Notes

Transition-Metal-Substituted Diphosphenes. 33.[1] Preparation of the η^2-1,2-Diphosphaallyl Complex $(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})\overline{\text{FeP(SiMe}_3\text{)P}}{=}\text{C(SiMe}_3)_2$ and Reaction with Ni(CO)_4 and PMe_3. Formation of the η^3-Ferradiphosphaallyl Complex $[(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})(\mu\text{-CO})\overline{\text{FeP}{=}\text{PC(SiMe}_3)_3]\text{Ni}}(\text{CO})_2$

Lothar Weber* and Ralf Kirchhoff

Fakultät für Chemie der Universität Bielefeld, Universitätsstrasse 25,
D-33615 Bielefeld, Germany

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*Summary: Irradiation of the η^1-1,2-diphosphaallyl complex $(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{FeP(SiMe}_3)\text{P}{=}\text{C(SiMe}_3)_2$ (**1a**) afforded the η^2-diphosphaallyl complex $(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})\overline{\text{FeP(SiMe}_3)\text{P}}{=}\text{C(SiMe}_3)_2$ (**4**) with liberation of 1 equiv of CO. Thermolabile **4** was characterized in solution by spectroscopic means (IR; ^{1}H, ^{13}C, ^{31}P NMR) and by selected chemical reactions. Treatment of **4** with Ni(CO)_4 led to regeneration of **1a**, whereas the addition of PMe_3 induced a rearrangement to give the metallodiphosphene **8**. **8** was converted by an excess of Ni(CO)_4 to the complex $[(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})(\mu\text{-CO})\overline{\text{FeP—PC(SiMe}_3)_3]\text{Ni}}(\text{CO})_2$ (**9**). Structures for **8** and **9** are proposed on the basis of spectroscopic data and elemental analyses.*

The concepts of the diagonal relationship of C/P in the periodic table and of isoelectronic compounds proved to be fruitful in the synthetic design as well as in the understanding of the structures of many organophosphorus compounds and their transition-metal complexes.[2–4] Numerous phosphorus analogues of classical transition-metal π complexes demonstrate the exceptional ability of phosphorus to replace carbon in the skeleton of any typical unsaturated hydrocarbon π-complex.[2,5] For example, the thermal conversion of η^1-phosphaallyl complexes[4] as well as η^1-1,3-diphosphaallyl complexes[6] into the corresponding η^3 complexes parallels the familiar σ/π rearrangement of allyl complexes.

We recently synthesized 1-metalla-1,2-diphosphapropenes which formally may be regarded as η^1-1,2-diphosphaallyl complexes:[7,8]

$$\text{Cp}^*(\text{CO})_2\text{Fe}-\text{P(SiMe}_3)_2 \xrightarrow[-\ \text{Me}_3\text{SiCl}]{+\ \text{ClP}=\text{C(SiMe}_3)\text{R}} \text{Cp}^*(\text{CO})_2\text{Fe}-\text{P(SiMe}_3)\text{P}=\text{C(SiMe}_3)\text{R}$$

1a R = Me_3Si

1b R = Ph

In order to effect a σ/π rearrangement complex **1a** was heated in methylcyclohexane solution at 85 °C for 4 h. Instead of the expected η^3-1,2-diphosphaallyl complex **2**, compound **3** was formed as the result of the insertion of the P=C moiety into an aliphatic C—H bond of a ring methyl substituent.[8,9]

Under comparable conditions **1b** was isomerized to a metallodiphosphirane.[8] From this it is clear that a σ/π-1,2-diphosphaallyl rearrangement cannot be realized thermally. In this paper we describe the photolysis of **1a** and the reaction of the obtained product with Ni(CO)_4 and PMe_3.

Experimental Section

General Information. Standard inert-atmosphere techniques were used for the manipulation of all reagents and reaction products. Infrared spectra were recorded on a Mattson Polaris and modified Perkin-Elmer PE 238 grating spectrometer (FT-IR)/Atari 1040 STF. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were taken in C_6D_6 solution at 22 °C on Bruker AC 100 (^{1}H, 100.131 MHz; ^{13}C, 25.180 MHz; ^{31}P, 40.539 MHz) and Bruker AM 300 (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{31}P, 121.7 MHz) spectrometers. Spectral standards were SiMe_4 (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P). Electron impact mass spectra were recorded on a Varian MAT CH5-DF spectrometer (70 eV, 250 °C). Elemental analyses were obtained from the Microanalytical Laboratory KOLBE, Mülheim, Germany.

Materials. The compounds $(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{FeP(SiMe}_3)\text{P}{=}\text{C}$-

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[1] Part 32: Weber, L.; Buchwald, S.; Rühlicke, A.; Stammler, H.-G.; Neumann, B. *Z. Anorg. Allg. Chem.* **1993,** *619,* 934.

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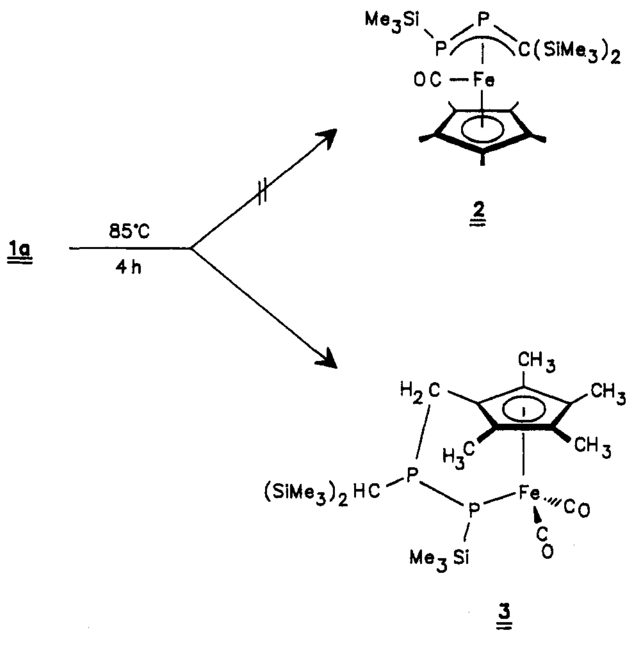


$(SiMe_3)_2$[7] and PMe_3[10] were prepared as described in the literature. $Ni(CO)_4$ was bought from Strem Chemicals. All solvents were rigorously dried with an appropriate drying agent and distilled before use.

Photolysis of (η^5-C_5Me_5)$(CO)_2$FeP($SiMe_3$)P=C($SiMe_3$)$_2$ (1a). A solution of 0.25 g (0.46 mmol) of **1a** in 2 mL of C_6D_6 was cooled to 0 °C and irradiated for 5 h by means of a 125-W mercury lamp. CO was freed and removed by pumping off repeatedly after every 30 min. The obtained solution of **4** was submitted to NMR spectroscopy. ^1H NMR: δ 0.34 (dd, $^3J_{PH}$ = 4.1, $^4J_{PH}$ = 0.3 Hz, 9H, $PSiMe_3$), 0.40 (d, $^4J_{PH}$ = 1.1 Hz, 9H, $CSiMe_3$), 0.40 (s, 9H, $CSiMe_3$), 1.65 (dd, $^4J_{PH}$ = 1.3, 0.7 Hz, 15H, C_5Me_5). $^{13}C\{^1H\}$ NMR: δ 2.7 (dd, $^2J_{PC}$ = 9.7, $^3J_{PC}$ = 2.1 Hz, $PSi(CH_3)_3$), 3.0 (dd, $^3J_{PC}$ = 5.0, $^4J_{PC}$ = 2.4 Hz, $CSi(CH_3)_3$), 3.1 (d, $^3J_{PC}$ = 8.5 Hz, $CSi(CH_3)_3$), 10.4 (dd, $^3J_{PC}$ = 5.4, 1.1 Hz, $C_5(CH_3)_5$), 91.9 (d, $^2J_{PC}$ = 0.5 Hz, $C_5(CH_3)_5$), 154.5 (dd, $^1J_{PC}$ = 61.4, $^2J_{PC}$ = 13.4 Hz, P=C), 223.8 (dd, $^2J_{PC}$ = 26.1, $^3J_{PC}$ = 1.8 Hz, FeCO). $^{31}P\{^1H\}$ NMR: δ −338.2 (d, $^1J_{PP}$ = 521.8 Hz, $PSiMe_3$), 409.1 (d, $^1J_{PP}$ = 521.8 Hz, P=C).

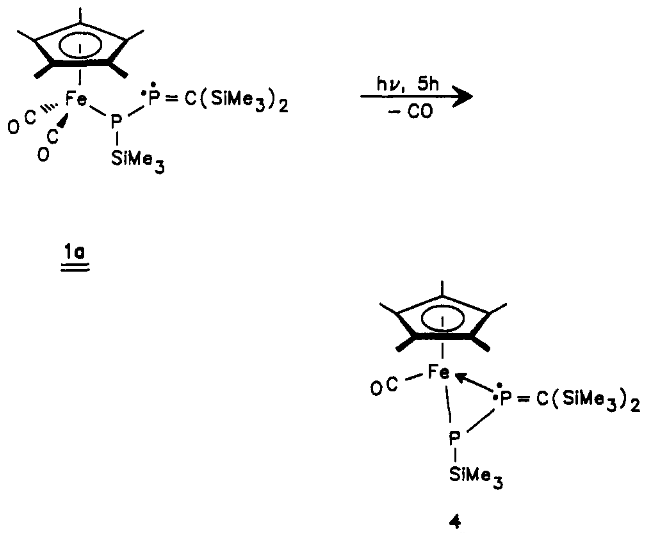
Reaction of 4 with $Ni(CO)_4$. A cooled solution (0 °C) of 5.35 g (9.90 mmol) of **1a** in 30 mL of *n*-pentane was irradiated over 5 h with permanent removal of carbon monoxide. The $^{31}P\{^1H\}$ NMR spectrum of the solution indicated complete conversion of **1a** to **4**. An IR spectrum of the solution shows one intense ν(CO) band at 1925 cm^{-1}. A solution of 2.82 g (16.5 mmol) of $Ni(CO)_4$ in 15 mL of *n*-pentane was added dropwise with stirring. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture was characterized by the resonances of **1a** and **4**. The formation of **1a** was completed after 2 h of stirring at 20 °C. The presence of minor impurities prevented the isolation of pure **1a**.

Preparation of (η^5-C_5Me_5)(CO)(PMe_3)FeP=PC($SiMe_3$)$_3$ (8). A solution of 3.25 g (6.34 mmol) of **1a** in 30 mL of *n*-pentane was irradiated as described before. To the obtained solution of **4** was added a solution of 0.50 g (6.57 mmol) of PMe_3 at 20 °C, and the mixture was stirred for 2 h. All volatiles were removed in vacuo. The dark residue was dissolved in 15 mL of *n*-pentane and stored at −30 °C. Recrystallization of the black precipitate from *n*-pentane yielded 1.38 g (37%) of black microcrystalline **8**. IR (KBr): δ 2974 s, 2949 s, 2906 s, 1917 vs [ν(CO)], 1481 w, 1420 w, 1376 m, 1280 m, 1249 s [$\delta(Si(CH_3)_3)$], 1025 w, 949 s, 950 s, 840 vs [$\rho(Si(CH_3)_3)$], 659 s cm^{-1}. ^1H NMR: δ 0.56 (s, 27H, $SiMe_3$), 0.94 (dd, $^2J_{PH}$ = 8.8, $^4J_{PH}$ = 0.3 Hz, 9H, PMe_3), 1.49 (m, C_5Me_5). $^{13}C\{^1H\}$ NMR: δ 5.44 (dd, $^3J_{PC}$ = 5.3, $^4J_{PC}$ = 3.9 Hz, $PSi(CH_3)_3$), 10.12 (d, $^3J_{PC}$ = 6.2 Hz, $C_5(CH_3)_5$), 18.53 (ddd, $^1J_{PC}$ = 27.3, $^2J_{PC}$ = 4.2, $^4J_{PC}$ = 1.9 Hz, $C(SiMe_3)_3$), 42.01 (ddd, $^1J_{PC}$ = 94.0, $^3J_{PC}$ = 2.7, $^4J_{PC}$ = 1.0 Hz, $P(CH_3)_3$), 93.27 (s, C_5Me_5), 220.97 (dd, $^2J_{PC}$ = 30.4, 16.8 Hz, FeCO). $^{31}P\{^1H\}$ NMR: δ 889.6 (dd, $^1J_{PP}$ = 672.0, $^2J_{PP}$ = 4.4 Hz, Fe–P), 570.4 (dd, $^1J_{PP}$ = 672.0, $^3J_{PP}$ = 4.4 Hz, $PCSi_3$), 24.3 ("t", $^2J_{PP}$ = 4.4 Hz, $P(CH_3)_3$). MS (EI): *m/z* 588 (M^+), 512 ($M^+ - PMe_3$), 484 ($M^+ - PMe_3 - CO$), 411 ($M^+ - PMe_3 - CO - SiMe_3$), 253 ($M^+ - PMe_3 - CO - C(SiMe_3)_3$), 191 ($C_5Me_5Fe^+$), 73 ($SiMe_3^+$). Anal. Calcd for $C_{24}H_{51}FeOP_3Si_3$ (M_r 588.7): C, 48.97; H, 8.73; Fe, 9.96. Found: C, 48.40; H, 9.18; Fe, 9.59.

[(η^5-C_5Me_5)(CO)(μ-CO)FeP=PC($SiMe_3$)$_3$]$Ni(CO)_2$ (9). A solution of 0.77 g (4.51 mmol) of $Ni(CO)_4$ in 10 mL of *n*-pentane was added at 20 °C to the solution of 1.25 g (2.12 mmol) of **7** in 20 mL of *n*-pentane. The mixture was stirred for 4 days at ambient temperature. Volatiles were removed in vacuo, and the oily black residue was dissolved in 10 mL of *n*-pentane. The solution was stored at −30 °C. Recrystallization of the black precipitate yielded 0.31 g (22%) of black crystalline **9**. IR (KBr): ν 2972 w, 2955 w, 2903 w, 2042 vs [ν(CO)], 1995 vs [ν(CO)], 1979 vs [ν(CO)], 1863 s [ν(CO)], 1487 w, 1474 w, 1457 w, 1429 w, 1380 m, 1258 s, 1249 s [$\delta(Si(CH_3)_3)$], 1029 m, 848 vs [$\rho(Si(CH_3)_3)$], 659 m, 568 m cm^{-1}. ^1H NMR: δ 0.52 (dd, $^4J_{PH}$ = 0.9, $^5J_{PH}$ = 0.4 Hz, 27H, $SiMe_3$), 1.37 (d, $^4J_{PH}$ = 0.5 Hz, 15H, C_5Me_5). $^{13}C\{^1H\}$ NMR: δ 5.3 (dd, $^3J_{PC}$ = 5.6, $^4J_{PC}$ = 3.3 Hz, $Si(CH_3)_3$), 8.9 (d, $^3J_{PC}$ = 7.4 Hz, $C_5(CH_3)_5$), 18.9 (d, $^1J_{PC}$ = 21.9 Hz, P–CSi_3), 96.9 (d, $^3J_{PC}$ = 0.8 Hz, $C_5(CH_3)_5$), 194.9 (d, $^2J_{PC}$ = 11.2 Hz, NiCO), 202.6 (d, $^2J_{PC}$ = 8.1 Hz, NiCO), 214.5 (d, $^2J_{PC}$ = 15.6 Hz, FeCO), 225.0 (d, $^2J_{PC}$ = 9.0 Hz, μ-CO). $^{31}P\{^1H\}$ NMR: δ 180.2 (d, $^1J_{PP}$ = 533.0 Hz, PC), 352.0 (d, $^1J_{PP}$ = 533.0 Hz, FeP). MS (CI): *m/z* 540 ($M^+ - Ni(CO)_2$), 512 ($M^+ - Ni(CO)_2 - CO$), 484 ($M^+ - Ni(CO)_2 - 2CO$), 247 ($C_5Me_5(CO)_2Fe^+$), 219 ($C_5Me_5(CO)Fe^+$), 191 ($C_5Me_5Fe^+$), 135 ($C_5Me_5^+$), 73 ($SiMe_3^+$). Anal. Calcd for $C_{24}H_{42}FeNiO_4P_2Si_3$ (M_r 655.4): C, 43.99; H, 6.46. Found: C, 43.84; H, 6.51.

Results and Discussion

Irradiation of a C_6D_6 solution of **1a** over 5 h led to the development of CO and a darkening of the reaction mixture. From the $^{31}P\{^1H\}$ NMR spectrum of the solution (δ −338.2 d and 409.1 d, $^1J_{PP}$ = 522 Hz) the formation of a η^3-diphosphaallyl complex has to be excluded. In such species both ^{31}P resonances are expected in the high-field region of the spectrum.



Unfortunately, all attempts to isolate the product of the photolysis **4** were thwarted by decomposition. Solutions of **4** in C_6H_6, methylcyclohexane, or *n*-pentane may be stored at −30 °C for a few days. At ambient temperatures they decompose completely within 12 h.

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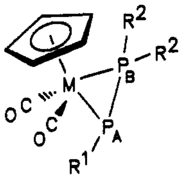
The characterization of 4 as an η^2 complex (or alternatively as a methyleneferradiphosphirane) was based on spectroscopic evidence and on the chemical behavior of the compound.

The IR spectrum of 4 in *n*-pentane displays one intense and sharp ν(CO) stretch at ν 1925 cm^{-1}. The ^{31}P{^{1}H} NMR spectrum is characterized by a doublet in the high-field region typical for three-membered rings (δ −338.2, PSiMe$_3$) and a second doublet in the low-field region of phosphaalkenes (δ 409.1, P=C; $^1J_{PP}$ = 521.8 Hz). The cyclization 1a → 4 is accompanied by a significant shielding for both phosphorus atoms ($\Delta\delta$ = −307.9 and −93.8, respectively). The PP coupling is markedly increased by the ring closure (ΔJ = 227 Hz). This may be mainly attributed to the rehybridization of both phosphorus atoms and, to a lesser extent, to multiple bonding.

Malisch[11] and Lindner[12] independently studied molecules of the type 5, the ^{31}P NMR parameters of which (**5a**, δ_P = −238.5, δ_P = 31.4, $^1J_{AB}$ = 498.0 Hz; **5b**, δ_P = −186.6, δ_P = 20.3, $^1J_{AB}$ = 472 Hz) are comparable with the data for 4. The considerably short P–P bond in **5b** (2.114(2) and 2.125(2) Å) parallels the high $^1J_{PP}$ coupling.[12a]



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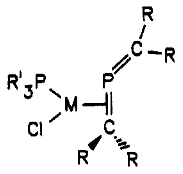
a) M = W; R^1 = Me; R^2 = Bu^t

b) M = Mo; R^1 = Ph; R^2 = Ph



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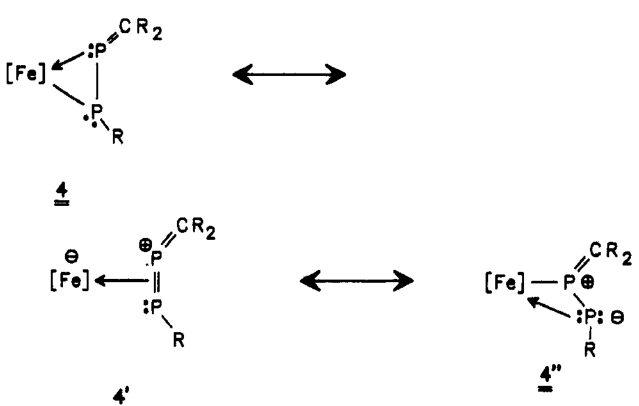
M = Ni ; R' = Et , Bu^n ; R = SiMe$_3$

M = Pt ; R' = Ph ; R = SiMe$_3$

A doublet of doublets at δ 154.5 ($^1J_{PC}$ = 61.4, $^2J_{PC}$ = 13.4 Hz) in the ^{13}C{^{1}H} NMR spectrum of 4 is in accord with the exocyclic P=C functionality.

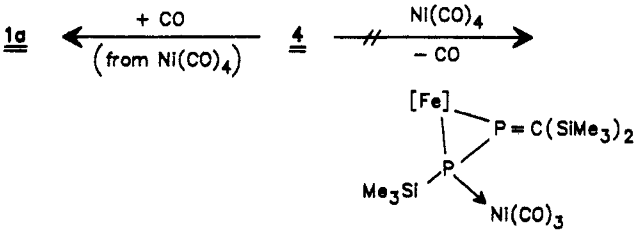
In keeping with this and with respect to the situation in 2-phosphonioallene complexes 6,[13] the bonding in 4 may be described by means of the three resonance formulas 4, 4′, and 4″. 4′ expresses the π interaction of a 1-phospha-2-phosphonioallene type ligand and a metalate, whereas 4″ displays a metallo(phosphinidene)methylenephosphorane type structure with an intramolecular stabilization of a coordinatively unsaturated metal atom by the phosphinidene center.



[Fe] = (η^5 − C$_5$Me$_5$)(CO)Fe

R = SiMe$_3$

We tried to stabilize the photolysis product by complexation with Ni(CO)$_3$. A large excess of Ni(CO)$_4$, however, did not furnish the expected adduct. Instead, the formation of 1a was observed. Obviously 4 suffers from an facile ring opening by CO, which is freed from decomposing Ni(CO)$_4$.



[Fe] = (η^5 − C$_5$Me$_5$)(CO)Fe

A different situation was encountered when in situ generated 4 was allowed to react with PMe$_3$ instead of CO. After 2 days compound 4 is completely converted into the metallodiphosphene 8, which was isolated as air- and moisture-sensitive black crystals (37% yield).

Complex 8 readily dissolves in *n*-pentane, benzene, and ether without decomposition. THF solutions of 8 decompose completely within 2 days.

The IR spectrum of 8 is dominated by an intense ν(CO) stretch at 1917 cm^{-1}. The position of this absorption is comparable with the ν(CO) band of 4.

The ^{31}P{^{1}H} NMR spectrum shows an AMX spin system with resonances at δ 889.6 and 570.4 for the phosphorus atoms of the P=P moiety ($^1J_{PP}$ = 672.0 Hz). Both nuclei are further coupled to the phosphorus of the PMe$_3$ ligand with the result of doublets of doublets ($^2J_{PP}$ = $^3J_{PP}$ = 4.4 Hz). A triplet at δ 24.3 is assigned to the PMe$_3$ group. Interestingly, the replacement of one CO ligand in (η^5-C$_5$Me$_5$)(CO)$_2$FeP=PC(SiMe$_3$)$_3$ by PMe$_3$ causes a marked deshielding of the metalated phosphorus ($\Delta\delta$ = 101.4), whereas the alkylated P atom experiences a high-field shift of only $\Delta\delta$ = 31.9 ppm.

There is no spectroscopic evidence for the intermediacy of the metallodiphosphapropene 7 at any time of the reaction. Obviously the severe steric congestion at the metalated phosphorus in 7 is relieved by the 1,3-silyl migration from phosphorus to carbon with the formation of 8. A similar rearrangement was invoked for the

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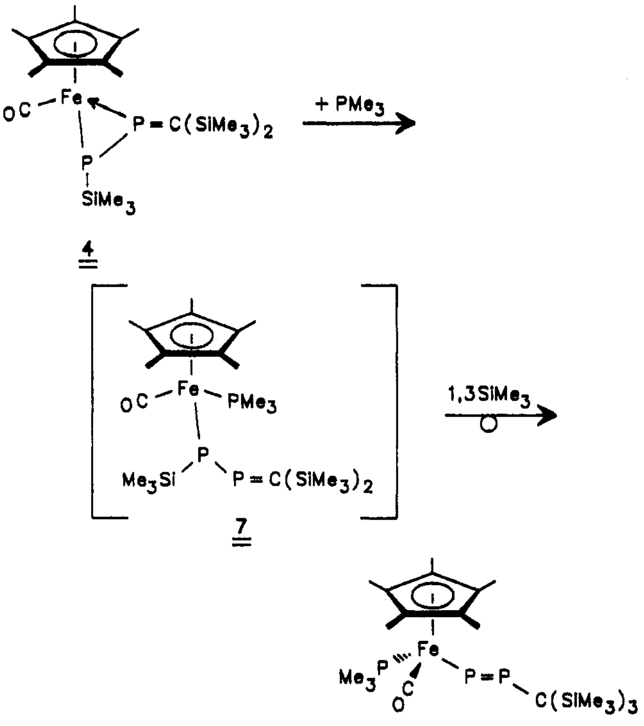

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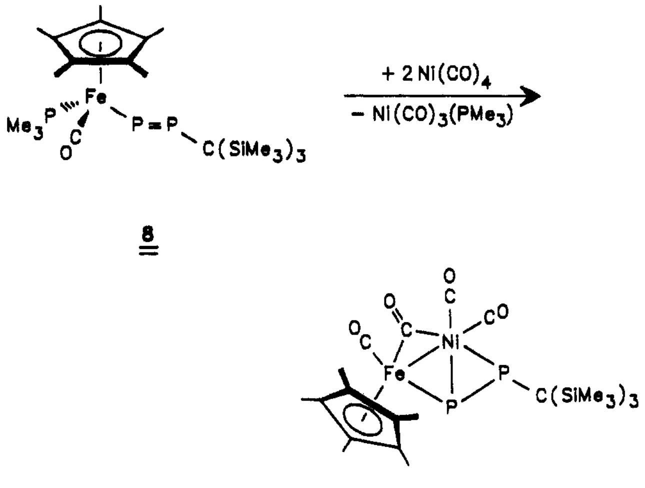
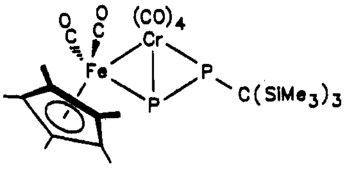
8



8

9



10

generation of Mes*P=PC(SiMe$_3$)$_3$ from LiP(SiMe$_3$)Mes* and ClP=C(SiMe$_3$)$_2$.[14]

In order to test the ligating properties of 8, the compound was allowed to react with an excess of Ni(CO)$_4$ in *n*-pentane. After 4 days the $^{31}P\{^1H\}$ NMR spectrum of the black reaction mixture showed doublets at δ 352.0 and 180.2 ($^1J_{PP}$ = 532.8 Hz) in addition to a singlet at δ −18.8. The last signal is readily assigned to the nickel phosphane complex Ni(CO)$_3$PMe$_3$ by comparison with data given in the literature.[15] The doublets are due to the black microcrystalline compound 9, which was isolated in 22% yield. The air- and moisture-sensitive solid is soluble in *n*-pentane, methylcyclohexane, benzene, and ether. Solutions of 9 completely decompose within a few days.

The IR spectrum of 9 shows four intense bands in the region for carbonyl ligands. A band at ν 1863 cm^{-1} is assigned to an edge-bridging CO ligand, whereas the absorptions at ν 2042 and 1995 cm^{-1} are caused by the terminal CO ligands of the Ni(CO)$_2$ moiety. A band at ν 1979 cm^{-1} is due to the ν(CO) stretch of the Fe(CO) unit.

The doublets in the $^{31}P\{^1H\}$ NMR spectrum indicate a η^3 coordination of the metallodiphosphene to the carbonylnickel fragment. A similar situation was previously seen with molecule 10 (δ 431.5 d, Fe–P, 134.9 d, P–C; $^1J_{PP}$ = 524 Hz).[7] In terms of the Wade–Mingos rules both compounds may also be considered as arachno complexes featuring 42 valence electrons.[16]

An X-ray crystal structure analysis of 9 was tried with small platelets grown from *n*-pentane at −30 °C. Unfortunately, the poor quality of the crystals did not allow a satisfactory refinement of the structure. Preliminary data, however, underline the proposed geometry of the molecule.

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