

Transition metal-substituted phosphalkenes and acylphosphanes. XXIX. ¹ Metallophosphalkene ($\eta^5\text{-C}_5\text{Me}_5$)(CO)₂FeP=C(NMe₂)₂, a versatile molecule in coordination chemistry

Lothar Weber^{*}, Olaf Kaminski, Beate Quasdorff, Hans-Georg Stammler, Beate Neumann

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

Received 19 March 1996; revised 9 May 1996

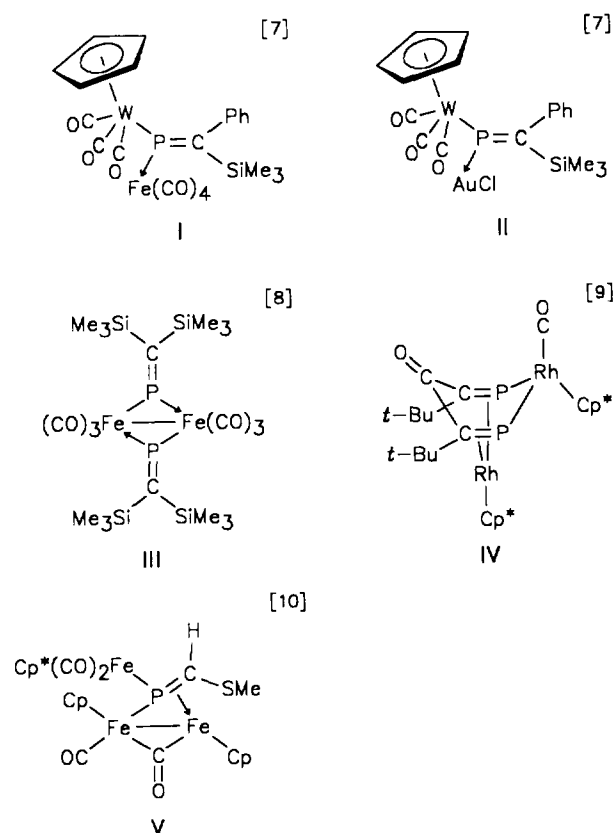
Abstract

The metallophosphalkene ($\eta^5\text{-C}_5\text{Me}_5$)(CO)₂FeP=C(NMe₂)₂ (**2**) undergoes reaction with isocyanides to afford complexes ($\eta^5\text{-C}_5\text{Me}_5$)(CO)(RNC)Fe–P=C(NMe₂)₂ (**4a**: R = 2,6-Me₂C₆H₃; **4b**: ¹Bu; **4c**: *c*-C₆H₁₁). Compound **2** is converted into its [(CO)₃Ni]-adduct ($\eta^5\text{-C}_5\text{Me}_5$)(CO)₂Fe–P[Ni(CO)₃]=C(NMe₂)₂ (**5**) by exposure to Ni(CO)₄. In contrast, condensation of one ring methyl group is observed during reaction of **2** with [(*Z*)-cyclooctene]Cr(CO)₅ to yield $\eta^5\text{-C}_5\text{Me}_4\text{CH}=\text{C}(\text{NMe}_2)\text{PH}[\text{Cr}(\text{CO})_5]\text{-Fe}(\text{CO})_2$ (**8**). Irradiating an equimolar mixture of **2** and Fe₂(CO)₉ furnishes complex $\eta^2\text{-}(\text{C.P})[\eta^5\text{-C}_5\text{Me}_5(\text{CO})_2\text{Fe-P}[\text{C}(\text{O})\text{NMe}_2]\text{CNMe}_2]\text{Fe}(\text{CO})_3$ (**10**) containing a phosphinocarbene ligand. The molecular structures of **4a**, **5**, **8** and **10** are established by single crystal X-ray analysis.

Keywords: Metallophosphalkene; Coordination chemistry; Metal carbonyls; Isocyanides; Phosphinocarbene complex

1. Introduction

The reactivity of metallophosphalkenes such as ($\eta^5\text{-C}_5\text{Me}_5$)(CO)₂FeP=C(SiMe₃)₂ (**1**) and ($\eta^5\text{-C}_5\text{Me}_5$)(CO)₂FeP=C(NMe₂)₂ (**2**) has attracted considerable interest over the last few years [2]. Compound **1** undergoes [2 + 1]-cycloadditions with isocyanides to afford metal-functionalized phosphiranes [3], whereas **2** is involved in [2 + 2]-cycloadditions with electron-deficient alkenes [4]. With alkyl diazoacetates, [2 + 3]-cycloadditions are observed [5]. A sequence of [2 + 2]-cycloadditions, cycloreversions and Diels–Alder reactions occurs with a variety of electrophilic alkynes [1,6]. Owing to the presence of donor sites at the phosphorus atom and at the PC π-bond, metallophosphalkenes, like classical phosphalkenes R¹P=CR²R³ (with R¹, R², R³ organosubstituents), should exhibit excellent ligating properties. Moreover, it is conceivable that ligand displacement processes at the metal center of **1** or **2** may also occur. Information on the coordination chemistry of metallophosphalkenes of the type L_{*n*}MP=CR¹R² is scarce, and comprises complexes I–V [7–10].



^{*} Corresponding author.

¹ XXVIII see Ref. [1].

We have therefore started a systematic investigation of the coordination chemistry displayed by such molecules.

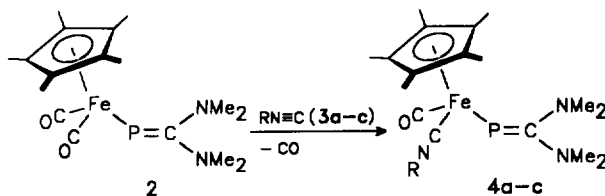
Here we report on carbonyl/isocyanide exchange reactions encountered with **2**, as well as on the ligand behavior of **2** towards binary metal carbonyls.

2. Results and discussion

2.1. CO / isocyanide exchange reactions

Contrary to **1**, the metallophosphaalkene (η^5 -C₅Me₅)(CO)₂FeP=C(NMe₂)₂ (**2**) [4] reacts with equimolar amounts of the isocyanides RN≡C (**3a–c**; **3a**: R = 2,6-Me₂C₆H₃; **4b**: ^tBu; **4c**: *c*-C₆H₁₁) [11] to give the isocyanide-functionalized metallophosphaalkenes (η^5 -C₅Me₅)(CO)(RNC)FeP=C(NMe₂)₂ (**4a–c**) by substitution of one carbonyl ligand. Complex **4a** is isolated as

dark red crystals, while **4b** and **4c** are obtained as dark red air- and moisture-sensitive oils.



3,4	R
a	2,6-Me ₂ C ₆ H ₃
b	^t -Bu
c	<i>c</i> -C ₆ H ₁₁

Table 1
Crystallographic details for **4a**, **5**, **8** and **10**

	4a	5	8	10
Empirical formula	C ₂₅ H ₃₆ FeN ₃ OP	C ₂₀ H ₂₇ FeN ₂ NiO ₅ P	C ₂₀ H ₂₀ CrFeNO ₇ P	C ₂₁ H ₂₇ Fe ₂ N ₂ O ₆ P
<i>M_r</i>	481.39	520.97	525.19	546.12
Color	dark red	black	yellow	dark red plates
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	36.86(2)	16.822(6)	10.337(4)	18.011(9)
<i>b</i> (Å)	8.388(3)	9.020(3)	10.868(5)	9.000(5)
<i>c</i> (Å)	18.389(7)	17.411(4)	12.488(7)	17.619(9)
α (°)	90	90	105.53(4)	90
β (°)	115.15(3)	113.86	100.97(4)	119.19(13)
γ (°)	90	90	115.14(3)	90
<i>V</i> (Å ³)	5147(4)	2416.1(13)	1146.9(9)	2493
<i>Z</i>	8	4	2	4
<i>D_c</i> (g cm ⁻³)	1.242	1.432	1.521	1.455
μ (mm ⁻¹)	0.669	1.477	1.215	1.265
<i>F</i> (000)	2048	1080	536	1128
Crystal size (mm ³)	1.0 × 0.70 × 0.30	0.50 × 0.30 × 0.10	0.60 × 0.40 × 0.30	0.60 × 0.40 × 0.05
Collection range, 2 θ _{max} (°)	55	55	55	50
	0 ≤ <i>h</i> ≤ 47	0 ≤ <i>h</i> ≤ 21	0 ≤ <i>h</i> ≤ 13	-21 ≤ <i>h</i> ≤ 18
	0 ≤ <i>k</i> ≤ 10	0 ≤ <i>k</i> ≤ 11	-14 ≤ <i>k</i> ≤ 12	-10 ≤ <i>k</i> ≤ 0
	-23 ≤ <i>l</i> ≤ 23	-22 ≤ <i>l</i> ≤ 20	-16 ≤ <i>l</i> ≤ 15	0 ≤ <i>l</i> ≤ 20
Scan speed (° min ⁻¹)	3.9–29.3	3.9–29.3	3.9–29.3	3.9–29.3
Independent reflections	5916	5555	5287	4309
No. of parameters	241	275	360	298
Absorption correction	semi-empirical from ψ -scans	semi-empirical from ψ -scans	none	semi-empirical from ψ -scans
<i>R_F</i> for reflections with <i>I</i> > 2 σ (<i>I</i>)	0.062 (for 4606 reflections)	0.063 (for 3110 reflections)	0.034 (for 4194 reflections)	0.064 (for 2494 reflections)
<i>R_F</i> ² for reflections with <i>I</i> > 2 σ (<i>I</i>)	0.1767	0.1225	0.076	0.1443
Goodness of fit	1.505	1.065	1.166	1.024
Residual electron density (e Å ⁻³)	1.2	0.5	0.5	0.7
Treatment of hydrogen atoms	riding model	riding model	refined isotropically	riding model

For all compounds: Siemens P2₁ diffractometer, temperature 173.2 K, Mo K α radiation ($\lambda = 0.71073$ Å), structure solution and refinement with program packages SHELXTL-PLUS and SHELXL-93, full-matrix least-squares refinement on *F*². All non-hydrogen atoms refined anisotropically (except the disordered Cp ligand of **4a**).

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the products display singlets at $\delta = 167.1\text{--}170.5$ ppm, which appear at markedly lower field than in precursor **2** ($\delta = 135.5$ ppm). The doublet of the ^{13}C nucleus of the P=C bond of **2** ($\delta = 202.4$ ppm; $^1J_{\text{PC}} = 97.0$ Hz) is slightly shielded in **4a–c** ($\delta = 200.3\text{--}200.7$ ppm, $^1J_{\text{PC}} = 95.5\text{--}97.1$ Hz). Downfield shifts are observed for the remaining carbonyl ligand of the isocyanide complexes [$\delta = 222.3\text{--}222.9$ ppm (s)] compared with **2** ($\delta^{13}\text{CO} = 220.3$ ppm). In line with an effective backbonding, ligation of the isocyanides to the electron-rich fragment $[(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})\text{FeP}=\text{C}(\text{NMe}_2)_2]$ is accompanied by a significant deshielding of the carbon atoms of the CN multiple bond ($\Delta^{13}\text{C} = 20.6\text{--}24.0$ ppm) [12,13]. Consis-

Table 2

Atomic coordinates ($\times 10^4$) and isotropic displacement parameters U_{iso} or U_{eq}^a [$\text{\AA}^2 \times 10^3$] for **4a**

Atom	x	y	z	U_{eq}
Fe(1)	931(1)	989(1)	1863(1)	27(1)
P(1)	1229(1)	3474(1)	2157(1)	32(1)
O(1)	829(1)	452(3)	3316(1)	49(1)
N(1)	1525(1)	5480(3)	3440(2)	37(1)
N(2)	961(1)	4079(4)	3331(2)	42(1)
N(3)	1779(1)	-14(3)	2643(2)	37(1)
C(1)	313(1)	711(4)	1063(2)	32(1)
C(2)	497(1)	-805(3)	1217(2)	33(1)
C(3)	808(1)	-780(3)	958(2)	33(1)
C(4)	815(1)	751(3)	644(2)	36(2)
C(5)	509(1)	1672(3)	709(2)	37(1)
C(6)	-31(1)	1212(6)	1244(3)	77(3)
C(7)	384(1)	-2198(5)	1590(3)	66(2)
C(8)	1082(1)	-2142(5)	1008(3)	54(2)
C(9)	1097(1)	1302(5)	302(3)	53(2)
C(10)	409(1)	3375(5)	447(3)	68(2)
C(1A)	333(1)	1451(5)	921(3)	36(2)
C(2A)	390(1)	-169(5)	1150(2)	36(2)
C(3A)	709(1)	-759(5)	995(2)	32(2)
C(4A)	849(1)	497(5)	670(2)	42(3)
C(5A)	616(1)	1862(5)	624(2)	31(2)
C(6A)	24(2)	2544(8)	982(4)	94(4)
C(7A)	153(2)	-1101(8)	1497(4)	94(4)
C(8A)	871(2)	-2428(7)	1148(4)	63(3)
C(9A)	1185(2)	397(8)	417(4)	60(3)
C(10A)	662(2)	3469(7)	314(4)	72(3)
C(11)	877(1)	765(4)	2749(2)	33(1)
C(12)	1231(1)	4344(4)	2999(2)	32(1)
C(13)	1387(1)	6981(4)	3624(2)	55(1)
C(14)	1873(1)	5647(5)	3273(2)	48(1)
C(15)	1087(1)	3914(6)	4184(2)	63(1)
C(16)	539(1)	4119(5)	2847(3)	55(1)
C(17)	1446(1)	397(4)	2344(2)	31(1)
C(18)	2180(1)	-293(4)	3136(2)	36(1)
C(19)	2329(1)	155(4)	3941(2)	40(1)
C(20)	2733(1)	-154(5)	4407(2)	56(1)
C(21)	2971(1)	-830(6)	4096(3)	65(1)
C(22)	2815(1)	-1281(5)	3294(2)	55(1)
C(23)	2417(1)	-1004(4)	2799(2)	39(1)
C(24)	2068(1)	929(5)	4269(2)	50(1)
C(25)	2240(1)	-1456(5)	1927(2)	52(1)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3

Selected bond lengths (\AA) and angles ($^\circ$) for **4a**

Fe(1)–C(11)	1.733(3)	Fe(1)–C(17)	1.792(3)
P(1)–C(12)	1.708(3)	O(1)–C(11)	1.158(4)
N(1)–C(12)	1.411(4)	N(1)–C(14)	1.447(4)
N(1)–C(13)	1.450(5)	N(2)–C(12)	1.389(4)
N(2)–C(16)	1.427(5)	N(2)–C(15)	1.442(5)
N(3)–C(17)	1.166(4)	N(3)–C(18)	1.386(4)
C(11)–Fe(1)–C(17)	91.5(2)	C(12)–P(1)–Fe(1)	114.55(11)
C(12)–N(1)–C(14)	118.4(3)	C(12)–N(1)–C(13)	117.5(3)
C(14)–N(1)–C(13)	113.2(3)	C(12)–N(2)–C(16)	121.1(3)
C(12)–N(2)–C(15)	122.4(3)	C(16)–N(2)–C(15)	116.1(3)
C(17)–N(3)–C(18)	167.5(3)	O(1)–C(11)–Fe(1)	172.8(3)
N(2)–C(12)–N(1)	111.9(3)	N(2)–C(12)–P(1)	127.0(2)
N(1)–C(12)–P(1)	121.1(2)	N(3)–C(17)–Fe(1)	178.4(3)

tently, the C \equiv N stretching vibration of free **3a** ($\nu = 2119.2\text{ cm}^{-1}$) [14] is shifted by 56 cm^{-1} to lower wavenumbers upon complexation. An intense band at $\nu = 1911\text{ cm}^{-1}$ is assigned to the CO stretching vibration of **4a**. In **4b** and **4c** the bathochromic shifts of the CN stretching vibrations are much less pronounced ($\Delta\nu = 12\text{ cm}^{-1}$).

2.1.1. X-ray structural analysis of **4a**

Molecule **4a** (Tables 1–3; Fig. 1) is best described as having a distorted ‘piano-stool’ geometry with three different legs [P(1)–Fe(1)–C(11) = $96.4(1)^\circ$; P(1)–Fe(1)–C(17) = $80.5(1)^\circ$; C(11)–Fe(1)–C(17) = $91.5(2)^\circ$]. One leg is represented by a non-linear terminal CO ligand [Fe(1)–C(11)–O(1) = $172.8(3)^\circ$], the iron–carbon bond length of which [Fe(1)–C(1) = $1.733(3)\text{ \AA}$] is significantly shorter than the respective contact to the isocyanide ligand [Fe(1)–C(17) = $1.792(3)\text{ \AA}$]. [In $\text{Fe}_2(\text{CNET})_9$ the Fe–C bond lengths to the terminal ligands range from $1.818(14)$ to $1.854(10)\text{ \AA}$, see Ref. [15]; in *cis*- $\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{CN}^t\text{Bu})$ the bond distances Fe–C(CO) and FeC(CN t Bu) amount to $1.73(1)$ and $1.81(1)\text{ \AA}$ respectively, see Ref. [16].] Whereas the arrangement Fe(1)–C(17)–N(3) appears to be linear [Fe(1)–C(17)–N(3) = $178.4(3)^\circ$], there is a considerable deviation from linearity at N(3) [C(17)–N(3)–C(18) = $167.5(3)^\circ$]. Similar observations are made in $[(\eta^5\text{-C}_6\text{H}_5\text{CO}_2\text{Me})\text{Cr}(\text{CO})_2\{\text{CNC}(\text{O})\text{Ph}\}]$, where the CNC angle is $168(1)^\circ$ [17]. The phosphalkenyl ligand is attached to the metal center via an Fe–P single bond of length $2.311(1)\text{ \AA}$. This distance corresponds to that in **2** [$2.325(2)\text{ \AA}$] and falls in the usual range for iron–phosphorus bond lengths determined in low-valent carbonyliron complexes [$2.12\text{--}2.39\text{ \AA}$] [18]. The structural features within the phosphalkenyl ligands of **4a** and **2** are closely related to each other. Thus, the P=C bond in **4a** [$1.708(3)\text{ \AA}$] remains unchanged [$1.709(5)\text{ \AA}$ in **2**] and falls in the typical region of $1.70\text{--}1.76\text{ \AA}$ for amino-functionalized phosphalkenes [19]. The valence angle at the dicoordinate phosphorus atom of **4a** is

slightly compressed [114.55(11)°] in comparison with the respective angle in **2** [117.9(2)°]. The atom N(2) at the planar carbon atom C(12) in *cis* position to Fe(1) is planar in contrast to N(1), which is slightly pyramidally configured (sum of angles 349.1°). Atoms N(1) and N(2) are displaced from the plane defined by the atoms Fe(1), P(1) and C(12) by 0.5250 and -0.4926 Å, respectively. In order to avoid steric encumbrance between the two bulky ligands, the phosphalkenyl unit is twisted away from the *o*-xylyl ring, as reflected by the torsion angles C(12)–P(1)–Fe(1)–C(11) = -8.8° and C(12)–P(1)–Fe(1)–C(17) = -99.9° . In **2** these angles are determined as 22.7 and -75.4° respectively.

The C₅Me₅ ring of **4a** is disordered, the occupation being 57:43. Ring C(1A)–C(5A) is refined as an ideal five-membered ring with a C–C bond length of 1.412 Å.

2.2. Reaction of **2** with metal carbonyls

2.2.1. With Ni(CO)₄

Treatment of equimolar amounts of **2** and tetracarbonylnickel in *n*-pentane in the temperature range -30 to 25°C affords the tricarbonylnickel adduct **5** as black air- and temperature-sensitive crystals. In the IR spectrum of the complex (C₆D₆ solution), intense carbonyl bands at $\nu = 2038$ and 1958 cm^{-1} are assigned to the [Ni(CO)₃] group having the local symmetry of the point group C_{3v}. These absorptions are markedly shifted to lower wavenumbers than those of complex (CO)₃Ni[P(^tBu)₃] (2056.1, 1971.0 cm⁻¹ [20]). This indicates a remarkable charge transfer from the metallophosphaalkene to the [Ni(CO)₃]-unit. A similar situation is present in the anion { μ -PPh₂[Ni(CO)₃]₂}⁻ ($\nu(\text{CO})(\text{THF}) = 2039$ w, 2019 s, 1960 vs cm⁻¹) [21]. The terminal carbonyl ligands at the [Cp(CO)₂Fe] group give rise to strong absorptions at $\nu = 1979$ and 1925 cm^{-1} , which are close to those in **2** ($\nu(\text{CO}) = 1975, 1925\text{ cm}^{-1}$).

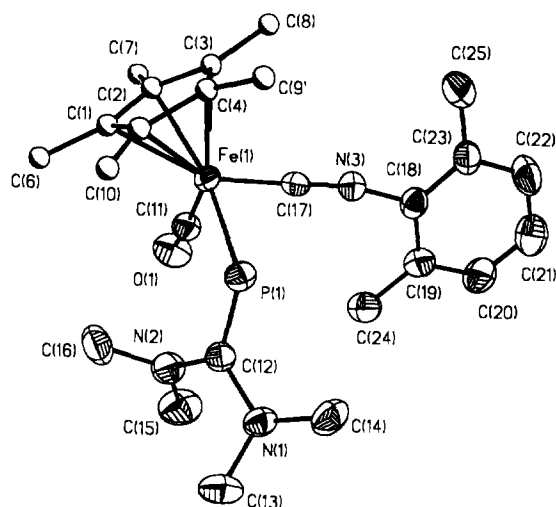


Fig. 1. Molecular structure of **4a** in the crystal.

Table 4

Atomic coordinates ($\times 10^4$) and isotropic displacement parameters U_{iso} or U_{eq}^a [$\text{\AA}^2 \times 10^3$] for **5**

Atom	x	y	z	U_{eq}
Ni(1)	2335(1)	2436(1)	5915(1)	50(1)
Fe(1)	1971(1)	531(1)	3660(1)	30(1)
P(1)	2766(1)	806(2)	5100(1)	37(1)
O(1)	1429(3)	3605(4)	3418(3)	56(1)
O(2)	3530(2)	679(4)	3335(2)	52(1)
O(3)	556(3)	3410(6)	4904(3)	84(2)
O(4)	3548(3)	4942(6)	6343(3)	86(2)
O(5)	2467(4)	501(6)	7304(3)	90(2)
N(1)	4166(3)	2384(5)	4995(3)	47(1)
N(2)	4465(3)	989(5)	6174(3)	49(1)
C(1)	1814(3)	-1801(5)	3563(3)	37(1)
C(2)	1519(3)	-1136(6)	2738(3)	38(1)
C(3)	836(3)	-165(5)	2650(3)	38(1)
C(4)	694(3)	-218(6)	3402(3)	39(1)
C(5)	1280(3)	-1247(6)	3952(3)	38(1)
C(6)	2503(4)	-2961(6)	3920(4)	63(2)
C(7)	1842(4)	-1502(7)	2068(4)	59(2)
C(8)	315(4)	737(7)	1886(3)	60(2)
C(9)	-48(4)	559(7)	3529(5)	69(2)
C(10)	1306(5)	-1737(8)	4792(4)	69(2)
C(11)	1671(3)	2402(6)	3537(3)	37(1)
C(12)	2922(3)	663(5)	3481(3)	37(1)
C(13)	3843(3)	1467(5)	5423(3)	38(1)
C(14)	3656(4)	3606(6)	4478(4)	53(2)
C(15)	5044(4)	2244(7)	5014(5)	67(2)
C(16)	5106(4)	2022(7)	6749(4)	78(2)
C(17)	4337(4)	-313(8)	6604(4)	68(2)
C(18)	1249(5)	3014(8)	5289(4)	64(2)
C(19)	3076(5)	3954(8)	6191(4)	61(2)
C(20)	2405(4)	1295(8)	6768(4)	65(2)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Upon complexation of the metallophosphaalkene to the [Ni(CO)₃] moiety its ³¹P NMR resonance is strongly shielded ($\Delta\delta = 120$ ppm). Usually, η^1 -coordination of phosphalkenes is accompanied by small downfield shifts ($\Delta\delta < 20$ ppm) [22–24].

The ¹³C{¹H} NMR spectrum of **5** shows a doublet at $\delta = 208.1$ ($^1J_{\text{PC}} = 77$ Hz) for the methylene carbon atom. In precursor **2** the respective signal is observed at $\delta = 202.4$ (d, $^1J_{\text{PC}} = 97.0$ Hz). A doublet at $\delta = 199.5$ ($^2J_{\text{PC}} = 7.0$ Hz) is due to the carbonyls at the nickel atom, while two singlets at $\delta = 219.65$ and 219.71 are attributed to the [Fe(CO)₂]-unit.

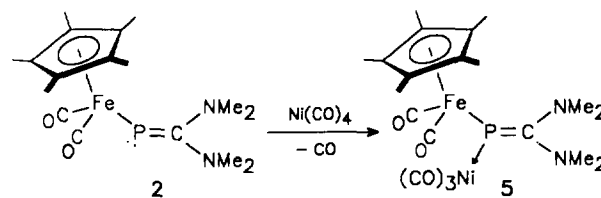


Table 5
Selected bond lengths (Å) and angles (°) for **5**

Ni(1)–C(20)	1.771(7)	Ni(1)–C(19)	1.782(8)
Ni(1)–C(18)	1.785(7)	Ni(1)–P(1)	2.352(2)
Fe(1)–C(11)	1.750(5)	Fe(1)–C(12)	1.753(5)
Fe(1)–P(1)	2.329(2)	P(1)–C(13)	1.770(5)
O(1)–C(11)	1.147(6)	O(2)–C(12)	1.148(6)
O(3)–C(18)	1.142(7)	O(4)–C(19)	1.151(8)
O(5)–C(20)	1.184(7)	N(1)–C(13)	1.364(7)
N(1)–C(14)	1.462(6)	N(1)–C(15)	1.468(7)
N(2)–C(13)	1.373(6)	N(2)–C(17)	1.454(7)
N(2)–C(16)	1.470(7)		
C(20)–Ni(1)–C(19)	114.7(3)	C(20)–Ni(1)–C(18)	112.7(3)
C(19)–Ni(1)–C(18)	111.8(3)	C(20)–Ni(1)–P(1)	102.2(2)
C(19)–Ni(1)–P(1)	106.9(2)	C(18)–Ni(1)–P(1)	107.7(2)
C(11)–Fe(1)–C(12)	98.8(2)	C(11)–Fe(1)–P(1)	92.3(2)
C(12)–Fe(1)–P(1)	91.0(2)	C(13)–P(1)–Fe(1)	116.5(2)
C(13)–P(1)–Ni(1)	97.1(2)	Fe(1)–P(1)–Ni(1)	122.26(6)
C(13)–N(1)–C(14)	121.9(5)	C(13)–N(1)–C(15)	123.7(5)
C(14)–N(1)–C(15)	114.4(5)	C(13)–N(2)–C(17)	122.0(5)
C(13)–N(2)–C(16)	121.1(5)	C(17)–N(2)–C(16)	112.5(5)
C(10)–C(5)–Fe(1)	129.6(4)	O(1)–C(11)–Fe(1)	176.0(5)
O(2)–C(12)–Fe(1)	176.1(5)	N(1)–C(13)–N(2)	113.1(5)
N(1)–C(13)–P(1)	127.8(4)	N(2)–C(13)–P(1)	119.0(4)
O(3)–C(18)–Ni(1)	178.3(6)	O(4)–C(19)–Ni(1)	177.9(6)
O(5)–C(20)–Ni(1)	176.6(6)		

According to an X-ray diffraction analysis of **5** (Tables 1, 4 and 5; Fig. 2), η^1 -ligation of **2** to the $[\text{Ni}(\text{CO})_3]$ moiety by virtue of the phosphorus lone pair causes a significant distortion of the metallophosphaalkene. Thus, the phosphorus atom is now trigonal-pyramidally coordinated (sum of angles 335.8°), forming single bonds to the atoms Fe, Ni and C(13). In comparison to **2**, the PC bond is elongated by 0.061 \AA . A similar bond lengthening is found in $\eta^1\text{-(F}_3\text{CP=C(F)NMe}_2\text{)}[\text{Cr}(\text{CO})_5]$ [25]. The $[\text{Ni}(\text{CO})_3]$ group is only weakly coordinated, as concluded from the long Ni–P bond [$2.352(2) \text{ \AA}$]. The corresponding bond lengths in

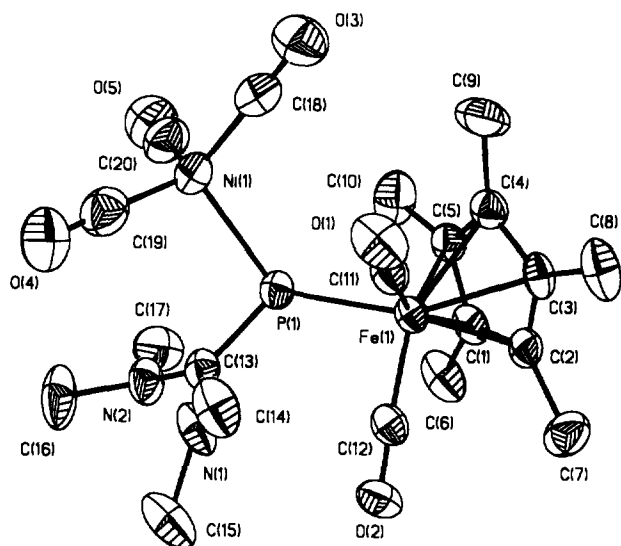
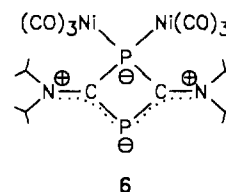


Fig. 2. Molecular structure of **5** in the crystal.

$\text{Mes}^* \text{P}[\text{Ni}(\text{CO})_3]=\text{C}=\text{CPh}_2$ or **6** amount to $2.234(1) \text{ \AA}$ [26] or $2.271(1) \text{ \AA}$ [27] respectively. The Fe–P bond in **5** is slightly longer than that in **2**.



The methylene carbon atom C(13) of **5** is trigonal planar (sum of angles 359.9°). The same is true for nitrogen atom N(1) in the vicinity of the iron center (sum of angles 359.0°), whereas atom N(2) deviates slightly from planarity (sum of angles 355.6°). Bond lengths C(13)–N(1) [$1.364(7) \text{ \AA}$] and C(13)–N(2) [$1.373(6) \text{ \AA}$] are comparable and shorter than the standard value of a $\text{C}(\text{sp}^2)\text{--N}(\text{sp}^2)$ single bond [1.45 \AA].

In the crystal molecule **5** adopts a configuration with orthogonal orientation of the bond P(1)–Ni(1) and the vector $\text{Cp}_c^* \text{--Fe}$ (where Cp_c^* is the center of the Cp^* ring) [torsion angle $\text{Cp}_c^* \text{--Fe--P(1)--Ni} = -96.9^\circ$].

According to a Newman projection of **5** (Fig. 3), the lone pair at the phosphorus atom is presumably directed towards the Cp^* ring, leading to a nearly eclipsed position of the vectors Fe–C(12)–O(2) and P–C(13) (torsion angle $\text{C(12)--Fe--P--C(13)} = 150^\circ$).

2.2.2. With [(Z)-cyclooctene]Cr(CO)₅

The reaction of metallophosphaalkene **2** with [(Z)-cyclooctene]Cr(CO)₅ takes an unexpected course. Instead of the anticipated η^1 -complex $\text{Cp}^*(\text{CO})_2\text{Fe--P}[\text{Cr}(\text{CO})_5]=\text{C}(\text{NMe}_2)_2$ (**7**), compound **8** is isolated as yellow crystals.

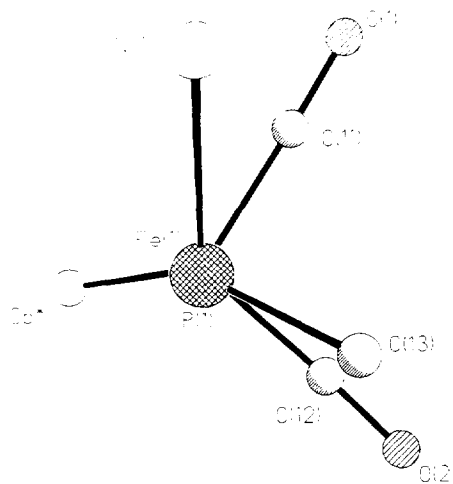
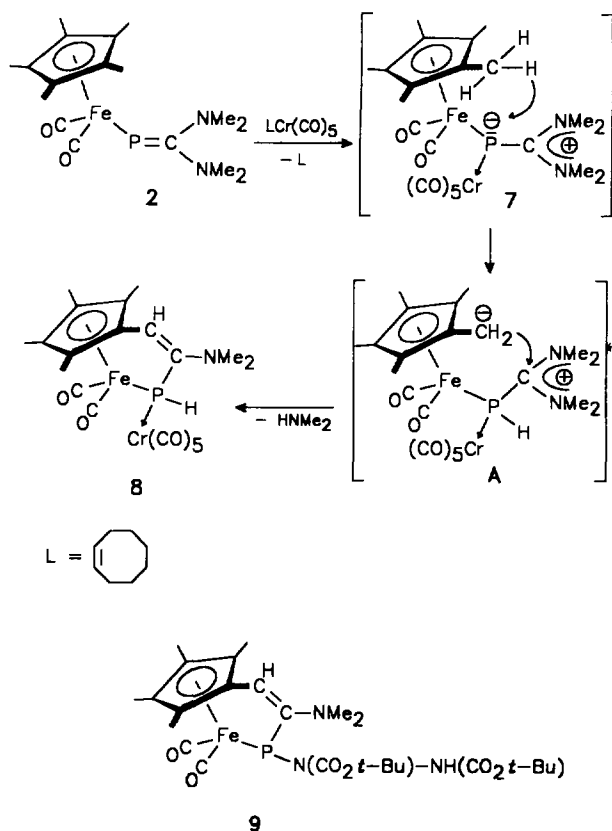


Fig. 3. Newman projection of **5** with view along the P(1)–Fe(1) vector.



The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **8** is characterized by a singlet at $\delta = 4.6$ ppm, which in the ^1H -coupled spectrum is split into a doublet of doublets. The large coupling constant of 267 Hz is consistent with a PH-function. The small coupling ($^3J_{\text{PH}} = 35$ Hz) is caused by the methyne proton at the C=C double bond. This assignment is substantiated by the ^1H NMR spectrum, where the respective hydrogen atoms are observed at $\delta = 4.78$ ($^1J_{\text{PH}} = 267.0$ Hz) and $\delta = 4.58$ ($^3J_{\text{PH}} = 35.1$ Hz). The remaining dimethylamino group in **8** gives rise to a singlet at $\delta = 2.49$ ppm. Four discrete singlets for the ring methyl hydrogens clearly indicate that the fifth ring methyl substituent of the precursor must have been involved in a chemical transformation. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum features a doublet at $\delta = 98.8$ ($^2J_{\text{PC}} = 17.9$ Hz) for the olefinic methyne carbon atom, whereas the amino-functionalized carbon atom of the C=C bond is attributed to a doublet at $\delta = 164.7$ ppm ($^1J_{\text{PC}} = 13.1$ Hz). In the previously described condensation product **9**, the olefinic carbon atoms are encountered as a broad singlet at $\delta = 88.9$ ppm (CH) and as a doublet at $\delta = 167.3$ ppm ($^1J_{\text{PC}} = 39.6$ Hz) [28]. The ^{13}C nuclei of the terminal carbonyl ligands at the iron center give rise to two doublets at $\delta = 213.7$ ($^2J_{\text{PC}} = 8.9$ Hz) and 215.3 ppm ($^2J_{\text{PC}} = 11.4$ Hz). Doublets at $\delta = 219.1$ ($^2J_{\text{PC}} = 10.8$ Hz) and 223.9 ppm ($^2J_{\text{PC}} = 6.2$ Hz) are due to the equatorial and axial carbonyls of the $[\text{Cr}(\text{CO})_5]$ -unit.

The IR spectrum of **8** (KBr) shows six intense bands in the region of carbonyl stretching modes, which points to a local symmetry of the $[\text{Cr}(\text{CO})_5]$ moiety lower than that of the point group C_{4v} . Bands at $\nu = 2051$, 1989, 1927 and 1894 cm^{-1} are attributed to this fragment, whereas the remaining absorptions at $\nu = 2017$ and 1967 cm^{-1} are due to the $[\text{Fe}(\text{CO})_2]$ building block. A weak band at $\nu = 2274\text{ cm}^{-1}$ is tentatively assigned to the PH stretching mode.

Obviously, one methyl group of the $\eta^5\text{-C}_5\text{Me}_5$ ligand of **2** is involved in a condensation process with the result of C=C double bond formation. This observation is explained by a strong polarization of the P=C bond induced by complexation to the electron-withdrawing $[\text{Cr}(\text{CO})_5]$ group in transient **7**. Transprotonation from a ring methyl group to the phosphorus leads to intermediate **A**. Subsequent C–C coupling and dimethylamine elimination affords **8**. This is the second example of a facile condensation involving one methyl substituent of an $\eta^5\text{-C}_5\text{Me}_5$ ligand under very mild conditions [28], and casts a new light on the characteristics of Cp^* ligands.

In addition to its electron-richness and steric bulk, it is the relative inertness which renders the Cp^* -ring useful as a spectator ligand in numerous complexes. There are only a few exceptions from that ‘rule of thumb’, and they are usually observed in electron-deficient and coordinatively unsaturated complexes of the early transition metals. CH-activation of one methyl group is met in bis(pentamethylcyclopentadienyl)titanium [29], $(\eta^5\text{-C}_5\text{Me}_5)(\eta^5, \eta^1\text{-Me}_4\text{C}_5\text{CH}_2)\text{TiCH}_3$ [30], $(\eta^5\text{-C}_5\text{Me}_5)(\eta^5, \eta^1\text{-Me}_4\text{C}_5\text{CH}_2)\text{ZrPh}$ [31] and $(\eta^5\text{-C}_5\text{Me}_5)(\eta^5, \eta^1\text{-Me}_4\text{C}_5\text{CH}_2)\text{HfCH}_2\text{Ph}$ [32]. Two adjacent methyl groups of the same C_5Me_5 ring are converted to the η^3, η^4 -1,2,3-trimethyl-4,5-dimethylenecyclopentadienyl ligand in $(\eta^5\text{-C}_5\text{Me}_5)[\eta^3, \eta^4\text{-Me}_3\text{C}_5(\text{CH}_2)_2]\text{Ti}$ [33], $(\eta^5\text{-$

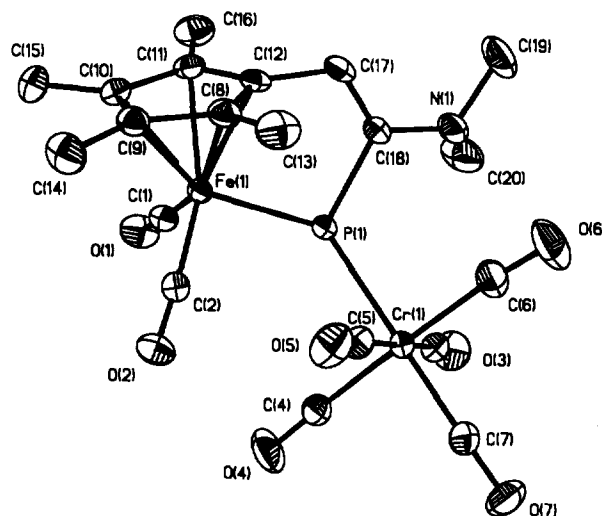


Fig. 4. Molecular structure of **8** in the crystal.

$C_5Me_5[\eta^3, \eta^4-Me_3C_5(CH_2)_2]W$ [34] and $[\eta^3, \eta^4-Me_3C_5(CH_2)_2]Ga(H)_2(PMe_2)_2$ [35]. In one case the insertion of a P=C fragment into the CH bond of a ring methyl group has been described [36].

An X-ray structure study was desirable to confirm the conclusion drawn from spectroscopic evidence and to determine the geometry of the condensation product. Single crystals of **8** were grown from toluene at $-30^\circ C$. The analysis (Fig. 4, Tables 1, 6 and 7) sustains the presence of the unusual 3-tetramethylcyclopentadienyl-1-phospha-2-propenyl system coordinated in an η^5, η^4 -fashion to the $[Fe(CO)_2]$ moiety. The cyclopentadienyl ring is unsymmetrically bound to the iron atom. Owing to the tether P(1)–C(18)–C(17), the iron–carbon distance Fe–C(12) [2.065(2) Å] is significantly shorter than the remaining bond lengths [2.092(3)–2.114(4) Å]. The phosphorus atom is tetrahedrally configured, featuring single bonds to the adjacent atom C(18) [1.862(2) Å] and hydrogen [1.35(3) Å].

The Fe–P distance in **8** [2.2881(14) Å] is significantly shorter than in the precursor **2**. The carbon–

Table 6
Atomic coordinates ($\times 10^4$) and isotropic displacement parameters U_{iso} or U_{eq} ^a [$\text{\AA}^2 \times 10^3$] for **8**

Atom	x	y	z	U_{eq}
Fe(1)	2503(1)	–40(1)	7010(1)	18(1)
Cr(1)	–1765(1)	–3073(1)	6917(1)	21(1)
P(1)	803(1)	–2322(1)	6879(1)	19(1)
O(1)	2359(2)	–1170(2)	4572(2)	39(1)
O(2)	314(2)	935(2)	6519(2)	41(1)
O(3)	–2741(2)	–6127(2)	5176(2)	45(1)
O(4)	–2539(3)	–2365(2)	4779(2)	55(1)
O(5)	–858(2)	29(2)	8516(2)	41(1)
O(6)	–1235(3)	–3760(3)	9110(2)	58(1)
O(7)	–4983(2)	–4132(2)	6882(2)	48(1)
N(1)	1358(2)	–3931(2)	8161(2)	35(1)
C(1)	2366(3)	–753(3)	5520(2)	25(1)
C(2)	1133(3)	505(3)	6698(2)	26(1)
C(3)	–2364(3)	–4990(3)	5848(2)	29(1)
C(4)	–2216(3)	–2620(3)	5587(2)	31(1)
C(5)	–1158(3)	–1126(3)	7921(2)	27(1)
C(6)	–1366(3)	–3510(3)	8276(2)	35(1)
C(7)	–3749(3)	–3720(3)	6892(2)	31(1)
C(8)	3488(3)	1092(3)	8854(2)	25(1)
C(9)	4099(3)	2101(2)	8297(2)	24(1)
C(10)	4828(3)	1588(2)	7590(2)	24(1)
C(11)	4685(2)	261(2)	7691(2)	24(1)
C(12)	3839(3)	–55(3)	8459(2)	24(1)
C(13)	2772(4)	1277(4)	9773(2)	38(1)
C(14)	4051(4)	3504(3)	8476(3)	36(1)
C(15)	5696(3)	2372(3)	6913(3)	37(1)
C(16)	5381(3)	–595(3)	7152(3)	37(1)
C(17)	3330(3)	–1402(3)	8709(2)	30(1)
C(18)	1986(3)	–2603(3)	8007(2)	25(1)
C(19)	2182(5)	–3937(4)	9237(3)	56(1)
C(20)	766(4)	–5282(3)	7135(3)	56(1)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 7
Selected bond lengths (Å) and angles ($^\circ$) for **8**

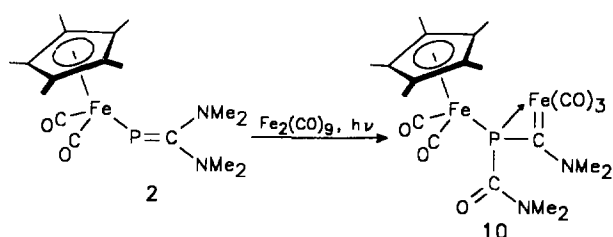
Fe(1)–C(1)	1.766(3)	Fe(1)–C(2)	1.769(2)
Fe(1)–C(12)	2.065(2)	Fe(1)–C(8)	2.092(3)
Fe(1)–C(11)	2.100(2)	Fe(1)–C(9)	2.108(3)
Fe(1)–C(10)	2.114(3)	Fe(1)–P(1)	2.2881(14)
Cr(1)–C(7)	1.855(3)	Cr(1)–C(4)	1.885(3)
Cr(1)–C(5)	1.897(3)	Cr(1)–C(3)	1.898(3)
Cr(1)–C(6)	1.900(3)	Cr(1)–P(1)	2.4373(13)
P(1)–C(18)	1.862(2)	P(1)–H(1)	1.35(3)
O(1)–C(1)	1.146(3)	O(2)–C(2)	1.143(3)
O(3)–C(3)	1.138(3)	O(4)–C(4)	1.144(3)
O(5)–C(5)	1.143(3)	O(6)–C(6)	1.142(3)
O(7)–C(7)	1.155(3)	N(1)–C(18)	1.394(3)
N(1)–C(20)	1.450(4)	N(1)–C(19)	1.451(4)
C(12)–C(17)	1.473(3)		
C(1)–Fe(1)–C(2)	94.79(11)	C(1)–Fe(1)–P(1)	92.11(10)
C(2)–Fe(1)–P(1)	95.30(9)	C(7)–Cr(1)–C(4)	90.11(12)
C(7)–Cr(1)–C(5)	90.56(12)	C(4)–Cr(1)–C(5)	89.34(12)
C(7)–Cr(1)–C(3)	90.29(12)	C(5)–Cr(1)–C(3)	177.11(10)
C(7)–Cr(1)–C(6)	87.98(12)	C(4)–Cr(1)–C(6)	177.74(11)
C(5)–Cr(1)–C(6)	89.45(12)	C(3)–Cr(1)–C(6)	93.34(12)
C(7)–Cr(1)–P(1)	177.57(8)	C(4)–Cr(1)–P(1)	89.33(9)
C(5)–Cr(1)–P(1)	91.80(9)	C(3)–Cr(1)–P(1)	87.33(9)
C(6)–Cr(1)–P(1)	92.62(9)	C(18)–P(1)–Fe(1)	101.78(9)
C(18)–P(1)–Cr(1)	113.91(9)	Fe(1)–P(1)–Cr(1)	125.05(4)
C(18)–P(1)–H(1)	101.7(11)	Fe(1)–P(1)–H(1)	106.0(11)
Cr(1)–P(1)–H(1)	105.8(11)	C(18)–N(1)–C(20)	117.6(2)
C(18)–N(1)–C(19)	116.1(2)	C(20)–N(1)–C(19)	112.7(3)
O(1)–C(1)–Fe(1)	176.4(2)	O(2)–C(2)–Fe(1)	176.2(2)
O(3)–C(3)–Cr(1)	177.6(2)	O(4)–C(4)–Cr(1)	177.7(2)
O(5)–C(5)–Cr(1)	177.0(2)	O(6)–C(6)–Cr(1)	173.8(2)
O(7)–C(7)–Cr(1)	179.3(2)	C(18)–C(17)–C(12)	119.6(2)
C(17)–C(18)–N(1)	125.3(2)	C(17)–C(18)–P(1)	114.7(2)
N(1)–C(18)–P(1)	119.4(2)		

carbon distance within the handle C(17)–C(18) [1.336(4) Å] compares well with the corresponding bond length in **9** [1.338(9) Å] and is in agreement with a double bond. The pyramidal dimethylamino group (sum of angles 346.6°) is connected to C(18) via a single bond of length 1.394(3) Å. In **2** the respective CN bonds amount to 1.372(8) and 1.410(7) Å. The $[(CO)_5Cr]$ -unit is attached to the phosphorus via a single bond of length 2.4373(13) Å. This CrP bond distance is comparable with those in $F_3CP[Cr(CO)_5]=C(F)(NMe_2)$ (2.45 Å) [25] and in $[Cr(CO)_5]_2[F_3CP=C(F)NMe_2]$ [2.459(2), 2.457(2) Å] [37] and is located at the upper range of Cr–P bond distances in pentacarbonyl chromium complexes (2.25–2.48 Å) [38,39].

2.2.3. With $Fe_2(CO)_9$

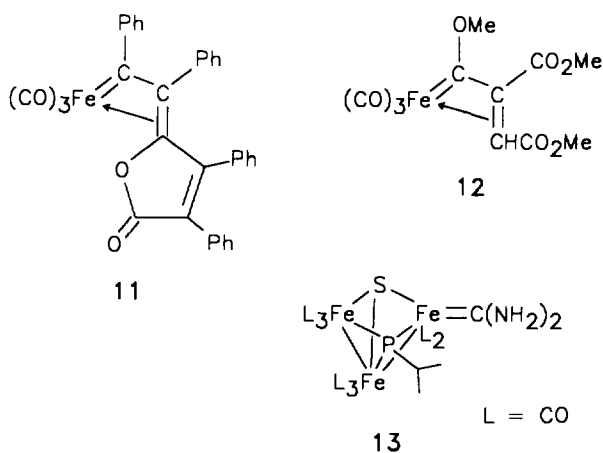
Treatment of phosphalkenes [2,40,41] with binary iron carbonyls usually leads to the formation of η^1 -phosphalkene adducts by virtue of the lone pair at the phosphorus atom. The photochemical reaction of **2** with $Fe_2(CO)_9$ in *n*-hexane, however, takes a completely different course, affording black crystalline **10** in 70% yield. The thermal reaction of **2** and $Fe_2(CO)_9$ is com-

plicated and leads to a number of products, one of which is complex **10** (^{31}P NMR control).



Prior to the discussion of the spectroscopic data, consideration of the structural features of compound **10**, as given by an X-ray analysis (Fig. 5; Tables 1, 8 and 9), seems appropriate.

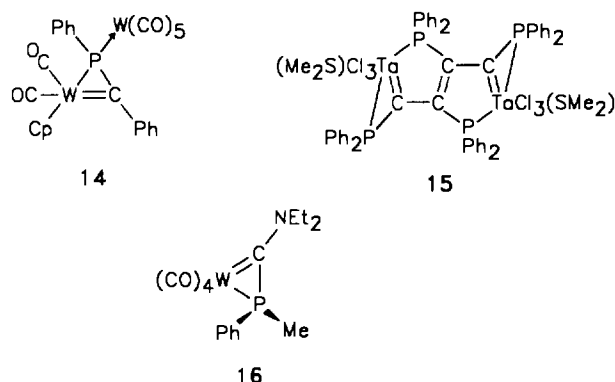
The core of the molecule is a three-membered ring containing the atoms P(1), Fe(2) and C(18). The phosphorus atom possesses the configuration of a distorted trigonal pyramid, with angles ranging from $52.6(2)^\circ$ [C(18)–P(1)–Fe(2)] to $128.97(9)^\circ$ [Fe(2)–P(1)–Fe(1)]. Thereby the endocyclic bond length Fe(2)–P(1) [2.252(2) Å] is close to the exocyclic bond distance Fe(1)–P(1) [2.268(2) Å] and has to be regarded as a single bond. The iron–carbon bond length Fe(2)–C(18) [1.832(7) Å] is remarkably short and compares well with the Fe–C double bond in iron carbene complexes **11** [1.834(2) Å] [42] and **12** [1.819(3) Å] [43].



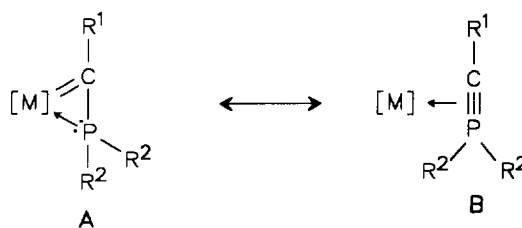
Fe=C($_{sp^2}$) bonds in carbene iron complexes range from 1.724(9) Å in [Cp(CO)(Ph₃P)Fe=CF₂]⁺BF₄[−] [44] to 2.037 Å in cluster **13** [45]. The average Fe=C distance from 60 structures amounts to 1.90 Å [46,47].

The bond length P(1)–C(18) of 1.746(7) Å is amidst that of PC single and double bonds (1.85 and 1.65 Å

respectively) [2] and corresponds to the PC bond length in complex **14** [1.775(8) Å] [48].

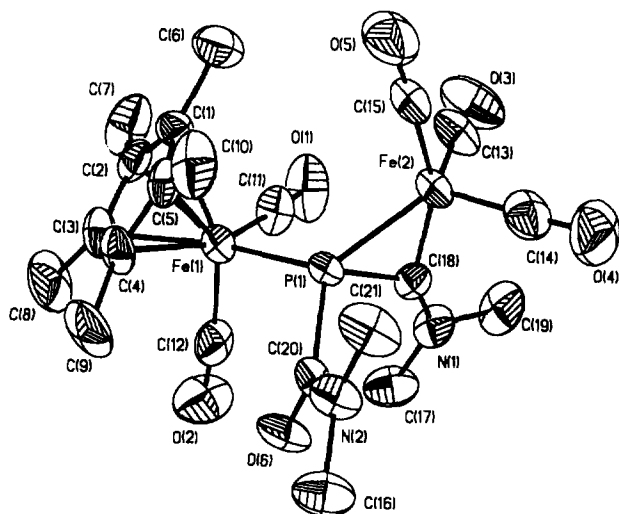


In complexes related to **10**, PC bond lengths vary from 1.683(11) Å in **15** [49] to 1.807 Å in the tungsten derivative **16** [50]. The endocyclic angles in **10**, P(1)–Fe(2)–C(18), Fe(2)–P(1)–C(18) and Fe(2)–C(18)–P(1), are determined as $49.9(2)^\circ$, $52.6(2)^\circ$ and $77.6(2)^\circ$ respectively. The bonding situation in such three-membered rings may be described by two canonical formulae **A** and **B**. Structure **A** considers the molecule as an η^2 -phosphinocarbene complex, whereas **B** seems to be best viewed as a λ^5 -phosphaalkyne- η^2 complex and is realized in most of the tantalum derivatives.



In our case, the X-ray crystal structure analysis of **10** is in favor of formula **A**.

Only a few stable non-coordinated λ^5 -phosphaalkynes are known. Usually they feature two amino groups at phosphorus and a trimethylsilyl group at carbon, with only the two exceptions of (TMPip)(Ph)P≡C–SiMe₃ (TMPip = 2,2,6,6-tetramethylpiperidino) and [(ⁱPr₂N)₂P≡C–PH(NⁱPr₂)₂]⁺CF₃SO₃[−]. The X-ray structure analysis of the salt reveals a planar tricoordinate phosphorus atom with a PC bond length of 1.548(4) Å. This value is in the range for a phosphorus carbon triple bond, whereas the PC bond length to the tetracoordinate phosphorus atom amounts to 1.605(5) Å. The PCP angle of $164.1(4)^\circ$ – $165.1(4)^\circ$ is rather large [51].

Fig. 5. Molecular structure of **10** in the crystal.

A double bond of length 1.313(8) Å between nitrogen atom N(1) and ring carbon atom C(18) agrees well with the coplanarity of the atoms C(17), C(19), N(1), C(18),

Table 8
Atomic coordinates ($\times 10^4$) and isotropic displacement parameters U_{iso} or U_{eq}^a [$\text{\AA}^2 \times 10^3$] for **10**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Fe(1)	6858(1)	1188(1)	2069(1)	37(1)
Fe(2)	7773(1)	-2118(1)	3883(1)	41(1)
P(1)	7806(1)	-584(2)	2889(1)	33(1)
O(1)	6701(5)	2083(7)	3566(4)	87(2)
O(2)	8061(4)	3471(7)	2250(6)	103(3)
O(3)	7084(5)	-1045(8)	4967(5)	99(2)
O(4)	9098(5)	-4243(7)	4972(5)	95(2)
O(5)	6506(5)	-4364(7)	2805(4)	86(2)
O(6)	8936(3)	586(5)	2488(4)	57(2)
N(1)	8869(4)	610(7)	4585(4)	51(2)
N(2)	8986(4)	-1893(6)	2435(4)	48(2)
C(1)	5679(4)	112(9)	1404(4)	48(2)
C(2)	5564(4)	1654(9)	1229(5)	48(2)
C(3)	6042(5)	2049(8)	817(5)	54(2)
C(4)	6458(5)	729(9)	753(4)	47(2)
C(5)	6215(5)	-444(8)	1100(4)	43(2)
C(6)	5247(6)	-803(11)	1803(6)	84(3)
C(7)	5009(6)	2700(12)	1411(6)	90(3)
C(8)	6073(7)	3567(10)	462(7)	94(3)
C(9)	7025(6)	608(12)	341(6)	83(3)
C(10)	6409(6)	-2060(9)	1068(5)	70(3)
C(11)	6780(5)	1739(8)	2993(5)	54(2)
C(12)	7651(5)	2512(9)	2228(5)	56(2)
C(13)	7331(6)	-1514(9)	4509(6)	60(2)
C(14)	8567(6)	-3383(9)	4521(6)	60(2)
C(15)	7016(5)	-3490(9)	3242(5)	52(2)
C(16)	9666(5)	-1795(9)	2207(6)	66(2)
C(17)	9128(6)	1972(9)	4343(6)	70(3)
C(18)	8372(4)	-397(8)	4030(4)	38(2)
C(19)	9126(6)	466(11)	5514(5)	74(3)
C(20)	8673(4)	-630(8)	2568(4)	41(2)
C(21)	8686(6)	-3368(8)	2457(6)	62(2)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 9
Selected bond lengths (Å) and angles (°) for **10**

Fe(1)–C(11)	1.771(8)	Fe(1)–C(12)	1.775(9)
Fe(1)–P(1)	2.268(2)	Fe(2)–C(13)	1.733(8)
Fe(1)–C(14)	1.743(10)	Fe(2)–C(15)	1.777(9)
Fe(2)–C(18)	1.832(7)	Fe(2)–P(1)	2.252(2)
P(1)–C(18)	1.764(7)	P(1)–C(20)	1.904(7)
O(1)–C(11)	1.129(9)	O(2)–C(12)	1.124(9)
O(3)–C(13)	1.173(9)	O(4)–C(14)	1.185(10)
O(5)–C(15)	1.168(9)	O(6)–C(20)	1.227(8)
N(1)–C(18)	1.313(8)	N(1)–C(17)	1.448(10)
N(1)–C(19)	1.474(10)	N(2)–C(20)	1.338(8)
N(2)–C(21)	1.441(9)	N(2)–C(16)	1.467(9)
C(11)–Fe(1)–C(12)	94.9(4)	C(11)–Fe(1)–P(1)	89.0(2)
C(12)–Fe(1)–P(1)	94.2(2)	C(13)–Fe(2)–C(14)	106.3(4)
C(13)–Fe(2)–C(15)	100.0(4)	C(14)–Fe(2)–C(15)	95.1(4)
C(13)–Fe(2)–C(18)	93.8(3)	C(14)–Fe(2)–C(18)	102.7(3)
C(15)–Fe(2)–C(18)	153.4(3)	C(13)–Fe(2)–P(1)	119.8(3)
C(14)–Fe(2)–P(1)	125.3(3)	C(15)–Fe(2)–P(1)	103.6(2)
C(18)–Fe(2)–P(1)	49.9(2)	C(18)–P(1)–C(20)	103.8(3)
C(18)–P(1)–Fe(2)	52.6(2)	C(20)–P(1)–Fe(2)	123.7(2)
C(18)–P(1)–Fe(1)	119.8(2)	C(20)–P(1)–Fe(1)	107.3(2)
Fe(2)–P(1)–Fe(1)	128.97(9)	C(18)–N(1)–C(17)	124.5(7)
C(18)–N(1)–C(19)	119.8(7)	C(17)–N(1)–C(19)	115.4(7)
C(20)–N(2)–C(21)	125.7(6)	C(20)–N(2)–C(16)	118.4(6)
C(21)–N(2)–C(16)	115.9(6)	O(1)–C(11)–Fe(1)	177.6(8)
O(2)–C(12)–Fe(1)	170.3(7)	O(3)–C(13)–Fe(2)	175.1(8)
O(4)–C(14)–Fe(2)	178.1(9)	O(5)–C(15)–Fe(2)	178.2(8)
N(1)–C(18)–P(1)	136.0(6)	N(1)–C(18)–Fe(2)	146.1(6)
P(1)–C(18)–Fe(2)	77.6(3)	O(6)–C(20)–N(2)	121.3(6)
O(6)–C(20)–P(1)	115.6(5)	N(2)–C(20)–P(1)	123.1(5)

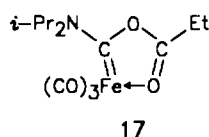
P(1) and Fe(2). The coordination sphere about the phosphorus atom is completed by a planar dimethylamino-carbonyl group. The carbon–phosphorus bond P(1)–C(20) [1.904(7) Å] is significantly lengthened in comparison with the standard value of 1.85 Å. Carbon–phosphorus single bond distances ranging from 1.87 to 1.95 Å, however, are quite common in phosphino-carbonyl compounds [52].

The assignment of the spectral data to structure **10** is straightforward. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum a singlet at $\delta = -108.0$ ppm appears in the highfield region typical for three-membered phosphorus heterocycles [53].

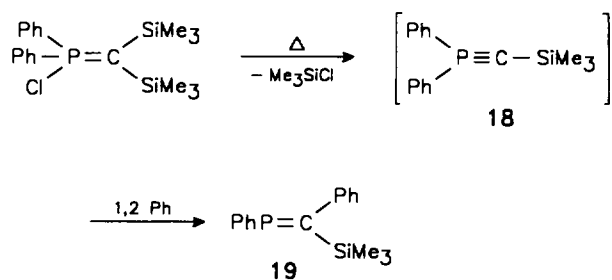
As in typical dimethylaminocarbene complexes, the ^1H NMR spectrum of **10** (500 MHz) shows two sharp singlets at $\delta = 3.14$ and 3.34 ppm for protons of the two chemically and magnetically different methyl groups at N(1). In complex $(\text{CO})_4\text{Fe}=\text{C}(\text{Ph})(\text{NMe}_2)$ the respective resonances are observed at $\delta = 3.22$ and 4.04 ppm (in acetone- d_6) [54]. At 22°C two broad singlets at $\delta = 2.48$ and 3.06 ppm are assigned to the protons of the two methyl groups at the dimethylaminocarbonyl function. At 50°C coalescence of these resonances to a broad singlet at $\delta = 2.79$ ppm is observed. Accordingly, ΔG^\ddagger for the rotation about the bond C(20)–N(2) is estimated to be 14.3 ± 0.5 kcal mol $^{-1}$.

In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (22 °C) a pair of sharp doublets at $\delta = 47.0$ ($J_{\text{PC}} = 6.9$ Hz) and $\delta = 48.7$ ppm ($J_{\text{PC}} = 3.6$ Hz) are assigned to the different methyl carbons at N(1), whereas two broad singlets at $\delta = 36.5$ and 39.0 ppm are due to the methyl carbons at N(2). The carbonyl group of the $[\text{Me}_2\text{NC}(\text{O})\text{P}]$ -unit gives rise to a doublet at $\delta = 171.4$ ($^1J_{\text{PC}} = 9.3$ Hz). The carbonyl ligands at Fe(1) are observed as doublets at $\delta = 213.0$ ($^2J_{\text{PC}} = 16.8$ Hz) and 217.6 ppm ($^2J_{\text{PC}} = 13.0$ Hz). A singlet at $\delta = 223.3$ is due to the $[\text{Fe}(2)(\text{CO})_3]$ carbonyls. The carbene carbon atom gives rise to a doublet at $\delta = 246.3$ ($^1J_{\text{PC}} = 94.8$ Hz), which is in good agreement with the respective resonance in **17** ($\delta = 244.3$ ppm) [47] or in **11** ($\delta = 247.6$ ppm).

The IR spectrum of **10** (KBr) shows three intense bands at $\nu = 2013$, 1969 and 1886 cm^{-1} for the stretching vibrations of the terminal carbonyl ligands. A medium intense absorption at $\nu = 1596$ cm^{-1} is tentatively assigned to the $\nu(\text{CO})$ mode of the dimethylamino-carbonyl group.



Compound **10** is the first iron complex featuring an η^2 -phosphinocarbene (or λ^5 -phosphaacetylene) ligand. The conversion of a metallophosphaalkene into such a ligand in the coordination sphere of a carbonyliron complex is unusual. An opposite transformation takes place during the elimination of Me_3SiCl from P-halomethylene phosphoranes. The transient formation of λ^5 -phosphaacetylene **18** was postulated to explain the generation of phosphaalkene **19** [55].



Other synthetic routes have been used for the type of complexes discussed here. Tungsten derivatives are available either from cationic carbyne complexes and KPMePh [50], from cationic tungstaphosphabi-

cyclo[1.1.0]butanones by mild thermolysis [56] or, alternatively, from neutral tungsten carbynes, diorganochlorophosphanes and NaBPh_4 [57].

Tantalum derivative **15** is synthesized from $\text{Ph}_2\text{P}-\text{C}\equiv\text{C}-\text{PPh}_2$ and $\text{Ta}_2\text{Cl}_6(\text{SMe}_2)_3$, whereas in the remaining η^2 - λ^5 -phosphaacetylene tantalum complexes the π -ligand is derived from PMe_3 [35,58] or PhPMe_2 [59].

3. Experimental details

3.1. General comments

All manipulations were performed under dry argon or N_2 . Solvents were rigorously dried with an appropriate drying agent and distilled before use. $[(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{FeP}=\text{C}(\text{NMe}_2)_2]$ (**2**) [4], the isocyanides [11], $\text{Fe}_2(\text{CO})_9$ [60] and $(\eta^2\text{-cyclooctene})\text{Cr}(\text{CO})_5$ [61] were prepared as described in the literature. $\text{Ni}(\text{CO})_4$ was purchased commercially (Strem).

IR spectra: Mattson Polaris (FT-IR)/Atari 1040 STF. ^1H , ^{31}P , ^{13}C NMR spectra: Bruker AC 100 (^1H , 100.131; ^{13}C , 25.180; ^{31}P , 40.539 MHz), Bruker AM 300 (^1H , 300.1; ^{13}C , 75.5; ^{31}P , 121.7 MHz) and Bruker DRX 500 (^1H , 500.133, ^{13}C , 125.771, ^{31}P , 202.456 MHz). Standards: SiMe_4 (^1H , ^{13}C), 85% H_3PO_4 (^{31}P). Mass spectra: Varian MAT CH5-DF spectrometer.

3.2. Synthesis of $(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{-NC})\text{FeP}=\text{C}(\text{NMe}_2)_2$ (**4a**)

To a solution of **2** (0.85 g, 2.25 mmol) in 30 ml of *n*-pentane at 20 °C was added a solution of 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{NC}$ (**3a**) (0.29 g, 2.25 mmol) in 20 ml of *n*-pentane within 1 h. After stirring for 24 h, the reaction mixture was filtered, and the filtrate was freed from the solvent and volatile components in vacuo. The red viscous residue was crystallized from 10 ml of *n*-pentane at 0 °C for 48 h to yield 0.43 g (36%) of dark red crystalline **4a**. IR (KBr): ν 2970 w, 2915 m, 2850 w, 2771 w, 2063 vs [$\nu(\text{CN})$], 1911 vs [$\nu(\text{CO})$], 1590 w, 1555 w, 1464 m, 1377 m, 1347 w, 1305 w, 1260 w, 1119 w, 1092 w, 1076 m, 1025 w, 771 w, 678 w, 577 w, 552 m, 517 w cm^{-1} . ^1H NMR (C_6D_6): δ 1.73 (s, 15H, C_5Me_5), 2.32 (s, 6H, $\text{Me}_2\text{C}_6\text{H}_3$), 2.84 (s, 6H, NMe_2), 2.85 (s, 6H, NMe_2), 6.74 (s, 3H, H-aryl). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 9.68 [d, $^3J_{\text{PC}} = 8.7$ Hz, $\text{C}_5(\text{CH}_3)_5$], 19.18 [s, 2,6- $(\text{CH}_3)_2\text{-C}_6\text{H}_3$], 43.11 [s, $\text{N}(\text{CH}_3)_2$], 43.25 [s, $\text{N}(\text{CH}_3)_2$], 94.15 [s, $\text{C}_5(\text{CH}_3)_5$], 125.92 s, 131.51 s, 133.97 s, 134.17 (s, C-aryl), 190.05 (d, $^2J_{\text{PC}} = 4.4$ Hz, FeCN), 200.67 (d, $^1J_{\text{PC}} = 97$ Hz, $\text{P}=\text{C}$), 222.28 (s, CO). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 157.4$ s; (*n*- C_5H_{12}): $\delta = 167.1$ s. MS(FAB): m/z 482 ($\text{M}^+ + \text{H}$), 454 ($\text{M}^+ + \text{H}$, $-\text{CO}$), 322 ($\text{M}^+ - \text{CO}$, $-2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC}$). Anal. Found: C, 62.12; H, 7.34; N,

8.74. $C_{25}H_{36}FeN_3OP$ (481.38) Calc.: C, 62.38; H, 7.54; N, 8.72%.

3.3. Synthesis of $(\eta^5-C_5Me_5)(CO)(tBuNC)-FeP=C(NMe_2)_2$ (**4b**)

Analogously, dark red oily **4b** (0.47 g, 44%) was obtained from **2** (0.94 g, 2.49 mmol) and **1BuNC** (**3b**) (0.21 g, 2.49 mmol). IR (Csl): ν 2977 m, 2911 m, 2125 s [$\nu(CN)$], 1936 s [$\nu(CO)$], 1673 m, 1554 m, 1497 w, 1463 m, 1382 m, 1263 w, 1207 w, 1074 m, 1030 m, 982 w, 572 m, 557 mcm^{-1} . 1H NMR (C_6D_6): δ 1.07 (s, 9H, **1Bu**), 1.65 (s, 15H, C_5Me_5), 2.87 (s, br, 12H, NMe_2). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 9.61 [d, $^2J_{PC} = 9.1$ Hz, $C_5(CH_3)_5$], 31.36 [s, $C(CH_3)_3$], 43.98 s and 43.12 [s, $N(CH_3)_2$], 56.36 [s, $C(CH_3)_3$], 93.02 [s, $C_5(CH_3)_5$], 178.46 (s, FeCN), 200.40 (d, $^1J_{PC} = 95.6$ Hz, P=C), 222.83 (s, CO). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 163.8; (*n*- C_5H_{12}): δ 168.9 s. Anal. Found: C, 57.39; H, 8.11; N, 8.89. $C_{21}H_{36}FeN_3OP$ (433.34) Calc.: C, 58.21; H, 8.37; N, 9.69%. Repeated attempts at purification did not provide better C and N values.

3.4. Synthesis of $(\eta^5-C_5Me_5)(CO)(c-C_6H_{11}NC)-FeP=C(NMe_2)_2$ (**4c**)

Analogously, dark red oily **4c** (0.48 g, 46%) was prepared from **2** (0.85 g, 2.25 mmol) and *c*- $C_6H_{11}NC$ (**3c**) (0.25 g, 2.25 mmol). IR (Csl): ν 2933 s, 2858 m, 2128 s [(CN)], 1929 s [$\nu(CO)$], 1674 w, 1554 m, 1491 w, 1450 m, 1380 m, 1263 w, 1072 m, 982 w, 811 w, 658 w, 572 m, 553 mcm^{-1} . 1H NMR (C_6D_6): δ 1.68 (s, 15H, C_5Me_5), 2.90 (s, 12H, NMe_2) (the protons of the cyclohexyl group appear as a broad hump between $\delta = 0.9$ and 1.5). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 9.68 [d, $^3J_{PC} = 9.0$ Hz, $C_5(CH_3)_5$], 23.60 s, 23.61 s, 25.29 s, 34.07 s and 34.40 (s, CH_2), 43.24 s and 43.38 [s, $N(CH_3)_2$], 54.89 [s, $(CH_2)_5CH-NC$], 93.11 [d, $^2J_{PC} = 0.8$ Hz, $C_5(CH_3)_5$], 178.21 (d, $^2J_{PC} = 2.8$ Hz, FeCN), 200.41 (d, $^1J_{PC} = 95.5$ Hz, P=C), 222.85 (s, CO). $^{31}P\{^1H\}$ NMR (*n*- C_5H_{12}): δ 170.5 s. Anal. Found: C, 60.11; H, 8.26; N, 8.64. $C_{23}H_{38}FeN_3OP$ (459.37) Calc.: C, 60.14; H, 8.34; N, 9.14%.

3.5. Synthesis of $(\eta^5-C_5Me_5)(CO)_2FeP-[Ni(CO)_3]=C(NMe_2)_2$ (**5**)

Metallophosphaalkene **2** (0.64 g, 1.69 mmol) was treated with nickeltetracarbonyl (0.29 g, 1.69 mmol) in 40 ml of *n*-pentane at $-30^\circ C$. The mixture was warmed to $20^\circ C$, and stirring was continued for 2 h. The solution was freed from the solvent and volatile components in vacuo. The dark residue was dissolved in 25 ml of *n*-pentane and filtered. The filtrate was stored at $-30^\circ C$ for 24 h to afford black crystals (0.65 g, 74%) of **5**. IR (KBr): ν 2918 m, 2034 s [$\nu Ni(CO)$], 1983 s [$\nu Fe(CO)$],

1973 s [$\nu Fe(CO)$], 1957 vs [$\nu Ni(CO)$], 1950 vs [$\nu Ni(CO)$], 1917 s [$\nu Fe(CO)$], 1652 w, 1560 w, 1502 m-w, 1485 m-w, 1452 m-w, 1367 m-w, 1344 m-w, 1261 w, 1121 w, 1107 w, 1078 m, 877 w, 637 w, 582 m, 453 wcm^{-1} . IR (C_6D_6): $\nu(CO) = 2038$ s, 1979 vs, 1958 vs, 1925 scm^{-1} . 1H NMR (C_6D_6): δ 1.52 [d, $^4J_{PH} = 0.7$ Hz, 15H, $C_5(CH_3)_5$], 2.72 (s, 6H, NMe_2), 2.74 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 9.1 [d, $^3J_{PC} = 7.4$ Hz, $C_5(CH_3)_5$], 42.9 [s, $N(CH_3)_2$], 43.0 [s, $N(CH_3)_2$], 96.3 [s, $C_5(CH_3)_5$], 199.5 (d, $^2J_{PC} = 7.0$ Hz, NiCO), 208.1 (d, $^1J_{PC} = 77.7$ Hz, P=C), 219.65 (s, FeCO), 219.71 (s, FeCO). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 15.0 s. MS/El: *m/z* 521 (M^+), 493 ($M^+ - CO$), 465 ($M^+ - 2CO$), 437 ($M^+ - 3CO$). Anal. Found: C, 45.71; H, 5.29; N, 5.19. $C_{20}H_{27}FeN_2NiO_5P$ (520.94) Calc.: C, 46.11; H, 5.22; N, 5.38%.

3.6. Synthesis of $\eta^5-Me_4C_5CH=C(NMe_2)-PH[Cr(CO)_5]Fe(CO)_2$ (**8**)

A solution of $(\eta^2-Z\text{-cyclooctene})Cr(CO)_5$ (0.63 g, 2.09 mmol) in 20 ml of *n*-pentane was added dropwise to a chilled solution ($-30^\circ C$) of **2** (0.79 g, 2.09 mmol) in 30 ml of *n*-pentane. Stirring of the mixture was continued for four days at ambient temperature. Solvent and volatile components were removed in vacuo, the dark residue was dissolved in toluene (30 ml) and filtered. The filtrate was stored at $-30^\circ C$ for 48 h to yield yellow crystals of **8** (0.72 g, 66%). IR (KBr): ν 2917 w, 2863 w, 2833 w, 2785 w, 2274 w [νPH], 2051 s [$\nu Cr(CO)$], 2017 s [$\nu Fe(CO)$], 1989 s [$\nu Cr(CO)$], 1967 s [$\nu Fe(CO)$], 1927 vs [$\nu Cr(CO)$], 1894 vs [$\nu Cr(CO)$], 1592 w, 1449 w, 1386 w, 1316 w, 1204 w, 1096 w, 1080 w, 1033 w, 918 w, 872 w, 800 m, 766 w, 708 w, 670 s, 660 s, 625 w, 602 w, 587 m, 568 w, 466 wcm^{-1} . 1H NMR (C_6D_6): δ 1.23 (s, 3H, C_5CH_3), 1.30 (s, 3H, C_5CH_3), 1.34 (s, 3H, C_5CH_3), 1.65 (s, 3H, C_5CH_3), 2.49 (s, 6H, NMe_2), 4.58 (d, $^3J_{PH} = 35.1$ Hz, $C_5CH=CN$), 4.78 (d, $^1J_{PH} = 267.0$ Hz, PH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 8.9 (s, C_5CH_3), 9.5 (s, C_5CH_3), 9.6 (s, C_5CH_3), 9.7 (s, C_5CH_3), 41.7 (s, NCH_3), 41.8 (s, NCH_3), 93.1 [s, $C_5(CH_3)_4$], 93.3 [s, $C_5(CH_3)_4$], 96.8 [s, $C_5(CH_3)_4$], 98.8 (d, $^2J_{PC} = 17.9$ Hz, $C_5CH=CN$), 101.2 [s, $C_5(CH_3)_4$], 108.7 [d, $^3J_{PC} = 6.7$ Hz, $C_5(CH_3)_4$], 164.7 (d, $^1J_{PC} = 13.1$ Hz, $CH=CP$), 213.7 (d, $^2J_{PC} = 8.9$ Hz, FeCO), 215.3 (d, $^2J_{PC} = 11.4$ Hz, FeCO), 219.1 (s, $^2J_{PC} = 10.8$ Hz, $CrCO_{eq}$), 223.9 (d, $^2J_{PC} = 6.2$ Hz, $CrCO_{ax}$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 4.6 s. MS/LSIMS (+), matrix nitrobenzylalcohol: *m/z* 526 ($M^+ + H$). Anal. Found: C, 45.61; H, 3.77; N, 2.60. $C_{20}H_{20}CrFeNO_7P$ (525.20) Calc.: C, 45.74; H, 3.84; N, 2.67%.

3.7. $\eta^2(P,C)-[(\eta^5-C_5Me_5)(CO)_2FeP\{C(O)NMe_2\}-CNMe_2]Fe(CO)_3$ (**10**)

A mixture of **2** (0.47 g, 1.24 mmol) and $Fe_2(CO)_9$ (0.45 g, 1.24 mmol) in 50 ml of *n*-hexane ($20^\circ C$) was

irradiated for 1 h by means of a 125 W Hg arc lamp. The resulting mixture was stored for 48 h at 20 °C, whereupon black crystalline and analytically pure **10** (0.48 g, 70%) separated out. IR (KBr): ν 2953 w, 2918 m, 2873 w, 2013 s, [$\nu(\text{CO})$], 1969 vs [$\nu(\text{CO})$], 1886 vs [$\nu(\text{CO})$], 1596 m, 1544 m, 1456 w, 1396 m, 1384 m, 1250 w, 1167 w, 1100 m, 1030 w, 800 w, 750 w, 620 m, 604 m, 579 mcm^{-1} . $^1\text{H NMR}$ (C_6D_6): δ 1.47 (s, 15H, C_5Me_5), 2.48 (s, 3H, NMe), 3.06 (s, 3H, NMe), 3.14 (s, 3H, NMe), 3.34 (s, 3H, NMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 9.0 [d, $^3J_{\text{PC}} = 3.2$ Hz, $\text{C}_5(\text{CH}_3)_5$], 36.5 (s, br, NMe), 39.0 (s, br, NMe), 47.0 (d, $J_{\text{PC}} = 6.9$ Hz, NMe), 48.7 (d, $J_{\text{PC}} = 3.6$ Hz, NMe), 97.2 [s, $\text{C}_5(\text{CH}_3)_5$], 171.4 [s, $\text{C}(\text{O})\text{NMe}_2$], 213.0 (d, $^2J_{\text{PC}} = 16.8$ Hz, Cp^+FeCO), 217.6 (d, $^2J_{\text{PC}} = 13.0$ Hz, Cp^+FeCO), 223.3 [s, $\text{Fe}(\text{CO})_3$], 246.3 (d, $^1J_{\text{PC}} = 94.8$ Hz, $\text{PC}=\text{Fe}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ -108.0 s. MS/El: m/z 546 (M^+), 518 ($\text{M}^+ - \text{CO}$), 490 ($\text{M}^+ - 2\text{CO}$), 462 ($\text{M}^+ - 3\text{CO}$), 434 ($\text{M}^+ - 4\text{CO}$), 406 ($\text{M}^+ - 5\text{CO}$), 378 ($\text{M}^+ - 4\text{CO}$, -Fe). Anal. Found: C, 45.86; H, 4.88; N, 5.01. $\text{C}_{21}\text{H}_{27}\text{Fe}_2\text{N}_2\text{O}_6\text{P}$ (514.13) Calc.: C, 46.19; H, 4.98; N, 5.13%.

References

- [1] L. Weber, O. Kaminski, B. Quasdorff, A. Rühlicke, H.-G. Stammler and B. Neumann, *Organometallics*, **15** (1996) 123.
- [2] L. Weber, *Angew. Chem.*, **108** (1996) 293; *Angew. Chem., Int. Ed. Engl.*, **35** (1996) 271.
- [3] L. Weber, A. Rühlicke, H.-G. Stammler and B. Neumann, *Organometallics*, **12** (1993) 4653.
- [4] L. Weber, O. Kaminski, H.-G. Stammler, B. Neumann and V. Romanenko, *Z. Naturforsch.*, **48b** (1993) 1784.
- [5] L. Weber, O. Kaminski, H.-G. Stammler and B. Neumann, *Organometallics*, **14** (1995) 581.
- [6] L. Weber, O. Kaminski, H.-G. Stammler, B. Neumann and R. Boese, *Z. Naturforsch.*, **49b** (1994) 1693.
- [7] E. Niecke, H.-J. Mettermich, M. Nieger, D. Gudat, P. Wenderoth, W. Malisch, C. Hahner and W. Reich, *Chem. Ber.*, **126** (1993) 1299.
- [8] A.M. Arif, A.H. Cowley and S. Quashie, *J. Chem. Soc., Chem. Commun.*, (1985) 428.
- [9] P.B. Hitchcock, M.J. Maah and J.F. Nixon, *Heteroat. Chem.*, **2** (1991) 243.
- [10] L. Weber, I. Schumann, H.-G. Stammler and B. Neumann, *Organometallics*, **14** (1995) 1626.
- [11] W.P. Weber, G.W. Gokel and I.K. Ugi, *Angew. Chem.*, **84** (1972) 587; *Angew. Chem., Int. Ed. Engl.*, **11** (1972) 530.
- [12] D. Lentz, B. Pötter, R. Marschall, I. Brüdgam and J. Fuchs, *Chem. Ber.*, **123** (1990) 257.
- [13] G. Simonneaux, P. Le Maux, G. Jaouen and R. Dabard, *Inorg. Chem.*, **18** (1979) 3167.
- [14] R.W. Stephany, M.J.A. de Bie and W. Drenth, *Org. Magn. Reson.*, **6** (1974) 45.
- [15] J.-M. Bassett, G.K. Barker, M. Green, J.A.K. Howard, F.G.A. Stone and W.C. Wolsey, *J. Chem. Soc., Dalton Trans.*, (1981) 219.
- [16] R.D. Adams, F.A. Cotton and J.M. Troup, *Inorg. Chem.*, **13** (1974) 257.
- [17] P. Le Maux, G. Simonneaux, G. Jaouen, L. Quahab and P. Batail, *J. Am. Chem. Soc.*, **100** (1978) 4312.
- [18] L. Weber, M. Frebel and R. Boese, *New J. Chem.*, **13** (1989) 303 and references cited therein.
- [19] A.N. Chernega, A.V. Ruban, V.D. Romanenko, L.N. Markovskii, A.A. Korin, M.Y. Antipin and Y.T. Struchkov, *Heteroat. Chem.*, **2** (1991) 229 and references cited therein.
- [20] C.A. Tolman, *J. Am. Chem. Soc.*, **92** (1970) 2953.
- [21] K. Jonas and L. Schieferstein, *Angew. Chem.*, **88** (1976) 682; *Angew. Chem., Int. Ed. Engl.*, **15** (1976) 622.
- [22] O.J. Scherer, *Angew. Chem.*, **97** (1985) 905; *Angew. Chem., Int. Ed. Engl.*, **24** (1985) 924.
- [23] H. Eshtiagh-Hosseini, H.W. Kroto, J.F. Nixon, M.J. Maah and M.J. Taylor, *J. Chem. Soc., Chem. Commun.*, (1981) 199.
- [24] Th.C. Klebach, R. Lourens, F. Bickelhaupt, C.H. Stam and A. van Herk, *J. Organomet. Chem.*, **210** (1981) 211.
- [25] J. Grobe, D. Le Van, J. Nientiedt, B. Krebs and M. Dartmann, *Chem. Ber.*, **121** (1988) 655.
- [26] R. Appel, F. Knoch and V. Winkhaus, *J. Organomet. Chem.*, **307** (1986) 93.
- [27] J. Grobe, D. Le Van, M. Hegemann, B. Krebs and M. Läge, *Angew. Chem.*, **104** (1992) 94; *Angew. Chem., Int. Ed. Engl.*, **31** (1992) 95.
- [28] L. Weber, O. Kaminski, R. Boese and D. Bläser, *Organometallics*, **14** (1995) 820.
- [29] J.E. Bercaw, *J. Am. Chem. Soc.*, **96** (1974) 5087.
- [30] C. McDade, J.C. Green and J.E. Bercaw, *Organometallics*, **1** (1982) 1629.
- [31] L.E. Schock, C.P. Brock and T.J. Marks, *Organometallics*, **6** (1987) 232.
- [32] A.R. Bulls, W.P. Schäfer, M. Serfas and J.E. Bercaw, *Organometallics*, **6** (1987) 1219.
- [33] J.W. Pattiasina, C.E. Hissink, J.L. de Boer, A. Meetsma, J.H. Teuben and A.L. Spek, *J. Am. Chem. Soc.*, **107** (1985) 7758.
- [34] F.G.N. Cloke, J.C. Green, M.L.H. Green and C.P. Morley, *J. Chem. Soc., Chem. Commun.*, (1995) 945.
- [35] V.C. Gibson, T.P. Kee, S.T. Carter, R.D. Sanner and W. Clegg, *J. Organomet. Chem.*, **418** (1995) 197.
- [36] L. Weber, R. Kirchhoff and R. Boese, *J. Chem. Soc., Chem. Commun.*, (1992) 1182; *Chem. Ber.*, **126** (1993) 1963.
- [37] J. Grobe, D. Le Van, B. Krebs, R. Fröhlich and A. Schiemann, *J. Organomet. Chem.*, **389** (1990) C29.
- [38] H.J. Platas, J.M. Stewart and S.O. Grim, *Inorg. Chem.*, **12** (1973) 265.
- [39] G. Huttner, G. Mohr, P. Friedrich and H.G. Schmid, *J. Organomet. Chem.*, **160** (1978) 59; J. von Seyerl, D. Neugebauer and G. Huttner, *Chem. Ber.*, **112** (1979) 3637.
- [40] J.F. Nixon, *Chem. Rev.*, **88** (1988) 1327.
- [41] R. Appel, in M. Regitz and O. Scherer (eds.), *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, Thieme, Stuttgart, 1990, p. 157.
- [42] J. Klimes and E. Weiss, *Angew. Chem.*, **94** (1982) 207; *Angew. Chem., Int. Ed. Engl.*, **21** (1982) 205; *Angew. Chem. Suppl.*, (1982) 477.
- [43] K. Nakatsu, T. Mitsudo, H. Nakanishi, Y. Watanabe and T. Takegami, *Chem. Lett.*, (1977) 1447.
- [44] A.M. Crespi and D.F. Shriver, *Organometallics*, **4** (1985) 1830.
- [45] B. Eber, G. Huttner, Z. Zsolnai and W. Imhof, *J. Organomet. Chem.*, **402** (1991) 221.
- [46] U. Schubert, in *Transition Metal Carbene Complexes*, Verlag Chemie, Weinheim, 1983, p. 73 and references cited therein; J. Daub, G. Endress, U. Erhardt, K.H. Jogun, J. Kappler, A. Laumer, R. Pfiz and J.J. Sterzowski, *Chem. Ber.*, **115** (1982) 1787; J. Park, S. Kang, D. Whang and K. Kim, *Organometallics*, **10** (1991) 3413; F. Carre, R.J.P. Corriu, C. Guerin, B.J.L. Henner, W.W. Choy and W.C. Mau, *Organometallics*, **8** (1989) 313.
- [47] E.O. Fischer, J. Schneider and K. Ackermann, *Z. Naturforsch.*, **39b** (1984) 468.

- [48] N.H. Tran Huy, J. Fischer and F. Mathey, *Organometallics*, 7 (1988) 240.
- [49] F.A. Cotton, L.R. Falvello and R.C. Najjar, *Organometallics*, 1 (1982) 1640.
- [50] E.O. Fischer, R. Reitmeier and K. Ackermann, *Angew. Chem.*, 95 (1983) 419; *Angew. Chem., Int. Ed. Engl.*, 22 (1983) 411; *Angew. Chem. Suppl.*, (1983) 488; E.O. Fischer and R. Reitmeier, *Z. Naturforsch.*, 38b (1983) 582.
- [51] G. Bertrand and R. Reed, *Coord. Chem. Rev.*, 137 (1994) 323.
- [52] G. Becker, O. Mundt and M. Rössler, *Z. Anorg. Allg. Chem.*, 468 (1980) 55; L. Weber, K. Reizig and R. Boese, *Organometallics*, 4 (1985) 1890, 2097.
- [53] M. Baudler, *Pure Appl. Chem.*, 52 (1980) 755; *Z. Chem.*, 24 (1984) 352.
- [54] E.O. Fischer, H.-J. Beck, C.G. Kreiter, J. Lynch, J. Müller and E. Winkler, *Chem. Ber.*, 105 (1972) 162.
- [55] R. Appel, J. Peters and R. Schmitz, *Z. Anorg. Allg. Chem.*, 475 (1981) 18, 6204.
- [56] F.R. Kreißl, M. Wolfgruber and W.J. Sieber, *Organomet. Chem.*, 270 (1984) C4.
- [57] F.R. Kreißl, J. Ostermeier and C. Ogric, *Chem. Ber.*, 128 (1995) 289.
- [58] H.M. Anstice, H.H. Fielding, V.C. Gibson, C.E. Housecroft and T.P. Kee, *Organometallics*, 10 (1991) 2183; V.C. Gibson, T.P. Kee and W. Clegg, *J. Chem. Soc., Chem. Commun.*, (1990) 313; M.L.H. Green, P.M. Hare and J.A. Bandy, *J. Organomet. Chem.*, 330 (1987) 61.
- [59] N. Hovnanian and L.G. Hubert-Pfalzgraf, *J. Organomet. Chem.*, 299 (1986) C29; N. Hovnanian, L.G. Hubert-Pfalzgraf and G. Le Borgne, *Inorg. Chem.*, 24 (1985) 4647.
- [60] W.P. Fehlhammer, W.A. Herrmann and K. Öfele, in G. Brauer (ed.), *Handbuch der Präparativen Anorganischen Chemie*, Vol. III, Enke, Stuttgart, 1981, p. 1827.
- [61] F.W. Grevels and V. Skibbe, *J. Chem. Soc., Chem. Commun.*, (1984) 681.