N-(N',N',N'',N''-tetramethyl) guanidine-substituted phosphines as monodentate, bidentate or tridentate ligands in transition metal chemistry [1]

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Abstract

The diorganophosphinous-N-(N',N',N'',N''-tetramethyl)guanidinides 1a and 1b and the organophosphonous-bis-N-(N',N',N'',N''-tetramethyl)guanidinides 2 and 3 are used as ligands towards carbonyls of zerovalent transition metals. In most cases coordination via phosphorus is observed. 1b and 2 act as PN-donors towards the (tetracarbonyl)molybdenum fragment, forming chelate complexes involving one five-membered ring. 3 acts as a PNN'-donor towards molybdenum carbonyls, forming a bicyclic chelate complex. X-ray structure determinations were performed for the octacarbonyldimanganese compound 7, the tricarbonylnickel complex 8 and the tetracarbonyliron derivative 10. The dimanganese compound 7 was found to be diaxially substituted with short MnC bonds but standard MnP bond lengths. The nickel compound 8 exhibited short PNi bonds, long NiC bonds and short CO bonds, consistent with enhanced π-back donation from metal to phosphorus. The coordination geometry at the iron atom in 10 was found to be trigonal bipyramidal with phosphorus in the axial position, strongly distorted towards square pyramidal.

Keywords: Carbonyls; Transition metal chemistry; Coordination geometry

1. Introduction

The coordination chemistry of amidines (e.g. see Ref. [1]) and substituted guanidines [2] has been extensively studied. To the best of our knowledge, only one report concerning the behaviour of guanidine-substituted phosphorus compounds towards transition metals has appeared [3]. During the past few years a range of new and/or novel types of phosphorus compounds have been synthesised in our laboratory. These compounds have been extensively studied regarding their use as ligands in transition metal chemistry [4]. As we have recently studied some N-(N',N',N'',N''-tetramethyl)guanidine(TMG)-substituted phosphorus compounds [5,6], it seemed interesting to extend our work to coordination compounds of TMG-substituted phosphorus(III) compounds.

A number of different modes of coordination of transition metals with these compounds can be envisaged (Fig. 1). The simplest coordination type is A, i.e. coordination to the metal atom via the phosphorus atom. This is the form of bonding encountered most frequently in complexes of phosphorus(III) compounds. In type B, involving a phosphorus(III)-substituted tetramethylguanidine derivative, the metal is bonded to the amino nitrogen atom, whereas the phosphorus atom is not involved in the bonding to the metal. Only a few examples are known for coordination of type C, where the nitrogen atom adjacent to phosphorus is bound to the metal atom. This type of bonding is found in compounds formed in the reaction of some phosphorus(III) amides with boron compounds [7], and in the case of boron trifluoride interacting with methylphosphonic-bis-N-(N',N',N'',N''-tetramethyl)guanidinide [6]. The bonding mode observed in some copper(I) complexes of trithiophosphites, where a sulphur atom adjacent to the phosphorus atom is involved in the bonding to the transition metal, is similar [8]. C represents the normal coordination mode for substituted

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[1] Dedicated to Professor Jörn Müller on the occasion of his 60th birthday.

guanidines [2]. Coordination of type **D** is found in most cases of chelate formation involving ligands with a PN-donor set, similar to the title compounds [9–12]. Likewise, a PNN-donor set leads in most cases to coordination of type **E** [11,13,14]. Even though it would be expected, at least for the early transition and the main group metals, coordination of type **F** is rarely found in the coordination chemistry of phosphorus–nitrogen compounds. One of the few examples, formally, results from dialkylaminophosphinous-bis-*N*-(*N'*,*N'*,*N''*,*N'''*-tetramethyl)guanidinide and aluminium trichloride [15].

Our aim was to determine whether the high basicity of the imino nitrogen atoms in the TMG substituent or

the chelate effect are more important for the reactivity of the title compounds towards zerovalent transition metals.

2. Results and discussion

The reaction of the diorganophosphinous-*N*-(*N'*,*N'*,*N''*,*N'''*-tetramethyl)guanidinides **1a** and **1b** with Mo(CO)$_6$ led to the monosubstituted complexes **4a** and **4b**, respectively (Eq. (1) in Scheme 1). There was no sign of displacement of a second CO-group through the same guanidine system with formation of a chelate. The compounds were clearly characterised by their NMR
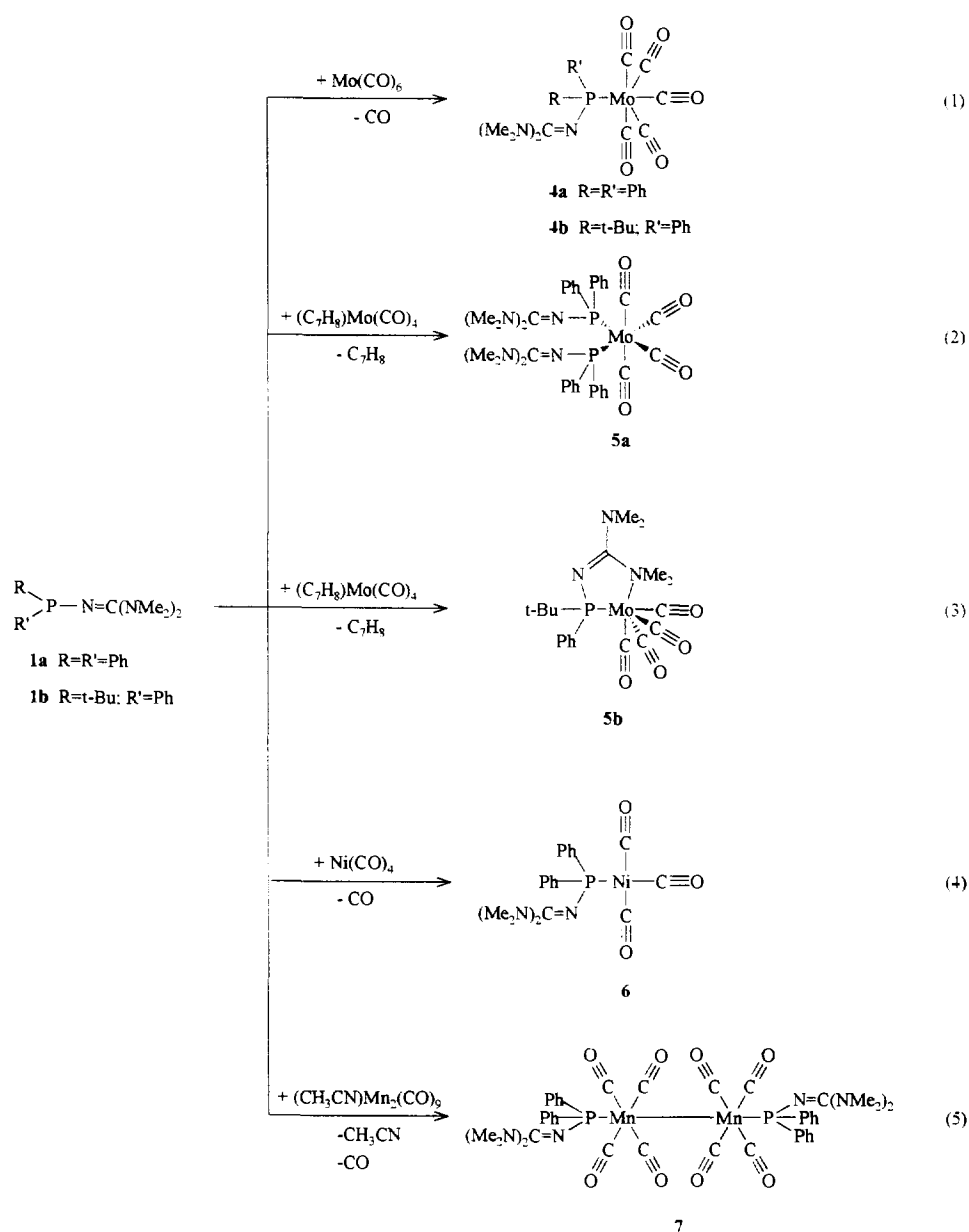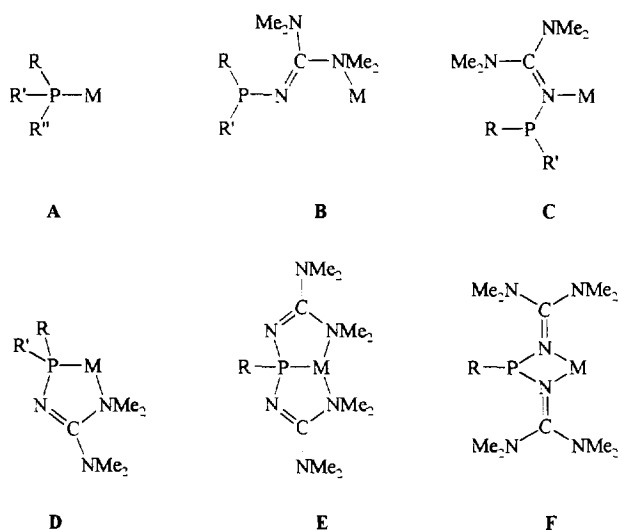

Scheme 1.

Fig. 1.

and mass spectra. In the ^{31}P NMR spectra both compounds showed one signal, ca. 25 ppm downfield from the signals of the starting materials (Table 1). In the ^{13}C NMR spectrum of **4b**, signals for two different carbonyl groups were observed. The signal at lower field (δ = 211.11 ppm) was assigned to the carbonyl group trans to phosphorus. In the EI-mass spectrum of **4a** the molecular ion was observed, whereas in the mass spectrum of **4b** only the ion formed by loss of one CO group was found. For both compounds the fragments resulting from the successive loss of the CO groups were observed. The IR spectrum of **4a** exhibited three bands in the CO stretching region (local C_{4v} symmetry), as expected (Table 2).

When **1a** was allowed to react with norbornadiene(tetracarbonyl)molybdenum in a molar ratio of 1 : 1, only compound **5a** was obtained, where two molecules of **1a** were coordinated to the metal (Eq. (2) in Scheme 1). No evidence for the formation of a chelate could be found. The $\delta(^{31}$P) value of **5a** was observed 28 ppm downfield from that of the educt (3 ppm further downfield from the $\delta(^{31}$P) value of **4a**). For a chelate complex where the phosphorus atom would be part of a five-membered ring, an additional shift of 20–40 ppm to lower field by the ring effect would be expected [16]. In the IR spectrum of **5a** the four CO stretching frequencies, expected for a cis-$L_2M(CO)_4$ compound with local C_{2v} symmetry, were observed (Table 2). In the EI-mass spectrum the molecular ion was observed for **5a**, as were signals arising from the subsequent loss of the CO groups and the loss of one ligand.

From **1b** and norbornadiene(tetracarbonyl)molybdenum, the chelate complex **5b** was formed (Eq. (3) in Scheme 1). The EI-mass spectrum showed peaks due to the molecular ion and the subsequent loss of the four CO groups. The $\delta(^{31}$P) value of **5b** was shifted 38 ppm downfield to that of the ligand (Table 2). This shift is

caused, partly, by the formation of the five-membered chelate ring. The IR spectrum of **5b** exhibited only three signals for the CO stretching vibration (Table 2). The signal at 1864 cm^{-1} was quite broad, and some bands may accidentally be degenerate. The ligand asymmetry and steric interactions due to the bulky *tert*-butyl group could be the reason for this.

The reaction of aminophosphines with tetracarbonyl-nickel often led to higher substitution when the starting materials were employed in a 1 : 1 molar ratio [17]. To avoid this, and to obtain the chelate complex, a large excess of the metal compound was used in the reaction with **1a**. Only the monosubstituted product **6** was obtained (Eq. (4) in Scheme 1). The $\delta(^{31}$P) signal of **6** was 25 ppm downfield to that of **1a** (Table 1). This is in good agreement with the shift observed for the pentacarbonylmolybdenum compound **4a**, where one molecule of **1a** acts as a monodentate ligand. In the IR spectra, two signals were observed for ν(CO) (Table 2). This is expected for a tricarbonyl nickel compound of C_{3v} symmetry.

When **1b** was allowed to react with acetonitrile-(nonacarbonyl)dimanganese, two main products were observed in the reaction mixture by ^{31}P NMR. Only one of these products was isolated. It was identified as the diaxially substituted octacarbonyldimanganese derivative **7** (Eq. (5) in Scheme 1). The second main product could not be separated from other by-products. The $\delta(^{31}$P) value of **7** lies at unusually low field (Table 2). This shift should correspond to that of a chelate complex, but the X-ray analysis (see below) showed that both acetonitrile molecules and one molecule of CO had been displaced, with formation of the symmetric complex **7**.

The reaction of **2** with tetracarbonylnickel led, in the same way as reaction (3), to the complex **8** by substitution of only one molecule of CO (Eq. (6) in Scheme 2). The $\delta(^{31}$P) value lay only 9 ppm downfield to that of **2** (Table 1). In the IR spectrum, three signals for the CO

Table 1
^{31}P NMR data for the compounds **1a/b–11**

Compound	$\delta(^{31}$P)	$\Delta(^{31}$P)
Ph$_2$PTMG **1a**	32.87	—
t-Bu(Ph)PTMG **1b**	51.25	—
MeP(TMG)$_2$ **2**	64.40	—
t-BuP(TMG)$_2$ **3**	81.61	—
[Ph$_2$PTMG]Mo(CO)$_5$ **4a**	58.34	25.47
[t-Bu(Ph)PTMG]Mo(CO)$_5$ **4b**	78.73	27.48
[Ph$_2$PTMG]$_2$Mo(CO)$_4$ **5a**	61.40	28.53
[t-Bu(Ph)PTMG]Mo(CO)$_4$ **5b**	89.58	38.33
[Ph$_2$PTMG]Ni(CO)$_3$ **6**	58.94	26.07
[Ph$_2$PTMG]Mn(CO)$_4$Mn(CO)$_4$[Ph$_2$PTMG] **7**	94.14	61.27
[MeP(TMG)$_2$]Ni(CO)$_3$ **8**	73.46	9.06
[MeP(TMG)$_2$]Mo(CO)$_4$ **9**	99.65	35.25
[t-BuP(TMG)$_2$]Fe(CO)$_4$ **10**	89.41	7.80
[t-BuP(TMG)$_2$]Mo(CO)$_3$ **11**	161.54	79.93

Table 2
Selected IR data for the compounds 4a/b–11

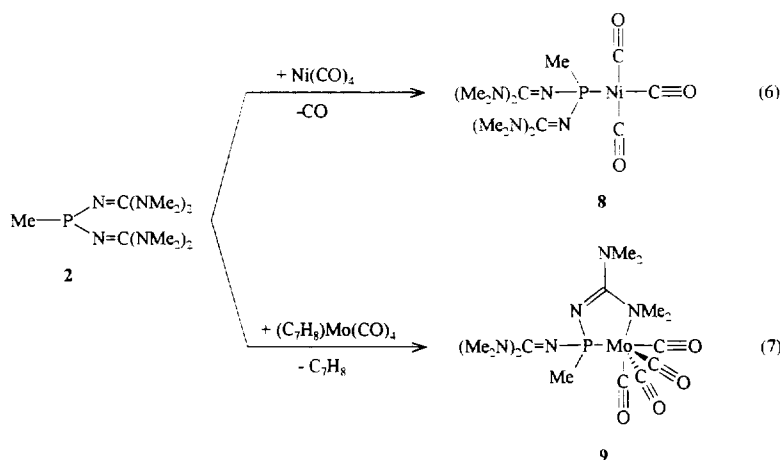| Compound	IR ṽ (CO) [cm^{-1}] (mode [a])				
[Ph$_2$PTMG]Mo(CO)$_5$ 4a [b]	2065 m (A$_1$)	1979 m, sh (B$_1$)	1914 vs, br (E + A$_1$)		
[Ph$_2$PTMG]$_2$Mo(CO)$_4$ 5a [c]	2040 s (A$_1$)	1925 vs (A$_1$)	1880 vs (B$_1$)	1810 m (B$_2$)	
[t-Bu(Ph)PTMG]Mo(CO)$_4$ 5b [b]	2006 w (A$_1$)	1925 w (A$_1$)	1864 vs		
[Ph$_2$PTMG]Ni(CO)$_3$ 6 [d]	2080 m (A$_1$)	2010 vs (E)			
[Ph$_2$PTMG]Mn(CO)$_4$Mn(CO)$_4$[Ph$_2$PTMG] 7 [c]	2020 m	2005 m	1955 vs	1920 m, sh	
[MeP(TMG)$_2$]Ni(CO)$_3$ 8 [d]	2060 s (A$_1$)	1985 vs, br (E)	1945 s (E)		
[MeP(TMG)$_2$]Mo(CO)$_4$ 9 [b]	2002 vw (A$_1$)	1892 vs (A$_1$)	1782 vs	1760 vs	
[t-BuP(TMG)$_2$]Fe(CO)$_4$ 10 [d]	2050 m	1965 m	1935 s	1930 s, sh	
[t-BuP(TMG)$_2$]Mo(CO)$_3$ 11 [b]	2003 s	1920 m, sh	1874 vs, br	1845 vs	1790 vs

vw = very weak, w = weak, m = medium, s = strong, vs = very strong. [a] Tentative assignment. [b] Recorded as KBr Pellet. [c] Recorded in toluene solution. [d] Recorded in n-hexane solution. [e] Recorded in CDCl$_3$ solution.

stretching vibrations were observed instead of the expected two bands for local C_{3v} symmetry (Table 2). This splitting of the E mode has been observed before and has been attributed to the distortion of the symmetry of the complex by steric interaction of the ligand with the CO groups [18]. In the case of 8 the distortion of the symmetry might also be caused by interaction of the ligand NMe$_2$ groups with the nickel atom. To decide whether there is any interaction between the metal atom and the ligand nitrogen atoms in the solid state, the structure of 8 was determined by X-ray diffraction (see below).
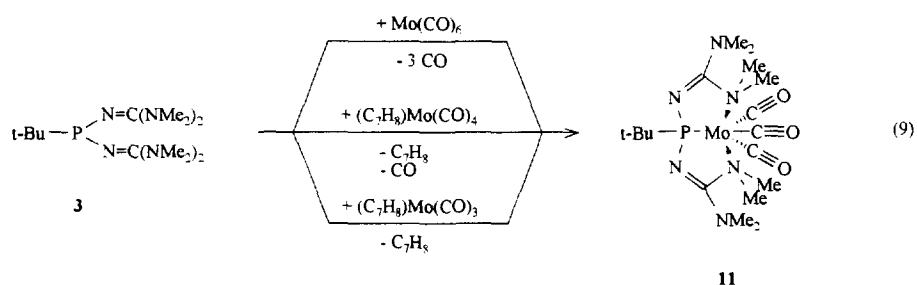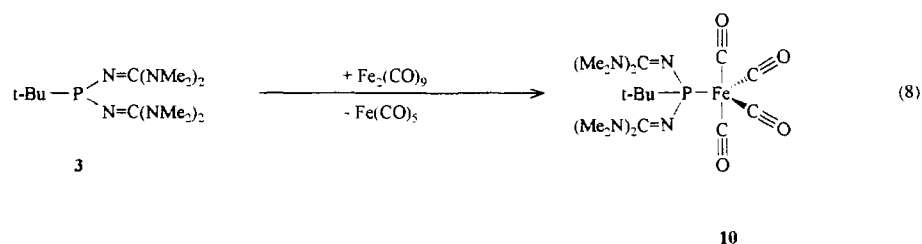
In accordance with the observations made in the reaction of 1b with norbornadiene(tetracarbonyl)-molybdenum, the corresponding reaction performed with 2 led to the chelate complex 9 (Eq. (7) in Scheme 2). The δ(^{31}P) value lay 35 ppm to lower field than that of 2 (Table 1). This shift is comparable to that observed for 5b, caused by the coordination of the phosphorus atom to the metal and by the formation of a five-membered chelate ring [16]. In the IR spectrum, four signals assigned to the CO stretching vibration were observed (Table 2). This corresponds to local C_{2v} symmetry for the CO groups. The frequency of the vibrations was

unusually low, which can be explained by the lack of π-backbonding from the metal atom to the nitrogen donor. Such low frequencies were not observed for the other compounds discussed here (except for 11). In the ^{1}H NMR spectrum of 9, one broad singlet at 2.80 ppm was observed for the protons of the NMe$_2$ groups, and one weak, very broad signal around 1.4 ppm, for the protons of the PMe group. Neither in the proton-coupled ^{31}P NMR, nor in the ^{1}H NMR spectra, was a ^{2}J(PH) coupling constant observed. The signals in the ^{1}H NMR spectrum were broad and, therefore, the structure of 9 in solution must be at least somewhat fluxional, possibly involving an exchange of the coordinating nitrogen atoms. Unfortunately, the complex was not stable in CD$_2$Cl$_2$, the only solvent suitable for temperature-dependent NMR studies of 9.

In the reaction of tert-butylphosphonous-bis-N-(N',N',N'',N''-tetramethyl)guanidinide 3 with nonacarbonyldiiron, the monosubstituted, mononuclear complex 10 was formed (Eq. (8) in Scheme 3). The δ(^{31}P) value of 10 was shifted only slightly to lower field from that of the starting material (Table 1), indicating monosubstitution without chelate formation. The IR spectrum of 10 exhibited four signals for the CO stretching vibra-

Scheme 2.

$$t\text{-Bu} - P \begin{array}{c} N=C(NMe_2)_2 \\ N=C(NMe_2)_2 \end{array}$$

3

$$\xrightarrow[-\ Fe(CO)_5]{+\ Fe_2(CO)_9}$$

$$\begin{array}{c} (Me_2N)_2C=N \\ t\text{-Bu} - P - Fe \\ (Me_2N)_2C=N \end{array}$$

(8)

10

$$t\text{-Bu} - P \begin{array}{c} N=C(NMe_2)_2 \\ N=C(NMe_2)_2 \end{array}$$

3

$$\begin{array}{c} +\ Mo(CO)_6 \\ -\ 3\ CO \\ +\ (C_7H_8)Mo(CO)_4 \\ -\ C_7H_8 \\ -\ CO \\ +\ (C_7H_8)Mo(CO)_3 \\ -\ C_7H_8 \end{array}$$

$$\begin{array}{c} NMe_2 \\ Me \\ Me \\ N \quad N \quad C=O \\ t\text{-Bu} - P - Mo - C\equiv O \\ N \quad N \quad C=O \\ Me \\ Me \\ NMe_2 \end{array}$$

(9)

11

Scheme 3.

tion, consistent with C_{2v} symmetry of an equatorially substituted $LM(CO)_4$ complex (Table 2). The X-ray structure determination of **10** showed axial substitution (see below). So, either **10** was equatorially substituted in solution (the IR spectrum was recorded in n-hexane) or the interaction of one nitrogen atom with the iron atom led to a disturbance of the symmetry, resulting in a splitting of the E mode.

The reaction of **3** with either hexacarbonylmolybde-num, norbornadiene(tetracarbonyl)molybdenum or cy-cloheptatriene(tricarbonyl)molybdenum led to the same product. It was identified as the bicyclic complex **11**, where **3** acted as a tridentate ligand (Eq. (9) in Scheme 3). In the reaction of tridentate ligands, displacement of one molecule of CO from precursors such as norborna-diene(tetracarbonyl)molybdenum was reported previ-
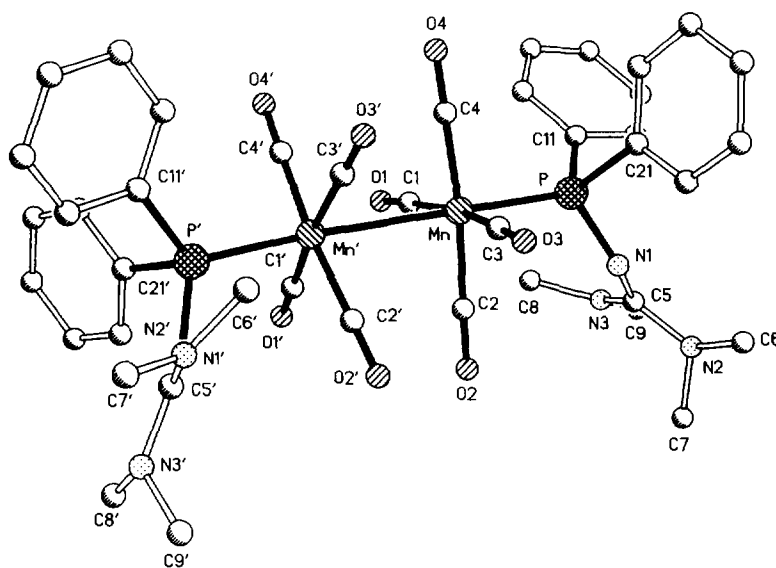
Fig. 2. Molecular structure of **7**.

Table 3
Bond lengths (pm) and angles (deg) for **7**

Mn–C(1)	182.3(3)	Mn–C(2)	183.5(3)
Mn–C(4)	183.7(3)	Mn–C(3)	184.0(3)
Mn–P	225.70(9)	Mn–Mn'	290.23(9)
P–N(1)	164.5(2)	P–C(21)	183.5(2)
P–C(11)	183.9(2)	O(1)–C(1)	114.8(3)
O(2)–C(2)	114.3(3)	O(3)–C(3)	114.2(3)
O(4)–C(4)	114.5(3)	N(1)–C(5)	128.4(3)
N(2)–C(5)	138.9(3)	N(2)–C(6)	144.3(4)
N(2)–C(7)	146.0(4)	N(3)–C(5)	136.4(3)
N(3)–C(8)	145.0(4)	N(3)–C(9)	145.3(4)
C(11)–C(12)	139.0(3)	C(11)–C(16)	139.1(3)
C(12)–C(13)	138.6(3)	C(13)–C(14)	138.0(4)
C(14)–C(15)	138.6(4)	C(15)–C(16)	137.5(4)
C(21)–C(26)	138.1(3)	C(21)–C(22)	140.0(3)
C(22)–C(23)	137.6(4)	C(23)–C(24)	137.4(4)
C(24)–C(25)	138.2(4)	C(25)–C(26)	138.0(4)
Mn'–C(3')	183.2(3)	Mn'–C(4')	183.2(3)
Mn'–C(2')	183.4(3)	Mn'–C(1')	183.5(3)
Mn'–P'	225.01(9)	P'–N(1')	165.5(2)
P'–C(21')	183.3(2)	P'–C(11')	183.7(2)
O(1')–C(1')	114.2(3)	O(2')–C(2')	114.5(3)
O(3')–C(3')	114.3(3)	O(4')–C(4')	114.2(3)
N(1')–C(5')	128.8(3)	N(2')–C(5')	136.1(4)
N(2')–C(6')	144.1(4)	N(2')–C(7')	146.1(4)
N(3')–C(5')	138.6(3)	N(3')–C(8')	144.3(4)
N(3')–C(9')	146.3(4)	C(11')–C(12')	139.1(4)
C(11')–C(16')	139.4(3)	C(12')–C(13')	138.3(4)
C(13')–C(14')	138.0(4)	C(14')–C(15')	137.3(4)
C(15')–C(16')	138.8(4)	C(21')–C(22')	139.1(3)
C(21')–C(26')	139.7(3)	C(22')–C(23')	138.7(4)
C(23')–C(24')	137.6(4)	C(24')–C(25')	138.2(4)
C(25')–C(26')	138.5(4)		
C(1)–Mn–C(2)	87.67(11)	C(1)–Mn–C(4)	91.44(11)
C(2)–Mn–C(4)	173.98(11)	C(1)–Mn–C(3)	169.78(10)
C(2)–Mn–C(3)	88.89(10)	C(4)–Mn–C(3)	90.98(11)
C(1)–Mn–P	97.29(8)	C(2)–Mn–P	92.60(8)
C(4)–Mn–P	93.42(8)	C(3)–Mn–P	92.48(8)
C(1)–Mn–Mn'	84.48(8)	C(2)–Mn–Mn'	87.85(8)
C(4)–Mn–Mn'	86.13(8)	C(3)–Mn–Mn'	85.78(8)
P–Mn–Mn'	178.19(2)	N(1)–P–C(21)	100.30(10)
N(1)–P–C(11)	109.23(11)	C(21)–P–C(11)	98.80(11)
N(1)–P–Mn	115.45(8)	C(21)–P–Mn	112.06(8)
C(11)–P–Mn	118.28(8)	C(5)–N(1)–P	138.7(2)
C(5)–N(2)–C(6)	117.6(2)	C(5)–N(2)–C(7)	119.1(2)
C(6)–N(2)–C(7)	114.2(3)	C(5)–N(3)–C(8)	121.9(2)
C(5)–N(3)–C(9)	122.6(2)	C(8)–N(3)–C(9)	114.9(3)
O(1)–C(1)–Mn	177.5(2)	O(2)–C(2)–Mn	178.6(2)
O(3)–C(3)–Mn	178.3(2)	O(4)–C(4)–Mn	179.7(2)
N(1)–C(5)–N(3)	127.2(2)	N(1)–C(5)–N(2)	118.8(2)
N(3)–C(5)–N(2)	114.0(2)	C(12)–C(11)–C(16)	118.3(2)
C(12)–C(11)–P	122.3(2)	C(16)–C(11)–P	119.3(2)
C(13)–C(12)–C(11)	120.9(2)	C(14)–C(13)–C(12)	119.9(3)
C(13)–C(14)–C(15)	119.7(2)	C(16)–C(15)–C(14)	120.1(2)
C(15)–C(16)–C(11)	121.1(2)	C(26)–C(21)–C(22)	118.4(2)
C(26)–C(21)–P	120.9(2)	C(22)–C(21)–P	120.7(2)
C(23)–C(22)–C(21)	120.7(2)	C(24)–C(23)–C(22)	120.0(3)
C(23)–C(24)–C(25)	120.0(2)	C(26)–C(25)–C(24)	120.0(3)
C(25)–C(26)–C(21)	120.8(2)	C(3')–Mn'–C(4')	90.84(11)
C(3')–Mn'–C(2')	90.33(11)	C(4')–Mn'–C(2')	172.87(11)
C(3')–Mn'–C(1')	172.11(11)	C(4')–Mn'–C(1')	87.94(11)
C(2')–Mn'–C(1')	89.95(11)	C(3')–Mn'–P'	96.12(8)
C(4')–Mn'–P'	95.21(8)	C(2')–Mn'–P'	91.66(8)
C(1')–Mn'–P'	91.76(8)	C(3')–Mn'–Mn	84.83(8)

Table 3 (continued)

C(4')–Mn'–Mn	88.29(8)	C(2')–Mn'–Mn	84.80(8)
C(1')–Mn'–Mn	87.34(8)	P'–Mn'–Mn	176.35(2)
N(1')–P'–C(21')	99.16(10)	N(1')–P'–C(11')	109.14(11)
C(21')–P'–C(11')	99.98(11)	N(1')–P'–Mn'	113.93(8)
C(21')–P'–Mn'	112.90(8)	C(11')–P'–Mn'	119.11(8)
C(5')–N(1')–P'	137.5(2)	C(5')–N(2')–C(6')	121.7(2)
C(5')–N(2')–C(7')	122.2(3)	C(6')–N(2')–C(7')	115.4(3)
C(5')–N(3')–C(8')	117.9(2)	C(5')–N(3')–C(9')	119.0(2)
C(8')–N(3')–C(9')	114.0(3)	O(1')–C(1')–Mn'	178.0(2)
O(2')–C(2')–Mn'	178.3(2)	O(3')–C(3')–Mn'	179.0(2)
O(4')–C(4')–Mn'	178.2(2)	N(1')–C(5')–N(2')	128.2(2)
N(1')–C(5')–N(3')	118.0(2)	N(2')–C(5')–N(3')	113.9(2)
C(12')–C(11')–C(16')	118.3(2)	C(12')–C(11')–P'	119.7(2)
C(16')–C(11')–P'	122.0(2)	C(13')–C(12')–C(11')	120.6(3)
C(14')–C(13')–C(12')	120.4(3)	C(15')–C(14')–C(13')	119.8(3)
C(14')–C(15')–C(16')	120.2(3)	C(15')–C(16')–C(11')	120.7(3)
C(22')–C(21')–C(26')	118.5(2)	C(22')–C(21')–P'	122.2(2)
C(26')–C(21')–P'	119.3(2)	C(23')–C(22')–C(21')	120.3(2)
C(24')–C(23')–C(22')	120.8(3)	C(23')–C(24')–C(25')	119.5(2)
C(24')–C(25')–C(26')	120.4(2)	C(25')–C(26')–C(21')	120.5(2)

ously [14]. The $\delta(^{31}P)$ value of 11 was shifted by 80 ppm downfield to that of 3. The phosphorus atom in 11 is part of two five-membered rings. The downfield shift, caused by the incorporation of a phosphorus atom into a five-membered chelate ring, is of additive character [16]. Thus the large downfield shift observed for 11 is explained. In the ^1H NMR spectrum, three broad signals were observed for the NMe$_2$ groups. No temperature-dependent NMR spectra could be obtained because 11 was not stable in the only suitable solvent, CD$_2$Cl$_2$. The ^1H NMR resonances of the uncoordinated NMe$_2$ groups were observed at $\delta = 3.08$ ppm. The methyl groups of the coordinated NMe$_2$ groups were nonequivalent. The signals at $\delta = 2.83$ ppm and $\delta = 2.67$ ppm could not be assigned to the methyl groups in endo and exo position in the bicyclic compound 11. Similar inequivalence of the NMe$_2$ methyl groups in chelate rings has been observed before [10].

3. Molecular structure of 7 (Fig. 2)

The phosphorus-containing ligands are in axial positions with nearly linear angles P–Mn–Mn' (178.19(2)°) and Mn–Mn'–P' (176.35(2)°). All angles at manganese involving phosphorus are larger than 90° because of the steric requirements of the phosphine ligand (91.66(8)° C2'–Mn'–P' to 97.29(8)° C1–Mn–P). As in bis-[tetra-carbonyl(diphenylmethylphosphine)manganese-(0)] 12 [19] the Mn(CO)$_4$ groups are staggered, with an average torsion angle of 45° (Tables 3 and 4).

The Mn–Mn' (290.23(9) pm) and the Mn–P (225.70(9) pm) and Mn'–P' (225.01(9) pm) bond lengths do not differ significantly from those in 12 (Mn–Mn 290 pm, P–Mn 223 pm). However, the Mn–C and C–O bond lengths show a major difference. Whereas the

Mn–C distances (average 183.4 pm) are longer than in 12 (Mn–C 175 pm), the C–O bonds (average 114.4 pm) are significantly shorter (12 119 pm).

Both phosphorus atoms display distorted tetrahedral coordination geometry, with the largest deviations from ideal angles for C21–P–Mn (98.80(11)°) and C11'–P'–Mn' (119.0(2)°).

4. Molecular structure of 8 (Fig. 3)

All crystals were of poor quality, with broad and irregular profiles; this is reflected in the high R values and poor precision.

The asymmetric unit contains two independent molecules of compound 8. However, the differences in bond lengths and angles are not significant, so only one molecule is discussed. No other N–P–Ni systems are available for comparison in the Cambridge Crystallographic Data Base, so this structure is compared with that of [(H$_3$C)$_3$C]$_3$PNi(CO)$_3$ 13 [20]. As in 13, the nickel atom in 8 is tetrahedrally coordinated with the largest deviation from tetrahedral angles for C91–Ni–C92 (116.4(8)°) and C90–Ni–P (103.6(4)°) (Tables 5 and 6).

The Ni–P bond (224.3(4) pm) is shorter, the average Ni–C (178(2) pm) bond is insignificantly longer than in 13 (Ni–P 229.1(5) pm, average Ni–C 172(5) pm). The former effect may imply slightly better π-back donation in 8.

In the compound tricarbonyl-(trimethyl-1-methoxy-4-oxo-1,2-diphenyl-1,2-diphosphacyclopentene-3,3,5-tricarboxylate)nickel the corresponding Ni–P bond length is 220.0 pm [21]; in P, P', P'', P'''-tetrakis(tricarbonyl-nickel)-tetraphosphorus-hexaoxide the Ni–P bond length is 215.0 pm [22].

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (pm$^2 \times 10^{-1}$) for **7**

	x	y	z	U_{eq}
Mn	1949.4(3)	4521.(3)	2445.8(2)	22.8(1)
P	216.5(5)	3217.1(5)	2351.6(3)	22.6(1)
O(1)	3219(2)	2920(2)	1406.8(12)	40.3(4)
O(2)	1036(2)	5114(2)	934.3(11)	40.6(4)
O(3)	973(2)	6477(2)	3396.5(11)	39.6(4)
O(4)	3094(2)	4078(2)	3961.5(12)	45.8(5)
N(1)	−921(2)	3253(2)	1678.6(12)	27.9(4)
N(2)	−2633(2)	2803(2)	711.6(13)	38.5(5)
N(3)	−1059(2)	1857(2)	419.1(14)	42.9(6)
C(1)	2745(2)	3538(2)	1823.7(15)	28.0(5)
C(2)	1395(2)	4900(2)	1518.2(15)	28.3(5)
C(3)	1348(2)	5721(2)	3042.6(14)	28.0(5)
C(4)	2654(2)	4252(2)	3381(2)	30.8(5)
C(5)	−1476(2)	2655(2)	970.9(15)	31.2(5)
C(6)	−3256(2)	3421(3)	1313(2)	46.0(7)
C(7)	−2906(3)	2978(3)	−96(2)	65.5(10)
C(8)	231(3)	18893	416(2)	46.4(7)
C(9)	−1858(3)	832(3)	−130(2)	67.8(11)
C(11)	320(2)	1695(2)	2274.9(14)	26.5(5)
C(12)	1415(2)	13712	2468(2)	31.1(5)
C(13)	1449(2)	227(2)	2455(2)	37.3(6)
C(14)	390(3)	−611(2)	2231(2)	42.0(7)
C(15)	−707(3)	−300(2)	2031(2)	40.3(6)
C(16)	−740(2)	841(2)	2064(2)	34.3(6)
C(21)	−473(2)	3509(2)	3282.6(14)	25.6(5)
C(22)	−130(2)	3046(2)	3925.8(15)	33.0(6)
C(23)	−615(3)	3298(2)	4635(2)	40.7(6)
C(24)	−1454(3)	4001(3)	4715(2)	41.8(7)
C(25)	−1801(2)	4467(3)	4087(2)	40.3(6)
C(26)	−1309(2)	4223(2)	3377(2)	33.7(6)
Mn′	4152.9(3)	6249.3(3)	2607.8(2)	23.1(1)
P′	5791.0(5)	7648.9(5)	2689.5(4)	23.9(1)
O(1′)	4270(2)	5149(2)	875.6(11)	42.0(5)
O(2′)	2492(2)	7711(2)	2113.8(13)	45.7(5)
O(3′)	3777(2)	7074(2)	4325.3(12)	48.6(5)
O(4′)	5563(2)	4546(2)	3015.8(13)	49.5(5)
N(1′)	5488(2)	8711(2)	2296.6(12)	29.3(5)
N(2′)	5299(3)	10367(2)	3320(2)	48.9(6)
N(3′)	5489(2)	10469(2)	2014.2(15)	39.8(5)
C(1′)	4212(2)	5582(2)	1536(2)	29.1(5)
C(2′)	3117(2)	7134(2)	2298(2)	31.7(6)
C(3′)	3920(2)	6747(2)	3666(2)	32.0(6)
C(4′)	5027(2)	5211(2)	2872(2)	31.4(5)
C(5′)	5422(2)	9786(2)	2558(2)	33.6(6)
C(6′)	4708(3)	9780(3)	3856(2)	54.7(8)
C(7′)	5918(4)	11574(3)	3693(2)	75.2(12)
C(8′)	5830(3)	9991(3)	1235(2)	48.7(7)
C(9′)	4625(3)	11238(3)	1989(3)	67.7(11)
C(11′)	6804(2)	8280(2)	3667.3(14)	29.1(5)
C(12′)	7611(2)	9335(2)	3793(2)	37.4(6)
C(13′)	8352(3)	9846(3)	4534(2)	49.5(7)
C(14′)	8309(3)	9308(3)	5157(2)	51.8(8)
C(15′)	7543(3)	8250(3)	5037(2)	44.1(7)
C(16′)	6790(2)	7736(2)	4297(2)	34.6(6)
C(21′)	6889(2)	7143(2)	2045.0(14)	24.8(5)
C(22′)	7893(2)	6758(2)	2344(2)	32.7(6)
C(23′)	8687(2)	6358(2)	1832(2)	38.1(6)
C(24′)	8494(3)	6328(2)	1021(2)	39.4(6)
C(25′)	7491(2)	6693(2)	713(2)	34.5(6)
C(26′)	6689(2)	7093(2)	1217.6(15)	30.7(5)
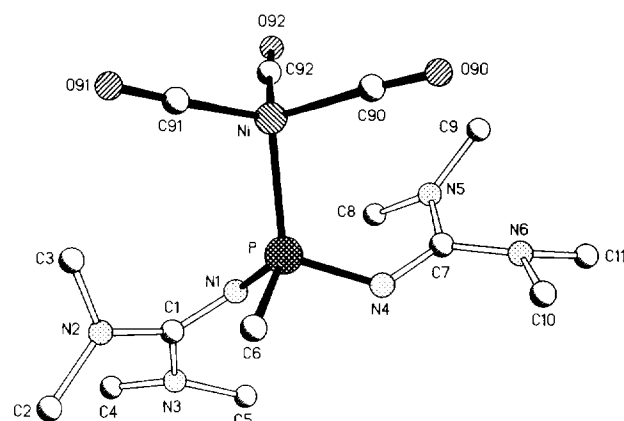
Fig. 3. Molecular structure of **8**.

The phosphorus atom displays a tetrahedral coordination geometry with the largest deviation from ideal angles for N4–P–C6 (96.9(6)°) and N1–P–Ni (119.0(4)°). In contrast to **13**, in which the carbonyl carbon atoms and the carbon atoms of the *tert*-butyl group are eclipsed, the substituents at phosphorus and ligands at nickel are staggered, with an average torsion angle of 34°.

Table 5
Bond lengths (pm) and angles (deg) for **8**

| Ni–C(91)	176(2)	Ni–C(92)	177(2)
Ni–C(90)	181.4(14)	Ni–P	224.3(4)
P–N(4)	165.4(10)	P–N(1)	168.3(11)
P–C(6)	181.7(14)	N(1)–C(1)	128(2)
N(2)–C(1)	135(2)	N(2)–C(3)	143(2)
N(2)–C(2)	146(2)	N(3)–C(1)	140(2)
N(3)–C(5)	143(2)	N(3)–C(4)	144(2)
N(4)–C(7)	131(2)	N(5)–C(7)	139(2)
N(5)–C(9)	144(2)	N(5)–C(8)	150(2)
N(6)–C(7)	134(2)	N(6)–C(10)	145(2)
N(6)–C(11)	146(2)	O(90)–C(90)	111(2)
O(91)–C(91)	115(2)	O(92)–C(92)	115(2)
C(91)–Ni–C(92)	116.4(8)	C(91)–Ni–C(90)	110.8(8)
C(92)–Ni–C(90)	110.0(7)	C(91)–Ni–P	107.1(5)
C(92)–Ni–P	108.2(5)	C(90)–Ni–P	103.6(4)
N(4)–P–N(1)	106.8(5)	N(4)–P–C(6)	96.9(6)
N(1)–P–C(6)	105.2(6)	N(4)–P–Ni	112.7(4)
N(1)–P–Ni	119.0(4)	C(6)–P–Ni	113.7(5)
C(1)–N(1)–P	133.4(10)	C(1)–N(2)–C(3)	120.9(11)
C(1)–N(2)–C(2)	122.8(12)	C(3)–N(2)–C(2)	115.8(12)
C(1)–N(3)–C(5)	119.0(11)	C(1)–N(3)–C(4)	120.3(11)
C(5)–N(3)–C(4)	116.1(12)	C(7)–N(4)–P	128.6(9)
C(7)–N(5)–C(9)	123.3(11)	C(7)–N(5)–C(8)	120.0(11)
C(9)–N(5)–C(8)	116.1(11)	C(7)–N(6)–C(10)	120.6(11)
C(7)–N(6)–C(11)	121.8(12)	C(10)–N(6)–C(11)	113.6(11)
N(1)–C(1)–N(2)	127.9(12)	N(1)–C(1)–N(3)	116.8(12)
N(2)–C(1)–N(3)	115.3(11)	N(4)–C(7)–N(6)	118.7(12)
N(4)–C(7)–N(5)	124.6(11)	N(6)–C(7)–N(5)	116.7(11)
O(90)–C(90)–Ni	176.2(14)	O(91)–C(91)–Ni	179(2)
O(92)–C(92)–Ni	176(2)		

5. Molecular structure of 10 (Fig. 4)

The iron atom displays distorted trigonal bipyramidal coordination geometry. The sum of the squares of the angle deviations at iron from idealised values is a measure of the degree of distortion from trigonal bipyramidal or square pyramidal geometry. This sum amounts to 518 (trigonal bipyramidal) or 1091 (square

Table 6

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (pm$^2 \times 10^{-1}$) for **8**

	x	y	z	U_{eq}
Ni	1167.5(6)	6030(2)	7153.7(10)	36.6(5)
P	1104.3(11)	4754(3)	8351(2)	27.7(7)
N(1)	1555(4)	4755(11)	9075(6)	35(2)
N(2)	2097(4)	2951(12)	8736(7)	41(2)
N(3)	2037(4)	3808(12)	10119(7)	40(2)
N(4)	624(4)	5139(11)	8873(6)	35(2)
N(5)	663(4)	7660(11)	9037(7)	39(2)
N(6)	-48(4)	6440(12)	8982(7)	40(2)
C(1)	1883(4)	3867(13)	9263(8)	34(2)
C(2)	2241(5)	1528(15)	8997(11)	54(4)
C(3)	2140(4)	3272(16)	7849(9)	43(3)
C(4)	2529(5)	3626(19)	10336(10)	59(4)
C(5)	1760(5)	4474(18)	10750(9)	51(4)
C(6)	970(5)	2894(14)	8161(9)	43(3)
C(7)	423(4)	6378(13)	8973(7)	30(2)
C(8)	1118(5)	7748(16)	9545(9)	48(3)
C(9)	469(5)	8990(14)	8736(9)	46(3)
C(10)	-333(5)	5232(16)	8706(8)	41(3)
C(11)	-293(5)	7412(15)	9545(9)	47(3)
O(90)	183(3)	6633(12)	6691(8)	63(3)
O(91)	1600(5)	4221(15)	5893(8)	92(4)
O(92)	1650(5)	8661(14)	7617(8)	78(4)
C(90)	561(5)	6418(14)	6839(9)	40(3)
C(91)	1429(6)	4924(17)	6399(11)	66(5)
C(92)	1469(5)	7618(19)	7413(10)	56(4)
Ni'	3857.0(6)	4102(2)	1911.2(10)	32.5(4)
P'	3874.3(10)	5277(3)	3155(2)	25.9(7)
N(1')	3404(3)	5281(10)	3772(6)	29(2)
N(2')	2902(4)	7167(13)	3332(7)	41(2)
N(3')	2924(4)	6352(12)	4717(7)	40(2)
N(4')	4327(4)	4849(11)	3806(7)	34(2)
N(5')	4992(4)	3451(13)	4040(7)	42(3)
N(6')	4261(4)	2313(12)	3893(8)	46(3)
C(1')	3096(4)	6247(13)	3907(8)	33(2)
C(2')	2806(6)	8641(15)	3502(11)	55(4)
C(3')	2853(5)	6726(18)	2436(9)	49(3)
C(4')	3163(6)	5624(17)	5405(9)	53(4)
C(5')	2456(5)	6818(19)	4878(10)	61(4)
C(6')	4014(5)	7145(13)	3030(9)	42(3)
C(7')	4501(5)	3561(14)	3924(8)	37(3)
C(8')	5189(6)	2431(18)	4651(10)	58(4)
C(9')	5293(5)	4652(18)	3828(10)	54(3)
C(10')	3786(6)	2247(17)	4238(11)	59(4)
C(11')	4452(7)	987(16)	3589(11)	66(4)
O(90')	4850(4)	3357(13)	1768(7)	63(3)
O(91')	3308(4)	1529(14)	2068(9)	78(4)
O(92')	3551(5)	6053(14)	559(7)	74(4)
C(90')	4458(5)	3654(14)	1815(9)	41(3)
C(91')	3511(5)	2572(19)	1994(10)	55(4)
C(92')	3669(5)	5287(17)	1090(11)	53(4)
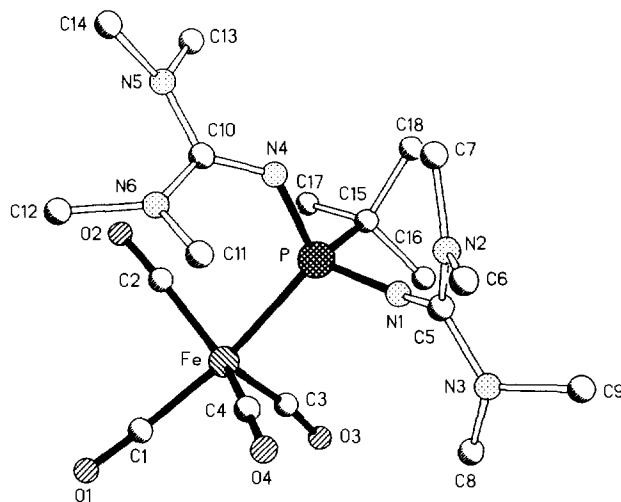
Fig. 4. Molecular structure of **10**.

pyramidal), which means that the coordination at the iron atom can be described as trigonal bipyramidal considerably distorted towards square pyramidal with axial C3. In the comparable complex $(Me_2N)_3PFe(CO)_4$ the geometry is nearly ideal trigonal bipyramidal with sums of 23 (trigonal bipyramidal) and 2387 (square pyramidal) [23]. In both complexes the phosphorus-containing ligand is axial, with a (C1–Fe–P) angle of 169.2(3)° in **10** (Tables 7 and 8).

The angles between phosphorus and equatorial carbonyl groups vary from 84.1(3)° (C2–Fe–P) to 95.2(3)° (C3–Fe–P). In $(Me_2N)_3PFe(CO)_4$ all angles at iron between phosphorus and the equatorial carbon atoms are smaller than 90°.

The Fe–P bond (230.1(2) pm) is longer than that in $(Me_2N)_3PFe(CO)_4$ (224.5(1) pm). The bond lengths Fe–C1 (179.2(1) pm), Fe–C2 (180.3(8) pm) and Fe–C4 (179.4(9) pm) are essentially the same as in $(Me_2N)_3PFe(CO)_4$ (178.1(5) pm to 179.3(6) pm), but Fe–C3 (175.8(10) pm) is considerably shorter.

The phosphorus atom displays distorted tetrahedral coordination geometry, with angles from 98.9(4)° (N1–P–C15) to 115.9(3)° (N1–P–N4). The equatorial substituents at the iron atom are staggered with respect to the substituents at phosphorus, with an average torsion angle between neighbouring atoms of 45°.

6. Experimental

All operations were carried out in a nitrogen atmosphere, employing standard vacuum and inert gas techniques. The solvents were dried by standard procedures and were freshly distilled before use. FT-IR spectra were recorded on a BIORAD 165 spectrometer. The ^{1}H (200.1 MHz), ^{13}C (50.3 MHz) and ^{31}P (80.1 MHz) NMR spectra were recorded on a Bruker AC-200 spec-

trometer using, unless indicated otherwise, $CDCl_3$ as solvent. All shifts are reported relative to TMS (^{1}H, ^{13}C) and H_3PO_4 (^{31}P). The EI-mass spectra were recorded on a Finnigan MAT 8430 spectrometer at 70 eV. The abbreviation "i.v." indicates a pressure of 0.1 mm Hg.

The following compounds were prepared according to published methods: 1a, 1b, 2 and 3 [5], norbornadiene(tetracarbonyl)molybdenum [24] and cycloheptatriene(tricarbonyl)molybdenum [25]. Other reagents were commercially available.

6.1. Reaction of diphenylphosphinous-N-(N′,N′,N″,N″-tetramethyl)guanidinide 1a with hexacarbonylmolybdenum; Formation of compound 4a

To a suspension of 0.43 g (1.6 mmol) of hexacarbonylmolybdenum in 20 ml of dimethoxyethane, 0.56 g

(1.87 mmol) of 1a were added at room temperature. The mixture was heated with stirring at 60°C for 16 h. The solvent was removed i.v., and 20 ml of n-hexane were added to the crude product. Upon stirring, an amorphous solid formed, which was filtered off, washed twice with 10 ml of n-hexane, and dried i.v. Yield 0.62 g (72.4%) pale brown solid, dec.: > 80°C. ^{1}H NMR: δ = 2.73 (s, 12 H, N(CH_3)$_2$); δ = 7.95–7.59, 7.33–7.29 (m, 10 H, P(C$_6$$H_5$)$_2$). ^{31}P NMR: δ = 58.34 (s). EI-MS: m/z (%): 537 (< 0.1) [M]$^+$, 509 (1.5) [M − CO]$^+$, 481 (1) [M − 2 CO]$^+$, 453 (7) [M − 3 CO]$^+$, 425 (< 0.1) [M − 4 CO]$^+$, 397 (13) [M − 5 CO]$^+$, 315 (51) [Ph$_2$P(:O)TMG]$^+$, 299 (6) [Ph$_2$PTMG]$^+$, 202 (100) [Ph$_2$P(:O)H]$^+$, 201 (96) [Ph$_2$P(:O)]$^+$, 152 (7) [PhPNMe$_2$]$^+$, 108 (8) [PhP]$^+$, 77 (19) [Ph]$^+$, 71 (14) [HNCNMe$_2$]$^+$. Anal. Found: C, 51.08; H, 4.61; N, 8.34. Calc.: C, 49.36; H, 4.14; N, 7.85%. C$_{22}$H$_{22}$MoN$_3$O$_5$P (535.35).

Table 7
Bond lengths (pm) and angles (deg) for 10

Fe–C(3)	175.8(10)	Fe–C(1)	179.2(10)
Fe–C(4)	179.4(9)	Fe–C(2)	180.3(8)
Fe–P	230.1(2)	R–N(1)	161.5(4)
P–N(4)	163.8(6)	P–C(15)	186.6(10)
O(1)–C(1)	111.8(12)	O(2)–C(2)	113.0(9)
O(3)–C(3)	117.6(12)	O(4)–C(4)	113.3(10)
N(1)–C(5)	128.6(9)	N(2)–C(5)	135.3(11)
N(2)–C(7)	144.1(11)	N(2)–C(6)	146.9(11)
N(3)–C(5)	138.7(10)	N(3)–C(8)	145.3(12)
N(3)–C(9)	146.6(8)	N(4)–C(10)	129.2(10)
N(5)–C(10)	136.2(10)	N(5)–C(13)	142.6(14)
N(5)–C(14)	144.8(12)	N(6)–C(10)	135.9(11)
N(6)–C(11)	144.4(9)	N(6)–C(12)	146.2(11)
C(15)–C(18)	149.7(14)	C(15)–C(16)	153.3(13)
C(15)–C(17)	153.4(9)		
C(3)–Fe–C(1)	95.6(4)	C(3)–Fe–C(4)	108.2(4)
C(1)–Fe–C(4)	90.2(4)	C(3)–Fe–C(2)	118.9(4)
C(1)–Fe–C(2)	90.2(4)	C(4)–Fe–C(2)	132.6(5)
C(3)–Fe–P	95.2(3)	C(1)–Fe–P	169.2(3)
C(4)–Fe–P	87.0(3)	C(2)–Fe–P	84.1(3)
N(1)–P–N(4)	115.9(3)	N(1)–P–C(15)	98.9(4)
N(4)–P–C(15)	99.6(4)	N(1)–P–Fe	111.4(3)
N(4)–P–Fe	114.4(2)	C(15)–P–Fe	115.2(3)
C(5)–N(1)–P	147.8(7)	C(5)–N(2)–C(7)	122.3(7)
C(5)–N(2)–C(6)	123.3(7)	C(7)–N(2)–C(6)	114.3(7)
C(5)–N(3)–C(8)	119.0(6)	C(5)–N(3)–C(9)	119.7(8)
C(8)–N(3)–C(9)	114.3(7)	C(10)–N(4)–P	133.1(6)
C(10)–N(5)–C(13)	118.9(8)	C(10)–N(5)–C(14)	123.8(8)
C(13)–N(5)–C(14)	114.9(8)	C(10)–N(6)–C(11)	122.1(6)
C(10)–N(6)–C(12)	123.8(6)	C(11)–N(6)–C(12)	113.9(8)
O(1)–C(1)–Fe	176.7(8)	O(2)–C(2)–Fe	175.9(8)
O(3)–C(3)–Fe	174.2(10)	O(4)–C(4)–Fe	173.8(9)
N(1)–C(5)–N(2)	126.0(7)	N(1)–C(5)–N(3)	118.4(8)
N(2)–C(5)–N(3)	115.6(6)	N(4)–C(10)–N(6)	126.6(7)
N(4)–C(10)–N(5)	119.4(8)	N(6)–C(10)–N(5)	114.0(8)
C(18)–C(15)–C(16)	107.3(8)	C(18)–C(15)–C(17)	109.5(7)
C(16)–C(15)–C(17)	108.6(8)	C(18)–C(15)–P	109.1(7)
C(16)–C(15)–P	111.1(7)	C(17)–C(15)–P	111.1(6)

Table 8
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (pm$^2 \times 10^{-1}$) for 10

	x	y	z	U_{eq}
Fe	1567.7(13)	9084.3(7)	3047.7(5)	23.7(3)
P	3367(3)	8210.1(12)	2558.1(8)	19.3(4)
O(1)	−979(9)	9868(5)	3786(4)	53(2)
O(2)	2114(8)	8298(5)	4664(3)	47(2)
O(3)	2987(12)	10688(5)	2660(4)	70(3)
O(4)	−147(10)	8661(5)	1578(4)	56(2)
N(1)	3471(9)	8243(4)	1558(3)	22.9(15)
N(2)	2995(8)	7084(4)	690(3)	27(2)
N(3)	2756(10)	8452(5)	207(3)	35(2)
N(4)	3372(8)	7269(4)	2973(3)	23.2(13)
N(5)	2789(9)	6307(5)	3981(3)	34(2)
N(6)	949(8)	6812(5)	3173(3)	28(2)
C(1)	−1(11)	9584(6)	3485(4)	32(2)
C(2)	1927(12)	8576(6)	4027(4)	38(2)
C(3)	2486(12)	10024(6)	2809(4)	39(2)
C(4)	526(11)	8779(7)	2156(4)	37(2)
C(5)	3103(9)	7917(5)	857(4)	29(2)
C(6)	2005(12)	6738(6)	61(4)	42(2)
C(7)	3821(11)	6460(6)	1134(4)	37(2)
C(8)	2583(15)	9345(6)	374(5)	51(3)
C(9)	3267(12)	8258(7)	−634(3)	45(3)
C(10)	2392(9)	6829(6)	3349(3)	23(2)
C(11)	408(12)	6830(6)	2331(4)	33(2)
C(12)	−186(12)	6719(8)	3802(4)	45(3)
C(13)	4174(14)	6423(9)	4361(5)	53(3)
C(14)	2116(13)	5500(6)	4141(5)	42(2)
C(15)	5258(11)	8543(6)	2813(4)	29(2)
C(16)	5707(14)	9315(8)	2303(5)	49(3)
C(17)	5408(12)	8757(8)	3738(4)	48(3)
C(18)	6283(11)	7846(8)	2596(5)	44(3)

6.2. Reaction of tert-butylphenylphosphinous-N-(N',N',N'',N''-tetramethyl)guanidinide 1b with hexacarbonylmolybdenum; formation of compound 4b

To a suspension of 1.16 g (4.4 mmol) of hexacarbonylmolybdenum in 20 ml of toluene was added a solution of 1.13 g (4.0 mmol) of 1b in 10 ml of toluene at room temperature. The mixture was heated with stirring to 60°C for 14 h. The solution was decanted from oily material and ca. 80% of the solvent was removed i.v. The solid thus formed was filtered off, washed twice with 10 ml portions of petroleum ether (30/40), and dried i.v. Yield 1.20 g (58.6%) colourless solid, m.p.: 104°C. ^{1}H NMR: δ = 1.04 (d, ^3J(PH) = 15.22, 9 H, C(CH_3)$_3$); δ = 2.69 (s, 12 H, N(CH_3)$_2$); δ = 7.34–7.63 (m, 5 H, C$_6H_5$). ^{13}C NMR: δ = 26.05 (d, ^2J(PC) = 7.24, C(CH_3)$_3$); δ = 37.55 (d, ^1J(PC) = 33.72, PC(CH$_3$)$_3$); δ = 40.38 (s, N(CH$_3$)$_2$); δ = 126.96 (d, ^3J(PC) = 8.45, aromatic m-C); δ = 129.49 (s, aromatic p-C); δ = 132.55 (d, ^2J(PC) = 12.53, aromatic o-C); δ = 138.67 (d, ^1J(PC) = 12.63, aromatic ipso-C); δ = 158.94 (d, ^2J(PC) = 8.14, N=C <); δ = 207.31 (d, ^2J(PC) = 9.19, cis-PMo(CO)$_4$); δ = 211.11 (d, ^2J(PC) = 22.96, trans-PMoCO). ^{31}P NMR: δ = 78.73 (s). EI-MS: m/z (%): 487 (<0.1) [M − CO]$^+$, 459 (<0.1) [M − 2 CO]$^+$, 403 (0.43) [M − 4 CO]$^+$, 377 (0.08)

[M − 5 CO]$^+$, 279 (22)[t-Bu(Ph)P(TMG)]$^+$, 222 (62) [PhP(TMG)]$^+$, 152 (100) [PhPNMe$_2$]$^+$, 109 (54) [PhPH]$^+$, 57 (6) [t-Bu]$^+$. IR [cm^{-1}] (KBr): $\tilde{\nu}$ = 2065 m, 1979 m, sh, 1914 vs, br, ν(CO); $\tilde{\nu}$ = 1577 m, 1552 s, 1504 m, 1474 w, ν(CN). Anal. Found: C, 46.62; H, 5.16; N, 8.04. Calc.: C, 46.61; H, 5.08; N, 8.15%. C$_{20}$H$_{26}$MoN$_3$O$_5$P (515.36).

6.3. Reaction of diphenylphosphinous-N-(N',N',N'',N''-tetramethyl)guanidinide 1a with norbornadiene(tetracarbonyl)molybdenum; formation of compound 5a

To a solution of 0.54 g (1.8 mmol) of norbornadiene (tetracarbonyl)molybdenum in 20 ml of n-hexane was added a solution of 0.59 g (2.0 mmol) of 1a in 10 ml of diethyl ether, dropwise over 30 min. After stirring for another 3 h the yellow precipitate was filtered off, and was dried i.v. Yield: 0.61 g (75.6%), dec.: > 115°C. ^{1}H NMR: δ = 2.47 (s, 24 H, N(CH_3)$_2$); δ = 7.61–7.54, 7.25–7.22 (m, 20 H, P(C$_6H_5$)$_2$). ^{31}P NMR: δ = 61.40 (s). EI-MS: m/z (%): 808 (0.3) [M]$^+$, 780 (0.1) [M − CO]$^+$, 752 (0.7) [M − 2 CO]$^+$, 724 (0.3) [M − 3 CO]$^+$, 696 (0.3) [M − 4 CO]$^+$, 539 (0.3) [Ph$_2$P(TMG)-Mo(CO)$_4$]$^+$, 509 (2.2) [Ph$_2$P(TMG)Mo(CO)$_4$]$^+$, 481 (3) [Ph$_2$P(TMG)Mo(CO)$_3$]$^+$, 453 (6) [Ph$_2$P(TMG)-Mo(CO)$_2$]$^+$, 397 (12) [Ph$_2$P(TMG)Mo]$^+$, 299 (100) [Ph$_2$P(TMG)]$^+$, 222 (34) [PhP(TMG)]$^+$, 186 (95) [Ph$_2$PH]$^+$, 185 (72) [Ph$_2$P]$^+$, 152 (26) [PhPNMe$_2$]$^+$, 108 (72) [PhP]$^+$. IR (cm^{-1}) (toluene): $\tilde{\nu}$ = 2040 m, 1925 vs, 1880 vs, 1810 m, ν(CO); $\tilde{\nu}$ = 1625 m, sh, 1570 s, br, 1435 s, br, ν(CN). Anal. Found: C, 55.88; H, 5.54; N, 10.29. Calc.: C, 56.58; H, 5.50; N, 10.42%. C$_{38}$H$_{44}$MoN$_6$O$_4$P$_2$ (806.69).

6.4. Reaction of tert-butylphenylphosphinous-N-(N',N',N'',N''-tetramethyl)guanidinide 1b with norbornadiene(tetracarbonyl)molybdenum; formation of compound 5b

To a solution of 0.95 g (3.2 mmol) of norbornadiene(tetracarbonyl)molybdenum in 25 ml of toluene, 0.96 g (3.4 mmol) of 1b were added at room temperature with exclusion of light. The mixture was stirred for 16 h. The solvent was removed i.v., and the residue was treated with 20 ml of n-hexane. The solid was filtered off, washed three times with 5 ml portions of n-hexane, and was dried i.v. Yield: 0.58 g (35.0%) of a cream coloured solid, m.p.: 134°C. ^{1}H NMR: δ = 1.09 (d, ^3J(PH) = 14.62, 9 H, C(CH_3)$_3$); δ = 2.68 (s, 6 H, N(CH_3)$_2$); δ = 2.70 (s, 6H, N(CH_3)$_2$); δ = 7.31–7.70 (m, 5 H, C$_6H_5$). ^{13}C NMR: δ = 26.74 (s, C(CH$_3$)$_3$); δ = 39.88 (d, ^1J(PC) = 17.44, PC(CH$_3$)$_3$); δ = 40.43 (s, N(CH$_3$)$_2$); δ = 126.41 (s, aromatic o-C); δ = 128.47 (s, aromatic p-C); δ = 132.86 (s, aromatic m-C); δ = 141.05 (s, aromatic ipso-C); δ = 156.31 (s, N=C <); δ = 215.47 (d, ^2J(PC) = 8.43, Mo(CO)$_4$).

^{31}P NMR: 89.57 (s). EI-MS: m/z (%): 487 (0.6) [M]$^+$, 459 (1.7) [M − CO]$^+$, 431 (0.2) [M − 2 CO]$^+$, 403 (2.7) [M − 3 CO]$^+$, 375 (1.4) [M − 4 CO]$^+$, 279 (28) [t-Bu(Ph)PTMG]$^+$, 222 (64) [PhPTMG]$^+$, 152 (100) [PhPNMe$_2$]$^+$, 109 (61) [PhPH]$^+$, 77 (12) [Ph]$^+$, 71 (39) [HNCNMe$_2$]$^+$, 57 (44) [t-Bu]$^+$. C$_{19}$H$_{26}$MoN$_3$O$_4$P (487.35). An elemental analysis of 5b was not obtained.

6.5. Reaction of diphenylphosphinous-N-(N',N',N'',N''-tetramethyl)guanidinide 1a with tetracarbonylnickel; synthesis of the tricarbonylnickel complex 6

To a solution of 4.0 g (23.4 mmol) of tetracarbonyl-nickel in 50 ml of n-hexane, a solution of 0.99 g (3.3 mmol) of 1a in 20 ml of toluene was added at room temperature. The mixture was stirred for 5 h and then cooled for 16 h to −20°C. The precipitate formed was filtered off, was washed twice with 10 ml portions of n-hexane, and was dried i.v. Yield: 1.08 g (74.0%) colourless solid, m.p.: 130°C (dec.). ^{1}H NMR (C$_6$D$_6$): δ = 2.36 (s, 12 H, N(CH$_3$)$_2$); δ = 7.85–8.00, 7.05–7.25 (m, 10 H, P(C$_6$H$_5$)$_2$). ^{31}P NMR (C$_6$D$_6$): δ = 58.94 (s). IR (cm^{-1}) (n-hexane): ṽ = 2080 m, 2010 vs, ν(CO); ṽ = 1645 m, 1565 m, sh, 1530 m, sh, 1480 m, sh, 1430 s, br, ν(CN). Anal. Found: C, 54.51; H, 5.14; N, 9.43. Calc.: C, 54.34; H, 5.02; N, 9.51%. C$_{20}$H$_{22}$N$_3$NiO$_3$P (442.08).

6.6. Reaction of diphenylphosphinous-N-(N',N',N'',N''-tetramethyl)guanidinide 1a with acetonitrile(nona-carbonyl)dimanganese; formation of compound 7

To a solution of 0.77 g (1.9 mmol) of freshly prepared acetonitrile(nonacarbonyl)dimanganese in 14 ml of acetonitrile, a solution of 0.57 g (1.9 mmol) of 1a in 10 ml of acetonitrile was added. The mixture was stirred at room temperature for 7 days. Subsequently, the volatile impurities and the solvent were removed i.v., and the remaining red oil was dissolved in 4 ml of CH$_2$Cl$_2$. To this solution 5 ml of n-hexane and 5 ml of diethyl ether were added, and the mixture was cooled to −20°C for 16 h. Yellow crystals and a red oil precipitated. The crystals were collected by filtration. Yield: 0.17 g (19.2%), dec.: > 65°C. ^{1}H NMR: δ = 2.73 (s, 24 H, N(CH$_3$)$_2$); δ = 7.2–7.4, 7.6–7.8 (m, 20 H, P(C$_6$H$_5$)$_2$). ^{31}P NMR: δ = 94.14 (s). IR (cm^{-1}) (CDCl$_3$): ṽ = 2020 m, 2005 m, 1955 vs, 1920 m, sh, ν(CO); ṽ = 1650 w, 1610 m, 1560 m, 1520 w, 1480 m, ν(CN). C$_{42}$H$_{44}$Mn$_2$N$_6$O$_8$P$_2$ (932.67). An elemental analysis for 7 was not obtained.

6.7. Reaction of methylphosphonous-bis-N-(N',N',N'',N''-tetramethyl)guanidinide 2 with tetracarbonylnickel; formation of compound 8

A solution of 0.88 g (3.2 mmol) of 2 in 20 ml of n-hexane was added at 0°C to a solution of 0.73 g (4.3

mmol) of tetracarbonylnickel in 20 ml of n-hexane. The mixture was allowed to reach room temperature, and was stirred for 4 h. Half of the solvent was evaporated, and the remaining solution was cooled to −20°C. The precipitate thus formed was filtered off and dried i.v. By crystallisation from petroleum ether (60/70) crystals suitable for the X-ray analysis were obtained. Yield: 1.04 g (77.9%) colourless crystals, m.p.: 46°C. ^{1}H NMR: δ = 0.79 (d, ^2J(PH) = 12.67, 3 H, PCH$_3$); δ = 2.74 (s, 24 H, N(CH$_3$)$_2$). ^{31}P NMR: δ = 73.46 (s). EI-MS: m/z (%): 416 (2) [M]$^+$, 388 (5) [M − CO]$^+$, 360 (54) [M − 2 CO]$^+$, 332 (33) [M − 3 CO]$^+$, 290 (56) [MeP(:O)(TMG)$_2$]$^+$, 274 (44) [MeP(TMG)$_2$]$^+$, 259 (96) [P(TMG)$_2$]$^+$, 189 (100) [Me$_2$NP(TMG)]$^+$, 119 (69) [P(NMe$_2$)$_2$]$^+$, 71 (64) [HNCNMe$_2$]$^+$. IR (cm^{-1}) (n-hexane): ṽ = 2060 s, 1985 vs, br, 1945 s, ν(CO); ṽ = 1630, s, sh, 1610, s, sh, 1580, s, br, 1565, s, br, ν(CN). Anal. Found: C, 40.42; H, 6.83; N, 20.42. Calc.: C, 40.32; H, 6.52; N, 20.15%. C$_{14}$H$_{27}$N$_6$NiO$_3$P (417.06).

6.8. Reaction of methylphosphonous-bis-N-(N',N',N'',N''-tetramethyl)guanidinide 2 with norbornadiene(tetracarbonyl)molybdenum; synthesis of compound 9

To a solution of 2.66 g (8.9 mmol) of norbornadiene(tetracarbonyl)molybdenum in 20 ml of toluene, 2.48 g (8.0 mmol) of 2 were added at room temperature. The mixture was stirred for 16 h. A yellow solid precipitated, was collected by filtration, and was redissolved in 5 ml of CH$_2$Cl$_2$. After addition of 20 ml of n-hexane the mixture was cooled to −20°C for 12 h. The yellow precipitate was filtered off, was washed with three 10 ml portions of n-hexane, and was dried i.v. Yield: 2.61 g (67.6%) yellow solid, m.p.: 90°C (dec.). ^{1}H NMR: δ = 1.4 (s, br, 3 H, PCH$_3$); δ = 2.80 (s, br, 24 H, N(CH$_3$)$_2$). ^{31}P NMR: δ = 99.65 (s). EI-MS: m/z (%): 484 (5) [M]$^+$, 456 (9) [M − CO]$^+$, 428 (2) [M − 2 CO]$^+$, 400 (< 1) [M − 3 CO]$^+$, 372 (9) [M − 4 CO]$^+$, 290 (36) [MeP(:O)TMG$_2$]$^+$, 256 (12) [PTMG$_2$]$^+$, 176 (13) [MePTMG]$^+$, 115 (54) [HTMG]$^+$, 71 (100) [NCNMe$_2$]$^+$. IR (cm^{-1}) (KBr): ṽ = 1892 vs, 1782 vs, 1760 vs, ν(CO); ṽ = 1542 vs, 1521 vs, 1471 s, ν(CN). Anal. Found: C, 36.31; H, 5.82; N, 17.23. Calc. C, 37.35; H, 5.64; N, 17.42%. C$_{15}$H$_{27}$MoN$_6$O$_4$P (482.33).

6.9. Reaction of tert-butylphosphonous-bis-N-(N',N',N'',N''-tetramethyl)guanidinide 3 with nonacarbonyldiiron; Formation of the tetracarbonyliron(0) derivative 10

To a solution of 0.89 g (2.4 mmol) of nonacarbonyldiiron in 20 ml of toluene, a solution of 0.77 g (2.4 mmol) of 3 in 10 ml of toluene was added with exclusion of light. The mixture was stirred for 16 h. The solvent and the pentacarbonyl iron formed in the reac-

tion were removed i.v. The residue was dissolved in 7 ml of dichloromethane. 10 ml of *n*-hexane were added to the solution and the mixture was cooled to −20°C for 16 h. The yellow crystals thus obtained were filtered off, and were dried i.v. Yield: 0.98 g (84.3%), dec.: > 65°C. ^{1}H NMR (C$_6$D$_6$): δ = 1.55 (d, ^3J(PH) = 16.49, 9 H, C(CH$_3$)$_3$); δ = 2.51 (s, 24 H, N(CH$_3$)$_2$). ^{31}P NMR (C$_6$D$_6$): δ = 89.41 (s). EI-MS: m/z (%): 456 (12) [M − CO]$^+$, 428 (36) [M − 2 CO]$^+$, 400 (100) [M − 3 CO]$^+$, 316 (21) [t-BuP(TMG)$_2$]$^+$, 302 (86) [t-BuP(NMe$_2$)(TMG)Fe]$^+$, 259 (38) [P(TMG)$_2$]$^+$, 189 (11) [(TMG)P(NMe$_2$)]$^+$, 119 (11) [P(NMe$_2$)$_2$]$^+$, 71 (6) [HNCNMe$_2$]$^+$. IR (cm^{-1}) (*n*-hexane): $\tilde{v}$ = 2050 m, 1965 m, 1935 s, 1930 s, ν(CO); $\tilde{v}$ = 1645 m, 1570 m, 1470 vs, br, ν(CN). Anal. Found: C, 44.71; H, 7.15; N, 17.45. Calc.: C, 44.64; H, 6.87; N, 17.35%. C$_{18}$H$_{33}$FeN$_6$O$_4$P (484.32).

6.10. Reaction of tert-butylphosphonous-bis-N-(N',N',N'',N''-tetramethyl)guanidinide 3 with hexacarbonylmolybdenum; Synthesis of the bis(chelate) complex 11

To a suspension of 1.44 g (5.5 mmol) of hexacarbonylmolybdenum in 40 ml of *n*-hexane, a solution of 1.73 g (5.5 mmol) of 3 in 20 ml of *n*-hexane was added.

The mixture was refluxed for 5 h. After cooling to room temperature the yellow precipitate formed was filtered off, was washed with 20 ml of *n*-hexane, and dried i.v. Yield 1.67 g (58.1%) yellow solid, dec.: > 75°C. ^{1}H NMR (CD$_2$Cl$_2$): δ = 0.81 (d, ^3J(PH) = 12.35, 9 H, C(CH$_3$)$_3$); δ = 2.67 (s, br, 6 H, Mo(N(CH$_3$)$_2$)C); δ = 2.83 (s, br, 6 H, Mo(N(CH$_3$)$_2$)C); δ = 3.08 (s, br, 12 H, N(CH$_3$)$_2$). ^{13}C NMR (CD$_2$Cl$_2$): δ = 23.92 (d, ^2J(PC) = 18.66, C(CH$_3$)$_3$); δ = 35.54 (d, ^1J(PC) = 30.32, PC(CH$_3$)$_3$); δ = 39.37–41.50 (m, N(CH$_3$)$_2$); δ = 165.50 (d, ^2J(PC) = 19.46, N=C <); δ = 206.10 (s, Mo(CO)); δ = 209.22 (s, Mo(CO)); δ = 223.71 (s, Mo(CO)). ^{31}P NMR: δ = 161.54 (s). IR (cm^{-1}) (KBr): $\tilde{v}$ = 2003 s, 1920 m, sh, 1874 vs, br, 1845 vs, 1790 vs, ν(CO); $\tilde{v}$ = 1524 vs, br, 1470 s, ν(CN). Anal. Found: C, 40.93, H, 6.41; N, 16.80. Calc.: C, 41.13; H, 6.70; N, 16.93%. C$_{17}$H$_{33}$MoN$_6$O$_3$P (496.40).

7. X-ray structure determinations

7.1. Data collection and reduction

Crystals were mounted on glass fibres in inert oil and were transferred to the cold gas stream of the diffractometer (Stoe STADI-4 for 7 and 10, Siemens P4 for 8,

Table 9
Crystal data for the compounds 7, 8 and 10

Compound	7	8	10
Formula	C$_{42}$H$_{44}$Mn$_2$N$_6$O$_8$P$_2$	C$_{14}$H$_{27}$N$_6$NiO$_3$P	C$_{18}$H$_{33}$FeN$_6$O$_4$P
M_r	932.65	417.10	484.32
Crystal habit	red prism	colourless prism	yellow prism
Crystal size (mm^3)	0.85 × 0.40 × 0.35	0.60 × 0.45 × 0.35	0.95 × 0.40 × 0.15
Temperature (°C)	−130	−100	−130
Crystal system	triclinic	monoclinic	orthorhombic
Space group	$P\bar{1}$	$P2_1/c$	$P2_12_12_1$
Cell constants			
a (pm)	1128.6(2)	2840.8(10)	920.9(2)
b (pm)	1209.8(3)	942.5(3)	1588.7(3)
c (pm)	1714.7(3)	1569.2(5)	1610.1(3)
α (deg)	103.90(2)	90	90
β (deg)	96.16(2)	91.87(3)	90
γ (deg)	99.86(2)	90	90
U (nm^{-3})	2.2120(8)	4.199(2)	2.3556(8)
Z	2	8	4
D_x (Mg m^{-3})	1.400	1.491	1.366
μ (mm^{-1})	0.701	1.613	0.743
$F(000)$	964	1989	1024
$2\theta_{max}$ (deg)	50	50	50
No. of reflns.:			
measured	7844	12568	1730
independent	7820	7373	1730
R_{int}	0.049	0.090	—
$wR(F^2$, all refl.)	0.111	0.406	0.1193
$R(F > 4\sigma(F))$	0.039	0.122	0.050
No. of parameters	549	469	282
S	1.053	1.10	1.075
Max. Δ/σ	< 0.001	< 0.001	< 0.001
Max. Δρ (e nm^{-3})	466	2010	399

both with Siemens LT-2 low temperature attachment). The cell constants for **7** (**10**) were refined from $\pm\omega$ angles of 58 (54) reflections in the 2θ range 20–23°. The orientation matrix for **8** was refined from setting angles of 50 reflections in the 2θ range 5–25° (monochromated Mo $K\alpha$ radiation). The crystal data for **7**, **8** and **10** are collected in Table 9.

7.2. Structure solution and refinement

The structures were solved by direct methods. All structures were refined anisotropically on F^2 (program system: SHELXL-93, G.M. Sheldrick, Universität Göttingen). H atoms were included using a riding model or rigid methyl groups. The weighting schemes were of the form $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ with $P = (F_o^2 + 2F_c^2)/3$. The absolute structure of **10** was determined using the method of Flack [26]; $x = -0.07(5)$. Full details of the structure determinations have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, from where this material may be obtained on quoting the full literature citation and the reference number CSD 404971 (**7**), CSD 404972 (**8**), and CSD 404973 (**10**).

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