

Phosphanyl-Amino Complexes of Nickel(II): Synthesis and Structure

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New neutral pentacoordinate nickel(II) complexes of the type $[\text{NiCl}_2(\text{PR}_3)(\text{P}^\wedge\text{N})]$ [$\text{PR}_3 = \text{PMe}_3, \text{PMe}_2\text{Ph}, \text{PMePh}_2$; $\text{P}^\wedge\text{N} = 2$ -(diphenylphosphanyl)aniline ($\text{P}^\wedge\text{NH}_2$), *N*-methyl-2-(diphenylphosphanyl)aniline ($\text{P}^\wedge\text{NHMe}$), *N,N*-dimethyl-2-(diphenylphosphanyl)aniline ($\text{P}^\wedge\text{NMe}_2$)], as well as cationic tetra-coordinate nickel(II) complexes of the type $[\text{NiCl}(\text{PR}_3)(\text{P}^\wedge\text{N})]^+$

have been synthesized and characterized both in the solid state and in solution. Interesting X-ray structural data have been collected for each class of compounds, which show, inter alia, that the pentacoordinate neutral complexes can be isolated in two different molecular forms, namely square-pyramidal or bipyramidal-trigonal.

Introduction

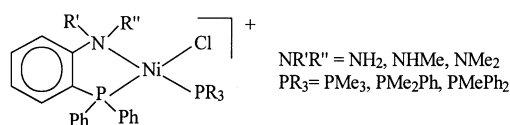
The synthesis of metal complexes stabilized by $\text{P}^\wedge\text{N}$ ligands and particularly phosphanyl-amines has attracted considerable attention in recent years^[1]. The ligands 2-(diphenylphosphanyl)pyridine and 2-(diphenylphosphanyl)aniline give rise to interesting examples. The first is known to exhibit a very versatile coordination behavior towards numerous transition metal centers^[2], both in mono- and polynuclear complexes. Remarkably, in these complexes it acts as either a monodentate, a bidentate chelating, or a bidentate bridging ligand. In its monodentate mode, the phosphane ligating site normally exhibits the strongest bonding ability towards metal centers such as nickel(II)^[3], cobalt(I)^[3], ruthenium(II)^{[4][5]}, rhodium(I)^{[4][6]}, and palladium(II)^{[4][7][8]}. Conversely, the coordination chemistry of 2-(diphenylphosphanyl)aniline^[9] has been widely investigated because of its ability to behave as a bidentate chelating amino^[10], amido^[11], or imido^[12] ligand. This behavior has been further developed in the synthesis of new macrocyclic chelate compounds such as P_2N_2 ligands, which have previously been tested in these laboratories^[13]. In particular, the reactivity of the tetradentate ligand *N,N'*-bis[2-(diphenylphosphanyl)phenyl]propane-1,3-diamine, H_2dppd , toward technetium and rhenium has been investigated. This

tetradentate phosphanyl-amine behaves both as a ligand and as a reducing agent towards $[\text{MO}_4]^-$ ($\text{M} = \text{Tc}, \text{Re}$) to give hexacoordinate neutral oxo- M^{V} phosphanyl-amido complexes of the general formula $[\text{MO}(\text{dppd})\text{X}]$, $\text{X} = \text{Cl}, \text{OH}, \text{OMe}, \text{OEt}, \text{O}_2\text{CCF}_3$.

Similarly, P_2N_2 ligands such as *N,N'*-bis[2-(diphenylphosphanyl)phenyl]ethane-1,2-diamine and *N,N'*-bis[2-(diphenylphosphanyl)phenyl]propane-1,3-diamine have been employed as efficient ligands for preparing unprecedented and previously elusive copper(II) phosphane complexes^[14]. These were subjected to X-ray structural analyses and were found to be characterized by authentic thermodynamic stability that was not attributable to kinetic inertness^[15]. The finely balanced *soft-hard* character of the $\{\text{P}_2\text{N}_2\}$ ligating set has been proposed to play a major role in underlying this important result.

The various properties of phosphanyl-amino ligands prompted us to undertake a systematic study aimed at preparing both neutral and cationic nickel(II) complexes of the type shown in Scheme 1 and to evaluate the potential of the cationic species as "SHOP"-type catalysts^[16].

Scheme 1



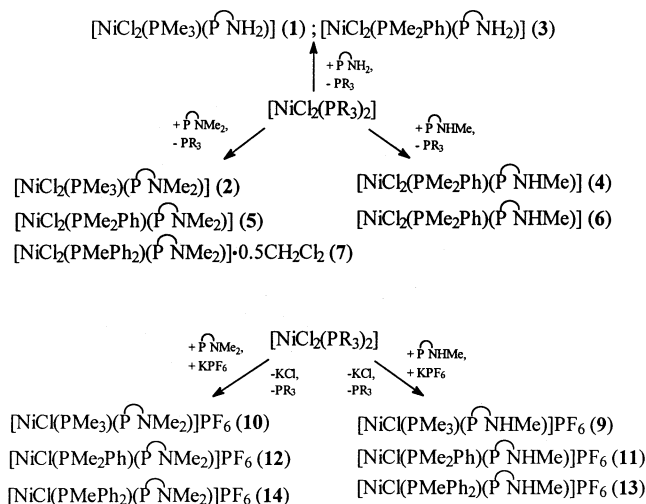
In this paper, we report on the detailed development of this project. Some of the results reported herein were anticipated in a preliminary report^[17].

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Results and Discussion

A general overview of the scope of the synthetic results is given in Scheme 2. The compounds are obtained upon substitution of one monodentate phosphane by the bidentate one, which chelates the metal through both the P and N atoms.

Scheme 2



$[\text{NiCl}_2(\text{PR}_3)_2]$ complexes react readily with 2-(diphenylphosphanyl)aniline, P^{NH}_2 , *N*-methyl-2-(diphenylphos-

phanyl)aniline, P^{NHMe} , and *N,N*-dimethyl-2-(diphenylphosphanyl)aniline, P^{NHMe_2} (hereafter referred to as P^{N}), usually in MeCN solution, to give pentacoordinate species of the type $[\text{NiCl}_2(\text{PR}_3)(\text{P}^{\text{N}})]$ (Table 1).

The same reaction, carried out in CH_2Cl_2 in the presence of KPF_6 as a scavenger of one Cl^- ligand per Ni atom, successfully leads to tetracoordinated species of the type $[\text{NiCl}(\text{PR}_3)(\text{P}^{\text{N}})]^+$ (Table 1), except in the case of P^{NH}_2 . The action of this tertiary phosphanyl-primary amine on $[\text{NiCl}_2(\text{PR}_3)_2]$ ($\text{PR}_3 = \text{PMe}_2\text{Ph}$ and PMePh_2) leads to the bis-bidentate species $[\text{Ni}(\text{P}^{\text{NH}}_2)_2]^{2+}$ [18], and/or to the mononuclear phosphorane-imino complex $[\text{NiCl}(\text{PMe}_3)(\text{P}^{\text{N}}\text{NP})]^+$ [19], $[\text{P}^{\text{N}}\text{NP} = N\text{-(trimethylphosphoranyl)-2-(diphenylphosphanyl)aniline}]$, when PMe_3 is incorporated into the starting material as a mono-tertiary phosphane.

The formation of the pentacoordinate $[\text{NiCl}_2(\text{PR}_3)(\text{P}^{\text{N}})]$ complexes is achieved under stoichiometric conditions in a homogeneous phase after a few hours of reaction time at room temperature. The products can be isolated as analytically pure species either upon spontaneous precipitation or after the addition of Et_2O . All these compounds are rather unstable in solution when exposed to air. Nevertheless, they can be recrystallized from e.g. CH_2Cl_2 (see Experimental Section) and their MeCN solutions provide conductivity measurements consistent with non-conducting species (Table 1).

Table 1. Selected synthetic and physicochemical data of $[\text{NiCl}_2(\text{PR}_3)(\text{P}^{\text{N}})]$ and $[\text{NiCl}(\text{PR}_3)(\text{P}^{\text{N}})]^{+[\text{a}]}$ complexes

Complex	Color	Crystal structure ^[b]	μ_{eff} [BM]	$\Lambda_{\text{M}}^{[\text{c}]}$ [$\Omega^{-1}\text{cm}^2\text{mol}^{-1}$]	$\nu_{\text{N-H}}$ $\delta_{\text{N-H}}$ [cm^{-1}] ^[d]	^1H NMR $\delta^{[\text{e}]}$	$\text{P}\{^1\text{H}\}$ NMR $\delta^{[\text{e}]}$	$\lambda_{\text{max}}^{[\text{f}]}$ [nm] in solution	$\lambda_{\text{max}}^{[\text{d}]}$ [nm] in the solid state
2	Blue	n.d.	1.3	n.c. ^[g]		Paramagnetic solutions, signals from +18.0 to -2.0		485, 570, 725	380, 600, 800
3	Blue	spy	Diam. ^[h]	n.c. ^[g]	$\nu_{\text{as}}^{[\text{i}]} 3236 \text{ m}, \nu_{\text{s}}^{[\text{i}]} 3134 \text{ m}, \delta 1602 \text{ m}$	1.78 (s, 6 H), 2.67 (m, 2 H), 6.33–8.38 (m, 19 H)	-5.2 (br s, 1P), 38.6 (br s, 1P)	475, 610 sh	490 sh, 620
4 ·0.5 MeCN	Blue	n.d.	0.7	n.c. ^[g]	3241 s	Paramagnetic solutions, signals from +18.0 to -2.0		475, 630 sh	550, 690 sh
6 ·C ₆ H ₆	Green	tb	3.4	n.c. ^[g]	3262 s	Paramagnetic solutions, signals from +18.0 to -1.0		430, 610 sh, 1055	400 sh, 620, 1050
9	Yellow	sp	Diam. ^[h]	180	3191 m	1.23 (s, 9 H), 2.87 (d, 3 H), 4.85 (m, 1 H), 7.20–7.95 (m, 14 H)	-144 (sept, 1 P), -9.8 (dd, 1 P), 42.5 (d, 1 P)	265 (4.49), 290 sh, 430 (2.89)	430
10	Yellow	n.d.	Diam. ^[h]	190		1.26 (d, 9 H), 3.19 (s, 6 H), 7.12–8.15 (m, 14 H)	-144 (sept, 1 P), -9.51 (d, 1 P), 38.1 (d, 1 P)	240 (4.16), 270 sh, 435 (2.76)	445
11	Red-orange	n.d.	Diam. ^[h]	158	3229 m	1.64 (s, 6 H), 2.04 (d, 3 H), 4.94 (m, 1 H), 7.12–8.15 (m, 19 H)	-144 (sept, 1 P), 1.30 (m, 1 P), 48.0 (m, 1 P)	295 (4.06), 322 (4.05), 430 (2.76)	450
13 ·C ₆ H ₆	Yellow	sp	Diam. ^[h]	171	3251 m	2.01 (d, 3 H), 2.33 (s, 3 H), 7.10–7.84 (m, 24 H)	-146 (sept, 1 P), 6.91 (d, 1 P), 37.6 (d, 1 P)	275 (4.08), 310 (4.02), 435 (2.81)	445

[a] PF_6^- salts. – [b] X-ray authenticated: n.d. = not determined; spy = square-pyramidal; tb = trigonal-bipyramidal; sp = square-planar. – [c] In MeCN. – [d] KBr plates. – [e] CDCl_3 for **2**, **3**, **4**·0.5 MeCN, and **6**·C₆H₆; CD_2Cl_2 for **9**, **10**, **11**, and **13**·C₆H₆. – [f] The data refer to solutions in CH_2Cl_2 , ca. 10^{-2} M for **2**, **3**, **4**·0.5 MeCN, and **6**·C₆H₆ and 10^{-3} – 10^{-5} M for **9**, **10**, **11**, and **13**·C₆H₆; lg ϵ values in parentheses. – [g] n.c. = non-conducting. – [h] Diam. = diamagnetic. – [i] ν_{as} = ν asymmetric. – [j] ν_{s} = ν symmetric.

The formation of the tetracoordinate $[\text{NiCl}(\text{PR}_3)(\text{P}^\wedge\text{N})]^+$ complexes can also be readily achieved under essentially stoichiometric conditions, by removal of KCl, concentration of the reaction solution, and addition of Et_2O . Cationic complexes $[\text{NiCl}(\text{PR}_3)(\text{P}^\wedge\text{N})]^+$ can be readily recrystallized from suitable solvent mixtures, such as $\text{CH}_2\text{Cl}_2/\text{EtOH}/\text{Et}_2\text{O}$ or $\text{CH}_2\text{Cl}_2/\text{EtOH}/\text{C}_6\text{H}_6$.

The ability of nickel(II) to give charged and neutral pentacoordinate complexes is well-documented in the literature^[20]. Thus, numerous high-spin distorted trigonal-bipyramidal and square-pyramidal complexes are known, which usually contain *hard* donor sites. Quite a few low-spin distorted trigonal-bipyramidal complexes have also been described and, conversely, they typically exhibit an overall *soft* coordination sphere. To the best of our knowledge, only four examples of pentacoordinate complexes with an $\{\text{NP}_2\text{Cl}_2\}$ donor set have been reported in the literature^{[17][21][22]}; the data presented herein allow the possibility of analyzing this coordination sphere, which is otherwise only poorly documented. The geometry of complex **3** (vide infra) is intermediate between square-pyramidal and trigonal-bipyramidal and this complex is diamagnetic. On the other hand, complexes **5**, **6**· CH_2Cl_2 , and **7** are trigonal-bipyramidal and paramagnetic. Ligand sets high in the spectrochemical series are predicted^[20] to give diamagnetic trigonal-bipyramidal complexes, but in our case the situation is reversed. Apparently, the ligand field exerted by our ligand set is not large enough to produce a singlet fundamental electronic state. Moreover, complexes **2** and **4** are characterized by magnetic moment values formally corresponding to less than two unpaired electrons (Table 1), which have previously been observed and discussed^[23] in terms of a thermally controlled equilibrium between singlet and triplet states. However, the data collected prevent us from invoking such an equilibrium as the sole factor responsible for the magnetic behavior of complexes **2** and **3**.

The $\{\text{NP}_2\text{Cl}\}$ chromophore invariably produces square-planar nickel(II) complexes for all the PR_3 and $\text{P}^\wedge\text{N}$ ligands employed, the structures of which have been validated by single-crystal X-ray analyses. The spectra in the visible range and the diamagnetism of all the complexes **9**, **10**, **11**, and **13**· C_6H_6 are in accordance with this structure^[20]. The position of the *d-d* band at 430–450 nm (Table 1) indicates that the $\{\text{NP}_2\text{Cl}\}$ chromophore is appreciably lower in the spectrochemical series than e.g. $\{\text{P}_2(\text{CN})_2\}$ ^[24], for which this band appears at ca. 350 nm. These bands are also observed in solution (lg ϵ values are also reasonable) and the conductivity figures are consistent with classical behavior of these square-planar nickel complexes.

Proton NMR spectra of the paramagnetic pentacoordinate complexes in CDCl_3 show signals spread over the range from $\delta = +20$ to -14 . Conversely, complexes **1** and **3**, which retain the unsubstituted phosphanyl-amine $\text{P}^\wedge\text{NH}_2$, are diamagnetic; their spectra allow the assignment of the coordinated phosphanyl-amine protons at $\delta = 2.60$ and of the methyl groups of the mono-tertiary phosphanes at $\delta = 1.26$ and 1.78 for **1** and **3**, respectively. These diamag-

netic species are subject to fluxional behavior at room temperature in CDCl_3 solution, since the $^{31}\text{P}\{^1\text{H}\}$ spectra exhibit broad signals that lack the multiplicity that would be expected given the presence of two magnetically non-equivalent phosphorus donors in the coordination sphere.

On the other hand, the $^{31}\text{P}\{^1\text{H}\}$ spectra of square-planar cationic complexes indicate the existence of two types of phosphorus donors; in fact, a double doublet pattern is usually observed, the position of which is primarily determined by the nature of the mono-tertiary phosphane. In addition, a septuplet centred at $\delta = -144$ establishes the presence of the hexafluorophosphate counterion. The methyl groups incorporated at the phosphorus and/or nitrogen donors are distinguishable on the basis of their chemical shifts and relative integrals in the proton spectra, which, where appropriate, also show the coordinated amine protons at $\delta = 4.90$.

X-ray Structure Analysis

In the neutral complexes **3** (Figure 1) and **6**· CH_2Cl_2 (Figure 2), the coordination around the Ni^{II} center is distorted trigonal-bipyramidal with the two axial positions occupied by the phosphorus atom of the monodentate phosphane and by the nitrogen atom of the bidentate ligand ($\text{P}^\wedge\text{NH}_2$ in **3** and $\text{P}^\wedge\text{NHMe}$ in **6**· CH_2Cl_2). The equatorial sites accommodate the remaining phosphorus of the phosphanylamine and the two Cl donors. The Ni atom is displaced from the equatorial plane in the direction of P(2), by 0.13 Å in **3** and by 0.18 Å in **6**· CH_2Cl_2 . The $\text{P}^\wedge\text{N}$ ligand mean plane of **3** makes a dihedral angle of 94.6° with the equatorial plane, while the corresponding angle in **6**· CH_2Cl_2 is 67.5° . The five-membered chelate ring, roughly planar in **3** (maximum deviation of 0.05 Å by the nitrogen atom; torsion angles between -6.8° and $+9.3^\circ$), assumes an envelope (C_s) conformation in **6**· CH_2Cl_2 , as shown by the deviation (0.29 Å) of the nitrogen atom and the torsion angle values (from -30.5° to $+35.0^\circ$). Moreover, superposition of the two structures (Figure 3) gives a high r.m.s. value (0.56 Å) when the fitting is performed on the 12 atoms labelled in the pertinent figure. Based on these differences, the geometry of **3** could alternatively be described as distorted square-pyramidal (Figure 4). In this description, the base could be regarded as comprising the P,N donors of the ligand, the P(2) atom of the monodentate phosphane, and Cl(1). The Ni atom is displaced from the base by $+0.27$ Å in the direction of Cl(2), but the deviations of the other donors are also dramatic [P(1) -0.31 Å, N(1) $+0.35$ Å, Cl(1) -0.32 Å and P(2) $+0.28$ Å]. Moreover, the *trans* angle P(1)–Ni–Cl(1) is only $148.29(6)^\circ$, while the *cis* angle P(1)–Ni–Cl(2) is widened to $110.82(6)^\circ$. In conclusion, the coordination geometry of **3** is intermediate between trigonal-bipyramidal and square-pyramidal and, accordingly, application of the τ index^[25] gives a value of 0.46 (1.0 for trigonal-bipyramidal; 0.0 for square-pyramidal).

In the cationic complexes **9** (Figure 5) and **13**·MeOH (Figure 6), the coordination geometry around Ni^{II} can be

Figure 1. ORTEP view of complex **3**; hydrogen atoms are omitted for clarity; the thermal ellipsoids are drawn at 40% probability

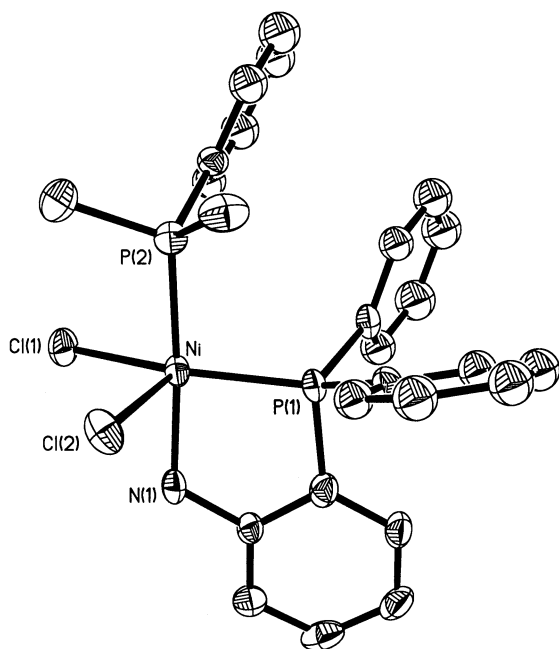
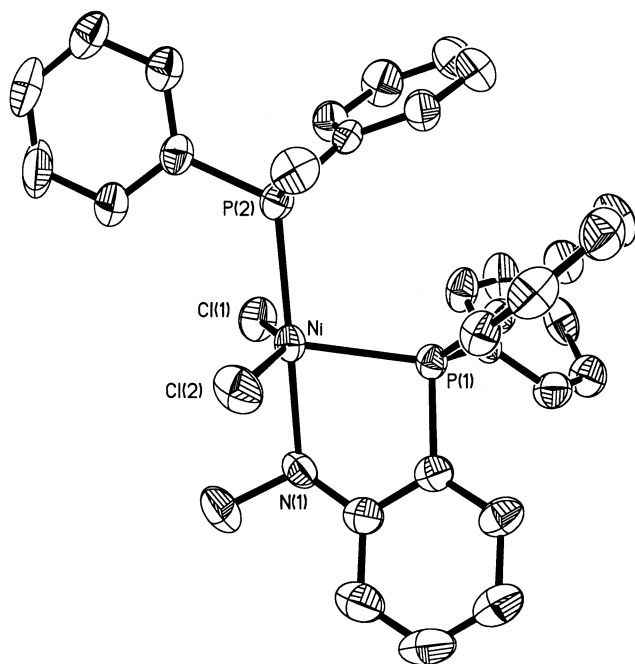


Figure 2. ORTEP view of complex **6**·CH₂Cl₂; hydrogen atoms and the CH₂Cl₂ molecule are omitted for clarity; the thermal ellipsoids are drawn at 40% probability



described as square-planar, with the two phosphorus donors located in a mutual *cis* arrangement and the remaining two positions occupied by the secondary amine nitrogen of the bidentate P⁺NHMe ligand and by the Cl donor. The nickel coordination spheres are distorted (Table 2) and the four donor atoms deviate from the mean coordination plane by ± 0.17 Å in **9** and by ± 0.10 Å in **13**·MeOH. The P⁺N ligand mean plane makes a dihedral angle with the mean coordination plane of 18.8° in **9** and of 23.9° in **13**·

Figure 3. Superposition of geometries of **3** (—) and **6**·CH₂Cl₂ (---)

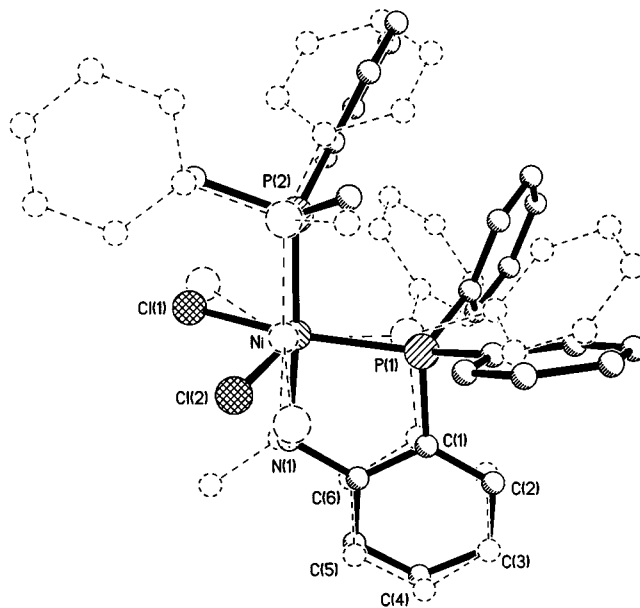
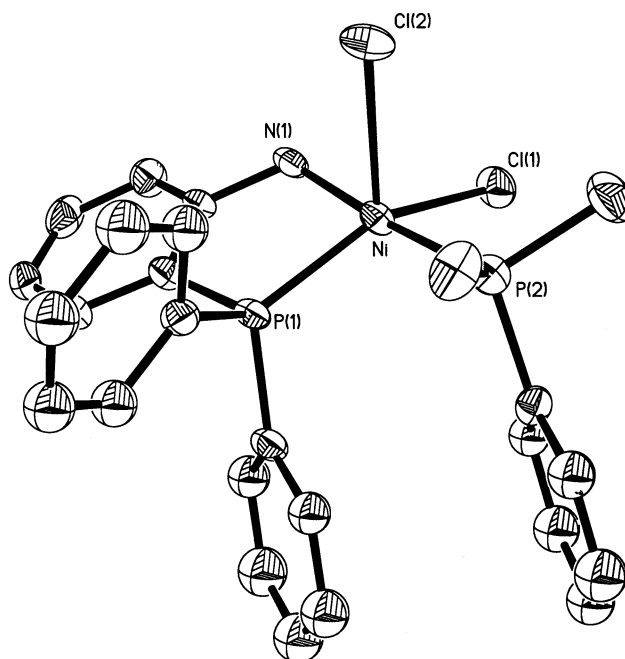


Figure 4. ORTEP view of complex **3** showing the square-pyramidal geometry; hydrogen atoms are omitted for clarity; the thermal ellipsoids are drawn at 40% probability



MeOH. The conformation of the five-membered NiPCCN chelate ring results in a twist-envelope (*C*₂) form (torsion angles between -14.2° and 13.2° in **9** and between -24.2° and 19.4° in **13**·MeOH) and superposition of the two structures (Figure 7) reveals only minor differences in the relative orientations of the phenyl rings, the r.m.s. value being 0.13 Å when the fitting is performed on the 11 atoms labelled in the pertinent figure.

For each of the four complexes, the packing does not give rise to intermolecular contacts shorter than the sum of the

Figure 5. ORTEP view of complex **9**; hydrogen atoms and the PF_6^- anion are omitted for clarity; the thermal ellipsoids are drawn at 40% probability

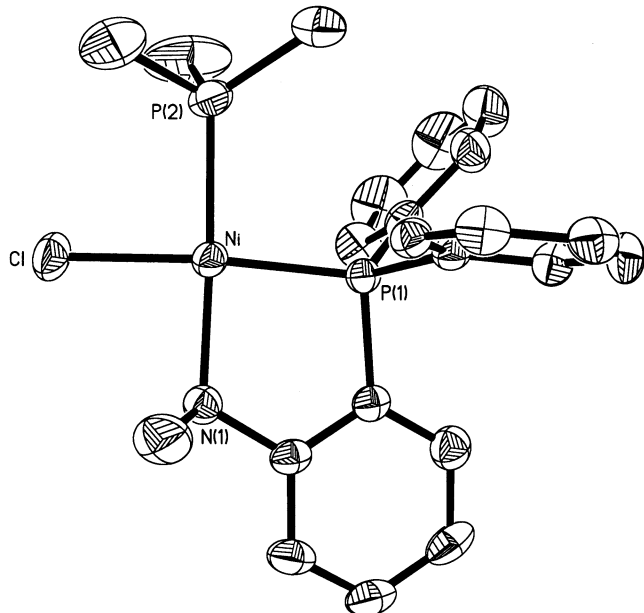


Figure 6. ORTEP view of complex **13**·MeOH; hydrogen atoms, the PF_6^- anion and the MeOH molecule are omitted for clarity; the thermal ellipsoids are drawn at 40% probability

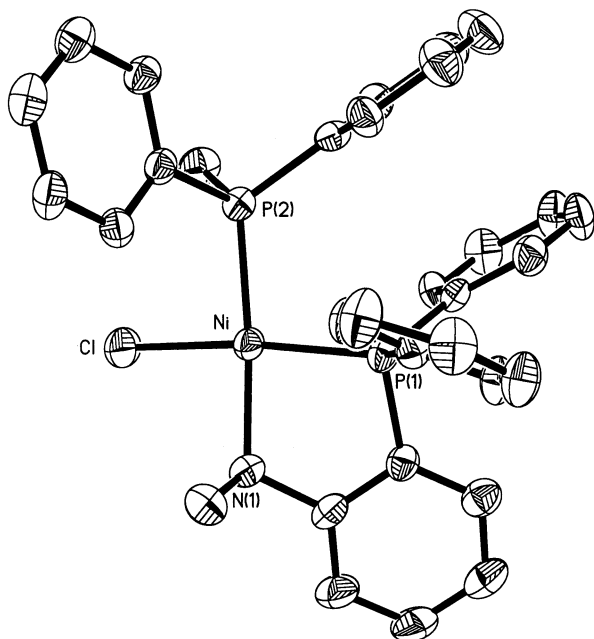


Figure 7. Superposition of geometries of **9** (—) and **13**·MeOH (---)

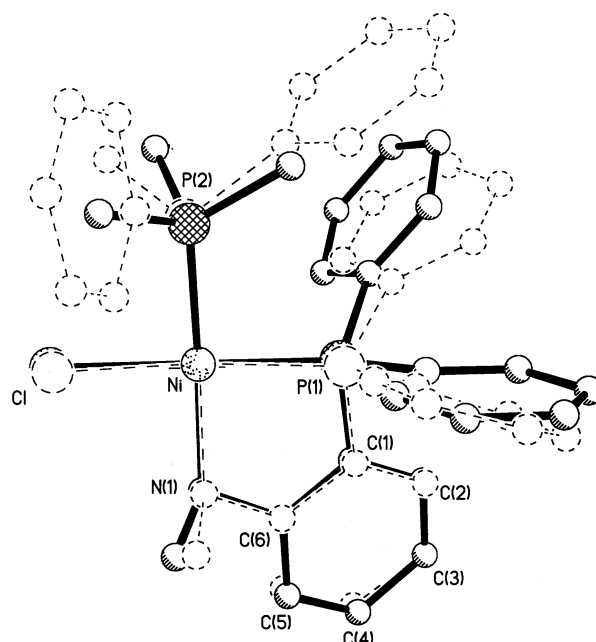


Table 2. Selected bond lengths [Å] and angles [°] for **3**, **6**· CH_2Cl_2 , **9**, and **13**·MeOH

	3	6 · CH_2Cl_2
Ni—Cl(1)	2.249(2)	2.307(2)
Ni—Cl(2)	2.565(2)	2.298(2)
Ni—P(1)	2.170(2)	2.330(2)
Ni—P(2)	2.189(2)	2.380(2)
Ni—N(1)	1.963(4)	2.212(4)
Cl(1)—Ni—Cl(2)	99.78(6)	144.59(6)
Cl(1)—Ni—P(1)	148.29(6)	109.17(6)
Cl(1)—Ni—N(1)	87.5(1)	84.8(1)
Cl(2)—Ni—P(2)	90.65(6)	92.24(6)
Cl(2)—Ni—P(1)	110.82(6)	104.09(6)
P(2)—Ni—N(1)	175.6(1)	177.6(1)
	9	13 ·MeOH
Ni—Cl	2.200(2)	2.177(2)
Ni—P(1)	2.137(1)	2.156(2)
Ni—P(2)	2.195(2)	2.204(2)
Ni—N(1)	1.987(4)	1.998(6)
Cl—Ni—P(1)	165.91(6)	171.36(9)
Cl—Ni—P(2)	89.53(6)	88.68(9)
Cl(1)—Ni—N(1)	88.7(1)	87.9(1)
P(1)—Ni—P(2)	95.87(6)	98.05(8)
P(1)—Ni—P(2)	87.0(1)	85.8(2)
P(2)—Ni—N(1)	174.8(1)	174.0(2)

van der Waals radii and there are no possibilities for hydrogen bonding. The Ni(II)—donor atom bond lengths in the $[\text{NiCl}_2(\text{PR}_3)(\text{P}^\wedge\text{N})]$ and $[\text{NiCl}(\text{PR}_3)(\text{P}^\wedge\text{N})]^+$ complexes merit some comment. Thus, the spread of their values (Table 3) might seem unexpectedly large (Ni—Cl in the range 2.177–2.567 Å; Ni—P 2.139–2.400 Å and Ni—N 1.963–2.353 Å), but this can be rationalized on the basis of coordination number, c.n., and/or geometry arguments. In fact, comparison of the distances with the pertinent “ref-

erence” values retrieved from the Cambridge Structural Database (CSD)^[26] reveals the following features. (i) The Ni^{II}—Cl distances (mean value of 2.196 Å when c.n. = 4, and of 2.288 Å with c.n. = 5) are slightly shorter than the corresponding CSD values [2.22 (219 obs.) and 2.34 Å (88 obs.), respectively], but they confirm the finding that on going from c.n. 4 to 5 the distance increases. This trend also holds for the Ni—P and Ni—N distances. The Ni—Cl(2) distance in **3** [2.567(2) Å] represents an exception, being the

Table 3. Selected structural data for $[\text{NiCl}_2(\text{PR}_3)(\text{P}^\wedge\text{N})]$ and $[\text{NiCl}(\text{PR}_3)(\text{P}^\wedge\text{N})]\text{PF}_6$ complexes

	Geometry ^[a]	Ni–Cl [Å]	Ni–PR ₃ [Å]	Ni–P [Å]	Ni–N [Å]	P [⊖] N _{bite} [°]	Ni–N–C _{chelate} [°]	Ref. ^[b]
$[\text{NiCl}_2(\text{PMe}_2\text{Ph})(\text{P}^\wedge\text{NMe}_2)]$	tb	2.276(2) 2.284(2)	2.372(2)	2.290(2)	2.353(4)	77.9(1)	109.2(5)	5
$[\text{NiCl}_2(\text{PMePh}_2)(\text{P}^\wedge\text{NHMe})]\cdot\text{CH}_2\text{Cl}_2$	tb	2.298(2) 2.307(2)	2.380(2)	2.330(2)	2.212(4)	79.9(1)	112.3(3)	6 ·CH ₂ Cl ₂
$[\text{NiCl}_2(\text{PMePh}_2)(\text{P}^\wedge\text{NMe}_2)]\cdot 0.5\text{CH}_2\text{Cl}_2$	tb	2.288(3) 2.272(3)	2.400(5)	2.310(3)	2.325(8)	78.7(2)	108.5(5)	7
$[\text{NiCl}_2(\text{PMe}_2\text{Ph})(\text{P}^\wedge\text{NH}_2)]$	tb/spy	2.249(2) 2.567(2)	2.189(2)	2.170(2)	1.963(4)	86.3(2)	119.8(3)	3
$[\text{NiCl}(\text{PMe}_3)(\text{P}^\wedge\text{NP})]\text{PF}_6$ ^[c]	sp	2.217(2)	2.192(2)	2.159(3)	2.011(7)	83.1(2)	113.8(5)	8
$[\text{NiCl}(\text{PMe}_3)(\text{P}^\wedge\text{NHMe})]\text{PF}_6$	sp	2.200(2)	2.195(2)	2.137(1)	1.987(4)	87.0(1)	116.7(3)	9
$[\text{NiCl}(\text{PMePh}_2)(\text{P}^\wedge\text{NHMe})]\text{PF}_6\cdot\text{MeOH}$	sp	2.177(2)	2.177(2)	2.156(2)	1.998(6)	85.8(2)	115.2(5)	13 ·MeOH
$[\text{NiCl}(\text{PMePh}_2)(\text{P}^\wedge\text{NMe}_2)]\text{PF}_6$	sp	2.189(5)	2.207(5)	2.139(5)	2.056(8)	86.8(2)	114.9(6)	14

^[a] tb = trigonal-bipyramidal; spy = square-pyramidal; sp = square-planar. – ^[b] **3**, **6**·CH₂Cl₂, **9**, **13**·MeOH in present work; **5** in ref. ^[21], **7** and **14** in ref. ^[17]; **8** in ref. ^[19]. – ^[c] P[⊖]NP = N-(trimethylphosphoranyl)-2-(diphenylphosphanyl)aniline.

second longest distance ever reported in the literature^[27]. In the square-pyramidal description (Figure 4), this axial elongation can be correlated with the electron density in the d_{z^2} orbital for the d^8 ion, leading to a pronounced metal–halide electron-electron repulsion. (ii) The geometry seems to govern the Ni–P bond lengths. The corresponding mean values in the trigonal-bipyramidal complexes average 2.310 Å and 2.384 Å for the chelating phosphane ligand and the unidentate ligand axially bonded to Ni^{II}, respectively. The magnitude of this “axial effect” (ca. 0.07 Å) is consistent with similar values encountered in the CSD file. In square-planar complexes, the corresponding mean values are 2.148 Å and 2.193 Å and a parallel situation is presented by **3**, since values of 2.189 Å and 2.170 Å are observed. (iii) The Ni^{II}–N distances in cationic complexes with c.n. = 4 (mean value 2.01 Å) are dramatically shorter than those in the neutral complexes with c.n. = 5 (mean value 2.30 Å), but the paucity of literature data prevents us from making a reliable comparison. In any case, the Ni–N(C_{sp²})H₂ value of **3** (1.963 Å) conforms to those of the square-planar complexes. Similarly, the P–Ni–N bite angle (86.3°) of **3** closely approaches the mean value (85.6°) found in the four analogous complexes with c.n. 4, while it is compressed to 78.8° in those with c.n. = 5. Finally, the Ni–N–C angle of the five-membered chelate ring averages 115.2° in complexes with c.n. = 4, while it is compressed to 110.0° when the c.n. becomes 5.

Conclusions

Phosphanyl-amines P[⊖]NH₂, P[⊖]NHMe, P[⊖]NMe₂ exhibit good coordination properties towards the nickel(II) center, affording stable neutral pentacoordinate $[\text{NiCl}_2(\text{PR}_3)(\text{P}^\wedge\text{N})]$ and cationic tetracoordinate $[\text{NiCl}(\text{PR}_3)(\text{P}^\wedge\text{N})]^+$ complexes starting from the corresponding $[\text{NiCl}_2(\text{PR}_3)_2]$ precursor.

The neutral pentacoordinate species $[\text{NiCl}_2(\text{PR}_3)(\text{P}^\wedge\text{N})]$ feature a rather unusual {NP₂Cl₂} donor set. Their behavior can be satisfactorily accounted for considering the data collected in the course of this study. The range of magnetic moments they exhibit is unexpected in view of the

donor set {NP₂Cl₂} and of their crystal structures. While it is possible to assign a trigonal-bipyramidal structure to complex **6**, in analogy to related compounds such as $[\text{NiCl}_2(\text{PMe}_2\text{Ph})(\text{P}^\wedge\text{NMe}_2)]$ ^[21] and $[\text{NiCl}_2(\text{PMePh}_2)(\text{P}^\wedge\text{NMe}_2)]\cdot 0.5\text{CH}_2\text{Cl}_2$ ^[17], complex **3** has a structure intermediate between trigonal-bipyramidal and square-pyramidal, which accounts for the very long Ni–Cl distance.

The cationic tetracoordinate species $[\text{NiCl}(\text{PR}_3)(\text{P}^\wedge\text{N})]^+$ can be derived from the corresponding $[\text{NiCl}_2(\text{PR}_3)_2]$ precursor only by the addition of KPF₆ in order to remove one Cl[–] ligand per Ni atom. NMR spectra and crystal structures indicate that these complexes consist of the *cis*-P,P isomer. Comparison of some structural features such as the Ni–N, Ni–Cl, and Ni–P bond lengths confirms the finding that on going from c.n. = 4 to 5 the distances increase. In particular, Ni–N is dramatically shorter than the CSD reference value, but the paucity of literature data prevents us from making firm conclusions from this observation.

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Experimental Section

General: All chemicals and solvents were of analytical grade and were used as received unless otherwise stated. The starting $[\text{NiCl}_2(\text{PR}_3)_2]$ (PR₃ = PMe₃, PMe₂Ph, PMePh₂) complexes were prepared according to the literature^{[28][29]}, as were the ligands P[⊖]NH₂^[9], P[⊖]NHMe^[9], and P[⊖]NMe₂^[30]. – IR: Mattson 3030 Fourier-transform spectrometer. – UV/Vis in the solid state: Cary 5-E spectrophotometer (1200–220 nm), diffuse reflectance method. – UV/Vis in solution: Cary 17D spectrophotometer (1200–220 nm), ca. 10^{–2} M solutions in CH₂Cl₂ for the pentacoordinate complexes in 0.1-cm cells and 10^{–3}–10^{–5} M solutions in CH₂Cl₂ for square-planar and cationic complexes in 1-cm cells. – NMR: Bruker AC-200 (200 MHz for ¹H and ³¹P). For ¹H NMR, CDCl₃ or CD₂Cl₂ as solvent, TMS as internal standard; for ³¹P{¹H} NMR, CDCl₃ or CD₂Cl₂ as solvent, 85% aqueous H₃PO₄ as external standard. – Conductivity measurements: Amel conductimeter Mod. 131, ca. 10^{–3} M solutions in MeCN at 25°C. – Magnetic susceptibility measurements: Cahn 2000 microbalance. – Elemental analyses (C, H, N): Fisons EA 1108 elemental analyzer.

[NiCl₂(PMe₃)(P[^]NMe₂)] (2): To a solution of 0.196 g of [NiCl₂(PMe₃)₂] (0.68 mmol) in 10 ml of MeCN was added 0.209 g of P[^]NH₂ (0.68 mmol). The blood-red solution immediately darkened and was stirred under dinitrogen at room temperature for 3 h. The solution was then concentrated to a volume of 3 ml under a flow of dinitrogen. A dark-blue powder precipitated, which was collected by filtration, washed with 5 ml of Et₂O, 5 ml of *n*-hexane and 0.5 ml of EtOH, and dried in vacuo. Yield: 0.140 g (40%). – IR (KBr): $\tilde{\nu}$ = 3047 cm⁻¹ s, 1580 m, 1481 m, 1437 s, 1094 s, 959 vs, 753 m, 514 m. – ¹H NMR (CDCl₃): Several signals in the region δ = +18.0 to –2.0. – C₂₃H₂₉Cl₂NNiP₂ (483.01): calcd. C 54.05, H 5.73, N 2.74; found C 54.64, H 5.67, N 2.43.

[NiCl₂(PMe₂Ph)(P[^]NH₂)] (3): To a solution of 0.108 g of [NiCl₂(PMe₂Ph)₂] (0.27 mmol) in 10 ml of MeCN was added 0.075 g of P[^]NH₂ (0.27 mmol) and the mixture was stirred under dinitrogen at room temperature. The blood-red solution immediately turned dark. After 5 min, a blue compound precipitated and after 15 min the solid was collected by filtration, washed several times with MeCN, and dried in vacuo. Yield: 0.111 g (85%). Crystals were grown by slow evaporation of the solvent from CH₂Cl₂ solutions. – IR (KBr): $\tilde{\nu}$ = 3236 cm⁻¹ m, 3179 m, 3093 s, 1555 m, 1478 m, 1433 s, 1095 m, 914 vs, 698 m, 512 m. – ¹H NMR (CDCl₃): δ = 1.78 [s, 6 H, P(CH₃)₂], 2.67 (m, 2 H, NH₂), 6.33–8.38 (m, 19 H, aromatic). – ³¹P{¹H} NMR (CDCl₃): δ = –5.2 (br. s, 1 P, PMe₂), 38.6 (br., 1 P, P[^]NH₂). – C₂₆H₂₇Cl₂NNiP₂ (545.08): calcd. C 57.29, H 5.00, N 2.57; found C 57.17, H 5.37, N 2.57.

[NiCl₂(PMe₂Ph)(P[^]NHMe)] (4): To a solution of 0.100 g of [NiCl₂(PMe₂Ph)₂] (0.25 mmol) in 5 ml of MeCN was added 0.073 g of P[^]NHMe (0.25 mmol) and the mixture was stirred under dinitrogen at room temperature. After 30 min, a blue compound precipitated and after 3 h the solid was collected by filtration, washed twice with 6 ml of *n*-hexane, and dried in vacuo. Yield: 0.065 g (44%). – IR (KBr): $\tilde{\nu}$ = 3246 cm⁻¹ w, 3051 s, 2247 w, 1580 m, 1481 m, 1435 s, 1098 s, 913 s, 742 m, 487 s. – ¹H NMR (CDCl₃): Several signals in the region δ = +18.0 to –2.0. – C₂₇H₂₉Cl₂NNiP₂·0.5 CH₃CN (579.64): calcd. C 58.02, H 5.31, N 3.62; found C 57.75, H 5.06, N 3.64.

[NiCl₂(PMePh₂)(P[^]NHMe)] (6): To a blood-red solution of 0.101 g of [NiCl₂(PMePh₂)₂] (0.19 mmol) in 10 ml of MeCN and 0.5 ml of CH₂Cl₂ was added 0.055 g of P[^]NHMe (0.19 mmol). The red solution immediately turned brown. After stirring under dinitrogen at room temperature for 3 h, the solution was concentrated to dryness under reduced pressure. The residue was washed with 0.4 ml of MeCN and 0.4 ml of CH₂Cl₂, and then redissolved in 10 ml of CH₂Cl₂ and 1.5 ml of C₆H₆. Addition of 23 ml of Et₂O caused the precipitation of a green solid, which was collected by filtration, washed with 5 ml of Et₂O, and dried in vacuo. Yield: 0.080 g (60%). Crystals were grown by slow evaporation of the solvent from CH₂Cl₂ solutions. – IR (KBr): $\tilde{\nu}$ = 3262 cm⁻¹ w, 1580 m, 1471 s, 1434 s, 1099 m, 885 s, 685 vs, 502 s. – ¹H NMR (CDCl₃): Several signals in the region δ = +18.0 to –1.0. – C₃₂H₃₁Cl₂NNiP₂·C₆H₆ (699.3): calcd. C 65.26, H 5.34, N 2.00; found C 65.38, H 5.44, N 1.74.

[NiCl(PMe₃)(P[^]NHMe)]PF₆ (9): To a mixture of 0.131 g of [NiCl₂(PMe₃)₂] (0.46 mmol) and 0.117 g of KPF₆ (0.64 mmol) in 10 ml of CH₂Cl₂ was added 0.134 g of P[^]NHMe (0.46 mmol) under stirring. The blood-red mixture immediately turned dark-red. After 3 h, a yellow solid had been deposited, which was filtered off, washed with 2 ml of H₂O, recrystallized from a 1:2 MeCN/Et₂O solution (30 ml), and dried in vacuo. The filtrate was concentrated to dryness under reduced pressure and the residue was recrystallized as above, giving a second crop of the yellow solid.

Yield: 0.195 g (70%). Crystals suitable for X-ray analysis were grown by slow evaporation of the solvent from CH₂Cl₂ solutions. – IR (KBr): $\tilde{\nu}$ = 3191 cm⁻¹ m, 1583 m, 1462 m, 1104 w, 838 vs (P–F), 557 s. – ¹H NMR (CD₂Cl₂): δ = 1.23 [s, 9 H, P(CH₃)₃], 2.87 (d, ³J_{HH} = 6 Hz, 3 H, NCH₃), 4.85 (m, 1 H, NH), 7.20–7.95 (m, 14 arom. H). – ³¹P{¹H} NMR (CD₂Cl₂): δ = –144 (sept., J_{PF} = 711 Hz, 1 P, PF₆[–]), –7.80 (m, 1 P, PMe₃), 42.5 (m, 1 P, P[^]NHMe). – C₂₂H₂₇ClF₆NNiP₃ (606.56): C 43.56, H 4.50, N 2.31; found C 43.42, H 4.16, N 2.16.

[NiCl(PMe₃)(P[^]NMe₂)]PF₆ (10): To a mixture of 0.082 g of [NiCl₂(PMe₃)₂] (0.29 mmol) and 0.074 g of KPF₆ (0.40 mmol) in 10 ml of CH₂Cl₂ was added 0.089 g of P[^]NH₂ (0.25 mmol) and the mixture was stirred at room temperature. The blood-red solution immediately turned orange-red. After 3 h, the mixture was filtered and concentrated to a volume of 4 ml under a flow of dinitrogen. Addition of 12 ml of Et₂O caused the precipitation of a yellow-orange solid, which was collected by filtration, washed with H₂O, and dried in vacuo. The solid was recrystallized from CH₂Cl₂/EtOH/C₆H₆ (10:1:19) (20 ml). Yield: 0.121 g (67%). – IR (KBr): $\tilde{\nu}$ = 3070 cm⁻¹ w, 1580 m, 1483 m, 1436 s, 1097 m, 836 vs (P–F), 558 s. – ¹H NMR (CD₂Cl₂): δ = 1.26 [d, 9 H, ²J_{HP} = 12.5 Hz, P(CH₃)₃], 3.19 [s, 6 H, N(CH₃)₂], 7.12–8.15 (m, 14 H, aromatic). – ³¹P{¹H} NMR (CD₂Cl₂): δ = –144 (sept, 1 P, J_{PF} = 713 Hz, PF₆[–]), –9.51 (d, 1 P, ²J_{PP} = 107 Hz, PMe₃), 38.1 (d, 1 P, ²J_{PP} = 107 Hz, P[^]NMe₂). – C₂₃H₂₉ClF₆NNiP₃ (620.59): calcd. C 44.51, H 4.71, N 2.26; found C 44.41, H 4.56, N 2.26.

[NiCl(PMe₂Ph)(P[^]NHMe)]PF₆ (11): To a mixture of 0.155 g of [NiCl₂(PMe₂Ph)₂] (0.38 mmol) and 0.138 g of KPF₆ (0.75 mmol) in 1 ml of CH₂Cl₂ was added 0.111 g of P[^]NHMe (0.38 mmol) and the mixture was stirred at room temperature. The blood-red mixture slowly turned red-orange. After 3 h, the solution was filtered and concentrated to a volume of 5 ml under a flow of dinitrogen. Addition of 15 ml of Et₂O caused the precipitation of an orange solid, which was collected by filtration, washed with H₂O, and dried in vacuo. The solid was recrystallized from CH₂Cl₂/EtOH/C₆H₆ (7:1.5:19) (27.5 ml). Yield: 0.153 g (60%). – IR (KBr): $\tilde{\nu}$ = 3229 cm⁻¹ m, 1584 m, 1506 m, 1437 s, 1102 m, 837 vs (P–F), 557. – ¹H NMR (CD₂Cl₂): δ = 1.64 [s, 6 H, P(CH₃)₂], 2.96 (d, 3 H, ³J_{HH} = 6 Hz, NCH₃), 4.94 (m, 1 H, NH), 6.90–8.04 (m, 19 H, aromatic). – ³¹P{¹H} NMR (CD₂Cl₂): δ = –144 (sept, 1 P, J_{PF} = 713 Hz, PF₆[–]), 1.30 (m, 1 P, PMe₂Ph), 48.0 (m, 1 P, P[^]NHMe). – C₂₇H₂₉ClF₆NNiP₃ (668.63): calcd. C 48.55, H 4.38, N 2.10; found C 48.71, H 4.38, N 2.03.

[NiCl(PMePh₂)(P[^]NHMe)]PF₆ (13): To a mixture of 0.132 g of [NiCl₂(PMePh₂)₂] (0.25 mmol) and 0.092 g of KPF₆ (0.50 mmol) in 10 ml of CH₂Cl₂ was added 0.073 g of P[^]NHMe (0.25 mmol) and the mixture was stirred at room temperature. The blood-red mixture immediately turned red-orange. After 3 h, the solution was filtered and concentrated to a volume of 4 ml under a flow of dinitrogen. Addition of 16 ml of Et₂O caused the formation of a red-orange oil, which was separated by decantation. After dissolution of the oil in 7 ml of CH₂Cl₂, 18 ml of C₆H₆ was added and upon stirring an orange-yellow solid precipitated. This solid was collected by filtration, washed with H₂O, dried in vacuo, and recrystallized from CH₂Cl₂/EtOH/C₆H₆ (6:1.5:17) (24.5 ml). Yield: 0.112 g (60%). Crystals were grown from CH₂Cl₂/MeOH/C₆H₆/Et₂O solutions. – IR (KBr): $\tilde{\nu}$ = 3251 cm⁻¹ m, 1581 m, 1436 s, 1099 w, 840 vs (P–F), 557 s. – ¹H NMR (CDCl₃): δ = 2.01 (d, 3 H, ³J_{HP} = 13 Hz, PCH₃), 2.33 (s, 3 H, NCH₃), 7.10–7.84 (m, 26 H, aromatic). – ³¹P{¹H} NMR (CDCl₃): δ = –146 (sept., 1 P, J_{PF} = 713 Hz, PF₆[–]), 6.91 (d, 1 P, ²J_{PP} = 83 Hz, PMe₂Ph), 37.6 (d, 1 P, ²J_{PP} = 83 Hz, P[^]NHMe). – C₃₂H₃₁ClF₆NNiP₃·C₆H₆ (808.82): calcd. C 56.08, H 4.59, N 1.72; found C 56.99, H 4.55, N 1.65.

X-ray Crystal Structure Determinations: Many of the details of the structure analyses carried out on complexes **3**, **6**·CH₂Cl₂, **9**, and **13**·MeOH are listed in Table 4.

partially occupied sites with occupancies of ca. 0.7, 0.2, and 0.1, but efforts to refine these values were not successful and hence this matter was not pursued further. The PF₆[−] anion of **9** was modelled

Table 4. Crystallographic details for complexes **3**, **6**·CH₂Cl₂, **9**, and **13**·MeOH

	3	6 ·CH ₂ Cl ₂	9	13 ·MeOH
formula	C ₂₆ H ₂₇ Cl ₂ NNiP ₂	C ₃₃ H ₃₃ Cl ₄ NNiP ₂	C ₂₂ H ₂₇ ClF ₆ NNiP ₃	C ₃₃ H ₃₅ ClF ₆ NNiOP ₃
cryst. system	monoclinic	triclinic	monoclinic	triclinic
space group	P2 ₁ /n, (No.14)	P1 (No.2)	P2 ₁ /n, (No.14)	P1 (No.2)
a [Å]	11.937(5)	9.763(4)	11.856(3)	10.008(1)
b [Å]	13.348(4)	10.002(3)	13.669(4)	13.395(2)
c [Å]	15.575(4)	18.115(9)	16.575(5)	14.598(2)
α [°]	90	77.89(3)	90	101.50(1)
β [°]	92.37(3)	77.85(3)	96.54(2)	105.02(1)
γ [°]	90	87.36(3)	90	104.56(1)
V [Å ³]	2479(1)	1691(1)	2669(1)	1745.5(3)
Z	4	2	4	2
D _{calcd} [Mg/m ³]	1.460	1.251	1.510	1.444
μ [mm ^{−1}]	1.142	1.008	1.061	0.825
F(000)	1128	728	1240	784
cryst. size [mm]	0.20 × 0.30 × 0.20	0.15 × 0.10 × 0.20	0.25 × 0.25 × 0.25	0.15 × 0.15 × 0.15
Θ range [°]	2.3–25.0	2.6–22.5	2.5–22.5	2.2–21.5
indep. refl.	4387	4429	3500	4013
refl. with I > 2σ(I)	2633	3295	2956	2798
no. of parameters	215	385	289	414
R1 ^[a] , wR2 ^[b] [I > 2σ(I)]	0.043, 0.106	0.041, 0.112	0.045, 0.158	0.055, 0.139
R1, wR2 (all data)	0.082, 0.121	0.062, 0.123	0.054, 0.163	0.094, 0.165
GooF on F ²	0.745	0.987	1.509	1.182
max/min. resid. dens. [eÅ ^{−3}]	0.90, −0.48	0.53, −0.49	0.87, −0.84	0.69, −0.46
extinction coeff. F _c ^[c]	0.0000(6)	—	0.0039(11)	0.0000(11)

^[a] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. — ^[b] $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$. — ^[c] $F_c^* = kF_c[1 + (0.001 \times F_c^2 \lambda^3 / \sin 2\Theta)]^{-1/4}$.

Crystallographic measurements were made at 293 K with a Siemens Nicolet R3m/V four-circle diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) (ω –2 Θ scan technique). The unit cell was determined by the automatic indexing of 50 centered reflections at 2 $\Theta > 21^\circ$. The rather poor quality of crystals of **13**·MeOH was manifested in broad scan-widths during initial search routines with the diffractometer and the diffracting ability of the sample dropped with increasing Bragg angle; much of the higher angle data collected were deemed to be weak. As a consequence, the data collection for **13**·MeOH was restricted to 2 $\Theta = 43^\circ$. Corrections for Lorentz polarization effects and extinction were applied in all cases, while an empirical absorption correction, based on ψ scans for six reflections at $\chi \approx 90^\circ$, was applied only for compounds **3** and **13**·MeOH (minimum and maximum transmission factors 0.63–0.87 and 0.49–0.68 for **3** and **13**·MeOH, respectively). In fact, for **6**·CH₂Cl₂ and **9**, azimuthal scan data proved such correction to be unnecessary. The structures were solved by Patterson methods and refined by full-matrix least-squares methods on F² using the SHELXTL/PC^[31] and SHELXL-93^[32] suites of programs. Atomic scattering factors and anomalous dispersion parameters were taken from ref.^[33]. Non-hydrogen atoms were assigned anisotropic thermal parameters, with the exception of the disordered atoms of **6**·CH₂Cl₂, **9**, and **13**·MeOH. The hydrogen atoms were constrained to ride on the atom to which they were attached. The isotropic thermal parameters for the methyl H atoms were refined with 1.5 times, and for all phenyl H atoms with 1.2 times the U_{eq} value of the corresponding atom. On the contrary, the hydrogen atoms attached to nitrogen atoms were located in the final difference maps, but were not included in the refinement. During the refinement procedure it became apparent that the CH₂Cl₂ molecule in **6**·CH₂Cl₂, the PF₆[−] anion in **9**, and the MeOH molecule in **13**·MeOH were disordered. The CH₂Cl₂ molecule of **6**·CH₂Cl₂ was found to be severely disordered into a number of

using partial F atom occupancies, such that the central P atom had two 100%, four 66% and four 33% occupied F atoms around it. This model still gave rather high thermal parameters (ca. 0.10 Å² for all atoms), but resulted in an overall improvement in the structure. Finally, the MeOH molecule of **13**·MeOH was located in a disordered position and was included at half occupancy.

Selected bond lengths and angles are listed in Table 2.

Further details of the crystal structure determination can be ordered from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-408520 (**3**), -408521 (**6**·CH₂Cl₂), -408522 (**9**), -408523 (**13**·MeOH).

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