Synthesis, Structure, and Ligand Behavior of the 1,2-Diphosphaferrocene [(η^5-1,3-tBu$_2$C$_5$H$_3$)(η^5-{3,4-(Me$_3$SiO)$_2$-5-(Me$_3$Si)P$_2$C$_3$}Fe]☆

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Reaction of equimolar amounts of (η^5-1,3-tBu$_2$C$_5$H$_3$)(CO)$_2$FeP(SiMe$_3$)$_2$ with bis(trimethylsilyl)methylenechlorophosphane afforded the 1-metallo-1,2-diphosphapropene (η^5-1,3-tBu$_2$C$_5$H$_3$)(CO)$_2$FeP(SiMe$_3$)P=C(SiMe$_3$)$_2$ (**1b**). Treatment of **1b** with an excess of [(Z)-cyclooctene]Cr(CO)$_5$ furnished 1,2-diphosphaferrocene (η^5-1,3-tBu$_2$C$_5$H$_3$)(η^5-{1-[Cr(CO)$_5$]-3,4-(Me$_3$SiO)$_2$-5-(Me$_3$Si)P$_2$C$_3$}Fe (**4b**). Chromium complex **4b** was freed from the pentacarbonylchromium fragment by heating with 1.5 equiv. of [Fe$_2$(CO)$_9$] in toluene solution at 80–90 °C affording sandwich **5**. In contrast, treatment of **4c** with [Fe$_2$(CO)$_9$] in refluxing n-pentane yielded the trinuclear complex (η^5-1,3-tBu$_2$C$_5$H$_3$){η^5-1,2-[Fe$_2$(CO)$_7$]-3,4-(Me$_3$SiO)$_2$-5-(Me$_3$Si)P$_2$C$_3$}Fe (**6**). The ligation of sandwich **5** to the [Fe(CO)$_4$] unit in **7** was achieved by irradiation with [Fe(CO)$_5$] in n-pentane solution. A tricarbonylnickel adduct **8** resulted from the reaction of **4b** with an excess of [Ni(CO)$_4$] in toluene at ambient temperature. The molecular structures of the complexes **6** and **8** were established by single-crystal X-ray structure analyses. Cyclovoltammetric studies with **4b**, **5**, and **8** revealed an anodic shift of the oxidation potential when changing from **5** to **8** and **4**.

Mono- and polyphosphacyclopentadienide anions [P$_n$(CR)$_{5-n}$]$^-$ (n = 1–5) are of considerable current interest, since they not only exhibit significant electron delocalization but also readily form η^5-transition metal complexes[1–7].

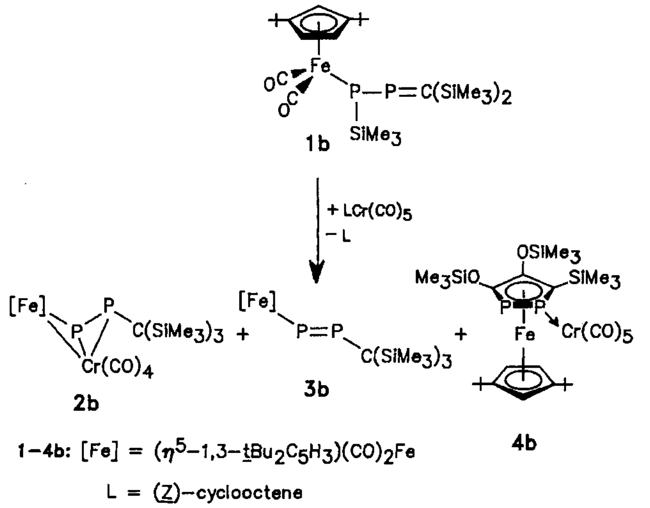
Recently, we have described the preparation of the 1-metallo-1,2-diphosphapropene (η^5-C$_5$Me$_5$)(CO)$_2$FeP(SiMe$_3$)-P=C(SiMe$_3$)$_2$ (**1a**) and its pentacarbonylchromium-induced rearrangement to the butterfly complex [(η^5-C$_5$Me$_5$)(CO)$_2$Fe–P=P–C(SiMe$_3$)$_3$]Cr(CO)$_4$ (**2a**), the ferriodiphosphene (η^5-C$_5$Me$_5$)(CO)$_2$Fe–P=P–C(SiMe$_3$)$_3$ (**3a**), and a few crystals of the novel 1,2-diphosphaferrocene (η^5-C$_5$Me$_5$){η^5-1-[Cr(CO)$_5$]-3,4-(Me$_3$SiO)$_2$-5-(Me$_3$Si)P$_2$C$_3$}Fe (**4a**)[3]. We were interested in the conditions favoring the formation of the sandwich compound compared with the other products, and in the chemistry of our 1,2-diphosphacyclopentadienyl complexes. An obvious prerequisite for those studies was an efficient synthetic approach to the latter. Markovskii and coworkers reported on the thermally induced 1,3-sigmatropic Me$_3$Si shift in 1,2-diphosphapropenes R^1(Me$_3$Si)P–P=C(SiMe$_3$)$_2$ to the isomeric diphosphenes R^{1}P=P–C(SiMe$_3$)$_3$. They pointed out that the ease of silyl migration is highly dependent on the steric requirements of the group R^1 [8,9]. In keeping with this observation it was anticipated that the reduction of the bulkiness of the (C$_5$R$_5$)(CO)$_2$Fe fragment in 1-metallo-1,2-diphosphapropenes might suppress the 1,3-silyl shift to metallo-diphosphenes in favor of sandwich formation. Independently, Niecke and coworkers obtained a 1,2-diphosphaferrocene, (η^5-C$_5$H$_5$)[η^5-3,4-(Me$_3$SiO)$_2$-5-(Me$_3$Si)P$_2$C$_3$]Fe, by heating a mixture of (η^5-C$_5$H$_5$)(CO)$_2$FeBr, (Me$_3$Si)$_2$P–P=C(SiMe$_3$)$_2$, and (Me$_2$N)$_3$PO in toluene[4a]. More recently Mathey et al. described the preparation of 1,2-diphospholides and the conversion of one representative into a 1,2-diphosphaferrocene[4b].

Results and Discussion

The reaction of the metallophosphane (η^5-1,3-tBu$_2$C$_5$H$_3$)(CO)$_2$Fe–P(SiMe$_3$)$_2$[10] with an equimolar amount of ClP=C(SiMe$_3$)$_2$[11] in n-pentane yielded the metallo-1,2-diphosphapropene (η^5-1,3-tBu$_2$C$_5$H$_3$)(CO)$_2$Fe–P(SiMe$_3$)-P=C(SiMe$_3$)$_2$ (**1b**) as a black thermolabile, oxygen- and moisture-sensitive powder. Even when stored at −30 °C under nitrogen **1b** slowly decomposed to [(η^5-1,3-tBu$_2$C$_5$H$_3$)(CO)$_2$Fe]$_2$, P(SiMe$_3$)$_3$, and other unidentified species. The ^{31}P{^{1}H}-NMR spectrum of **1b** displays doublets at δ = −83.8 and 505.1 ($^1J_{P,P}$ = 262 Hz). In the spectrum of **1a** corresponding resonances are observed at δ = −30.3 and 502.9 ($^1J_{P,P}$ = 295 Hz)[3]. In comparison with (Me$_3$Si)$_2$P–P=C(SiMe$_3$)$_2$ (δ = −134.45, 434.46, $^1J_{P,P}$ = 238 Hz)[12] and Mes(Me$_3$Si)P–P=C(SiMe$_3$)$_2$ (δ = −70.7, 405.4, $^1J_{P,P}$ = 382 Hz)[13] metal substitution at the tricoordinate phosphorus leads to a marked deshielding of the dicoordinate phosphorus atom. The presence of a P=C-functionality in **1b** is further confirmed by a doublet of doublets at δ = 214.9 ($^1J_{P,C}$ = 100.7, $^2J_{P,C}$ = 2.9 Hz) in the ^{13}C{^{1}H}-NMR spectrum of the compound.

Treatment of **1b** with an excess of [(Z)-cyclooctene]Cr(CO)$_5$[14] afforded the 1,2-diphosphaferrocene pentacarbonylchromium adduct **4b** as a crystalline dark orange-red solid in 28% yield.

Scheme 1

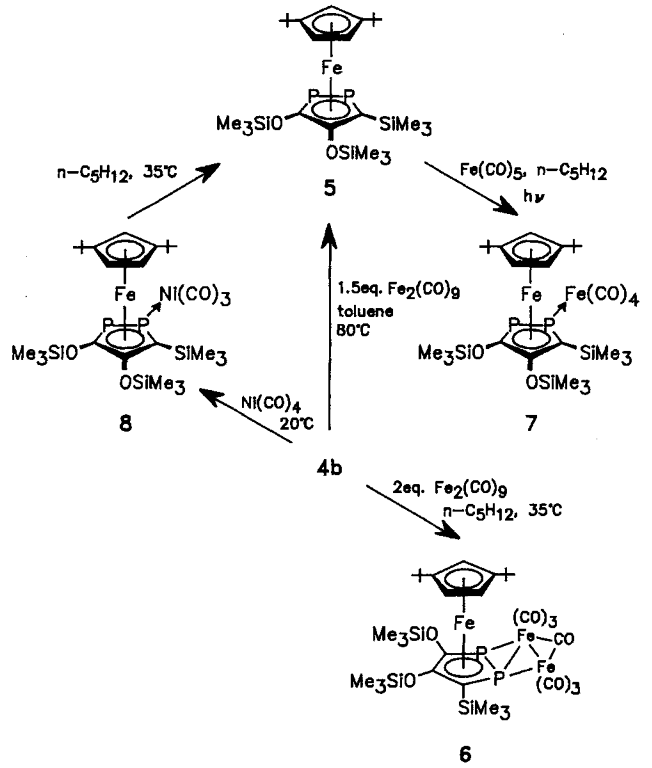


1–4b: [Fe] = (η^5-1,3-$\underline{t}Bu_2C_5H_3$)(CO)$_2$Fe
L = ($\underline{Z}$)-cyclooctene

The $^{31}P\{^1H\}$-NMR spectrum of the reaction mixture also displays signals at δ = 117.5 (d), 341.0 (d, $^1J_{P,P}$ = 525 Hz) and at δ = 612.8 (d), 740.8 ($^1J_{P,P}$ = 655 Hz) assigned to the butterfly complex **2b** and the metallodiphosphene **3b**, respectively. As neither compound could not be isolated in pure form due to decomposition, their identification was based on a comparison of the ^{31}P-NMR data with those of the related complexes **2a** (δ = 134.9, d; 431.5, d, $^1J_{P,P}$ = 525 Hz) and **3a** (δ = 602.3, d; 788.0, d, $^1J_{P,P}$ = 654.8 Hz)[3]. Compounds **2b**, **3b**, and **4b** were formed in a ratio of ca. 1:1:6. These findings are in accord with our assumption, that the release of the bulkiness around iron might favor the generation of the sandwich **4** compared with the diphosphene derivatives **2** and **3**. Complex **4b** is stable in air and toward moisture. It is readily soluble in benzene and THF but poorly soluble in ether and alkanes.

The conversion of the pentacarbonylchromium adduct **4b** into the 1,2-diphosphaferrocene **5** was effected by thermolysis of **4b** in the presence of 1.5 equivalents of [$Fe_2(CO)_9$] in toluene at 80–90 °C. The course of the reaction was monitored by ^{31}P-NMR spectroscopy. After heating for 5 h the spectrum exhibits two pairs of doublets at δ = 69.17; –162.7 ($^1J_{P,P}$ = 276.6 Hz) and at δ = 26.16; –114.71 ($^1J_{P,P}$ = 426.4 Hz) in a ratio of 2:1, which are assigned to the carbonyliron adducts **6** and **7**. After one day an AB pattern (δ_A = –64.75; δ_B = –74.49; $^1J_{A,B}$ = 381.4) indicates the additional formation of sandwich **5**. After 4 more days the spectrum displays exclusively the resonances of the carbonyl-free sandwich, which was isolated as a red crystalline solid in 44% yield. The successive appearance of signals for **6**, **7**, and **5** demonstrates that **5** was formed by thermal decomposition of carbonyliron-containing intermediates. They were synthesized independently under milder conditions. Thus, a 62% yield of black crystalline **6** was obtained by heating of a slurry of **4b** with a twofold excess of [$Fe_2(CO)_9$] in refluxing n-pentane for ca. 2 d. Orange-red microcrystalline **7** resulted from the photolysis of a mixture of sandwich **5** and [$Fe(CO)_5$] in n-pentane (78% yield). The transformation of **4b** into the tricarbonylnickel derivative **8** was achieved by treatment with an equimolar amount of [$Ni(CO)_4$] in toluene at 20 °C. Red crystalline **8** was isolated in 72% yield. The thermal stability of the 1,2-diphospholyl complexes in solution increases in the order **8** $\ll$ **6** $\approx$ **7** $\ll$ **5** < **4b**. Accordingly, the thermolysis of **8** to regenerate sandwich **5** (35% yield) proceeded already in boiling pentane.

Scheme 2



The ^{31}P NMR parameters of the AB spin system of the two adjacent phosphorus atoms of **5** are comparable with Niecke's data for (η^5-C_5H_5){η^5-3,4-($Me_3SiO)_2$-5-($Me_3Si)P_2C_3$}Fe (δ_A = –66.2, δ_B = –67.2, $^1J_{A,B}$ = 379 Hz)[4a]. The σ donation of the η^5-ligated 1,2-diphospholyl ring to carbonylmetal units M(CO)$_n$ via P1 (no isomers with a M–P(2) linkage have been detected) leads to a considerable deshielding of this phosphorus atom [δP(1) = 0.4 to –27.9] whereas the remaining nucleus P(2) experiences high-field shifts to δ values of –102.8 to –114.71. The $^1J_{P,P}$ coupling constants increase upon coordination from 381.4 Hz in **5** to 426.4 Hz in **7**. The situation in the trinuclear complex **6** is somewhat different. Phosphorus resonances are separated by as much as 231.87 ppm and the coupling constant $^1J_{P,P}$ has decreased to 276.6 Hz. These values may partly be rationalized by the marked elongation of the P–P bond, as detected by an X-ray study.

The presence of an unsymmetrically substituted 1,2-diphosphacyclopentadienyl ligand in **4b**, **5**, **7**, and **8** is the reason for two downfield resonances of the siloxy-substituted ring carbon atoms at δ = 129.27 to 135.93 with coupling constants $^1J_{P,C}$ of 27.1 to 72.1 Hz and $^2J_{P,C}$ of 4.6 to 17.4 Hz. With the exception of **8** the silylated ring carbon atoms in the complexes give rise to doublets of doublets at considerably higher field (δ = 66.31–77.87; $^1J_{P,C}$ = 53.4–77.5 Hz, $^2J_{P,C}$ = 1.6–15.3 Hz). The ^{1}H and ^{13}C resonances of the chemically and magnetically non-equivalent *tert*-butyl groups give rise to two singulets. The same holds for the carbon atoms and protons in the 4,5-positions of the cyclopentadienyl ring.

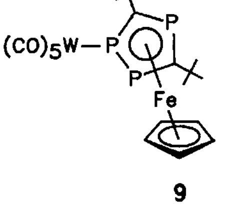
The IR spectra of the carbonyl metal adducts **4b**, **7**, and **8** show more ν(CO) absorptions than expected for a local C_{4v} or C_{3v} symmetry. The lowering of this local symmetry is clearly caused by coordination of $[Cr(CO)_5]$, $[Fe(CO)_4]$, and $[Ni(CO)_3]$ fragments to the unsymmetrical and bulky ligand **5**. Bands with highest wavenumbers in **4b**, **7**, and **8** correspond to those of the triphenylphosphane complexes $[(CO)_5Cr(PPh_3)]$ [ν(CO), hexane: 2064 m, 1984 vw, 1944 vs cm^{-1}] and $[(CO)_4Fe(PPh_3)]$ [ν(CO), hexane: 2052.2, 1979.7, 1946.6 cm^{-1}][15], indicating comparable σ-donor/π-acceptor properties of **5** and the phosphane.

Only the mass spectra of **4b** (CI) and **5** (EI) display the molecular ions as the parent peaks. Obviously, all the carbonyl metal fragments in **6**–**8** as well as in **4b** are easily cleaved to **5**$^+$ under the conditions in the MS. The latter ion is always fragmented into the molecular ion of the diphospholyl ring (*m*/*z*: 349) and the $(tBu_3C_5H_3Fe)^+$ unit (*m*/*z*: 233). Fragmentation of the heterocycle leads to the alkyne cation $(Me_3Si-O-C\equiv C-O-SiMe_3)^+$ (*m*/*z*: 202) and a species with *m*/*z*: 147 which we tentatively assign to the aromatic diphosphirenium ion $(\overline{P-P=C}SiMe_3^+)$.

X-Ray Structural of Analysis of 8

The molecular structure of **8** (Figure 1) is comparable with that of **4a**[3] and features the rare 1,2-diphosphacyclopentadienyl ligand in an η^5:η^1 mode of coordination to the iron and nickel atoms. The iron center is sandwiched between the two five-membered rings. The heterocycle is planar and nearly eclipsed to the planar cyclopentadienyl ligand enclosing a dihedral angle of 2.8°. The oxygen atoms O(1) and O(2) as well as the atom Si(3) are in the plane of the diphospholyl ring. The nickel atom is located 0.454 Å above that plane opposite to the iron. The iron atom is separated by 1.684 Å from the cyclopentadienyl and by 1.655 Å from the heterocyclic ligand.

The P–P and P–C bond lengths [2.126(2), 1.767(6), 1.775(6) Å] as well as the distance C(15)–C(16) [1.434(8) Å] compare well with the corresponding data in **9** [P–P = 2.098(2), P–C = 1.753(7), 1.764(8) Å][16] and are in good agreement with corresponding parameters in π-coordinated phosphaarenes[1,2,17].



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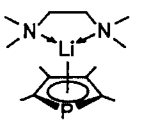
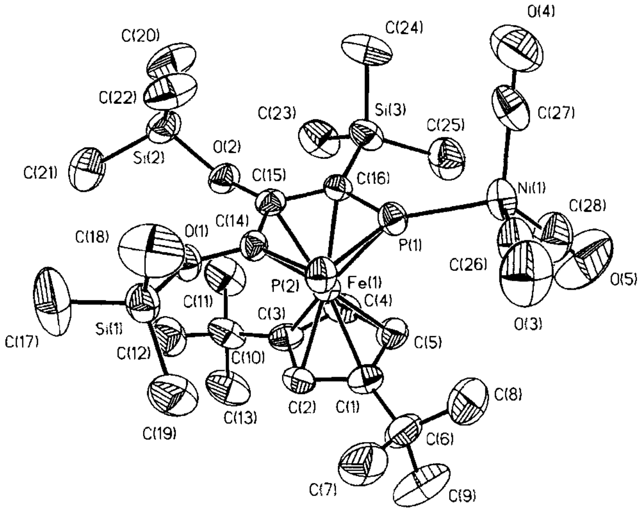


10

The endocyclic valence angles at the phosphorus atoms [C(16)–P(1)–P(2) = 98.4(2), P(1)–P(2)–C(14) = 91.9(2)°] are significantly more acute than the endocyclic angles at the carbon atoms C(14) [118.5(4)°], C(15) [118.1(5)°], and C(16) [112.7(4)°]. In the lithiumphospholyl complex $Li(tmeda)[PC_4Me_4]$ (**10**)[18] the endocyclic angle C–P–C was determined to be 90.5(2)°, whereas the P–C–C and C–C–C angles average to 112.4(4)°. Like in **4a** the iron atom is displaced significantly towards the three ring carbon atoms. The distances from iron to the carbon atoms of the heterocycle are slightly longer (average 2.116 Å) than the corresponding bond lengths to the cyclopentadienyl ring carbon atoms [average 2.072 Å]. The bond length Fe–P(1) of 2.283(2) Å is markedly shortened with respect to the distance Fe–P(2) [2.343(2) Å]. The shorter distance is found to the phosphorus atom coordinated to the $[Ni(CO)_3]$ unit. The Ni–P distance [Ni–P(1) = 2.226(2) Å] is comparable to the one in $[(\eta^1\text{-}Mes^*P=C=CPh_2)Ni(CO)_3]$ [2.234(1) Å[19]]. The carbonylnickel fragment is slightly distorted from C_{3v} symmetry by coordination to the P ligand as evidenced by the angles P(1)–Ni–C(26) = 103.3(2)°, P(1)–Ni–C(27) = 106.0(2)°, and P(1)–Ni–C(28) = 110.1(3)°.

Figure 1. Molecular structure of **8** in the crystal[a]

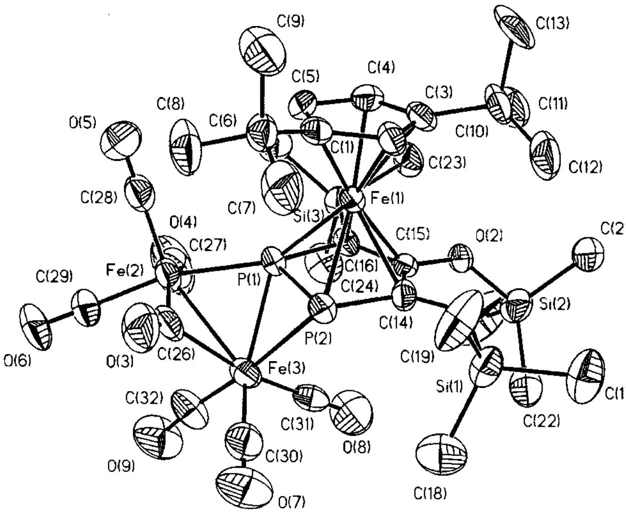


[a] Selected bond lengths [Å] and angles [°]: Ni–P(1) 2.226(2), P(1)–P(2) 2.126(2), P(2)–C(14) 1.775(6), P(1)–C(16) 1.767(6), C(15)–C(16) 1.434(8), C(14)–O(1) 1.375(6), C(15)–O(2) 1.371(6), C(16)–Si(3) 1.888(6), Fe–P(1) 2.283(2), Fe–P(2) 2.343(2), Fe–C(14) 2.121(6), Fe–C(15) 2.125(6), Fe–C(16) 2.102(6), Fe–C(1) 2.071(6), Fe–C(2) 2.064(6), Fe–C(3) 2.094(6), Fe–C(4) 2.065(6), Fe–C(5) 2.064(6). – P(1)–P(2)–C(14) 91.9(2), P(2)–C(14)–C(15) 118.5(4), C(14)–C(15)–C(16) 118.1(5), C(15)–C(16)–P(1) 112.7(4), C(16)–P(1)–P(2) 98.4(2).

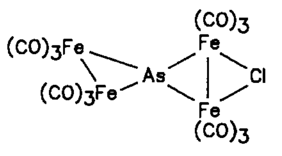
X-Ray Structural Analysis of 6

The molecular structure of **6** (Figure 2) may be described as that of a trinuclear complex where sandwich **5** functions as a bidentate ligand towards the two iron atoms of a $[Fe_2(CO)_7]$ fragment via the P–P unit of the 1,2-diphospholyl ring. The bond lengths Fe(2)–P(1) [2.207(3) Å], Fe(3)–P(1) [2.310(3) Å] and Fe(3)–P(2) [2.488(3) Å] are markedly different and may be interpreted in terms of an η^1 interaction between Fe(2) and P(1) and an η^2 coordination of the PP bond to Fe(3). Generally, Fe−P distances in low-valent carbonyliron complexes range from 2.09 to 2.38 Å[20]. The atom Fe(1) maintains its η^5 interaction with the heterocycle giving FeP distances [Fe(1)−P(1) = 2.251(3), Fe(1)−P(2) = 2.325(3) Å] which differ slightly from the corresponding figures in **8**. The contacts of the iron center to the carbon atoms of the heterocycle range from 2.127(8) to 2.167(8) Å [av. 2.146(8) Å]. As in **8** the Fe−C bonds Fe(1)−C(1) to Fe(1)−C(5) to the Cp ring are significantly shorter [av 2.104(9) Å]. The most obvious change **5** experiences upon ligation to [$Fe_2(CO)_7$] is an elongation of the PP bond to 2.281(4) Å. The standard value for a P−P double bond is 2.00 Å[21], whereas a distance of 2.22 Å[22] is accepted as an average for the P−P single bond. Compared to the above value the P=P-π bond is considered η^2-ligated to two different metal atoms Fe(1) as well as Fe(3) in a near *trans* orientation. The interplanar angle between planes defined by atoms Fe(1), P(1), and P(2) as well as Fe(3), P(1), and P(2) is 172.9°. Atoms Fe(2) and Fe(3) are linked by a single bond of 2.601(2) Å and by a semibridging carbonyl group [Fe(2)−C(26) = 1.936(12) Å; Fe(3)−C(26) = 2.032(11) Å]. The Fe−Fe separation is comparable to the corresponding bond length in e.g. [iPr$_2$NP−C(O)−PN−iPr$_2$]Fe$_2$(CO)$_6$ [2.603(2) Å][23]. Fe−Fe single bond distances in low-valent iron complexes range from 2.4606(22) Å in $Fe_2(CNEt)_9$[24] to 2.802(3) Å in **11**[25].

Figure 2. Molecular structure of **6** in the crystal[a]

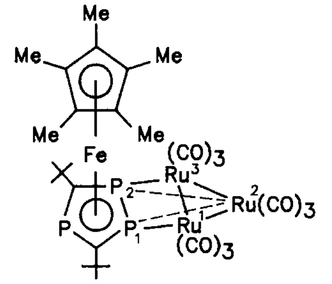


[a] Selected bond lengths [Å] and angles [°]: Fe(1)−P(2) 2.325(3), Fe(1)−P(1) 2.252(3), Fe(1)−C(14) 2.142(9), Fe(1)−C(15) 2.167(8), Fe(1)−C(16) 2.127(9), P(1)−P(2) 2.281(4), P(1)−C(16) 1.781(9), P(1)−Fe(3) 2.310(3), P(2)−C(14) 1.809(8), P(1)−Fe(2) 2.207(3), P(2)−Fe(3) 2.488(3), Fe(2)−Fe(3) 2.601(2), Fe(2)−C(26) 1.936(12), Fe(3)−C(26) 2.032(10), Fe(1)−C(1) 2.112(8), Fe(1)−C(2) 2.102(9), Fe(1)−C(3) 2.129(8), Fe(1)−C(4) 2.082(9), Fe(1)−C(5) 2.097(9). − P(2)−P(1)−C(16) 97.7(3), P(1)−P(2)−C(14) 88.0(3), P(2)−C(14)−C(15) 120.8(6), C(14)−C(15)−C(16) 119.8(7), C(15)−C(16)−P(1) 113.1(6), Fe(2)−P(1)−P(2) 118.92(12), P(1)−Fe(2)−C(26) 82.1(3).



11

The heterocycle slightly deviates from planarity being folded around the axis P(1)−C(15) by 7.2°. Note that atoms P(1), P(2), Fe(2), and C(26) lie in a plane [torsion angle C(26)−Fe(2)−P(1)−P(2) = 1.9°], which is η^4-bound to the [$(CO)_3Fe(3)$] fragment. In keeping with this view **6** might be envisaged as a slipped triple-decker complex with a 1-carbonyliron-1,2-diphospholyl middle deck attached to Fe(1) and Fe(3). The terminal decks are represented by the Cp ring at Fe(1) and the ensemble of three carbonyl groups at Fe(3). This mode of coordination can also account for the geometrical changes of the heterocycle in comparison with **4a** or **8**. The bonding situation in **6** is unusual. The only compound which is roughly comparable to **6** is the tetranuclear complex **12** where a 1,2,4-triphospholyl ligand is η^5-coordinated to a (C_5Me_5)Fe unit and additionally linked in a μ_3-η^2 fashion to a [$Ru_3(CO)_9$] fragment.



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Although in **12** the Ru(2)−P distances of 2.541(2) and 2.508(2) Å are in accord with a weak π interaction, no significant weaking of the PP bond [2.131(2) Å] was observed[26].

Electrochemical Investigation of 4b, 5, and 8

Cyclic voltammograms for complexes **4b**, **5**, and **8** were recorded at a Pt electrode in CH_2Cl_2 and in acetonitrile. Compounds **4b** and **5** undergo relatively undisturbed reversible one-electron oxidation in CH_2Cl_2, close to the ferrocenium/ferrocene redox transition under identical conditions (Table 1), whereas the corresponding transitions in acetonitrile are irreversible even at elevated scan rates (20 V/s). A second oxidation at more positive potential is irreversible in either solvent. An irreversible, not diffusion-controlled reduction, starting around −1 V (SCE) was found in acetonitrile, obviously accompanied by decomposition of the complex. A slightly more complicated pattern was observed for the oxidation of **8** in CH_2Cl_2. The oxidation wave is composed of two closely spaced waves of roughly equal height which on the reverse scan give rise to one single reduction peak. There is no obvious dependence of the relative peak heights on the scan rate (20−200 mV/s). Whereas peak separation of the first oxidation to this re-

Table 1. Redox potentials and peak separations for complexes **4b**, **5**, and **8** in CH_2Cl_2

Compound		$E_{1/2}$/V[a]	ΔE_p/mV	v/mV/s
5	$Cp(\underline{t}Bu)_2Fe\{P_2C_3(OSiMe_3)_2(SiMe_3)\}$	0.475/0.09	50	20
4b	$Cp(\underline{t}Bu)_2Fe\{P_2C_3(OSiMe_3)_2(SiMe_3)\}Cr(CO)_5$	0.66/0.275	65	20
8	$Cp(\underline{t}Bu)_2Fe\{P_2C_3(OSiMe_3)_2(SiMe_3)\}Ni(CO)_3$	0.465/0.07	60	100
		0.53/0.145	155	

[a] Potential value vs. SCE/ferrocene$^{+/0}$.

duction peak is in the normal range (60 mV), the difference of the second oxidation to the reduction peak, amounting to 155 mV, signalizes a chemical reaction. Since the reduction peak coincides with the one found for **5** the most probable explanation is a partial dissociation of the $[Ni(CO)_3]$ group in diluted solution (about 10^{-3} M in complex) of **8** generating some **5**. The single reduction peak would then signalize the ready and complete dissociation of a $Ni(CO)_3$ fragment into the monocationic species $\mathbf{8}^+$, leaving $\mathbf{5}^+$ as the sole electrode species to be reduced at the reverse scan, i.e. oxidation of **8** is irreversible. Application of the standard peak separation of about 60 mV to the oxidation of **8** leads to a redox potential of about 0.53 V (SCE, 0.145 V vs. ferrocene) for the $\mathbf{8}^{+/0}$ transition.

A comparison of these oxidation potentials with those of ferrocene or phosphaferrocenes is made difficult due to the presence of the different ring substituents. The closest approach to the present complexes where electrochemical potentials have been determined is (3,4-dimethyl-1-phospholyl)(η^5-cyclopentadienyl)iron[27], which oxidizes 0.08 V more positive than ferrocene. Two trimethylsiloxyl substituents may exert an (+)-M effect, whereas the second dicoordinate ring phosphorus atom in place of a CH unit causes a positive shift of the oxidation potentials. Obviously, these effects seem to compensate each other. As expected the binding of a $[Cr(CO)_5]$ group to P(1) of **5** affording **4b** effects an additional anodic shift of the redox potential. A similar observation was made with corresponding $[Cr(CO)_5]$ adducts of phosphaferrocenes[28]. The electronegative $[Cr(CO)_5]$ group removes electron density from the heterocycle and concomitantly from the iron. This effect is of the same magnitude as the shift exerted by an acetyl or carboxyl group at ferrocene [$\Delta E \approx 245$ mV][29]. A similar anodic shift but to a smaller extent is caused by a $[Ni(CO)_3]$ group.

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Experimental

All manipulations were performed under dry nitrogen. Solvents were rigorously dried with an appropriate drying agent and distilled before use. The compounds $[(\eta^5\text{-}1,3\text{-}t\mathrm{Bu}_2C_5H_3)(CO)_2FeP(SiMe_3)_2]$[10], $[(Z)\text{-cyclooctene}]Cr(CO)_5$[14], and $ClP{=}C(SiMe_3)_2$[11] were prepared as described in the literature. $[Ni(CO)_4]$, $[Fe(CO)_5]$, and $[Fe_2(CO)_9]$ were purchased.

IR spectra were recorded with a Mattson Polaris (FT-IR)/Atari 1040 STF. – ^{1}H-, ^{31}P-, ^{13}C-NMR spectra were measured with Bruker AC 100 (^{1}H, 100.131; ^{13}C, 25.180; ^{31}P, 40.539 MHz) and Bruker AM 300 (^{1}H, 300.1; ^{13}C, 75.5; ^{31}P, 121.7 MHz) instruments. Standards: $SiMe_4$ (^{1}H, ^{13}C), 85% H_3PO_4 (^{31}P). – Mass spectra were recorded with a Varian MAT CH5-DF spectrometer (70 eV, 250°C).

$(\eta^5\text{-}1,3\text{-}t\mathrm{Bu}_2C_5H_3)(CO)_2FeP(SiMe_3)P{=}C(SiMe_3)_2$ (**1b**): A solution of 1.90 g (8.57 mmol) of $ClP{=}C(SiMe_3)_2$ in 20 ml of *n*-pentane was dropwise added to a solution of 4.00 g (8.57 mmol) of $(\eta^5\text{-}1,3\text{-}t\mathrm{Bu}_2C_5H_3)(CO)_2FeP(SiMe_3)_2$ in 80 ml of *n*-pentane at −15°C. The mixture obtained was stirred for 2 h at 25°C, and the course of the reaction was monitored by ^{31}P-NMR spectroscopy. Solvents and volatile components were removed in vacuo. The oily residue obtained was dissolved in 30 ml of *n*-pentane and the solution was filtered through a pad of Na_2SO_4 (d = 5 cm). The filtrate was concentrated to a volume of 5 ml and stored at −30°C for 24 h. The dark brown precipitate was recrystallized from *n*-pentane to yield 3.70 g (75%) of **1b** as a dark brown solid. – IR (cm^{-1}, KBr): $\tilde{\nu}$ = 2963 s [$\nu(CH_3)$], 2907 w, 2873 w, 1990 vs [ν(CO)], 1958 vs [ν(CO)], 1491 w, 1464 w, 1363 w, 1262 vs [δ ($Si(CH_3)_3$], 1097 s, 1023 s, 801 vs, 686 w, 632 w, 581 w. – ^{1}H-NMR (C_6D_6): δ = 0.42 (d, $^4J_{P,H}$ = 1.8 Hz, 9H, (*E*)-$CSiMe_3$), 0.49 (d, $^3J_{P,H}$ = 3.4 Hz, 9H; $PSiMe_3$), 0.62 (s, 9H, (*Z*)-$CSiMe_3$), 1.37 (s, 18H, *t*Bu), 4.14 (d, $^4J_{H,H}$ = 1.9 Hz, 2H, 4,5-H_{Cp}), 4.41 (m, 1H, 2-H_{Cp}). – $^{13}C\{^1H\}$-NMR (C_6D_6): δ = 2.77 [d, $^2J_{P,C}$ = 13.9 Hz, $PSi(CH_3)_3$], 3.05 [d, $^3J_{P,C}$ = 9.1 Hz, (*Z*)-$CSi(CH_3)_3$], 4.72 [dd, $^3J_{P,C}$ = 8.9, $^4J_{P,C}$ = 2.8 Hz, (*E*)-$CSi(CH_3)_3$], 31.46 [s, $C(CH_3)_3$], 31.83 [s, $C(CH_3)_3$], 32.05 [s, $C(CH_3)_3$], 78.34 (s, C-2_{Cp}), 84.22 (s, C-4_{Cp}), 87.05 (s, C-5_{Cp}), 116.71 (s, C-$1,3_{Cp}$), 214.9 (dd, $^1J_{P,C}$ = 100.7; $^2J_{P,C}$ = 2.9 Hz, P=C), 216.6 (d, $^2J_{P,C}$ = 6.8 Hz, CO). – $^{31}P\{^1H\}$-NMR (C_6D_6): δ = −83.8 (d, $^1J_{P,P}$ = 262 Hz, Fe–P), 501 (d, $^1J_{P,P}$ = 262 Hz, P=C). – MS/CI), *m/z*: 582 [M^+], 554 [M^+ – CO], 526 [M^+ – 2 CO], 293 [$P(SiMe_3)P{=}C(SiMe_3)_2^+$], 290 [$t\mathrm{Bu}_2C_5H_3Fe(CO)_2H^+$], 262 [($t\mathrm{Bu}_2C_5H_3$-Fe)(CO)$H^+$], 234 [$t\mathrm{Bu}_2C_5H_3FeH^+$], 189 [$PC(SiMe_3)_2^+$], 73 [$SiMe_3^+$], 57 [$t\mathrm{Bu}^+$]. – $C_{25}H_{48}FeO_2P_2Si_3$ (582.71): calcd. C 51.53, H 8.30; found C 49.90, H 8.36. Repeated recrystallization did not provide better C values, but was accompanied by decomposition.

$[(\eta^5\text{-}1,3\text{-}t\mathrm{Bu}_2C_5H_3)(\eta^5\text{-}\{1\text{-}[Cr(CO)_5]\text{-}3,4\text{-}(Me_3SiO)_2\text{-}5\text{-}(Me_3Si)\text{-}P_2C_3\}Fe$ (**4b**): To a solution of 3.00 g (5.10 mmol) of **1b** in 70 ml of *n*-pentane at ambient temp. was added in one portion 4.60 g (15.3 mmol) of solid (*Z*)-(cyclooctene)pentacarbonyl chromium. The color of the reaction mixture slowly changed from black to brown. After of stirring for 24 h (^{31}P-NMR control) the reaction was stopped. The dark solution was decanted from a dark brown oil. This was crystallized from 25 ml of ether at 0°C to yield 1.10 g (28%) of orange-red crystalline **4b**. – IR (cm^{-1}, KBr): $\tilde{\nu}$ = 3854 m, 3105 w, 3091 w, 2960 vs [ν(CH)], 2908 m, 2873 m, 2065 vs [ν(CO)], 1993 m [ν(CO)], 1957 vs [ν(CO)], 1934 vs [ν(CO)], 1489 m,

1459 m, 1377 vs, 1294 m, 1254 vs [δ(SiMe$_3$), 1197 vs, 1165 m, 1059 vs, 903 m, 844 s [ρ(SiMe$_3$)], 752 m, 666 s, 649 s. – IR (cm^{-1}, *n*-C$_6$H$_{14}$): ν(CO) = 2064.0, 1991.3 w, 1953.5 s, 1945.5 s, 1934.3 m. – ^{1}H-NMR (C$_6$D$_6$): δ = 0.14 (s, 9H, OSiMe$_3$), 0.23 (d, $^{4}J_{\mathrm{P,H}}$ = 0.9 Hz, 9H, CSiMe$_3$), 0.47 (s, 9H, OSiMe$_3$), 1.16 (s, 9H, *t*Bu), 1.38 (s, 9H, *t*Bu), 4.07 (m, 1H) and 4.11 (m, 1H, 4,5-H$_{\mathrm{Cp}}$), 4.81 (m, 1H, 2-H$_{\mathrm{Cp}}$). – ^{13}C{^{1}H}-NMR (CD$_2$Cl$_2$): δ = 0.83 [d, $^{3}J_{\mathrm{P,C}}$ = 6.6 Hz, CSi(*C*H$_3$)$_3$], 1.56 [s, OSi(CH$_3$)$_3$], 2.31 [d, $^{4}J_{\mathrm{P,C}}$ = 2.7 Hz, OSi(CH$_3$)$_3$], 31.16 [s, *p*-C(*C*H$_3$)$_3$], 31.57 [s, *C*(CH$_3$)$_3$], 32.31 [d, $^{4}J_{\mathrm{P,C}}$ = 4.0 Hz, C(*C*H$_3$)$_3$], 32.58 [s, *C*(CH$_3$)$_3$], 66.31 (s, C-2$_{\mathrm{Cp}}$), 68.00 [dd, $^{1}J_{\mathrm{P,C}}$ = 59.2, $^{2}J_{\mathrm{P,C}}$ = 3.8 Hz, *C*Si(CH$_3$)$_3$], 69.44 (s) and 70.29 (d, $^{2}J_{\mathrm{P,C}}$ = 1.3 Hz, C-4,5$_{\mathrm{Cp}}$), 110.70 (d, $^{2}J_{\mathrm{P,C}}$ = 0.9 Hz) and 111.49 (s, C-1,3$_{\mathrm{Cp}}$), 133.50 ("t", $^{2}J_{\mathrm{P,C}}$ = 4.9 Hz, PC*C*O), 135.57 (d, $^{1}J_{\mathrm{P,C}}$ = 27.1 Hz, P*C*O), 216.71 [dd, $^{2}J_{\mathrm{P,C}}$ = 14.0, $^{3}J_{\mathrm{P,C}}$ = 3.0 Hz, Cr(CO)$_{\mathrm{eq}}$], 222.38 [d, $^{2}J_{\mathrm{P,C}}$ = 3.0 Hz, Cr(CO)$_{\mathrm{ax}}$]. – ^{31}P{^{1}H}-NMR (C$_6$D$_6$): δ = −102.8 (d, $^{1}J_{\mathrm{P,P}}$ = 397 Hz, CrP*P*), 0.4 (d, $^{1}J_{\mathrm{P,P}}$ = 397 Hz, Cr*P*P). – MS/CI, *m/z*: 774 [M$^+$], 582 [M$^+$ – Cr(CO)$_5$], 349 [(Me$_3$SiO)$_2$(Me$_3$Si)C$_3$P$_2^+$], 233 [*t*Bu$_2$C$_5$H$_3$Fe$^+$], 202 [Me$_3$SiOCCOSiMe$_3^+$], 147 [P$_2$CSiMe$_3^+$], 73 [SiMe$_3^+$]. – C$_{30}$H$_{48}$CrFeO$_7$P$_2$Si$_3$ (774.74): calcd. C 46.51, H 6.25; found C 46.61, H 6.10.

[(η^5-1,3-tBu$_2$C$_5$H$_3$)(η^5-{3,4-(Me$_3$SiO)$_2$-5-(Me$_3$Si)P$_2$C$_3$})Fe] (**5**): A sample of 1.06 g (2.91 mmol) of [Fe$_2$(CO)$_9$] was added to a solution of 1.50 g (1.94 mmol) of **4b** in 15 ml of toluene. The slurry was stirred at ca. 80–90°C for 5 d (^{31}P-NMR control!). Solvent and volatile components were removed in vacuo and the black residue was chromatographed on a column (8 × 2 cm) packed with Florisil (Riedel de Haën). With *n*-hexane a rose-red zone developed, which was completely eluted. From this fraction a yield of 0.51 g (44%) of red crystalline **5** was obtained. – IR (cm^{-1}, KBr): $\tilde{\nu}$ = 2962 s [ν(CH)], 2908 m, 2866 m, 1489 w, 1462 w, 1385 m, 1365 w, 1261 vs [δ(Si(CH$_3$)$_3$)], 1188 m, 1097 s, 1057 s, 1022 s, 909 w, 836 sh, 802 vs [ρ(Si(CH$_3$)$_3$)], 753 w, 695 w, 661 w. – ^{1}H-NMR (C$_6$D$_6$): δ = 0.23 (s, 9H, SiMe$_3$), 0.37 (s, 9H, OSiMe$_3$), 0.41 (s, 9H, OSiMe$_3$), 1.29 (s, 9H, *t*Bu), 1.33 (s, 9H, *t*Bu), 4.25 (m, 2H, 4,5-H$_{\mathrm{Cp}}$), 4.35 (s, 1H, 2-H$_{\mathrm{Cp}}$). – ^{13}C{^{1}H}-NMR: δ = 0.96 [d, $^{3}J_{\mathrm{P,C}}$ = 4.8 Hz, CSi(*C*H$_3$)$_3$], 1.36 [s, OSi(CH$_3$)$_3$], 1.59 [s, OSi(CH$_3$)$_3$], 31.20 [s, C(*C*H$_3$)$_3$], 31.52 [s, *C*(CH$_3$)$_3$], 31.93 [s, C(*C*H$_3$)$_3$], 32.08 [s, *C*(CH$_3$)$_3$], 66.19 (s, C-2$_{\mathrm{Cp}}$), 67.21 (s, C-4$_{\mathrm{Cp}}$), 68.87 (s, C-5$_{\mathrm{Cp}}$), 77.87 [dd, $^{1}J_{\mathrm{P,C}}$ = 77.5; $^{2}J_{\mathrm{P,C}}$ = 15.3 Hz, *C*Si(CH$_3$)$_3$], 106.52 (s) and 108.15 (s, C-1,3$_{\mathrm{Cp}}$), 132.52 ("t", $^{2}J_{\mathrm{P,C}}$ = 4.6 Hz, PC*C*O), 135.93 (dd, $^{1}J_{\mathrm{P,C}}$ = 72.1; $^{2}J_{\mathrm{P,C}}$ = 17.4 Hz, PCO). – ^{31}P{^{1}H}-NMR (C$_6$D$_6$): δ = −64.75 (d, $^{1}J_{\mathrm{P,P}}$ = 381.4 Hz), −74.49 (d, $^{1}J_{\mathrm{P,P}}$ = 381.4 Hz). – MS/EI, *m/z*: 582 [M$^+$], 567 [M$^+$ – CH$_3$], 348 [(Me$_3$SiO)$_2$(Me$_3$Si)C$_3$P$_2^+$ – H], 233 [*t*Bu$_2$C$_5$H$_3$Fe$^+$], 202 [Me$_3$SiOCCOSiMe$_3^+$], 147 [P$_2$CSiMe$_3^+$], 73 [SiMe$_3^+$], 57 [*t*Bu$^+$]. – C$_{25}$H$_{48}$FeO$_2$P$_2$Si$_3$ (582.71): calcd. C 51.53, H 8.30; found C 50.60; H 8.01.

(η^5-1,3-tBu$_2$C$_5$H$_3$)(η^5-{1,2-[Fe$_2$(CO)$_7$]-3,4-(Me$_3$SiO)$_2$-5-(Me$_3$Si)P$_2$C$_3$})Fe (**6**): A slurry of 0.50 g (0.65 mmol) of **4b** and 0.47 g (1.30 mmol) of [Fe$_2$(CO)$_9$] in 8 ml of *n*-pentane was heated at 35°C until the ^{31}P resonance of the starting reactant had completely disappeared (^{31}P-NMR control! for ca. 2 d). The mixture was freed from volatile components, and the black residue was chromatographed on Florisil (column: *l* = 12 cm, *d* = 2 cm). With *n*-hexane as the eluant three zones developed. The eluate of the first dark green zone containing [Fe$_3$(CO)$_{12}$] was discarded. The eluate of the third dark red zone was evaporated to dryness. The black residue was crystallized from 4 ml of a 3:1 mixture of ether and *n*-pentane at +5°C. Yield: 0.35 g (62%) of red black crystalline **6**. – IR (cm^{-1}, KBr): $\tilde{\nu}$ = 2962 s [ν(CH)], 2908 m, 2866 sh, 2055 vs [ν(CO)], 2042 vs [ν(CO)], 1995 vs [ν(CO)], 1982 vs [ν(CO)], 1969 vs [ν(CO)], 1954 vs [ν(CO)], 1932 sh [ν(CO)], 1794 vs [ν(μ-CO)], 1463 s, 1376 s, 1256 m [δ(Si(CH$_3$)$_3$)], 1184 m, 1165 sh, 1063 m, 975 w, 895 w, 844 vs [ρ(Si(CH$_3$)$_3$)], 748 w, 732 w, 680 w, 620 m, 598 s, 581 m, 531 m, 483 w. – IR (cm^{-1}, *n*-C$_6$H$_{14}$): $\tilde{\nu}$ = 2056 s, 2023 s, 1994 s, 1984 sh, 1966 s, 1955 sh, 1793 m. – ^{1}H NMR (C$_6$D$_6$): δ = 0.13 (s, 9H, OSiMe$_3$), 0.45 (d, $J_{\mathrm{P,H}}$ = 1.7 Hz, 9H, CSiMe$_3$), 0.53 (s, 9H, OSiMe$_3$), 1.06 (s, 9H, *t*Bu), 1.09 (s, 9H, *t*Bu), 4.36 (m, 1H) and 4.54 (m, 1H, 4,5-H$_{\mathrm{Cp}}$), 4.93 (m, 1H, 2-H$_{\mathrm{Cp}}$). – ^{13}C{^{1}H}-NMR (C$_6$D$_6$): δ = 1.33 [s, CSi(*C*H$_3$)$_3$], 1.82 [s, OSi(CH$_3$)$_3$], 1.95 [s, OSi(CH$_3$)$_3$], 31.15 [s, C(*C*H$_3$)$_3$], 31.50 [s, *C*(CH$_3$)$_3$], 58.05 (s, C-2$_{\mathrm{Cp}}$), 69.85 (s, PC*C*O), 73.73 (d, $^{1}J_{\mathrm{P,C}}$ = 24 Hz, PCSi), 79.87 (s, C-4$_{\mathrm{Cp}}$), 84.05 (s, C-5$_{\mathrm{Cp}}$), 113.57 (d, $^{1}J_{\mathrm{P,C}}$ = 62 Hz, PCO), 117.07 (s, C-1,3$_{\mathrm{Cp}}$), 210.43 (s, CO), 211.54 (s, CO), 212.21 (s, CO), 216.71 (m, CO), 244.07 (s, μ-CO). – ^{31}P{^{1}H}-NMR (C$_6$D$_6$): δ = 69.17 (d, $^{1}J_{\mathrm{P,P}}$ = 276.6 Hz, 1 P, PCO), −162.70 (d, $^{1}J_{\mathrm{P,P}}$ = 276.6 Hz, 1 P, PCSi). – MS/EI, *m/z*: 582 [M$^+$ – Fe$_2$(CO)$_7$], 233 [*t*Bu$_2$C$_5$H$_3$Fe$^+$], 202 [Me$_3$SiOCCOSiMe$_3^+$], 168 [Fe(CO)$_4^+$], 147 [P$_2$CSiMe$_3^+$], 140 [Fe(CO)$_3^+$], 112 [Fe(CO$_2$)$^+$], 84 [Fe(CO)$^+$], 73 [SiMe$_3^+$], 57 [*t*Bu$^+$], 56 [Fe$^+$]. – C$_{32}$H$_{48}$Fe$_3$O$_9$P$_2$Si$_3$ (890.48): calcd. C 43.16, H 5.43; found C 42.82, H 5.27.

[(η^5-1,3-tBu$_2$C$_5$H$_3$)(η^5-{1-[Fe(CO)$_4$]-3,4-(Me$_3$SiO)$_2$-5-(Me$_3$Si)-P$_2$C$_3$}Fe (**7**): To a solution of 0.45 g (0.77 mmol) of **5** in 20 ml of *n*-pentane 0.23 g (1.16 mmol) of [Fe(CO)$_5$] was added. The stirred mixture was irradiated until the CO evolution had ceased (ca. 45 min). After filtration, the solution was concentrated to ca. 5 ml and stored at −30°C. A yield of 0.45 g (78%) of orange-red microcrystalline **7** was obtained. – IR (cm^{-1}, KBr): $\tilde{\nu}$ = 2960 m, [ν(CH)], 2908 sh, 2047 vs [ν(CO)], 1976 vs [ν(CO)], 1940 vs [ν(CO)], 1489 w, 1464 w, 1382 m, 1344 w, 1294 w, 1254 s, [δ(Si(CH$_3$)$_3$)], 1194 m, 1166 sh, 1055 m, 899 m, 846 s, [ρ(Si(CH$_3$)$_3$)], 754 m, 744 sh, 693 w, 680 w, 620 s, 566 w, 524 w, 491 w, 456 w. – IR (cm^{-1}, *n*-C$_6$H$_{14}$): $\tilde{\nu}$(CO) = 2050.7 s, 1979.1 s, 1954.3 vs, 1945.8 vs. – ^{1}H-NMR (C$_6$D$_6$): δ = 0.17 (s, 9H, Me$_3$SiO), 0.22 (s, 9H, CSiMe$_3$), 0.52 (s, 9H, OSiMe$_3$), 1.15 (s, 9H, *t*Bu), 1.40 (s, 9H, *t*Bu), 4.18 (m, 2H, 4,5-H$_{\mathrm{Cp}}$), 5.11 (m, 1H, 2-H$_{\mathrm{Cp}}$). – ^{13}C{^{1}H}-NMR (C$_6$D$_6$): δ = 0.69 [d, $^{3}J_{\mathrm{P,C}}$ = 6.5 Hz, CSi(*C*H$_3$)$_3$], 1.51 [s, OSi(CH$_3$)$_3$], 2.17 [d, $^{4}J_{\mathrm{P,C}}$ = 1.1 Hz, OSi(CH$_3$)$_3$, 31.02 [s, C(*C*H$_3$)$_3$], 31.81 [s, *C*(CH$_3$)$_3$], 32.03 [d, $^{4}J_{\mathrm{P,C}}$ = 3.7 Hz, C(*C*H$_3$)$_3$], 32.33 [s, *C*(CH$_3$)$_3$], 66.31 [dd, $^{1}J_{\mathrm{P,C}}$ = 53.4, $^{2}J_{\mathrm{P,C}}$ = 1.6 Hz, *C*Si(CH$_3$)$_3$], 66.41 (s, C-2$_{\mathrm{Cp}}$), 69.85 s and 69.96 (s, C-4,5$_{\mathrm{Cp}}$), 111.12 (s) and 111.32 (s, C-1,3$_{\mathrm{Cp}}$), 132.13 (s) and 132.40 [m, *C*OSi(CH$_3$)$_3$], 214.29 (dd, $^{2}J_{\mathrm{P,C}}$ = 19.5, $^{3}J_{\mathrm{P,C}}$ = 2.8 Hz, FeCO). – ^{31}P{^{1}H}-NMR (C$_6$D$_6$): δ = 26.16 (d, $^{1}J_{\mathrm{P,P}}$ = 426.4 Hz, P*P*Fe), −114.71 (d, $^{1}J_{\mathrm{P,P}}$ = 426.4 Hz, *P*PFe). – MS/EI, *m/z*: 582 [M$^+$ – Fe(CO)$_4$], 567 [M$^+$ – Fe(CO)$_4$ – CH$_3$], 233 [*t*Bu$_2$C$_5$H$_3$Fe$^+$], 202 [Me$_3$SiOCCOSiMe$_3^+$], 147 [P$_2$CSiMe$_3^+$], 112 [Fe(CO)$_2^+$], 84 [Fe(CO)$^+$], 73 [SiMe$_3^+$], 57 [*t*Bu$^+$], 56 [Fe$^+$]. – C$_{29}$H$_{48}$Fe$_2$O$_6$P$_2$Si$_3$ (750.60): calcd. C 46.41, H 6.45; found C 45.96, H 6.38.

(η^5-1,3-tBu$_2$C$_5$H$_3$)(η^5-{1-[Ni(CO)$_3$]-3,4-(Me$_3$SiO)$_2$-5-(Me$_3$Si)-P$_2$C$_3$})Fe (**8**): At room temp. a sample of 0.11 g (0.65 mmol) of [Ni(CO)$_4$] was added to a solution of 0.50 g (0.65 mmol) of **4b** in 15 ml of toluene while the red color of the mixture immediately darkened to red-black. After stirring of the mixture for 2 h all **4b** was consumed (^{31}P-NMR control!) and volatile components were removed in vacuo. The residue was crystallized from 3 ml of ether at −30°C. Yield 0.34 g (72%) of red crystalline **8**. – IR (cm^{-1}, KBr): $\tilde{\nu}$ = 2958 m [ν(CH)], 2905 w, 2070 vs [ν(CO)], 2004 vs [ν(CO)], 1992 vs [ν(CO)], 1377 m, 1357 m, 1254 m [δ(Si(CH$_3$)$_3$)], 1191 m, 1049 m, 903 m, 842 s [ρ(Si(CH$_3$)$_3$)], 819 sh, 753 m, 696 w, 557 w, 527 w, 445 m. – ^{1}H-NMR (C$_6$D$_6$): δ = 0.16 (s, 9H, OSiMe$_3$), 0.25 (s, 9H, CSiMe$_3$), 0.35 (s, 9H, OSiMe$_3$), 1.17 (s, 9H, *t*Bu), 1.21 (s, 9H, *t*Bu), 4.13 (m, 1H) and 4.19 (m, 1H, 4,5-H$_{\mathrm{Cp}}$), 4.45 (m, 1H, 2-H$_{\mathrm{Cp}}$). – ^{13}C{^{1}H}-NMR (C$_6$D$_6$): δ = 0.76 [s, CSi(*C*H$_3$)$_3$], 1.53 [s, OSi(CH$_3$)$_3$], 1.94 [s, OSi(CH$_3$)$_3$], 31.10 [s, C(*C*H$_3$)$_3$], 31.61 [s, *C*(CH$_3$)$_3$], 32.18 [s, C(*C*H$_3$)$_3$], 32.48 [s, *C*(CH$_3$)$_3$], 67.83 (s, C-2$_{\mathrm{Cp}}$), 68.67 (s) and 69.19 (s, C-4,5$_{\mathrm{Cp}}$), 70.04 (d, $^{1}J_{\mathrm{P,C}}$ = 38.5 Hz, *C*SiMe$_3$), 109.06 and 109.34 (s, C-1,3$_{\mathrm{Cp}}$), 129.27 (s, P*C*O),

132.59 (s, PC*C*O), 195.10 (s, CO). – $^{31}P\{^1H\}$-NMR (C_6D_6): $\delta = -27.9$ (d, $^1J_{P,P} = 409.5$ Hz, P*P*Ni), −100.8 (d, $^1J_{P,P} = 409.5$ Hz, *P*PNi). – MS/EI, *m/z*: 582 [$M^+ - Ni(CO)_3$], 567 [$M^+ - Ni(CO)_3 - CH_3$], 348 [$(Me_3SiO)_2(Me_3Si)C_3P_2^+$], 233 [$t\text{Bu}_2C_5H_3Fe^+$], 202 [$Me_3SiOCCOSiMe_3^+$], 147 [$P_2CSiMe_3^+$], 142 [$Ni(CO)_3^+$], 114 [$Ni(CO)_2^+$], 86 [$Ni(CO)^+$], 73 [$SiMe_3^+$], 57 [$t\text{Bu}^+$]. – $C_{28}H_{48}FeNiO_5P_2Si_3$ (725.43): calcd. C 46.35, H 6.63; found C 46.33, H 6.23.

Thermolysis of **8**: A slurry of 0.60 g (0.83 mmol) of **8** in 10 ml of *n*-pentane was heated at reflux for 2–3 h. Analogous work-up afforded 0.17 g (35%) of **5**.

Electrochemistry: Cyclic voltammetry was performed with EG & G electrochemical equipment as previously described (U. Kölle, *J. Organomet. Chem.* **1978**, *152*, 225). Solutions were kept 0.1 M in Bu_4NPF_6 and about 10^{-3} M in the respective sandwich complex. Potential was referenced to an aqueous SCE separated from the solution by a ceramic frit. In situ potential calibration was performed after completion of each measurement by recording the ferrocene$^{+/0}$ peak (0.385 V vs. SCE) in the same solution.

X-Ray Crystal Structure Analysis of **6**[30]: Single crystal from ether, 0.9 × 0.6 × 0.1 mm, $T = 293$ K, Siemens $P2_1$ diffractometer; Mo-K_α (graphite monochromator); $\lambda = 0.71073$ Å, empirical formula $C_{32}H_{48}Fe_3O_9P_2Si_3$, space group $P2_1/c$; unit cell dimensions: $a = 16.664(7)$, $b = 12.384(7)$, $c = 20.393(7)$ Å; $\beta = 92.55(3)°$; $d_{\text{calcd.}} = 1.407$ g cm^{-3}, $V = 4204(3)$ Å^3, $Z = 4$; $\mu(\text{Mo-}K_\alpha) = 1.228$ mm^{-1}; range for data collection: $3 \le 2\Theta \le 50°$; ω scan; index ranges: $0 \le h \le 19$, $0 \le k \le 14$, $-24 \le l \le 24$; reflections collected 7687; independent reflections 7419; parameters 452; 54 restraints for disordered $(CH_3)_3Si$ group of Si(2); absorptions correction: Semiempirical from ψ scans. Program used: SHELXTL-plus and SHELXL-93. Structure solution: direct methods; structure refinement: Full-matrix least-squares on F^2, $R_F = 0.086$, $wR_F^2 = 0.1994$ based on 3935 refl. with $I > 2\sigma(I)$, with $w = 1/[\sigma^2(F_o^2) + (0.1140\,P)^2]$ where $P = (F_o^2 + 2\,F_c^2)/3$.

X-Ray Crystal Structure Analysis of **8**[30]: Single crystal from ether, 0.8 × 0.6 × 0.2 mm, $T = 293$ K, Siemens $P2_1$ diffractometer; Mo-K_α (graphite monochromator); $\lambda = 0.71073$ Å, empirical formula $C_{28}H_{48}FeNiO_5P_2Si_3$, space group $P2_1/n$; unit cell dimensions: $a = 12.438(5)$, $b = 16.646(8)$, $c = 18.622(6)$ Å; $\beta = 100.69(3)°$; $d_{\text{calcd.}} = 1.272$ g cm^{-3}, $V = 3789(3)$ Å^3, $Z = 4$; $\mu(\text{Mo-}K_\alpha) = 1.090$ mm^{-1}; range for data collection: $3 \le 2\Theta \le 50°$; ω scan; index ranges: $0 \le h \le 14$, $0 \le k \le 19$, $-22 \le l \le 21$; reflections collected 7033; independent reflections 6705; parameters 376; absorption correction: Semiempirical from ψ scans. Programm used: SHELXTL-plus and SHELXL-93. Structure solution: direct methods; structure refinement: Full matrix least-squares on F^2, $R_F = 0.0655$, $wR_F^2 = 0.1367$ based on 3925 refl. with $I > 2\sigma(I)$, with $w = 1/[\sigma^2(F_o^2) + (0.0646\,P)^2 + 0.0000\,P]$ where $P = (F_o^2 + 2\,F_c^2)/3$.

[☆] Dedicated to Professor *Manfred Regitz* on the occasion of his 60th birthday.

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[30] Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-58889.

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