene is formed, it has a higher affinity for dimerization than for addition to olefins. It may also be argued that the iPr$_2$N donor substituent reduces the presumed electrophilicity of **5**. However, increasing the electron density of the olefin, as in 1-methoxy-1-propene and 1-methoxy-1,3-cyclohexadiene, does not lead to phosphiranes (again in contrast to the reactions with [PhPW(CO)$_5$]),[1a, 6] but in these cases the cycloaddition may be hampered by complexation of the proposed intermediate **5** to the O-substituents.

The unequivocal intermediacy of [Fe(CO)$_4$]-complexed phosphinidene **5** could, however, be demonstrated in the reaction with 1,2-propadiene **7**, the parent allene (Scheme 3). Slowly heating a suspension of **3**, **4**, and **7** from −30 °C to room temperature gave the cycloaddition product methylenephosphirane **8** in 51 % yield along with the cluster **6**. The spectroscopic properties of **8** resemble those of the earlier reported W(CO)$_5$-complexed methylenephosphiranes.[7] Most characteristic are its ^{31}P NMR chemical shift ($\delta = -47.5$) and its mass spectrum, which shows indications for a retro allene addition from the decarbonylated Fe-phosphirane. Evidently, the affinity of allene **7** for **5** competes well with the dimerization pathway.



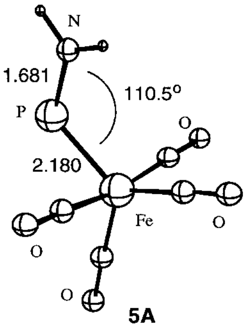
Scheme 3.

Incorporation of conjugated double bonds in the allene should increase its affinity for **5** and this can indeed be demonstrated for tetramethyldiallene **9** (Scheme 4). Heating a reaction mixture of **3**, **4**, and **9** from −30 °C to 0 °C, with isolation and purification of the product below −10 °C, results in the exclusive formation of phosphirane **10**. Monitoring of the reaction by ^{31}P NMR spectroscopy confirms the emergence of only one major singlet at $\delta = -20.4$, a minor resonance at $\delta = -29$, (assigned to the epimer of **10** but too small to integrate), and no trace of cluster **6**. The spectroscopic data show that cycloaddition has occurred at the conjugated double bond of **9**, which is also the least substituted one, and not at a terminal double bond to give **11**. The ^{1}H NMR spectrum shows a resonance signal for the phosphirane hydrogen atom at $\delta = 2.72$ which has ^5J couplings (confirmed by decoupling experiments) with two olefinic methyl groups at $\delta = 1.89$ and 2.12. The *syn*-configuration of phosphirane **10** is based on the assumption that the allene substituent and the sterically demanding iPr$_2$N group (more than [Fe(CO)$_4$]) are in a *trans* configuration.



Scheme 4.

An ab initio analysis of the reaction given in Scheme 4 was performed with the Amsterdam Density Functional (ADF) program[8] using a frozen core triple-ζ (TZP) basis set augmented with diffuse functions[9] and an uncontracted triple-ζ STO basis set for the five outer shells of Fe. All geometries were optimized at the NL-SCF level in the Vosko–Wilk–Nusair parametrization[10] with nonlocal corrections for exchange (Becke88)[11] and correlation (Perdew86).[12] Notation **A** is used to identify computed structures; a distinction is in the use of the H$_2$N substituent versus the iPr$_2$N group used in the experimental work. [H$_2$N–P=Fe(CO)$_4$] (**5A**) (Figure 1) has a strong P–Fe bond of 2.180 Å with σ and π interactions of a similar magnitude and electrophilic behavior, in accord with a recent analysis on related [M(CO)$_5$]-complexed phosphinidenes (M = Mo, Cr, W).[13] 1,2-Addition of **5A** to the diene part of **9A** (giving **10A**, Figure 2) is favored by 6 kcal mol^{-1} over reaction with one of its terminal olefinic bonds (giving **11A**, Figure 2), which is in accord with the experimental data. Even though **10A** is the more stable isomer, its significantly distorted phosphirane ring suggests that this compound is rather reactive. Particularly, its 1.944 Å long C–P bond length, which is even 0.041 Å longer than that of **11A**, is indicative for possible rearrangements initiated by cleavage of this bond.



5A

Figure 1. The calculated structure **5A**.

The [W(CO)$_5$]-complexed vinylphosphiranes are indeed known to undergo rearrangements and epimerizations in a

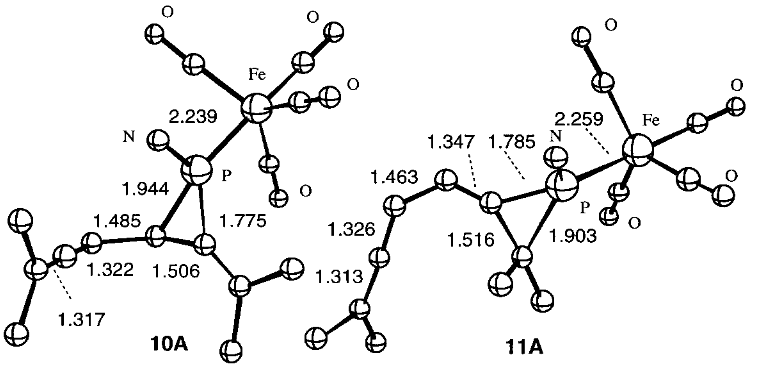


Figure 2. The calculated structures **10 A** and **11 A**.

manner similar to the well-documented vinylcyclopropanes.[1a, 6a, 14] Compound **10** is no exception as the computed geometry **10 A** already suggests. Thus, when a suspension of **3**, **4**, and **9** is warmed from −30 °C to room temperature only complexed phospholene **12** is obtained in 71 % yield. Monitoring of the reaction by ^{31}P NMR spectroscopy shows the disappearance at 0 °C of the singlet at $\delta = -20.4$ (**10**) and the emergence of a singlet at $\delta = +105.3$. A single-crystal X-ray structure determination confirmed the formation of this new phospholene structure **12**.[15] We are aware of only one report on a related phospholene oxide, for which no structural data are available.[16] The crystal structure of **12** with its two exocyclic isopropylidene groups reveals interesting features (Figure 3). The molecule is approximately C_s-symmetric with a trigonal-bipyramidal geometry at the pentacoordinate Fe atom. The phospholene is in an axial position (Fe–P 2.2798(9) Å), and the C_s symmetry is supported by the conformation of the iPr$_2$N group, which is planar at the nitrogen atom. Bond lengths of 1.349(5), 1.340(6), and 1.349(5) Å for the three alternating C=C bonds and of 1.460(5) Å for the two C–C single bonds of the phospholene do not suggest enhanced π-delocalization (towards a diradicaloid structure). The phospholene ring deviates slightly from planarity with the P atom moved 0.269(5) Å out of the C2-C3-C4-C5 plane in the direction of the less bulky Fe(CO)$_4$ group. While the C-P-N angles are close to the tetrahedral angle, the C-P-C angle is 91.63(14)°, clearly indicating a strained ring system. As a consequence, the P-C-C angles in the ring at the sp^2 atoms C2 and C5 are 106.68(23) and 106.69(23)°, respectively. In contrast the C-C-C angles at C3 and C4 are 116.54(30) and 116.83(30)°, respectively. The computed structure **12 A** (Figure 4) shows geometrical features similar to the X-ray structure, except for the out-of-plane tilting of the P atom. The NMR data of **12** are in accordance with expectations and do not display special features. This may well suggest that crystal packing forces underlie the phospholene distortion in the crystal structure.

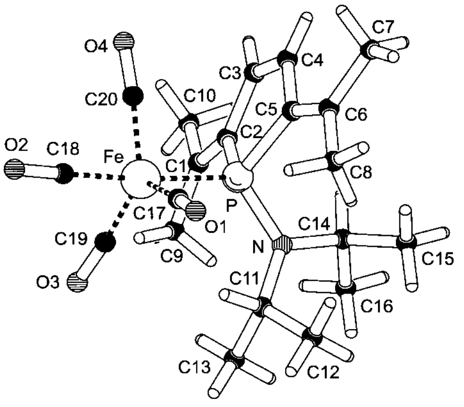


Figure 3. Molecular structure of **12**. Selected bond lengths [Å] and angles [°]: Fe–P 2.2798(9), P–N 1.675(3), P–C5 1.847(3), P–C2 1.851(3), C1–C2 1.349(5), C2–C3 1.460(5), C3–C4 1.340(5), C4–C5 1.460(5), C5–C6 1.349(5); C18-Fe-P 175.21(11), N-P-C5 109.00(14), N-P-C2 109.43(13), C5-P-C2 91.63(14), N-P-Fe 120.07(10), C5-P-Fe 112.15(10), C2-P-Fe 110.89(11), C2-C1-C9 124.0(3), C2-C1-C10 122.0(3), C9-C1-C10 113.9(3), C1-C2-C3 125.1(3), C1-C2-P 128.2(3), C3-C2-P 106.7(2), C4-C3-C2 116.5(3), C3-C4-C5 116.8(3), C6-C5-C4 124.9(3), C6-C5-P 128.4(3), C4-C5-P 106.7(2).

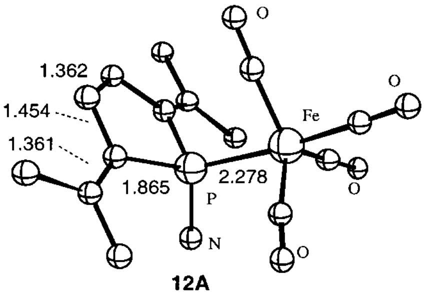


Figure 4. The calculated structure **12 A**.

The reaction energy for the formation of **10 A** from the cycloaddition of **5 A** to **9 A** is calculated to be 28 kcal mol^{-1}. The subsequent rearrangement to **12 A** is exothermic by another 40 kcal mol^{-1} which illustrates the driving force for this reaction. Interestingly, the formation of vinylphosphirane from the cycloaddition of **5 A** to *cis*-1,3-butadiene is like the formation of **10 A** exothermic by 24 kcal mol^{-1}. Because the reaction of the mixture of **3** and **4** with 2,3-dimethyl-1,3-butadiene does not occur under the same conditions used to generate **10**, it is evident that either steric reasons or rather kinetic factors also play a role in the reactivity of **5 A**.

In conclusion, the electrophilic [iPr$_2$NPFe(CO)$_4$] phosphinidene complex is conveniently generated in situ at low temperature and can be trapped by suitable olefins to form highly strained phosphiranes and phospholenes.

Experimental Section

All experiments were performed under an atmosphere of dry nitrogen. NMR spectra were recorded on Bruker AC 200, MSL 400 (^{1}H, ^{13}C), and WM 250 (^{31}P) spectrometers using SiMe$_4$ (^{1}H, ^{13}C) or 85 % H$_3$PO$_4$ (^{31}P) as external standards. High-resolution mass spectra (HR-MS) were recorded on a Finnigan MAT 90, UV/Vis spectra on a Varian Cary, and FT-IR spectra on a Mattson 630 Galaxy spectrophotometer. Elemental analysis was performed by the Microanalytischen Labor Pascher, Remagen-Bandorf (Germany).

8: To a suspension of **4** (0.58 g, 1.67 mmol) cooled to −78 °C in pentane (or diethyl ether) (25 mL) was added **3** (0.33 g, 1.67 mmol) and a solution of **7** (0.2 g, 5 mmol) in pentane (1.4 mL). The reaction mixture was allowed to warm slowly to −30 °C and then to 0 °C. After 30 minutes, the reaction mixture was cooled to −15 °C. At this temperature it was filtered, concentrated, and purified by flash chromatography (pentane, silica) to yield 288 mg (51 %) of a thermally unstable orange oil. ^{31}P NMR ($CDCl_3$): $\delta = -47.3$; ^{1}H NMR ($CDCl_3$): $\delta = 6.36$ (td, ^3J(P,H) = 16.7, ^4J(H,H) = 3.30 Hz, 1H; =CH), 6.12 (td, ^3J(P,H) = 37.1, ^4J(H,H) = 2.76 Hz, 1H; =CH), 3.39 (dsept., ^3J(H,H) = 6.73, ^3J(P,H) = 15.44 Hz, 2H, $(CH_3)_2CH$), 2.16 (tdd, ^1J(H,H) = 12.7, ^2J(P,H) = 7.56, ^4J(H,H) = 3.30 Hz, 1H, PCH), 1.54 (tdd, ^1J(H,H) = 12.7, ^2J(P,H) = 1.36, ^4J(H,H) = 2.84 Hz, 1H, PCH), 1.17 (d, ^3J(H,H) = 6.71 Hz, 6H; $(CH_3)_2CH$), 1.08 (d, ^3J(H,H) = 6.72 Hz, 6H; $(CH_3)_2CH$); ^{13}C NMR ($CDCl_3$): $\delta = 213.6$ (d, ^2J(P,C) = 22.6 Hz; CO), 135.6 (d, ^2J(P,C) = 4.1 Hz; =CP), 121.3 (s; $=CH_2$), 49.8 (d, ^2J(P,C) = 4.1 Hz; $(CH_3)_2CH$), 24.8 (d, ^1J(P,C) = 7.0 Hz; PCH_2), 23.0 (d, ^3J(P,C) = 2.1 Hz; $(CH_3)_2CH$); 22.1 (d, ^3J(P,C) = 3.3 Hz; $(CH_3)_2CH$); IR (KBr): $\tilde{\nu} = 2052$(m), 2017(w), 1942(s) cm^{-1} (CO); HR-MS: calcd. for $C_{13}H_{18}FeNO_4P$: 339.03223; found: 339.03206.

10: To a suspension of **4** (0.63 g, 1.82 mmol) cooled to $-78\,^{\circ}C$ in diethyl ether (25 mL) was added **3** (0.37 g, 1.82 mmol) and **9**[17] (0.24 g, 1.82 mmol). The mixture was allowed to warm to $-30\,^{\circ}C$ and then slowly to $0\,^{\circ}C$. Immediately thereafter, the solvent was removed, the residue was extracted with pentane and purified by flash chromatography (pentane, silica) at $-10\,^{\circ}C$ to yield a yellow oil. ^{31}P NMR ($CDCl_3$): $\delta = -20.4$; ^{1}H NMR ($CDCl_3$) $\delta = 4.87$ (m, 1H; allene-H), 3.45 (m, 2H; $(CH_3)_2CH$), 2.72 (m, 1H; PCH), 2.12 (d, ^5J(H,H) = 2.52 Hz, 3H; *trans*-$PC{=}CCH_3$), 1.89 (d, ^5J(H,H) = 2.20 Hz, 3H; *cis*-$PC{=}CCH_3$), 1.61 (d, ^5J(H,H) = 2.12 Hz, 6H; allene-CH_3), 1.13 (d, ^3J(H,H) = 6.40 Hz, 6H; $(CH_3)_2CH$), 1.12 (d, ^3J(H,H) = 6.50 Hz, 3H; $(CH_3)_2CH$); ^{13}C NMR ($CDCl_3$): $\delta = 213.8$ (d, ^2J(P,C) = 22.9 Hz; CO), 204.1 (d, ^3J(P,C) = 9.3 Hz; =C=), 146.4 (s; $PC{=}CMe_2$), 122.9 (d, ^1J(P,C) = 5.8 Hz; $P{-}C{=}CMe_2$), 97.3 (d, ^2J(P,C) = 4.8 Hz; $C{=}C{=}CMe_2$), 87.1 (d, ^4J(P,C) = 6.3 Hz; $HC{=}C{=}CMe_2$), 49.3 (d, ^2J(P,C) = 3.2 Hz; $(CH_3)_2CH$), 36.2 (d, ^3J(P,C) = 11.9 Hz; *trans*-$PC{=}CCH_3$), 25.2 (d, ^3J(P,C) = 6.5 Hz; *cis*-$PC{=}CCH_3$), 22.9 (s; $(CH_3)_2CH$), 22.5 (s; PCH), 22.4 (d, ^3J(P,C) = 2.9 Hz; $(CH_3)_2CH$), ^5J(P,C) = 6.0 Hz, allene-CH_3), 20.4 (d, ^5J(P,C) = 5.8 Hz; allene-CH_3).

12: The procedure was the same as described for **10**, but the mixture was allowed to warm to room temperature. After work-up and crystallization (pentane, $-20\,^{\circ}C$), this gave bright yellow crystals in 74 % yield. M.p. $143\,^{\circ}C$; ^{31}P NMR (C_6D_6): $\delta = 105.3$; ^{1}H NMR([D_8]toluene): $\delta = 6.25$ (d, ^3J(P,H) = 18.1 Hz, 2H; =CH), 3.93 (sept., ^3J(P,H) = 6.92 Hz, 2H; $(CH_3)_2CH$), 2.01 (s, 3H; *trans*-$C{=}CCH_3$), 1.54 (s, 3H; *cis*-$C{=}CCH_3$), 1.03 (d, ^3J(H,H) = 6.92 Hz, 12H; $(CH_3)_2CH$); ^{13}C NMR ($CDCl_3$): $\delta = 214.7$ (d, ^2J(P,C) = 14.5 Hz; CO), 139.1 (d, ^1J(P,C) = 55.0 Hz; P−C=), 138.1 (d, ^2J(P,C) = 10.7 Hz; =CH),128.5 (d, ^2J(P,C) = 18.1 Hz; $=CMe_2$), 51.0 (d, ^2J(P,C) = 8.0 Hz, $(CH_3)_2CH$), 25.1 (d, ^3J(P,C) = 8.6 Hz; *E*-CH_3), 24.0 (d, ^3J(P,C) = 3.0 Hz, $(CH_3)_2CH$), 22.0 (d, ^3J(P,C) = 9.8 Hz; *Z*-CH_3); IR (KBr): $\tilde{\nu} = 2043$(m), 1971(w), 1923(s) cm^{-1} (CO); UV/Vis (toluene): $\lambda_{max} = 316$ nm; MS (70 eV): m/z (%): 433 (2) [M^+], 377 (35) [$M^+ - 2CO$], 321 (100) [$M^+ - 4CO$]; HR-MS: calcd. for $C_{20}H_{28}FeNO_4P$: 433.1105; found: 433.1108; elemental analysis (%): calcd: C 55.46, H 6.26, P 7.15; found: C 54.56, H 6.51, P 7.15.

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[1] a) F. Mathey, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 275–286; *Angew. Chem.* **1987**, *99*, 285–296; b) *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. Scherer), Thieme, Stuttgart, **1990**; c) A. H. Cowley, *Acc. Chem. Res.* **1997**, *30*, 445–451; d) K. B. Dillon, F. Mathey, J. F. Nixon, *Phosphorus: The Carbon Copy*, Wiley, Chichester, **1998**, p. 19.

[2] A. Marinetti, F. Mathey, J. Fischer, A. Mitschler, *J. Am. Chem. Soc.* **1982**, *104*, 4484–4485; A. Marinetti, F. Mathey, *Organometallics* **1982**, *1*, 1488.

[3] a) A. Ostrowski, J. Jeske, P. G. Jones, R. Streubel, *J. Chem. Soc. Chem. Commun.* **1995**, 2507–2508; b) F. Mercier, B. Deschamp, F. Mathey, *J. Am. Chem. Soc.* **1989**, *111*, 9098–9100.

[4] See for example: a) P. B. Hitchcock, M. F. Lappert, W.-P. Leung, *J. Chem. Soc. Chem. Commun.* **1987**, 1282–1283; b) C. C. Cummins, R. R. Schrock, W. M. Davis, *Angew. Chem.* **1993**, *105*, 758–761; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 756–759; c) T. L. Breen, D. W. Stephan, *J. Am. Chem. Soc.* **1995**, *117*, 11914–11921.

[5] a) R. B. King, F. J. Wu, E. M. Holt, *J. Am. Chem. Soc.* **1987**, *109*, 7764–7775; b) R. B. King, G. S. Chorghade, *J. Organomet. Chem.* **1988**, *341*, 407–414; c) R. A. Bartlett, H. V. Rasika Dias, K. M. Flynn, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **1987**, *104*, 5699–5703; d) for a related approach: J. Borm, G. Huttner, O. Orama, *J. Organomet. Chem.* **1986**, *306*, 29.

[6] a) K. Lammertsma, J.-T. Hung, P. Chand, P. M. Gray, *J. Org. Chem.* **1992**, *57*, 6557–6560; b) J.-T. Hung, K. Lammertsma, *J. Org. Chem.* **1993**, *58*, 1800–1803; c) J.-T. Hung, S.-W. Yang, P. Chand, G. M. Gray, K. Lammertsma, *J. Am. Chem. Soc.* **1994**, *116*, 10966–10971; d) A. Marinetti, F. Mathey, *Organometallics* **1984**, *3*, 456–461; e) A. Marinetti, C. Charrier, F. Mathey, J. Fischer, *Organometallics* **1985**, *4*, 2134–2138.

[7] S. Krill, B. Wang, J.-T. Hung, C. J. Horan, G. M. Gray, K. Lammertsma, *J. Am. Chem. Soc.* **1997**, *119*, 8432–8437.

[8] a) C. Fonseca-Guerra, O. Visser, J. G. Snijders, G. te Velde, E. J. Baerends in *METECC-95* (Eds.: E. Clementi, C. Corongiu), STEF, Cagliari, **1995**, p. 307; b) E. J. Baerends, D. E. Ellis, P. Ros, *Chem. Phys.* **1973**, *2*, 41–51.

[9] a) J. G. Snijders, E. J. Baerends, P. Vernooijs, *At. Nucl. Data Tables* **1982**, *99*, 84; b) J. G. Snijders, P. Vernooijs, E. J. Baerends, *Internal report*, University of Amsterdam, Niederlande, **1981**.

[10] S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200–1211.

[11] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098.

[12] J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822.

[13] A. W. Ehlers, K. Lammertsma, E. J. Baerends, *Organometallics* **1998**, *17*, 2738–2741; G. Frison, F. Mathey, A. Sevin, *J. Organomet. Chem.* **1998**, *570*, 225–234; S. Creve, K. Pierloot, M. T. Nguyen, *Chem. Phys. Lett.* **1998**, *285*, 429.

[14] B. Wang, C. H. Lake, K. Lammertsma *J. Am. Chem. Soc.* **1996**, *118*, 1690.

[15] Crystal structure determination of **12**: $C_{20}H_{28}FeNO_4P$, $M_r = 433.25$, yellow block, $0.30 \times 0.25 \times 0.10\ mm^3$, triclinic, $P\bar{1}$ (no. 2), $a = 8.6083(2)$, $b = 10.2430(2)$, $c = 13.4667(3)$ Å, $\alpha = 78.7930(13)$, $\beta = 77.4930(11)$, $\gamma = 69.7903(12)^{\circ}$, $V = 1078.58(4)$ Å^3, $Z = 2$, $\rho = 1.334\ g\,cm^{-3}$. A total of 17694 reflections were measured on a Nonius Kappa CCD diffractometer with rotating anode ($\lambda = 0.71073$ Å) at a temperature of 150(2) K, of these 4908 reflections were unique ($R_{int} = 0.0828$). Absorption correction (multiscan, $\mu = 0.797\ mm^{-1}$, 0.55–0.92 transmission), molecular illustration, structure checking and calculations were performed the PLATON package.[18] Structure solved with Patterson methods (DIRDIF97[19]) and refined with SHELXL97[20] against F^2. Hydrogen atoms were introduced in calculated positions and refined as rigid groups. R values [$I > 2\alpha(I)$]: $R1 = 0.0559$, $wR2 = 0.1417$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-118488. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[16] J.-P. Lampin, F. Mathey, B. Bartel, *Bull. Soc. Chem.* **1971**, *1*, 317–329.

[17] M. S. Sigmon, B. Eaton, *J. Am. Chem. Soc.* **1996**, *118*, 11783–11788.

[18] A. L. Spek, PLATON, a multipurpose crystallographic tool, Utrecht University, The Netherlands, **1998**.

[19] P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits, C. Smykalla, DIRDIF97, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, **1997**.

[20] G. M. Sheldrick, SHELXL-97, Program for crystal structure refinement, Universität Göttingen, Germany, **1997**.