Nucleophilic Addition of Secondary Phosphines to Cationic Dienyl Tricarbonyliron Complexes: A Novel Route to Optically Active Phosphines**

Ulli Englert, Beate Ganter, Markus Käser, Elke Klinkhammer, Trixie Wagner and Albrecht Salzer*

Abstract: Secondary phosphines such as $HPPh_2$ add to the cationic iron dienyl complex $[(\eta^5\text{-}(1R)\text{-ethylnopadienyl})Fe(CO)_3]^+$ (**1**) by nucleophilic addition. The phosphonium salt initially formed is readily deprotonated to yield an optically active tertiary phosphine $[(\eta^4\text{-}(1R)\text{-ethylnopadienePPh}_2)Fe(CO)_3]$ (**2b**). A similar reaction also occurs with $[C_6H_7Fe(CO)_3]^+$ (**3**) and $[C_7H_9Fe(CO)_3]^+$ (**4**) to give $[(C_6H_7PPh_2)Fe(CO)_3]$ (**5**) and $[(C_7H_9PPh_2)Fe(CO)_3]$ (**6**) in good yields. The mechanism of formation of these novel phosphines is discussed. Complex **2b** crystallizes in the space group $P2_12_12_1$ (no. 19); **5** crystallizes in the space group $P2_1/c$ (no. 14). Like other monodentate optically active phosphines, **2b** is capable of coordinating to transition metal complexes. It forms palladium complexes on reaction with $[\{\mu\text{-chloro(allyl)palladium}\}_2]$ as well as with $[\{\mu\text{-chloro-}[(N,N\text{-dimethylamino-}\kappa N\text{-2-methyl})\text{phenyl-}\kappa C]\text{palladium}\}_2]$ (**11**). The latter reaction product crystallizes in the space group $P3_1$ (no. 144).

Keywords
carbonyl complexes · chiral ligands · iron complexes · phosphorus ligands

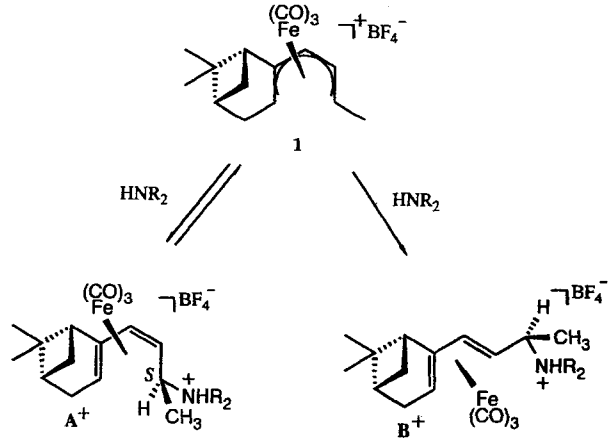
Introduction

There has been considerable recent interest in the synthesis and reactivity of tricarbonyl(η^5-pentadienyl)iron(1 +) complexes. Their usefulness as intermediates and reactants in organic synthesis, specifically in highly diastereoselective addition reactions of various nucleophiles, is well documented.[1] These addition reactions have also been the subject of detailed kinetic studies.[2]

Addition of N- and P-nucleophiles is generally very fast and reversible. We have used these reactions in the past to prepare a number of free or coordinated phosphonium salts and phosphonates[3] and to study their reactivity with respect to Wittig reactions.[4]

In a recent paper,[5] we also investigated the reactivity of an optically active dienyl complex, the easily accessible $[(1R)\text{-(ethylnopadienyl)}Fe(CO)_3]^+$ cation (**1**),[6] towards a variety of primary and secondary amines and were able to prepare a series of optically active amines in this manner. In the reaction with racemic phenylethylamine, we observed a kinetic resolution of the amine, the first example for this type of reaction. The addition of an amine to **1** leads to formation of an ammonium salt, which is then deprotonated by a second molecule of the amine or by another nonnucleophilic amine added to the reaction mixture. With longer reaction times, the inital (*E,Z*)-ammoniodiolefin complex $\mathbf{A}^+$ rearranges to the thermodynamically more stable (*E,E*)-isomer $\mathbf{B}^+$ (Scheme 1).

We have now investigated the same reaction, using secondary phosphines instead of amines with a view to extending this reaction to the synthesis of optically active, tertiary phosphines.



Scheme 1.

Results and Discussion

Treatment of **1** with the secondary phosphine $HPPh_2$ and subsequent deprotonation of the very rapidly formed phosphonium salt with the nonnucleophilic base NEt_3 led to formation of a diolefin complex with a diphenylphosphino substituent, but as a mixture of (*E,Z*) and (*E,E*) isomers (Scheme 2). The ^{31}P

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[+] X-ray crystal structure analyses.

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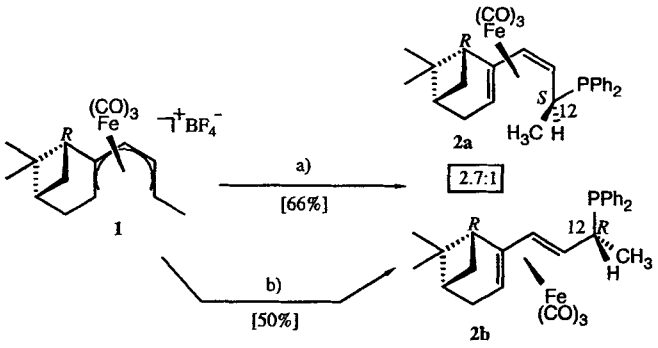
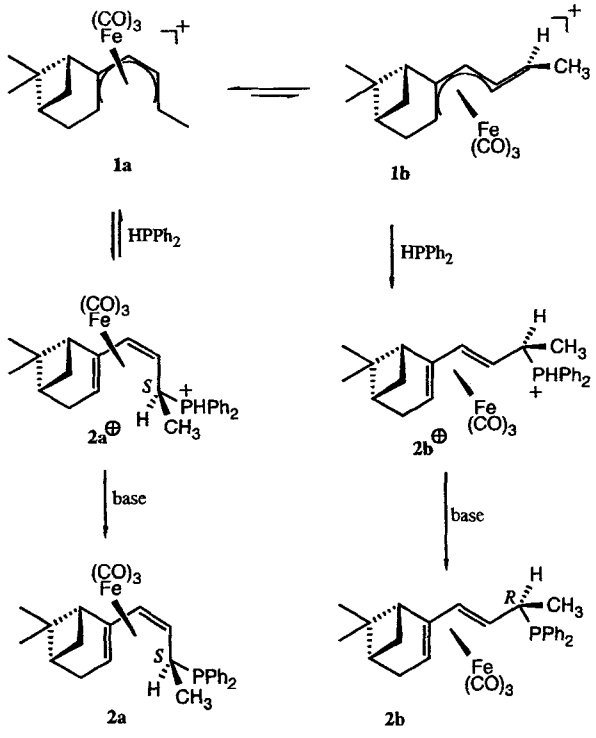


Scheme 2. a: 1) $HPPh_2$ (1.1 equiv), CH_2Cl_2, $-30\,^{\circ}C$, 1.5 h; 2) Na_2CO_3. b: 1) $HPPh_2$ (1.1 equiv), CH_2Cl_2, RT, 4 d; 2) Et_2O, NEt_3.

NMR ($CDCl_3$) shows two signals at $\delta = 2.22$ and 11.13. We assigned the signal at $\delta = 11.13$ to **2a** and that at $\delta = 2.22$ to **2b**. As with some of the amines investigated previously, it proved beneficial to extend reaction times to four days to allow the system to reach thermodynamic equilibrium. After this time, the only product isolated in good yields was the (*E,E*) diolefin complex **2b** as yellow crystals. The ^{31}P NMR (C_6D_6) shows only one signal at $\delta = 1.33$. The reaction therefore proceeds in a manner similar to that of primary and secondary amines (Scheme 3). The intermediate phosphonium salts were precipitated as solids and washed with ether. They were then immediately deprotonated, as they did not appear to be very stable even in the solid state in the absence of excess phosphine.



Scheme 3.

We have to postulate that the U-shaped dienyl complex **1a** is in a dynamic equilibrium with the S-shaped dienyl complex **1b** and that through a series of reversible equilibria the final (*E,E*) product **2b** is slowly formed, although the (*E,Z*) complex **2a** is initially favoured as the kinetically controlled product (Scheme 3). Such equilibria between U- and S-shaped dienyl complexes were first postulated by Pettit[7] and later extensively studied by Sorensen.[8] The addition of the phosphine occurs *trans* to the metal in both cases, establishing the (*S*) stereochemistry at the new chiral centre for the (*E,Z*)-diolefin complex[9] and (*R*) stereochemistry for the (*E,E*)-diolefin compound (see below). It is well established that phosphine addition to cationic metal complexes is still reversible at the phosphonium-ion stage.[2] In contrast to some amines, the basicity of the secondary phosphine is not high enough to deprotonate the phosphonium salt in situ. The addition of a strong, nonnucleophilic base is therefore required.

Cation **1a** offers various advantages over other dienyl cations: a) due to the central chirality introduced by the organic precursor and the planar chirality established by complex formation, the diastereoselectivity of addition and therefore the enantioselective formation of a new chiral centre is easily verified by NMR spectroscopy, and b) addition reactions occur exclusively at C-12 of the dienyl system, thereby limiting the number of possible addition products to the two observed.

As spectroscopic data were not sufficient to unequivocally establish the proposed stereochemistry of phosphine addition, crystals of **2b** were grown from a saturated hexane solution, cooled to $-30\,^{\circ}C$ (Fig. 1).[10] The stereochemistry of **2b** in the solid state is in agreement with the proposed rearrangement mechanism and the *trans* addition of the secondary phosphine to the S-shaped dienyl complex.

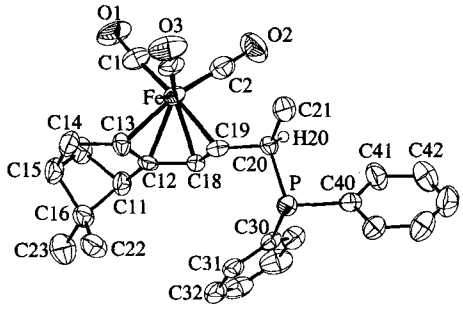
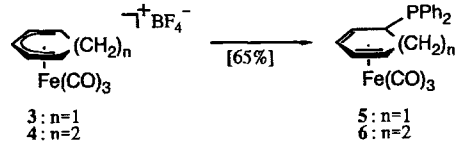


Fig. 1. Crystal structure of **2b** (PLATON plot, ellipsoids at the 30% probability level).

In order to test whether this reaction could be extended to other dienyl complexes and therefore be used as a general method to prepare phosphines with organometallic substituents, we also treated the well-known cyclic cations $[C_6H_7Fe(CO)_3]^+$ (**3**) and $[C_7H_9Fe(CO)_3]^+$ (**4**) with $HPPh_2$ under similiar conditions. As before, we observed a smooth formation of organometallic phosphines $[C_6H_7PPh_2Fe(CO)_3]$ (**5**) and $[C_7H_9PPh_2Fe(CO)_3]$ (**6**) in good yields (Scheme 4). In both cases, no rearrangement is possible and only one racemic product can be formed, since attack of the phosphine occurs *trans* to the metal and at both terminal carbons of the dienyl system. In principle, it should be possible to prepare optically active phosphines of this type, as optically active (cyclohexadienyl)$Fe(CO)_3$ derivatives are also known.[11]



3: n=1
4: n=2
5: n=1
6: n=2

Scheme 4. 1) $HPPh_2$ (1.1 equiv), CH_2Cl_2, RT, 1 h; 2) NEt_3, CH_2Cl_2, RT, 2 h.

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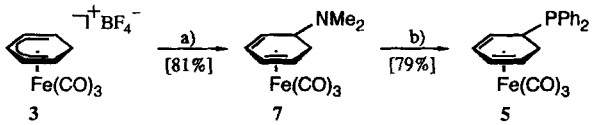
This reaction can be further extended to other secondary phosphines, such as the bicyclic phosphabicyclononane ("phobane") $C_8H_{14}PH$.[12] However, this phosphine, being a mixture of the [3.3.1] and [4.2.1] isomers, yielded a mixture of two phosphines, which could not be separated, and unlike other authors, we did not observe a preferential accumulation of one of these isomers.[13]

As an alternate method, it is also possible to first isolate the addition product with dimethylamine **7** and then substitute this amine by further reaction with $HPPh_2$ (Scheme 5). This synthetic approach resembles the methology successfully employed by Hayashi[14] and Togni[13, 15] in the synthesis of chiral ferrocenylphosphines, where NMe_2 and acetate substituents in chiral ferrocenes were replaced by secondary phosphines at elevated temperatures. This substitution proceeds with retention of configuration at carbon in optically active ferrocenes having both central and planar chirality, and it must be assumed that metal-stabilized carbocations are formed as short-lived configurationally stable intermediates. We prepared the ferrocenyl carbocation **8** and treated it immediately with $HPPh_2$; we also observed the formation of the ferrocenylphosphine **9** in good yields (Scheme 6).



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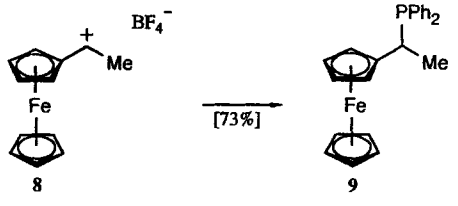
Scheme 5. a: excess $HNMe_2$, CH_2Cl_2, −30 °C, 15 min.; b: $HPPh_2$ (1.1 equiv), AcOH, 60 °C, 2 h.



8 9

Scheme 6. 1) $HPPh_2$ (1.2 equiv), CH_2Cl_2, 0 °C, 12 h; 2) NEt_3, CH_2Cl_2, RT, 2 h.

The Hayashi method via the amine adduct offers no advantages in our dienyl iron complexes, as the metal dienyl complexes **1**, **3** and **4** are themselves very stable and can therefore be stored indefinitely and used as required. A further advantage with these substrates is the fact that the chirality of **1** and **2b** originates from the "chiral pool" and no resolution is required at any stage. The methology of Lewis-base exchange also does not appear to work with **1**, as the dimethylamine adduct of **1** cannot be thermally converted to **2a** with $HPPh_2$, most probably because of the complicated rearrangement mechanisms involving U- and S-shaped dienyl complexes.

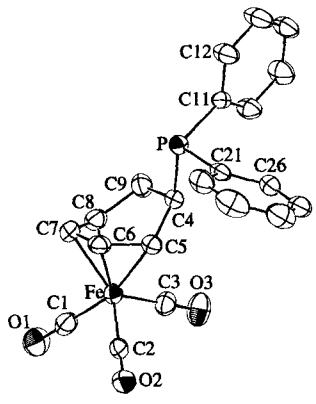


Fig. 2. Crystal structure of **5** (ORTEP plot, ellipsoids at the 30% probability level).

Complex **5** has also been characterized by an X-ray structure analysis. Single crystals were grown from hexane (Fig. 2).[16] The crystal structure of **5** also confirms the *trans* geometry of the diphenylphosphino group with respect to the $Fe(CO)_3$ moiety.

The reactions of secondary phosphines with cationic dienyl complexes therefore emerge as a useful and versatile method for the synthesis of novel chiral phosphines with bulky organometallic substituents.

We have also made several attempts to synthesize chelating diphosphines in this manner, starting from $HPhPCH_2CH_2PPhH$ and treating this with two equivalents of the respective cationic dienyl complexes. However, because these reactions generate chiral centres both at carbon and at phosphorus, complicated mixtures of single and double addition products and also diastereomeric mixtures were generated. We have not yet been able to separate these mixtures.

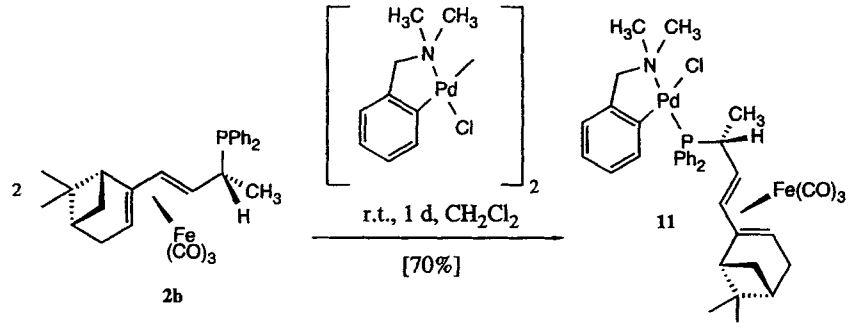
Hayashi has found several applications for monodentate optically active phosphine (MOP) ligands[17] in enantioselective catalysis,[18] particularly in connection with palladium complexes. In order to establish whether **2b** can act as an optically active ligand by coordinating to a second metal centre, despite its bulky $Fe(CO)_3$ substituent, we treated **2b** with two palladium complexes that normally form adducts with tertiary phosphines. The allyl palladium chloride dimer $[(C_3H_5PdCl)_2]$ is known to form monomeric complexes [(allyl)Pd(PR_3)Cl] on reaction with phosphines. In this respect, **2b** appears to behave like other phosphines. The monomeric complex **10** was formed at room temperature and isolated as pale yellow crystals. Like other allyl palladium complexes with a chiral ligand, it shows dynamic behaviour in solution, most likely due to fast $\pi-\sigma-\pi$ rearrangements of the allylic ligand, leading to an equilibrium between diastereomers **10a** and **10b** (Scheme 7). At −20 °C this rearrangement is sufficiently slow on the NMR time scale to allow the observation of two signals at $\delta = 32.92$ and 34.97 in the ^{31}P NMR spectrum. We were unable to grow single crystals of **10**. Nor could a similar palladium allyl complex of **5** be crystallized. Possibly, crystal formation is inhibited by the presence of diastereomers.

Scheme 7. R* = (η^4-(1*R*)-ethylnopadiene)$Fe(CO)_3$.

While we were now certain that organometallic phosphines such as **2b** were capable of reacting like regular phosphines, we still wanted structural evidence for the overall geometry of a coordinated phosphine complex of the type **2b**, in order to study the geometric restraints that might be imposed by this bulky phosphine on complexation.

Another well-known palladium system that is known to give crystalline phosphine adducts and has found some application in homogeneous catalysis is the dimeric complex [{μ-chloro-[(*N*,*N*-dimethylamino-κN-2-methyl)phenyl-κC]palladium}$_2$].[19] This compound was therefore treated with two equivalents of **2b** at room temperature. After one day we isolated the addition product **11** in good yields as an orange powder (Scheme 8). This complex shows no dynamic behaviour in solution and is readily characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy as a single isomer. The ^{31}P NMR signal is strongly shifted to lower field compared to that of the uncoordinated phosphine **2b** ($\delta = 50.1$ vs. 2.22).

Single crystals of **11** could be grown from benzene.[20] The crystal structure of **11** (Fig. 3) clearly proves that a sterically



Scheme 8.

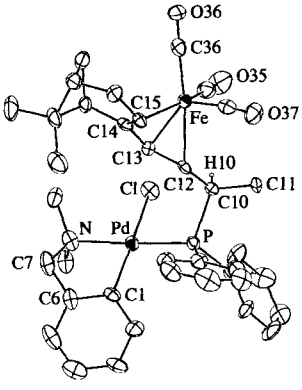


Fig. 3. Crystal structure of **11** (ORTEP plot, ellipsoids at the 30% probability level).

demanding phosphine such as **2b** can serve as a ligand in palladium chemistry. The bulky (diene)$Fe(CO)_3$ unit in the crystal adopts a position above the square plane defined by the ligands around palladium, and therefore should be perfectly suitable to serve as an MOP ligand.

We have established that bulky chiral phosphines can be generated from the reaction of secondary phosphines with cationic iron dienyl complexes. In addition, we have shown that such organometallic phosphines remain capable of coordinating to transition metals. Currently, we are investigating whether they might find some applications in homogeneous catalysis.

Experimental Procedure

All experiments were carried out under an atmosphere of nitrogen with standard Schlenk techniques. Diethyl ether was distilled from sodium benzophenone ketyl. Benzene was distilled over sodium. Dichloromethane and hexane were dried over molecular sieves 4 Å. The starting pentadienyl cation complex **1** [6], the cyclohexadienyl cation complex **3** [21], the cycloheptadienyl cation complex **4** [22], the ferrocenyl cation complex (**8**) [23] and the dimeric [{μ-chloro[(*N*,*N*-dimethylamino-κN-2-methyl)phenyl-κC]palladium}$_2$] [24] were prepared according to literature procedures. The dimeric [{μ-(chloro)(η^3-allyl)-palladium}$_2$] was purchased from Strem Chemicals. Diphenylphosphine was purchased from Fluka. ^{1}H NMR (300, 500 MHz) and ^{13}C NMR (75, 125 MHz) spectra were measured on a Varian VXR 300 and Varian Unity 500 instruments, respectively, with tetramethylsilane [δ = 0.0, ^{1}H NMR, ^{13}C NMR (C_6D_6)] or $CDCl_3$ (δ = 77.00, ^{13}C NMR) as internal standard. Carbon multiplicities were assigned by APT techniques. Phosphorus chemical shifts were externally referenced to 85% H_3PO_4 with downfield shifts reported as positive. IR spectra were recorded on a Perkin Elmer 1720X infrared spectrophotometer. The elemental analyses were performed by the microanalytical laboratory of our department.

(*R*)-Tricarbonyl{η^4-4-[(1*R*)-6,6-dimethylbicyclo[3.1.1]hept-2-ene-2-yl]-(*E*)-(2*R*)-2-diphenylphosphino-but-3-ene}iron (2b): The pentadienyl cation **1** (0.66 g, 1.64 mmol) was dissolved in dichloromethane (10 mL). Diphenylphosphine (0.3 mL, 1.81 mmol) was added, and the reaction mixture stirred for four days at room temperature. The solvent was removed under vacuum, and the residue washed with two portions of diethyl ether. The residue was redissolved in dichloromethane (10 mL), and triethylamine (0.25 mL, 1.81 mmol) added dropwise. After the mixture had been stirred for a further hour, the solvent was removed in vacuum and the product was extracted into hexane. After filtration to remove the ammonium salt, **2b** crystallized from the filtrate at −30 °C as a yellowish orange solid; yield 0.41 g (50%). ^{1}H NMR (500 MHz, C_6D_6): δ = 7.58–7.53, 7.42–7.37, 7.12–7.01 [3m, 10H; 2 × Ph], 4.06 (d, ^3J(H,H) = 8.5 Hz; =C*H*), 2.29–2.20, 1.85–1.75 (2m, 5H), 1.71–1.66 (m, 1H; C*H*), 1.45 (dd, ^3J(H,H) = 6.8 Hz, ^3J(P,H) = 15.3 Hz, 3H; CH_3), 1.39 (d, ^2J(H,H) = 10.3 Hz, 1H; C*H*), 1.18 (s, 3H; CH_3), 1.06–1.03 (m, 1H; C*H*), 0.72 (s, 3H; CH_3), 0.36 (ddd, ^3J(H,H) = 8.5, 6.1 Hz, ^3J(P,H) = 10.7 Hz, 1H; =C*H*). ^{13}C NMR (125 MHz, C_6D_6): δ = 213.67, 138.30 (d, ^1J(C,P) = 18.1 Hz), 136.51 (d, ^1J(C,P) = 17.5 Hz), 134.85, 133.92 (2d, ^2J(C,P) = 19.7 Hz), the other Ph signals are obscured by C_6D_6, 116.04, 84.13 (d, ^3J(C,P) = 3.3 Hz), 60.34 (d, ^2J(C,P) = 16.9 Hz), 54.09, 47.39, 42.57, 40.08, 38.43 (d, ^1J(C,P) = 15.9 Hz), 37.18, 29.72, 26.10, 22.14, 21.20 (d, ^2J(C,P) = 19.7 Hz). ^{31}P NMR (202 MHz, C_6D_6): δ = 1.33; IR (hexane): $\tilde{\nu}$(CO) = 2037, 1973, 1959 cm^{-1}; $C_{28}H_{29}FeO_3P$ (500.36): calcd C 67.21, H 5.84; found C 67.87, H 5.91.

Tricarbonyl[η^4-1-diphenylphosphinocyclohexa-2,4-diene]-iron (5): **Method A**: The diphenylphosphine (0.59 mL, 3.40 mmol) was added at room temperature to a suspension of the cyclohexadienyl cation complex **3** (0.95 g, 3.10 mmol) in dichloromethane (15 mL). After the reaction mixture had been stirred for 1 h, the solvent was removed in vacuo. The residue was carefully washed with ether and dried under vacuum. The residue was redissolved in dichloromethane (15 mL), and triethylamine (0.65 mL, 4.65 mmol) added dropwise. After a further 2 h of stirring, the solvent was removed in vacuo, and the product extracted into hexane. After filtration to remove the ammonium salt, the filtrate was cooled and **5** crystallized as yellow needles; yield 0.82 g (65%).
Method B: Diphenylphosphine (0.42 mL, 2.4 mmol) was added to a solution of **7** (0.60 g, 2.40 mmol) in glacial acetic acid (15 mL). The temperature was maintained at 60 °C for 2 h, and the solvent was then removed in vacuo. The residue was extracted into hexane, and the product (**5**) crystallized when the solution was cooled, yield 0.76 g (79%). ^{1}H NMR (500 MHz, C_6D_6): δ = 7.50–7.00 (m, 10H; 2 × Ph), 4.73, 4.55, 3.03, 2.83 (4m, 4H; 4 × =C*H*), 2.66 (m, 1H, CH(PPh$_2$)), 1.88, 1.46 (2m, 2H; CH_2). ^{13}C NMR (125 MHz, C_6D_6): δ = 212.24, 139.08 (d, ^1J(C,P) = 18.2 Hz), 138.12 (d, ^1J(C,P) = 17.0 Hz), 134.14 (d, ^2J(C,P) = 19.7 Hz), 132.92 (d, ^2J(C,P) = 18.6 Hz), the other Ph signals are obscured by C_6D_6, 85.39, 85.32, 63.41 (d, ^2J(C,P) = 10.4 Hz), 61.24 (d, ^3J(C,P) = 5.5 Hz), 35.76 (d, ^1J(C,P) = 15.9 Hz), 30.53 (d, ^2J(C,P) = 25.8 Hz). ^{31}P NMR (202 MHz, C_6D_6): δ = 8.03. IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 2048, 1980 cm^{-1}; $C_{21}H_{17}FeO_3P$ (404.22): calcd C 62.40, H 4.24; found C 63.07, H 4.58.

Tricarbonyl[η^4-1-diphenylphosphinocyclohepta-2,4-diene]iron (6): The diphenylphosphine (0.42 mL, 2.40 mmol) was added at room temperature to a suspension of the cycloheptadienyl cation complex **4** (0.70 g, 2.20 mmol) in dichloromethane (15 mL). After the mixture had been stirred for 1 h, the solvent was removed in vacuo. The residue was carefully washed with ether and dried under vacuum. The residue was dissolved in dichloromethane (10 mL), and triethylamine (0.35 mL, 2.40 mmol) added dropwise. After a further 2 h of stirring, the solvent was removed in vacuo, and the product extracted into hexane. After filtration to remove the ammonium salt, **6** crystallized from the cooled filtrate; yield 0.60 g (65%). ^{1}H NMR (500 MHz, C_6D_6): δ = 7.60–7.00 (m, 10H, 2 × Ph), 4.56, 4.46, 3.11, 2.90 (4m, 4H; 4 × =C*H*), 2.52 [m, 1H; CH(PPh$_2$)], 1.60 (m, 2H; CH_2), 1.03, 0.88 (2m, 2H; CH_2). ^{13}C NMR (125 MHz, C_6D_6): δ = 211.92, 137.85 (d, ^1J(C,P) = 19.0 Hz), 136.83 (d, ^1J(C,P) = 17.2 Hz), 134.23 (d, ^2J(C,P) = 19.2 Hz), 133.31 (d, ^2J(C,P) = 18.4 Hz), the other Ph-signals are obscured by C_6D_6, 88.83, 87.34, 60.07 (d, ^2J(C,P) = 9.2 Hz), 59.40, 37.75 (d, ^1J(C,P) = 17.8 Hz), 28.65 (d, ^3J(C,P) = 12.8 Hz), 27.03 (d, ^2J(C,P) = 19.4 Hz). ^{31}P NMR (202 MHz, C_6D_6): δ = 9.00. IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 2043, 1972 cm^{-1}; $C_{22}H_{19}FeO_3P$ (418.22): calcd C 63.18, H 4.57; found C 63.67, H 4.63.

Tricarbonyl[η^4-1-dimethylaminocyclohexa-2,4-diene)iron (7): The cyclohexadienyl cation complex **3** (1.00 g, 3.2 mmol) was suspended in dichloromethane (20 mL), and the suspension cooled to −30 °C. An excess of *N*,*N*-dimethylamine was condensed into the suspension, and the resulting solution was stirred for 15 min, before being allowed to warm to room temperature. The solvent was then removed in vacuo, and the product extracted into hexane. After filtration to remove the ammonium salt, the product crystallized from the cooled filtrate; yield 0.67 g (81%). ^{1}H NMR (500 MHz, C_6D_6): δ = 4.78, 4.68, 3.09, 2.52 (4m, 4H; 4 × =C*H*), 2.41 [m, 1H; CH(N(CH$_3$)$_2$)], 1.85 [s, 6H; N(CH_3)$_2$], 1.76, 1.14 (2m, 2H; CH_2). ^{13}C NMR (125 MHz, C_6D_6): δ = 212.36, 86.15, 85.06, 63.79, 58.61, 58.04, 40.99, 26.68. IR (hexane): $\tilde{\nu}$(CO) = 2050, 1980 cm^{-1}; $C_{11}H_{12}FeNO_3$ (262.07): calcd C 50.41, H 4.62; N 5.35, found C 50.60, H 4.64, N 5.39.

[1-(Diphenylphosphino)ethyl]ferrocene (9): The freshly prepared ferrocenyl cation complex **8** (0.52 g, 1.70 mmol) was dissolved in dichloromethane (15 mL), and the solution was cooled to 0 °C, prior to the addition of diphenylphosphine (0.35 mL, 2.04 mmol). After being stirred for an hour at this temperature, the solution was warmed to room temperature and stirred overnight. The solvent was removed in vacuo, and the residue was washed with ether and dried under vacuum. The residue was dissolved in dichloromethane (10 mL), and triethylamine (0.28 mL, 2.04 mmol) added dropwise. After a further 2 h of stirring, the solvent was removed in vacuo and the product extracted into toluene. After filtration to remove the ammonium salt, **9** was purified by chromatography (toluene, Al_2O_3) and obtained as a orange oil, yield 0.50 g (73%) ^{1}H NMR (500 MHz, C_6D_6): δ = 7.60–7.20 (m, 10H; 2 × Ph), 4.00 (s, 5H; Cp), 3.93, 3.88, 3.77, 3.54 (4m, 4H; Cp–R), 3.25 [m, 1H;

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$CH(PPh_2)$], 1.48 (dd, $^3J(P,H) = 14.3$ Hz, $^3J(H,H) = 7.2$ Hz, 3H; CH_3). ^{13}C NMR (125 MHz, C_6D_6): $\delta = 138.20$ (d, $^1J(C,P) = 6.7$ Hz), 137.88 (d, $^1J(C,P) = 8.0$ Hz), 134.52, 133.90 (2d, $^2J(C,P) = 19.6$ Hz), the other Ph signals are obscured by C_6D_6, 91.73 (d, $^2J(C,P) = 14.7$ Hz), 68.64, 69.17, 67.36, 66.99, 66.80, 32.66 (d, $^1J(C,P) = 15.3$ Hz), 18.17 (d, $^2J(C,P) = 19.0$ Hz). ^{31}P NMR (202 MHz, C_6D_6): $\delta = 4.59$; $C_{24}H_{23}FeP$ (398.27): calcd C 72.38, H 5.82; found C 72.15, H 5.79.

[(*R*)-Tricarbonyl-{η^4-4-[(1*R*)-6,6-dimethylbicyclo-[3.1.1]-hept-2-ene-2-yl]-(*E*)-(2*R*)-2-diphenylphosphino-1κ*P*-but-3-ene}iron]chloro(η^3-allyl)palladium (10): Complex **2b** (0.36 g, 0.72 mmol) was dissolved in dichloromethane (15 mL). Bis[μ-(chloro)(η^3-allyl)palladium] (0.13 g, 0.36 mmol) was added in one portion, and the reaction mixture stirred for 2 d at room temperature. After removal of the solvent in vacuo, the residue was dissolved in toluene/hexane (1:2) and filtered through Celite. After removal of the solvent and drying under vacuum, **10** was obtained as a yellow solid; yield 0.33 g (67%). ^1H NMR (300 MHz, C_6D_6): $\delta = 8.00-7.00$ (m, 10H; 2 × Ph), 5.00–4.20, 3.40–2.80 [4m, 5H; CH-(allyl), 2 × CH_2-(allyl)], 2.40–1.56 (m, 11H), 1.43 (d, $^2J(H,H) = 10.4$ Hz, 1H; CH), 1.14 (s, 3H; CH_3), 0.88 (s, 3H; CH_3); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 213.55$, 134.85, 133.26 (2d, $^1J(C,P) = 11.6$ Hz), 132.94, the other Ph signals are obscured by C_6D_6, 116.81, 84.30 (d, $^3J(C,P) = 3.6$ Hz), 79.31, 59.57, 57.51, 55.41, 47.56, 42.61, 40.18, 38.06 (d, $^1J(C,P) = 15.3$ Hz), 37.29, 29.83, 26.14, 22.58, 21.07 (d, $^2J(C,P) = 6.7$ Hz); ^{31}P NMR (253 K, 202 MHz, C_6D_6): $\delta = 34.97, 32.92$; IR (hexane): $\tilde{\nu}$(CO) = 2039, 2034, 1970, 1963, 1951 cm^{-1}; $C_{31}H_{34}ClFeO_3PPd$ (683.80): calcd C 54.49, H 5.01; found: C 54.56; H 5.30.

[(*R*)-Tricarbonyl{η^4-4-[(1*R*)-6,6-dimethylbicyclo[3.1.1]hept-2-ene-2-yl]-(*E*)-(2*R*)-2-diphenylphosphino-1κ*P*-but-3-ene}iron]chloro[(*N*,*N*-dimethylamino-κ*N*-2-methyl)-phenyl-κ*C*]palladium (11): **2b** (1.08 g, 2.16 mmol) was dissolved in dichloromethane (40 mL). Bis[μ-chloro{(*N*,*N*-dimethylamino-κ*N*-2-methyl)phenyl-κ*C*}palladium] (0.60 g, 1.08 mmol) was added, and the reaction mixture stirred overnight at room temperature. The solvent was removed in vacuo, and the residue dissolved in hexane/dichloromethane (1:1). After crystallization at −30 °C and drying under vacuum, **11** was obtained as an orange solid; yield 1.30 g (70%). ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.91-7.87$, 7.74–7.71, 7.47–7.39, 7.31–7.28 (4m, 10H; Ph), 6.96–6.95, 6.81–6.77, 6.48–6.44 [3m, 4H; CH-(Bz)], 5.94 (d, $^3J(H,H) = 8.5$ Hz, 1H; $=CH$), 4.18 [d, $^4J(P,H) = 13.2$ Hz, 1H; CHH-(Bz)], 3.85 [dd, $^4J(P,H) = 13.2$ Hz, $^2J(H,H) = 2.3$ Hz, 1H; CHH-(Bz)], 3.62–3.54 (m, 1H), 2.90, 2.69 [2d, $^4J(P,H) = 2.1$ Hz, 6H; $N(CH_3)_2$], 2.58–2.47, 2.15–2.08, 2.06–2.00, 1.97–1.90 (4m, 5H), 1.42 (s, 3H; CH_3), 1.42 (d, $^2J(H,H) = 10.1$ Hz, 1H), 1.30–1.22 (m, 1H; $=CH$), 1.11 (dd, $^3J(P,H) = 15.1$ Hz, $^3J(H,H) = 6.9$ Hz, 3H; CH_3), 0.95 (s, 3H; CH_3), -0.05 (ddd, $^3J(H,H) = 8.8$, 5.5 Hz, $^2J(P,H) = 10.3$ Hz, 1H; $=CH$); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 212.48$, 151.96, 147.88 (d, $^1J(C,P) = 2.1$ Hz), 137.10 (d, $J(C,P) = 10.4$ Hz), 135.50 (d, $J(C,P) = 10.4$ Hz), 133.86 (d, $J(C,P) = 9.9$ Hz), 130.81, 130.42 (2d, $J(C,P) = 2.1$ Hz), 128.54, 128.22 (d, $J(C,P) = 10.4$ Hz), 127.57 (d, $J(C,P) = 9.8$ Hz), 126.30 (d, $^2J(C,P) = 43$ Hz), 125.23 (d, $J(C,P) = 6$ Hz), 123.77, 122.26, 115.85, 83.24 (d, $^3J(C,P) = 3.8$ Hz), 72.20 (d, $^3J(C,P) = 2.5$ Hz), 57.27 (d, $^2J(C,P) = 2.8$ Hz), 53.58, 50.59, 49.65 (d, $^3J(C,P) = 2.1$ Hz), 47.58, 42.23, 40.09, 37.09 (d, $^1J(C,P) = 21.5$ Hz), 36.62, 29.66, 26.14, 22.20, 19.12; ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = 50.08$; IR (CH_2Cl_2): $\tilde{\nu}$(CO) = 2034, 1966 cm^{-1}; $\tilde{\nu}$(C=C) = 1637 cm^{-1}; $C_{37}H_{41}ClFeNO_3PPd \times CH_2Cl_2$ (862.37): calcd C 52.98, H 5.03, N 1.63; found C 51.68, H 5.09, N 1.48.

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[16] Compound **5** crystallizes in the monoclinic space group $P2_1/c$ (no. 14) with $a = 9.468(3)$, $b = 12.821(3)$, $c = 16.023(6)$ Å, $\beta = 99.74(3)°$, $V = 1917(2)$ Å^3, $Z = 4$, $d_{calcd} = 1.400$ g cm^{-3}, $F_{000} = 832$, $\mu = 8.83$ cm^{-1}. Intensity data were collected on an ENRAF-Nonius CAD4 diffractometer ($Mo_{K\alpha}$ radiation, 0.7107 Å, graphite monochromator) at −10 °C with the ω scan mode. For a pale yellow crystal of approximate dimensions 0.6 × 0.6 × 0.2 mm, 3959 reflections were recorded up to $2\theta < 50°$ in the $+h$, $+k$, $\pm l$ quadrant of the reflection sphere. Neither absorption nor extinction corrections were performed. The structure was solved by conventional Patterson and difference Fourier methods; full-matrix least-squares refinement on F [25] converged for 235 variables and 2156 independent reflection with $I > 2.0\sigma(I)$ at $R = 0.056$ and $R_w = 0.057$, GOF = 1.513. A final difference Fourier synthesis showed a maximum residual electron density of 0.557 e Å^{-3} close to the Fe atom [26].

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