

Tetra- and Triphosphane Pyridine Podands and Their Cobalt(II) and Nickel(II) Complexes

Stephan W. Kohl,^[a] Frank W. Heinemann,^[b] Markus Hummert,^[a] Hardy Weißhoff,^[c] and Andreas Grohmann^{*[a]}

Dedicated to Professor Robert Weiß on the occasion of his 65th birthday

Keywords: Cobalt / Nickel / N,P ligands

The reaction of the 2,6-diethylpyridine-derived tetraphosphane ligand $C_5H_3N[CMe(CH_2PMe_2)_2]_2$ (**1**_{Me}) with nickel(II) or cobalt(II) perchlorate or tetrafluoroborate in methanol produces complexes of approximate square-pyramidal geometry (NP₄ coordination). The nickel complexes are diamagnetic, with NMR spectral features (³¹P) that reflect a tetrahedral distortion of diametrically opposite phosphorus donors; this is also found in the solid state. In terms of bond lengths and angles, all complexes differ significantly from their analogues containing the phenyl-substituted ligand $C_5H_3N[CMe(CH_2PPh_2)_2]_2$. The ligand **1**_{Me} is readily and completely oxidised to the corresponding tetrakis(phosphane oxide) upon reaction with NO. Slow oxidation of the cobalt(II) tetrafluoroborate complex of **1**_{Me} with aerobic oxygen in acetonitrile produces a trinuclear cobalt complex containing two equivalents of partially oxidised ligand (C₂-symmetrical; donor set: [PMe₂]₂[P(O)Me₂]₂). Four phosphane oxide oxygen atoms coordinate the central cobalt(II) ion in tetrahedral fashion, whereas the lateral cobalt(II) ions are in a square-pyramidal environment provided by two PMe₂ do-

nors and three acetonitrile ligands in each case. The reaction of the cobalt(II) perchlorate complex of **1**_{Me} with carbon monoxide gives an octahedral, 19-valence-electron dicarbonyl complex in which one of the dimethylphosphanyl groups is uncoordinated. A structural relative of **1**_{Me}, $C_5H_3N[CMe(CH_2PMe_2)_2][CMe_2(CH_2PMe_2)]$ (**2**), which contains one fewer dimethylphosphanyl donor, can be prepared in a straightforward manner from 2-ethyl-6-isopropylpyridine in a four-stage process. In a series of mononuclear nickel(II) complexes, **2** employs only its three phosphane donors which, together with a monodentate ligand (acetonitrile, acetamide, or bromide), provide a tetragonal coordination environment for the metal ion which is intermediate between square planar and tetrahedral. The acetamide complex is generated from the acetonitrile complex by slow hydrolysis of the coordinated ligand. Full spectroscopic details for the complexes, as well as X-ray structure analyses, are reported.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2006)

Introduction

Phosphanes are the workhorse ligands of transition metal chemistry due to their variability in terms of steric demand and electronic properties. Both factors, which are mutually dependent, may be controlled within wide limits, depending on the bulk of substituents and the σ -donor/ π -acceptor balance they impart to the donor atom. The major application of phosphane complexes is in catalysis, where the phosphane-coordinated metal ion is the mediator of the

desired reaction.^[1] It is mainly for the mechanistic implications in catalysis that the reactivity, or lack thereof, of coordinated tertiary phosphanes themselves (e.g., metallation of C–H or C–P bonds) has become a focus of investigation.^[2]

Within this context, we have extended our study of tetrapodal pentadentate ligands^[3] to include tetraphosphane pyridine ligands (general formula: **1**). We are especially interested in mononuclear complexes of these ligands in which the “coordination cap” focuses the properties of several PR₂ donors on a single metal ion M. Such coordination modules can bind an additional monodentate ligand, L, to form complexes of pseudo-octahedral geometry. Previous reports have described the diphenylphosphanyl derivative **1**_{Ph}, whose steric bulk causes the metal centres to be largely inert with respect to further coordination (e.g., M = Co^{II}, L = O₂),^[4] and iron(II) complexes of the dimethylphosphanyl derivative (**1**_{Me}), which undergo unusual P–C bond breaking and re-forming reactions, depending on the nature of

[a] Technische Universität Berlin, Institut für Chemie, Sekretariat C2, Straße des 17. Juni 135, 10623 Berlin, Germany
Fax: +49-30-3142-2935,
E-mail: andreas.grohmann@chem.tu-berlin.de

[b] Universität Erlangen-Nürnberg, Institut für Anorganische Chemie,
Egerlandstraße 1, 91058 Erlangen, Germany

[c] Humboldt-Universität zu Berlin, Institut für Chemie,
Brook-Taylor-Str. 2, 12489 Berlin, Germany

the solvent (nucleophilic/non-nucleophilic), the anion, and other conditions.^[5] The present contribution summarises coordination chemistry aspects of this ligand with respect to nickel(II) and cobalt(II), and introduces a structural relative having only three PMe₂-substituted “tentacles” (2).

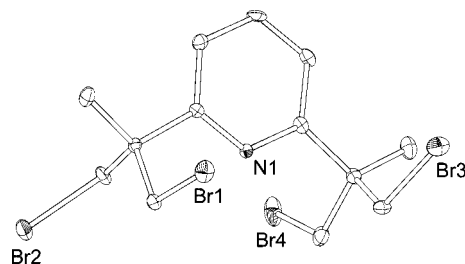
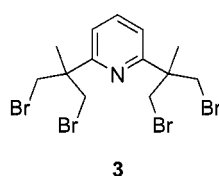
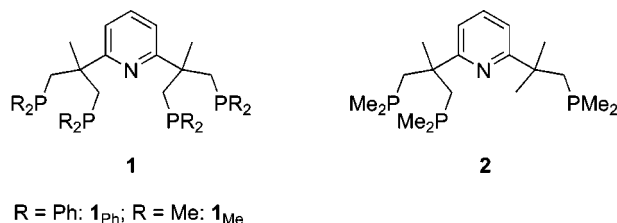
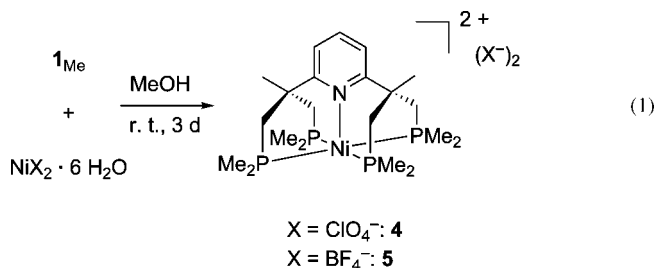


Figure 1. Structure of the tetrabromide **3**.

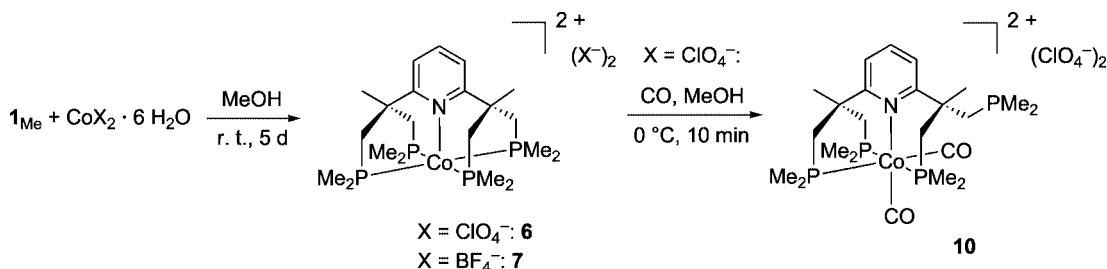
Compound **1**_{Me}, which is obtained as a colourless oil, has the expected spectroscopic signature (¹H, ¹³C, ³¹P), suggesting C_{2v} symmetry in solution. Upon mixing methanol solutions of equimolar amounts of **1**_{Me} and the hexahydrate salts of nickel(II) or cobalt(II) perchlorate or tetrafluoroborate at room temperature, complex formation is spontaneous, as judged by the immediate appearance of a deep red or brown colour. The reaction mixtures soon begin to deposit microcrystalline precipitates which, upon filtration and drying, analyse for the respective LMX₂ complexes [L = **1**_{Me}, M = Ni^{II}, X = ClO₄[−] (**4**) or BF₄[−] (**5**); M = Co^{II}, X = ClO₄[−] (**6**) or BF₄[−] (**7**); see Equation (1), Scheme 1, and Exp. Sect.].

Results and Discussion

The tetraphosphane **1**_{Me} {systematic name: 2,6-bis[1,3-bis(dimethylphosphanyl)-2-methylpropan-2-yl]pyridine; “py(PMe₂)₄”} may be prepared in good yield (>80%) from the reaction of the corresponding tetrabromide C₅H₃N[CMe(CH₂Br)₂]₂ (**3**)^[4] with four equivalents of LiPMe₂^[6] in diethyl ether.^[5] The yield of this reaction increases considerably with the purity of the halogenated precursor. Whereas **3** had previously been obtained as an oil or waxy solid, which reflected the presence of minor impurities introduced during the multi-stage synthesis, we have recently been able to obtain **3** in its crystalline form. The compound crystallises solvent-free in the space group *Pbca*, with no crystallographically imposed molecular symmetry (C₁; Figure 1). One of the 1,3-dibromo-2-methylprop-2-yl chains (involving Br3, Br4) adopts a “*syn*-pentane arrangement”, whereas the other has a more random orientation, also with respect to the pyridine ring. The bond distances and angles are unexceptional.^[7]



In the IR spectra of **4–7**, there is no indication for the coordination (if weak) of the perchlorate or tetrafluoroborate counterions, which would lead to a splitting of the respective anion bands owing to the reduction of local symmetry from T_d to C_{3v}.^[8] The nickel complexes **4** and **5** are diamagnetic, with well-resolved and very similar NMR spectra. In the ¹H NMR spectra, the pyridine protons appear as an AB₂ spin system (triplet/doublet), and in the ¹³C spectra there are three signals for the pyridine carbon atoms. These features and others, taken together, suggest



Scheme 1. Preparation of the cobalt complexes **6** and **7**, and reaction of **6** with CO to form **10**.

largely symmetrical (i.e., to a first approximation, square pyramidal) coordination of the ligand. The proton-decoupled ³¹P NMR spectra ([D₃]acetonitrile) contain two signals for the four ligand P atoms, at $\delta = -13$ ppm and -15 ppm, thus indicating a tetragonal distortion of the basal ligands (two diametrically opposite P donor atoms above and two below the NiP₄ best plane) in solution. This structural feature persists in the solid state in both the nickel(II) and the cobalt(II) complex. Figures 2 and 3 show the crystal structures of the cations in **4**·CHCl₃ and **7**·MeOH, respectively (the cation structure of **5**·MeOH is very similar; see deposited crystallographic data).

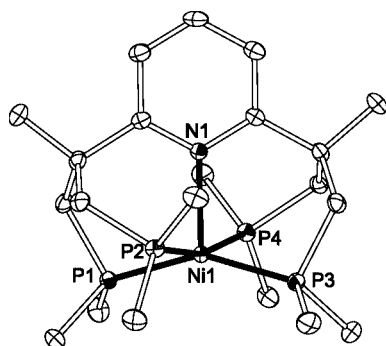


Figure 2. Structure of the dication in the nickel(II) complex **4**·CHCl₃ (perchlorate salt).

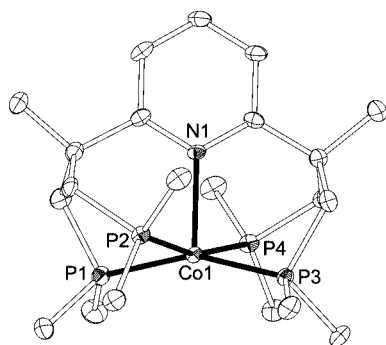


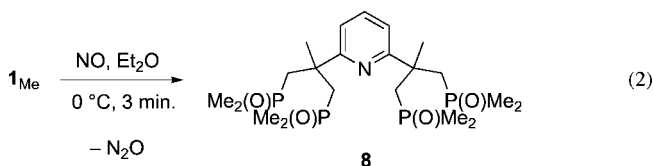
Figure 3. Structure of the dication in the cobalt(II) complex **7**·MeOH (tetrafluoroborate salt).

The bond lengths (see Table 1) involving the central ions in **4** and **7** are markedly shorter than in the structures of the phenyl-substituted ligand **1**_{Ph}.^[4] Whereas the metal–nitrogen distance is approximately 2.13 Å in both **4** and **7**, it is 2.28 and 2.19 Å in the nickel(II) and cobalt(II) complexes of **1**_{Ph}, respectively, and whereas the metal–phosphorus distances in **4** and **7** vary around 2.20 Å within a relatively narrow range, the range is much wider (2.23–2.33 Å) in the corresponding complexes of **1**_{Ph}. The N–M–P and P–M–P angles of the two sets of complexes vary accordingly. These differences reflect the considerable decrease in steric bulk of the ligand periphery upon going from **1**_{Ph} to **1**_{Me}.

Table 1. Selected bond distances [Å] and angles [°] in **4**·CHCl₃ and **7**·MeOH (standard deviations in parentheses). The structural parameters of **5**·MeOH are very similar (see CCDC data).

Distance or angle	4 ·CHCl ₃	7 ·MeOH
M1–N1	2.138(4)	2.131(4)
M1–P1	2.1806(13)	2.2261(15)
M1–P2	2.2018(13)	2.2119(15)
M1–P3	2.1797(13)	2.2177(14)
M1–P4	2.1900(15)	2.2203(14)
N1–M1–P1	104.34(10)	101.70(12)
N1–M1–P2	82.12(10)	81.54(13)
N1–M1–P3	104.72(11)	101.65(12)
N1–M1–P4	82.45(10)	81.77(13)
P1–M1–P2	89.59(5)	88.86(6)
P2–M1–P3	94.58(5)	93.31(6)
P3–M1–P4	89.26(5)	89.72(6)
P4–M1–P1	94.30(5)	94.84(6)
P1–M1–P3	150.94(5)	156.62(6)
P2–M1–P4	164.57(6)	163.31(6)

Steric factors, in addition to electronic ones, can also be expected to play a major role in determining the readiness with which the polyphosphane is oxidised. Whereas **1**_{Ph} does not react with nitrogen monoxide at 0 °C,^[4] the reaction of **1**_{Me} under the same conditions is quantitative after a few minutes, giving the tetrakis(phosphane oxide) **8** as a white microcrystalline material [Equation (2)]. Similar to the reaction of **1**_{Ph} under more forcing conditions, the reaction proceeds with concomitant formation of N₂O. The P=O stretching vibration appears as a strong band in the IR spectrum (KBr disc) at 1161 cm^{−1}, and the ³¹P chemical shift of the RP(O)Me₂ functions is $\delta = 44.95$ ppm (s), similar to the values reported for P(O)Me₃ ($\delta = 36.2$ or 41.0 ppm).^[9] The ligand properties of **8** are as yet unstudied. No oxidation of the ligand is observed when the nickel(II) complexes **4** or **5** are treated with NO under identical conditions.



Whereas the cobalt(II) complexes [**1**_{Ph}Co]X₂ (X = ClO₄, BF₄) were found to be unreactive towards aerobic oxygen,^[4] preliminary results indicate that the methyl derivative [**1**_{Me}Co](BF₄)₂ (**7**) does react to a minor extent, albeit with partial oxidation of the ligand and not with spontaneous formation of cobalt(III), as might initially be expected. While the processes involved require further study, we have been able to isolate (in very small amount) and characterise one oxidation product (**9**) structurally: it is the acetonitrile solvate of a trinuclear complex in which two symmetry-related molecular halves, each made up of a cobalt(II) ion and a partially oxidised ligand, hinge upon a central cobalt ion which is also in the +II oxidation state (space group C2/c; the central cobalt ion lies on a crystallographic twofold rotation axis). The overall charge of the trinuclear complex

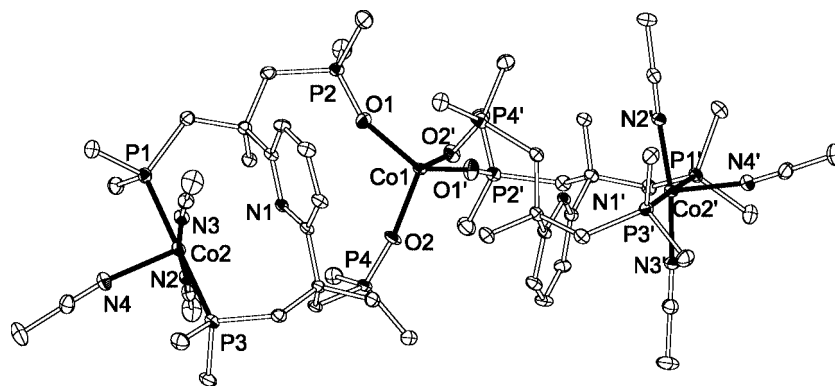


Figure 4. Structure of the hexacation in **9**·2CH₃CN (tetrafluoroborate salt).

is balanced by six tetrafluoroborate anions [Figure 4, composition: C₅₄H₁₀₀Co₃N₈O₄P₈(BF₄)₆·2CH₃CN]. The donor set of the chelate ligand is (PMe₂)₂[P(O)Me₂]₂, with the pyridine nitrogen atom remaining uncoordinated. The pairs of P(O)Me₂ donors in either ligand coordinate the central cobalt ion in a tetrahedral fashion, while the remaining pair of PMe₂ donors in each ligand coordinates an additional cobalt ion in a *trans* arrangement. These lateral cobalt(II) ions have three additional acetonitrile ligands, and thus approximate a square-pyramidal coordination geometry, with Co–P bond lengths slightly longer (at 2.27 Å; Table 2) than in **7**. The 1,3-didentate ligand side-arms each contain one PMe₂ and one P(O)Me₂ donor and are homochiral, thereby reducing the symmetry from C_{2v} in **1** to C₂ in the partially oxidised tetrapodal ligand (Figure 5). The formation of **9** parallels, to a certain extent, the partial oxidation of the triphos ligand, MeC(CH₂PPh₂)₃, upon reaction of its cobalt(II) complex with aerobic oxygen, as described by Huttner et al.^[10]

The pentacoordinate cobalt(II) complexes are 17-valence-electron species, and the coordination of an additional ligand is therefore possible in principle. We studied the behaviour of methanol solutions of the perchlorate salt **6** towards carbon monoxide (see Exp. Sect.), and obtained a well-defined product which, by elemental analysis and based on its IR spectroscopic and MS data, is a dicarbonylcobalt(II) complex in which one phosphane donor has become decoordinated, as shown in Scheme 1. In addition to two very strong bands for CO stretching vibrations (at 1988 and 1937 cm^{−1}), there is a prominent band at 875 cm^{−1} due to the P–C rocking deformation vibration of an uncoordinated dimethylphosphanyl group.^[11] Further, the mass spectrum (MALDI-TOF) has three prominent peaks associated with the parent ion {546 (28) [M – H]⁺, 430 (100) [M – H – Co – 2CO]⁺, 273.5 (18) [M]²⁺}, thus supporting the assignment of **10** as a 19-valence-electron, dicarbonylcobalt(II) complex of the pyridine-based tetraphosphane ligand. However, a 17-valence-electron species with an uncoordinated pyridine nitrogen atom is also possible.

There is a certain degree of similarity between the coordination mode adopted by the tetrapodal ligand in compound **10**, where it coordinates through an NP₃ donor subset, and the coordination mode adopted by a P–C bond

Table 2. Selected bond distances [Å] and angles [°] in **9**·2CH₃CN (standard deviations in parentheses).

Distance or angle	9 ·2CH ₃ CN
Co1–O1	1.924(3)
Co1–O2	1.924(3)
P2–O1	1.503(3)
P4–O2	1.507(3)
Co2–P1	2.2741(12)
Co2–P3	2.2655(12)
Co2–N2	1.899(3)
Co2–N3	2.100(4)
Co2–N4	1.899(3)
O1–Co1–O2	109.56(13)
O1'–Co1–O2'	109.56(13)
O1–Co1–O2'	107.23(14)
O2–Co1–O2'	106.02(19)
P2–O1–Co1	158.7(5)
P4–O2–Co1	155.2(2)
P1–Co2–P3	178.41(5)
P1–Co2–N2	90.26(11)
P1–Co2–N3	90.62(11)
P1–Co2–N4	90.69(11)
P3–Co2–N2	91.30(11)
P3–Co2–N3	87.79(11)
P3–Co2–N4	89.63(11)

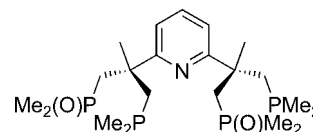
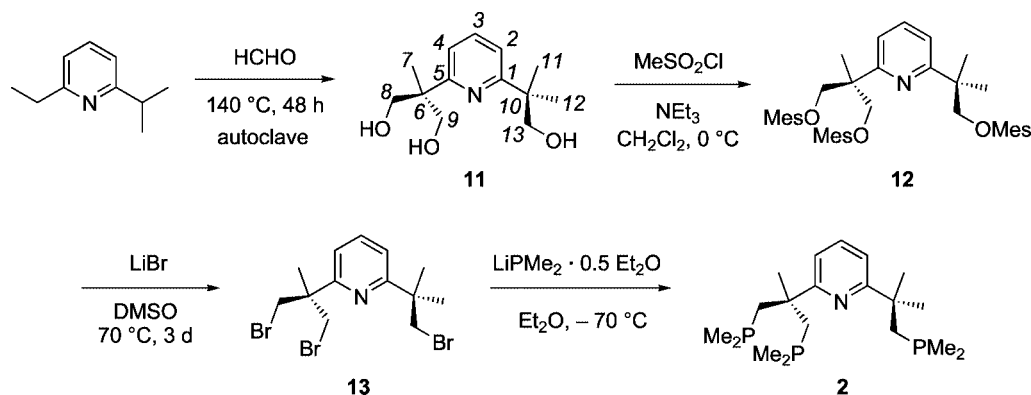


Figure 5. The partially oxidised, C₂-symmetrical tetrapodal ligand in **9**·2CH₃CN.

activated form of the same ligand in an iron(II) complex, where the donor set is likewise NP₃, augmented by a carbanionic methylene group which results from methanol-induced nucleophilic cleavage of one of the dimethylphosphanyl moieties.^[5] For this reason, we decided to synthesise a structural relative (**2**) of the tetraphosphane ligand **1**_{Me}, which can formally be derived from it by replacing one of the dimethylphosphanyl substituents by a hydrogen atom. The synthetic protocol is summarised in Scheme 2. It starts from 2-ethyl-6-isopropylpyridine, which is exhaustively hydroxymethylated in the reactive α -carbon positions by reaction with aqueous formaldehyde in an autoclave at elevated

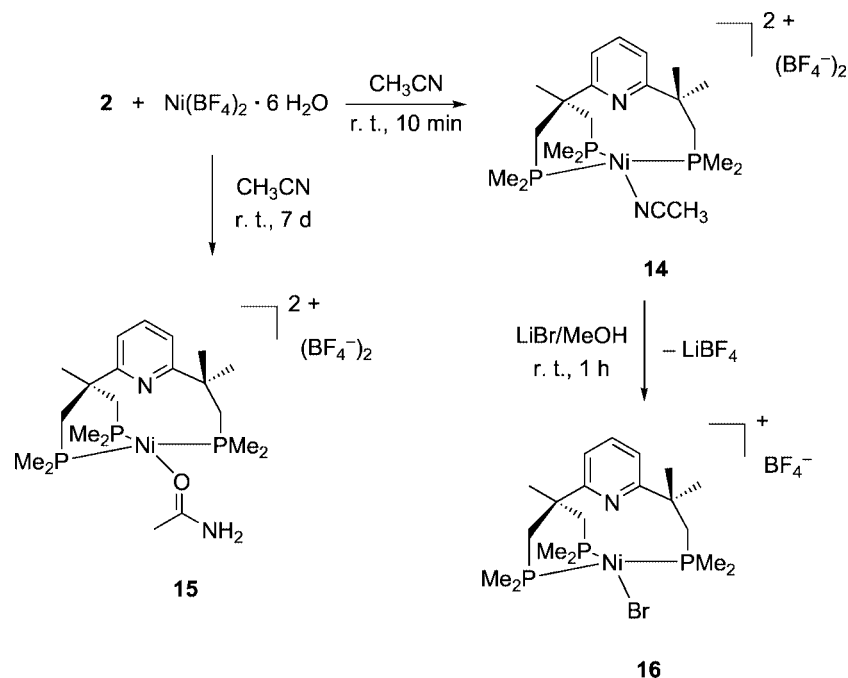
Scheme 2. Preparation of the tripodal tetradentate ligand **2**.

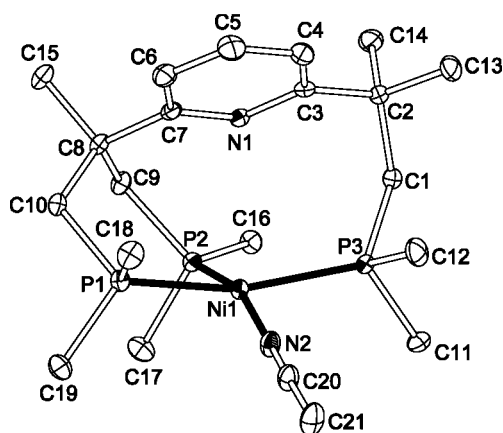
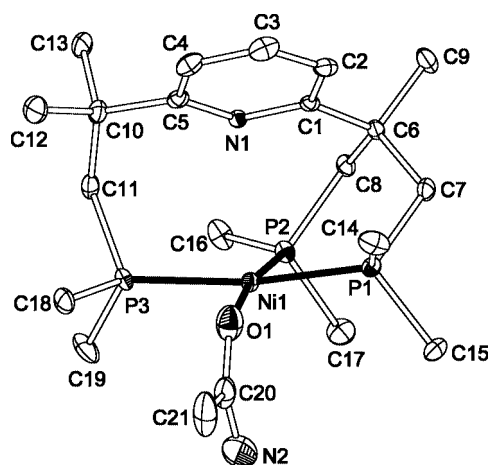
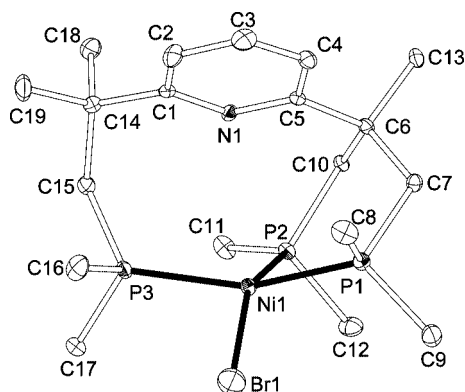
temperature. The triol **11** is then successively transformed into the mesylate **12**, the bromide **13** and, upon treatment with lithium dimethylphosphide according to a procedure described by Karsch et al.,^[6] into the triphosphane **2**. The intermediacy of the tribromide **13** is mandatory, as we found the mesylate, in a manner similar to the tosylated derivative, does not react cleanly with dimethylphosphide.

The reaction of **2** with Ni(BF₄)₂·6H₂O in anhydrous acetonitrile initially gives the CH₃CN-coordinated complex **14** (Scheme 3); when reaction mixtures are allowed to stand for several days, solvate water initiates hydrolysis of the coordinated, and hence activated, nitrile,^[12] to give the acetamide complex **15**. Freshly prepared nitrile complex **14** is transformed into the bromo complex **16** upon treatment with lithium bromide in methanol (Scheme 3). In every one of the complexes **14**–**16**, the chelate ligand **2** is tridentate, with an uncoordinated pyridine nitrogen atom, and there is one additional monodentate ligand (acetonitrile, acetamide

or bromide). The solid-state structures (Figures 6, 7 and 8, respectively) show the nickel ion in a coordination geometry intermediate between square planar and tetrahedral, with varying degrees of distortion. The following discussion applies to all three complexes, with complex **14** singled out for reference.

The exocyclic methyl substituents (**14**: C13, C14) are in different stereochemical environments, which makes the complex topologically chiral. It is diamagnetic in acetonitrile solution, as may be inferred from its fully assigned NMR spectra (see Exp. Sect. and Figure 6 for the numbering scheme used). Significantly, in solution at ambient temperature and on the NMR timescale, the cation has C_s symmetry, as indicated by the equivalence of the phosphanyl substituents P1 and P2, the methyl groups C13/14 (radiating from the quaternary carbon atom C2) and the methyl substituents C11/12 on P3. We are currently investigating whether or not the implied stereochemical flexibility of the P3-substituted ligand arm can be “frozen” in solution by

Scheme 3. Nickel(II) complexes of the tripodal ligand **2**.

Figure 6. Structure of the dication in **14** (tetrafluoroborate salt).Figure 7. Structure of the dication in **15** (tetrafluoroborate salt).Figure 8. Structure of the dication in **16** (tetrafluoroborate salt).

forcing the pyridine nitrogen atom to coordinate to the central metal: this would cause the newly formed N1-C3-C2-C1-P3-M chelate ring to adopt a boat conformation, which would force either the methyl group C13 or the methyl group C14 into closer proximity to the metal and thus make C2 a stereogenic centre, as in structurally related iron(II) complexes.^[5] The nickel–phosphorus bond lengths are within the normal range (Table 3), with the bond *trans*

to the monodentate ligand being the shortest in each complex. This resembles the situation in a structurally related chloro complex of the phenyl-substituted tetrapodal ligand **1_{Ph}**,^[4] in which one phosphane arm, in addition to the pyridine nitrogen atom, is uncoordinated. The non-bonded distances between nickel(II) and the pyridine nitrogen atom are similar in complexes **14–16**, ranging from 2.9 to 3.1 Å (Table 3).

Table 3. Selected bond distances [Å] and angles [°] in **14**, **15** and **16** (standard deviations in parentheses).

Distance or angle	14	15	16
Ni1–P1	2.2345(7)	2.2302(10)	2.2128(16)
Ni1–P2	2.1808(7)	2.1926(10)	2.1492(15)
Ni1–P3	2.2437(7)	2.2208(10)	2.2409(16)
Ni1–N2 (O1) (Br1)	1.890(2)	1.919(3)	2.3088(10)
Ni1...N1	3.010(2)	2.869(3)	3.128 (10)
N2–C20	1.132(3)	–	–
O1–C20	–	1.272(5)	–
P1–Ni1–P2	89.82(3)	89.35(4)	89.72(6)
P2–Ni1–P3	98.12(3)	96.39(4)	99.33(6)
P3–Ni1–N2 (O1), (Br1)	89.31(7)	88.78(9)	92.83(5)
P1–Ni1–N2 (O1), (Br1)	88.07(7)	86.88(10)	90.58(5)
P3–Ni1–P1	161.23(3)	168.70(4)	155.30(6)
P2–Ni1–N2 (O1), (Br1)	162.29(7)	170.82(11)	149.77(6)
Ni1–N2–C20	179.1(2)	–	–
Ni1–O1–C20	–	129.6(3)	–
N2–C20–C21	178.6(3)	–	–
O1–C20–C21	–	122.8(5)	–

Conclusions

Approximately square-pyramidal nickel(II) and cobalt(II) complexes are obtained with the pyridine-derived tetraphosphane ligand $\text{C}_5\text{H}_3\text{N}[\text{CMe}(\text{CH}_2\text{PMe}_2)_2]_2$ (**1_{Me}**), its NP_4 donor set being fully employed in coordination. The formal replacement of one dimethylphosphanyl group in **1_{Me}** by a hydrogen atom gives the new ligand $\text{C}_5\text{H}_3\text{N}[\text{CMe}(\text{CH}_2\text{PMe}_2)_2][\text{CMe}_2(\text{CH}_2\text{PMe}_2)]$ (**2**) which, in a series of nickel(II) complexes, acts as a chelating triphosphane, with no involvement of the pyridine nitrogen atom in coordination. Instead, two ten-membered chelate rings are formed. This contrasts sharply with the situation in a series of iron(II) complexes,^[5] where **2**, formed in situ by cleavage of one of the PMe_2 substituents in **1_{Me}**, coordinates through its complete NP_3 donor set. This forces one of the CMe_2 methyl substituents into close proximity to the metal and allows it to act as an agostic two-electron donor.

Experimental Section

CAUTION! The perchlorate complexes **4** and **6** (and possibly also **10**) are explosive in the solid state. They explode when put under mechanical stress (e.g., upon tapping with a metal spatula). They are to be prepared in quantities not exceeding 150 mg, and the utmost care is to be exercised in their handling.

Materials and Instrumentation: Unless noted otherwise, all reactions were carried out at room temperature in dried solvents under dry dinitrogen, using standard Schlenk techniques. **1_{Me}** and **3** were

prepared as described in the literature.^[5] Co(BF₄)₂·6H₂O, Co(ClO₄)₂·6H₂O, Ni(BF₄)₂·6H₂O, and Ni(ClO₄)₂·6H₂O were purchased from Aldrich and used without further purification. Carbon monoxide (99.997%) and nitrogen monoxide (99.99%) were purchased from Air Liquide, and 2-ethyl-6-isopropylpyridine was purchased from Alfa Aesar. The IR spectra of solids were measured using KBr disks. IR spectra were assigned on the basis of literature data.^[11] Spectroscopic data were obtained using the following instruments: IR spectroscopy: Nicolet Magna System 750; mass spectrometry: Varian 311A, Bruker Daltonics Esquire 3000+ and Voyager-DE Biospectrometry Workstation, PerSeptive Biosystems; NMR spectroscopy: Bruker ARX 200 and Bruker ARX 400. Signs of coupling constants in the ¹H, ¹³C, ¹⁹F, and ³¹P spectra were not determined. The atom numbering (superscripts) used for NMR assignments of compounds **2** and **11–13** follows the numbering scheme adopted for compound **11** (Scheme 2). The atom numbering (superscripts) used for NMR assignments of compounds **14** and **16** follows the labelling of the X-ray crystal structure of the compounds (Figures 6 and 8, respectively). Elemental analyses were carried out using a Thermo Finnigan, Flash EA, 1112 Series analyser.

Preparation of 2: A solution of **13** (1.2 g, 2.7 mmol) in diethyl ether (25 mL) was added from a dropping funnel over a period of 1 h at –70 °C to a suspension of LiPMe₂·0.5Et₂O (1.0 g, 9.5 mmol) in diethyl ether (20 mL). The mixture was warmed to room temperature overnight. The colour changed from brown to red, and all solid dissolved. After distilling off the solvent, the yellow residue was treated with pentane (25 mL) and filtered. The light-yellow solution was dried to yield a colourless oil (0.8 g, 83%). EI-MS (70 eV): *m/z* (%) 356 (100) [M – CH₃]⁺. ¹H NMR (200 MHz, [D₈]–THF, 25 °C, TMS): δ = 7.53 (t, ³J_{H,H} = 7.8 Hz, 1 H, H³), 7.15 (d, ³J_{H,H} = 7.9 Hz, 1 H, H²), 7.13 (d, ³J_{H,H} = 7.9 Hz, 1 H, H⁴), 2.14–1.86 (ddd, AB, ²J_{H,H} = 10.7, ²J_{P,H} = 3.5 Hz, 4 H, H^{8,9}), 1.87 (d, ²J_{P,H} = 3.4 Hz, 2 H, H¹³), 1.57 (s, 3 H, H⁷), 1.44 (s, 6 H, H^{11,12}), 0.85–0.63 (3 × d, ²J_{P,H} = 3.2 Hz 18 H, PCH₃) ppm. ¹³C{¹H} NMR (50.32 MHz, [D₈]THF, 25 °C, TMS): δ = 167.47 (s, 1 C, C¹), 165.83 (s, 1 C, C⁵), 136.81 (s, 1 C, C³), 118.17 (s, 1 C, C²), 117.48 (s, 1 C, C⁴), 49.50 (m, 3 C, C^{8,9,13}), 44.73 (t, 1 C, C⁶), 41.59 (d, 1 C, C¹⁰), 29.63 (m, 2 C, C^{11,12}), 26.48 (m, 1 C, C⁷), 16.18 (m, 6 C, PCH₃) ppm. ³¹P{¹H} NMR (80.95 MHz, [D₈]THF, 25 °C, 85% H₃PO₄): δ = –61.84 [s, 1 × P(Me₂)], –62.06 [s, 2 × P(Me₂)] ppm.

Preparation of 4: A solution of Ni(ClO₄)₂·6H₂O (87 mg, 0.239 mmol) in methanol (2.0 mL) was added over a period of 10 min at room temperature with stirring to a solution of **1** (103 mg, 0.239 mmol) in methanol (1.5 mL). The colour of the solution changed immediately from green to red, and a red microcrystalline precipitate began to form. After three days of continued stirring, the product was filtered off, washed with methanol (3 × 1.0 mL) and dried in vacuo to yield a red solid (148 mg, 90%). C₂₁H₄₁Cl₂NNiO₈P₄ (689.05): calcd. C 36.60, H 6.00, N 2.03; found C 36.92, H 5.81, N 1.97. IR (KBr): ν̄ = 2977 m, 2922 m, 1572 m, 1454 s, 1424 m, 1300 m, 1091 vs (ClO₄[–]), 944 s, 918 s, 622 s cm^{–1}. MALDI-TOF MS: *m/z* (%) 490 (100) [(py{PMe₂})₄Ni]⁺. ¹H NMR (200 MHz, [D₃]acetonitrile, 25 °C, TMS): δ = 8.11 (t, ³J_{H,H} = 7.9 Hz, 1 H, *para*-H), 7.88 (d, ³J_{H,H} = 8.0 Hz, 2 H, *meta*-H), 2.37–2.29 (m, 8 H, CH₂), 1.83 (s, 6 H, CH₃), 1.74 (m, 24 H, PCH₃) ppm. ¹³C{¹H} NMR (50.32 MHz, [D₃]acetonitrile, 25 °C, TMS): δ = 165.68 (s, 2 C, *ortho*-C), 141.89 (s, 1 C, *para*-C), 125.26 (s, 2 C, *meta*-C), 44.79 (s, 2 C, CCH₂), 36.72 (m, 4 C, CH₂), 33.07 (m, 2 C, CH₃), 16.72 (m, 8 C, PCH₃) ppm. ³¹P{¹H} NMR (80.95 MHz, [D₃]acetonitrile, 25 °C, 85% H₃PO₄): δ = –13.16 [m, 2 × P(Me₂)], –14.97 [m, 2 × P(Me₂)] ppm.

Compound 5: The procedure is similar to the preparation of compound **4** but with Ni(BF₄)₂·6H₂O (114 mg, 0.336 mmol) and **1** (145 mg, 0.336 mmol). Complex **5** was isolated as a red microcrystalline solid; yield: 203 mg (91%). C₂₁H₄₁B₂F₈NNiP₄ (663.75): calcd. C 38.00, H 6.23, N 2.11; found C 37.71, H 5.85, N 2.11. IR (KBr): ν̄ = 2978 m, 2929 m, 1575 m, 1453 s, 1425 m, 1306 m, 1055 vs (BF₄[–]), 946 s, 916 s, 520 m cm^{–1}. MALDI-TOF MS: *m/z* (%) 490 (100) [(py{PMe₂})₄Ni]⁺. ¹H NMR (200 MHz, [D₃]acetonitrile, 25 °C, TMS): δ = 8.12 (t, ³J_{H,H} = 7.9 Hz, 1 H, *para*-H), 7.88 (d, ³J_{H,H} = 8.0 Hz, 2 H, *meta*-H), 2.38–2.30 (m, 8 H, CH₂), 1.81 (s, 6 H, CH₃), 1.71 (m, 24 H, PCH₃) ppm. ¹³C{¹H} NMR (50.32 MHz, [D₃]acetonitrile, 25 °C, TMS): δ = 165.65 (s, 2 C, *ortho*-C), 141.91 (s, 1 C, *para*-C), 125.27 (s, 2 C, *meta*-C), 44.80 (s, 2 C, CCH₂), 36.71 (m, 4 C, CH₂), 33.11 (m, 2 C, CH₃), 16.73 (m, 8 C, PCH₃) ppm. ¹⁹F{¹H} NMR (188.31 MHz, [D₃]acetonitrile, 25 °C, CFCl₃): δ = –147.88 (s, 4 F, BF₄[–]) ppm. ³¹P{¹H} NMR (80.95 MHz, [D₃]acetonitrile, 25 °C, 85% H₃PO₄): δ = –13.15 [m, 2 × P(Me₂)], –14.99 [m, 2 × P(Me₂)] ppm.

Compound 6: The procedure is similar to the preparation of compound **4** but with Co(ClO₄)₂·6H₂O (55 mg, 0.15 mmol) and **1** (65 mg, 0.15 mmol). The reaction mixture changed colour from pink to brown and gave an olive-green microcrystalline precipitate; reaction time: five days. The product is an olive-green microcrystalline solid. Yield: 90 mg (87%). C₂₁H₄₁Cl₂CoNO₈P₄ (689.29): calcd. C 36.59, H 6.00, N 2.03; found C 36.82, H 6.02, N 2.02. IR (KBr): ν̄ = 2978 m, 2923 m, 1573 m, 1453 s, 1424 m, 1299 m, 1089 vs (ClO₄[–]), 944 s, 918 s, 622 s cm^{–1}. MALDI-TOF MS: *m/z* (%) 490 (80) [(py{PMe₂})₄Co]⁺, 430 (100) [M – H – Co]⁺.

Compound 7: The procedure is similar to the preparation of compound **4** but with Co(BF₄)₂·6H₂O (328 mg, 0.962 mmol) in methanol (4.0 mL) and **1** (415 mg, 0.962 mmol) in methanol (5.0 mL); addition time: 20 min at room temperature; observed colours as for compound **6**; reaction time: five days. The product is an olive-green microcrystalline solid. Yield: 543 mg (85%). C₂₁H₄₁B₂CoF₈NP₄ (663.99): calcd. C 37.99, H 6.22, N 2.11; found C 37.84, H 6.03, N 2.00. IR (KBr): ν̄ = 2975 m, 2924 m, 1574 m, 1454 s, 1426 m, 1300 m, 1054 vs (BF₄[–]), 945 s, 919 s, 520 s cm^{–1}. MALDI-TOF MS: *m/z* (%) 490 (81) [(py{PMe₂})₄Co]⁺, 430 (100) [M – H – Co]⁺. ³¹P{¹H} NMR (80.95 MHz, [D₄]methanol, 25 °C, 85% H₃PO₄): δ = 48.12 [br., 4 × P(Me₂)] ppm.

Preparation of 8: Nitrogen monoxide was bubbled through a solution of **1** (110 mg, 0.255 mmol) in diethyl ether (8.0 mL) at approximately 0 °C for three minutes. A white microcrystalline powder precipitated, which was filtered off and washed with diethyl ether (3 × 2.5 mL) to yield a white solid (124 mg, 98%). C₂₁H₄₁NO₈P₄ (495.45): calcd. C 50.91, H 8.34, N 2.83; found C 50.71, H 8.25, N 2.78. IR (KBr): ν̄ = 2978 m, 2911 m, 1653 m, 1574 m, 1457 s, 1420 m, 1384 s, 1295 s, 1161 vs (P=O), 941 s, 875 s, 745 m cm^{–1}. EI-MS (70 eV): *m/z* (%) 494 (100) [M – H]⁺. ¹H NMR (200 MHz, [D₃]acetonitrile, 25 °C, TMS): δ = 7.78 (t, ³J_{H,H} = 7.5 Hz, 1 H, *para*-H), 7.44 (d, ³J_{H,H} = 7.6 Hz, 2 H, *meta*-H), 2.69–2.61 (dd, AB, ²J_{H,H} = 6.0 Hz, 8 H, CH₂), 1.86 (s, 6 H, CCH₃), 1.35–1.28 (2 d, ²J_{P,H} = 2.4 Hz, 24 H, PCH₃) ppm. ³¹P{¹H} NMR (80.95 MHz, [D₃]acetonitrile, 25 °C, 85% H₃PO₄): δ = 44.95 [s, 4 × P(O)Me₂] ppm.

Preparation of 9: A solution of **7** (160 mg, 0.241 mmol) in acetonitrile (3.0 mL) was refluxed in air for five minutes, then placed in a Dewar vessel filled with hot water (80 °C), and the complete set-up cooled to 2 °C in a refrigerator. This produced a few single crystals of **9**·2CH₃CN within 7 d. Due to lack of material, the crystals were characterised solely by X-ray crystallography.

Preparation of 10: A brownish solution of **6** (105 mg, 0.152 mmol) in methanol (6.0 mL) was cooled in an ice bath, and a stream of

carbon monoxide was passed through the solution for five seconds. The colour of the solution darkened, and stirring was continued for a further ten minutes. The solvent was then evaporated, and the residue washed with a 1:2 mixture of methanol and diethyl ether (3 × 1.5 mL) to yield a brown solid (61 mg, 54%). $C_{23}H_{41}Cl_2CoNO_{10}P_4$ (745.31): calcd. C 37.06, H 5.54, N 1.88; found C 36.82, H 5.66, N 1.98. IR (KBr): $\tilde{\nu}$ = 2983 m, 2921 m, 1988 vs (CO), 1937 vs (CO), 1575 s, 1453 s, 1422 s, 1300 s, 1093 vs (ClO_4^-), 944 s (P–C, coordinated), 917 s (P–C, coordinated), 875 s (P–C, uncoordinated), 623 vs cm^{-1} . MALDI-TOF MS: m/z (%) 546 (28) $[M - H]^+$, 430 (100) $[M - H - Co - 2CO]^+$, 273.5 (18) $[M]^{2+}$.

Preparation of 11: An autoclave (volume: 2.1 L) was charged with 2-ethyl-6-isopropylpyridine (50 g, 0.33 mol) and an aqueous formaldehyde solution (37%, stabilised with 10% methanol; 250 mL, 3.30 mol) and the mixture heated to 140 °C for 48 h. After cooling to room temperature, the pressure was released and the solvent evaporated. The yellow oily residue was then heated to 100 °C for 24 h to remove excess formaldehyde. The residue was dissolved in trichloromethane (250 mL) and extracted with water (20 × 70 mL). The aqueous phase was separated, water removed on a rotary evaporator, and the remaining syrupy material dried for a further two days in vacuo at a temperature of 95 °C to yield a white solid, which was purified by washing with diethyl ether (27.7 g, 35%). $C_{13}H_{21}NO_3$ (239.31): calcd. C 65.25, H 8.84, N 5.75; found C 64.97, H 8.80, N 5.67. IR (KBr): $\tilde{\nu}$ = 3299 vs (OH), 2961 vs, 2873 vs, 1577 vs, 1461 vs, 1409 m, 1042 vs, 1027 vs, 756 cm^{-1} . EI-MS (70 eV): m/z (%) 239 (100) $[M]^+$. 1H NMR (400 MHz, $[D_1]$ trichloromethane, 25 °C, TMS): δ = 7.66 (t, $^3J_{H,H} = 7.9$ Hz, 1 H, H^3), 7.20 (d, $^3J_{H,H} = 8.0$ Hz, 1 H, H^2), 7.17 (d, $^3J_{H,H} = 8.0$ Hz, 1 H, H^4), 4.14 (br., 3 H, OH), 3.92–3.75 (dd, AB, $^2J_{H,H} = 11.2$ Hz, 4 H, $H^{8,9}$), 3.66 (s, 2 H, H^{13}), 1.29 (s, 6 H, $H^{11,12}$), 1.17 (s, 3 H, H^7) ppm. $^{13}C\{^1H\}$ NMR (100.64 MHz, $[D_1]$ trichloromethane, 25 °C, TMS): δ = 165.23 (s, 1 C, C^1), 163.27 (s, 1 C, C^5), 137.56 (s, 1 C, C^3), 118.95 (s, 1 C, C^2), 118.66 (s, 1 C, C^4), 71.83 (s, 1 C, C^{13}), 69.38 (s, 2 C, $C^{8,9}$), 45.97 (s, 1 C, C^6), 42.01 (s, 1 C, C^{10}), 24.95 (s, 2 C, $C^{11,12}$), 19.89 (s, 1 C, C^7) ppm.

Preparation of 12: A solution of **11** (11.0 g, 0.046 mol) and triethylamine (29.2 mL, 0.207 mol) in dichloromethane (200 mL) was cooled to –2 °C, and a solution of methanesulfonyl chloride (12.8 mL, 0.166 mol) in dichloromethane (50 mL) added dropwise, taking care that the temperature did not exceed +2 °C. The resulting suspension was warmed to room temperature and stirred for one hour. The reaction product was washed successively with hydrochloric acid (1 N, 1 × 50 mL), water (1 × 50 mL), sodium carbonate solution (1 × 50 mL), brine (1 × 50 mL) and finally again with water (1 × 50 mL). After drying over Na_2SO_4 and evaporating the solvent, the residue was dried in vacuo to yield the product as a colourless oil (20.3 g, 93%). IR (KBr): $\tilde{\nu}$ = 3029 vs, 2976 vs, 2941 vs, 1578 vs, 1352 vs, 1172 vs, 958 vs, 528 vs cm^{-1} . EI-MS (70 eV): m/z (%) 394 (100) $[M - CH_3SO_2]^+$. 1H NMR (200 MHz, $[D_1]$ trichloromethane, 25 °C, TMS): δ = 7.70 (t, $^3J_{H,H} = 8.0$ Hz, 1 H, H^3), 7.27 (d, $^3J_{H,H} = 7.9$ Hz, 1 H, H^2), 7.21 (d, $^3J_{H,H} = 7.9$ Hz, 1 H, H^4), 4.63–4.52 (dd, AB, $^2J_{H,H} = 8.8$ Hz, 4 H, $H^{8,9}$), 4.47 (s, 2 H, H^{13}), 2.96 (s, 6 H, SO_2-CH_3), 2.86 (s, 3 H, SO_2-CH_3), 1.50 (s, 3 H, H^7), 1.41 (s, 6 H, $H^{11,12}$) ppm. $^{13}C\{^1H\}$ NMR (50.32 MHz, $[D_1]$ trichloromethane, 25 °C, TMS): δ = 163.36 (s, 1 C, C^1), 158.42 (s, 1 C, C^5), 137.56 (s, 1 C, C^3), 119.13 (s, 1 C, C^2), 118.86 (s, 1 C, C^4), 77.64 (s, 1 C, C^{13}), 72.74 (s, 2 C, $C^{8,9}$), 45.14 (s, 1 C, C^6), 41.35 (s, 1 C, C^{10}), 36.84 (s, 2 C, SO_2CH_3), 36.74 (s, 1 C, SO_2CH_3), 24.57 (s, 2 C, $C^{11,12}$), 19.16 (s, 1 C, C^7) ppm.

Preparation of 13: Compound **12** (6.27 g, 0.013 mol) was dissolved in anhydrous dimethyl sulfoxide (150 mL) and heated to 70 °C. Vig-

orously dried (vacuo, 100 °C, 3 d) lithium bromide (5.17 g, 0.059 mol) was then added in one portion, and the solution stirred for two days at 70 °C. After cooling to room temperature, water (200 mL) was added, and the mixture stirred for 30 min. The milky solution was extracted with diethyl ether (7 × 70 mL), and the combined ether extracts washed with water (3 × 50 mL) to remove residual dimethyl sulfoxide. The organic phase was separated, dried with Na_2SO_4 , and the solvent evaporated to give an oily, crude product. Column chromatography (SiO_2 , 0.060–0.200 mm, pore diameter ca. 6 nm) using a combination of ethyl acetate and hexane (3:1) as eluent yielded the product as a colourless oil (3.1 g, 56%). IR (KBr): $\tilde{\nu}$ = 2969 vs, 2870 m, 1576 vs, 1458 vs, 1423 m, 1247 vs, 750 cm^{-1} . EI-MS (70 eV): m/z (%) 416 (32) $[M - CH_3]^+$, 414 (98) $[M - CH_3]^+$, 412 (100) $[M - CH_3]^+$, 410 (34) $[M - CH_3]^+$. 1H NMR (200 MHz, $[D_1]$ trichloromethane, 25 °C, TMS): δ = 7.66 (t, $^3J_{H,H} = 7.9$ Hz, 1 H, H^3), 7.23 (d, $^3J_{H,H} = 7.9$ Hz, 1 H, H^2), 7.18 (d, $^3J_{H,H} = 7.9$ Hz, 1 H, H^4), 4.00–3.86 (dd, AB, $^2J_{H,H} = 10.0$ Hz, 4 H, $H^{8,9}$), 3.80 (s, 2 H, H^{13}), 1.63 (s, 3 H, H^7), 1.49 (s, 6 H, $H^{11,12}$) ppm. $^{13}C\{^1H\}$ NMR (50.32 MHz, $[D_1]$ trichloromethane, 25 °C, TMS): δ = 164.07 (s, 1 C, C^1), 160.04 (s, 1 C, C^5), 137.07 (s, 1 C, C^3), 118.48 (s, 1 C, C^2), 118.36 (s, 1 C, C^4), 46.01 (s, 2 C, $C^{10,13}$), 42.10 (s, 3 C, $C^{6,8,9}$), 26.63 (s, 2 C, $C^{11,12}$), 23.09 (s, 1 C, C^7) ppm.

Preparation of 14: A solution of $Ni(BF_4)_2 \cdot 6H_2O$ (311 mg, 0.915 mmol) in acetonitrile (3.5 mL) was added over a period of 10 min at room temperature to a solution of **2** (340 mg, 0.915 mmol) in acetonitrile (2.5 mL). The solution changed colour immediately from green to red, and was stirred overnight. Diffusion of diethyl ether into this solution produced a red crystalline solid within 3 d. The product was filtered off and washed with diethyl ether (3 × 1.5 mL) to yield red crystals (442 mg, 75%). $C_{21}H_{39}B_2F_8N_2NiP_3$ (644.78): calcd. C 39.12, H 6.10, N 4.34; found C 39.09, H 6.19, N 4.30. IR (KBr): $\tilde{\nu}$ = 2970 s, 2932 s, 2292 m (CN), 1574 vs, 1426 vs, 1296 s, 1056 vs (BF_4^-), 948 vs, 920 vs, 520 cm^{-1} . ESI-MS: m/z (%) 236 (100) $[M]^{2+}$. 1H NMR (400 MHz, $[D_3]$ acetonitrile, 25 °C, TMS): δ = 7.88 (t, $^3J_{H,H} = 7.3$ Hz, 1 H, H^3), 7.53 (d, $^3J_{H,H} = 7.2$ Hz, 1 H, H^6), 7.52 (d, $^3J_{H,H} = 7.2$ Hz, 1 H, H^4), 2.50–2.00 (2 × m, 4 H, $CH_2^{9,10}$), 2.46 (s, 2 H, CH_2^1), 1.96 (s, 3 H, CH_3^{21}), 1.53–1.50 (m, 6 H, $PCH_3^{16,18}$), 1.51 (s, 3 H, CH_3^{15}), 1.46–1.43 (m, 6 H, $PCH_3^{17,19}$), 1.45 (2 × s, 6 H, $CH_3^{13,14}$), 1.26–1.22 (m, 6 H, $PCH_3^{11,12}$) ppm. $^{13}C\{^1H\}$ NMR (100.64 MHz, $[D_3]$ acetonitrile, 25 °C, TMS): δ = 166.78 (s, 1 C, C^3), 162.87 (s, 1 C, C^7), 139.79 (s, 1 C, C^5), 122.26 (s, 1 C, C^4), 121.22 (s, 1 C, C^6), 43.80 (s, 1 C, C^8), 42.25 (s, 1 C, C^2), 41.38 (d, $^1J_{PC} = 23.3$ Hz, 1 C, C^1), 37.69 (m, 2 C, $C^{9,10}$), 32.86 (s, 2 C, $C^{13,14}$), 32.13 (s, 1 C, C^{15}), 16.66 (m, 2 C, $PCH_3^{11,12}$), 15.62 (m, 4 C, PCH_3^{16-19}), 1.75 (s, 1 C, C^{21}) ppm. $^{19}F\{^1H\}$ NMR (188.31 MHz, $[D_3]$ acetonitrile, 25 °C, $CFCl_3$): δ = –147.90 (s, 4 F, BF_4^-) ppm. $^{31}P\{^1H\}$ NMR (80.95 MHz, $[D_3]$ acetonitrile, 25 °C, 85% H_3PO_4): δ = –3.53 (d, $^2J_{PP} = 70.5$ Hz, 2 P, $P^{2,1}$), –8.64 (t, $^2J_{PP} = 70.5$ Hz, 1 P, P^3) ppm.

Preparation of 15: Prepared similar to **14**, from $Ni(BF_4)_2 \cdot 6H_2O$ (150 mg, 0.441 mmol); solvent: acetonitrile (3.0 mL); addition time: 10 min at room temperature; **2**: 190 mg, 0.512 mmol; solvent: acetonitrile (2.0 mL); observed colours as for compound **14**; reaction time: seven days; appearance of product: orange blocks. $C_{21}H_{41}B_2F_8N_2NiOP_3$ (662.79): calcd. C 38.06, H 6.24, N 4.23; found C 38.29, H 6.39, N 4.34. ESI-MS: m/z (%) 245 (100) $[M]^{2+}$.

Preparation of 16: A solution of **14** (115 mg, 0.178 mmol) and LiBr (16 mg, 0.18 mol) in methanol (4.5 mL) was stirred at room temperature for 1 h. The solvent was evaporated, the residual red solid dried in vacuo, stirred in diethyl ether (10 mL) for 10 min, the mixture filtered, and the remaining solid dried again in vacuo. Dif-

fusion of diethyl ether into a saturated solution of **16** in methanol produced a red microcrystalline solid, as well as single crystals, within 4 d. The single crystals were separated, and the polycrystal-

line material filtered off and washed with diethyl ether (3 × 1.0 mL) to yield a red solid (85 mg, 80%). C₁₉H₃₆BBrF₄NNiP₃ (596.83); calcd. C 38.24, H 6.08, N 2.35; found C 38.20, H 6.06, N 2.30. ¹H

Table 4. Selected crystallographic data for **3**, **4**·CHCl₃, **7**·MeOH, **9**·2 CH₃CN, **14**, **15** and **16**.

	3	4 ·CHCl ₃	7 ·MeOH	9 ·2CH ₃ CN
Formula	C ₁₃ H ₁₇ Br ₄ N	C ₂₂ H ₄₂ Cl ₅ NNiO ₈ P ₄	C ₂₂ H ₄₅ B ₂ CoF ₈ NOP ₄	C ₅₈ H ₁₀₆ B ₆ Co ₃ F ₂₄ N ₁₀ O ₄ P ₈
<i>M_r</i> [g mol ⁻¹]	506.92	808.41	696.04	1952.94
Size [mm ³]	0.20 × 0.19 × 0.17	0.60 × 0.18 × 0.12	0.50 × 0.25 × 0.20	0.62 × 0.40 × 0.18
Colour	colourless	red	green	violet
<i>F</i> (000)	1936	3344	1772	4012
Crystal system	orthorhombic	orthorhombic	orthorhombic	monoclinic
Space group	<i>Pbca</i> (no. 61)	<i>Pna2</i> ₁ (no. 33)	<i>Pna2</i> ₁ (no. 33)	<i>C2/c</i> (no. 15)
<i>a</i> [Å]	11.2917(18)	21.794(4)	22.6555(6)	23.5131(9)
<i>b</i> [Å]	14.011(3)	9.583(2)	11.5947(3)	11.0384(3)
<i>c</i> [Å]	20.701(4)	32.694(5)	11.8607(3)	34.8349(11)
β [°]	90	90	90	99.759(2)
<i>V</i> [Å ³]	3275.2(10)	6828.0(2)	3115.6(1)	8910.5(5)
<i>Z</i>	8	8	4	4
ρ _{calc} [g cm ⁻³]	2.056	1.573	1.854	1.456
μ [mm ⁻¹]	9.814	1.190	0.877	0.792
Abs. correction	multi-scan	psi-scan	SADABS	SADABS
Temperature [K]	173(2)	180(2)	293(2)	293(2)
<i>T</i> _{max} / <i>T</i> _{min}	0.286/0.244	0.870/0.535	0.879/0.603	0.871/0.639
Scan	ω and ψ	ω and ψ	ω and ψ	ω and ψ
2θ range [°]	6.1–51.6	3.9–48.2	3.6–50.0	3.5–50.0
Measured reflections	10034	38301	19062	27646
Unique reflections	2663	10555	5290	7838
Obsd. reflections ^[a]	2077	8292	4561	5704
Refined parameters	165	761	380	657
<i>wR2</i> (all data) ^[b]	0.0637	0.0634	0.1277	0.1426
<i>R1</i> (obs. data) ^[c]	0.0375	0.0340	0.0525	0.0566
ρ _{fin} (max./min.) [e Å ⁻³]	0.623/–0.491	0.654/–0.440	0.588/–0.511	0.609/–0.770
Weighting scheme ^[d]	<i>k</i> = 0.0289/ <i>l</i> = 3.5634	<i>k</i> = 0.0267/ <i>l</i> = 0.0000	<i>k</i> = 0.0654/ <i>l</i> = 4.5591	<i>k</i> = 0.0584/ <i>l</i> = 16.9833
Abs. struct. parameter	–	0.448(12)	0.00(2)	–
	14	15	16	
Formula	C ₂₁ H ₃₉ B ₂ F ₈ N ₂ NiP ₃	C ₂₁ H ₄₁ B ₂ F ₈ N ₂ NiOP ₃	C ₁₉ H ₃₆ BBrF ₄ NNiP ₃	
<i>M_r</i> [g mol ⁻¹]	644.78	662.80	596.83	
Size [mm ³]	0.72 × 0.67 × 0.55	0.25 × 0.17 × 0.14	0.09 × 0.09 × 0.08	
Colour	yellow	orange	red	
<i>F</i> (000)	2672	2752	1224	
Crystal system	orthorhombic	monoclinic	monoclinic	
Space group	<i>Pbca</i> (no. 61)	<i>P2</i> ₁ / <i>n</i> (no. 14)	<i>P2</i> ₁ / <i>c</i> (no. 14)	
<i>a</i> [Å]	13.391(3)	19.419(2)	12.6633(14)	
<i>b</i> [Å]	18.763(3)	15.591(1)	11.845(4)	
<i>c</i> [Å]	23.050(3)	21.099(2)	16.986(2)	
β [°]	90	109.981(5)	96.337(10)	
<i>V</i> [Å ³]	5791.4(18)	6003.4(9)	2532.4(9)	
<i>Z</i>	8	8	4	
ρ _{calc} [g cm ⁻³]	1.479	1.467	1.565	
μ [mm ⁻¹]	0.902	0.875	2.570	
Abs. correction	psi-scan	SADABS	multi-scan	
Temperature [K]	150(2)	100(2)	173(2)	
<i>T</i> _{max} / <i>T</i> _{min}	0.637/0.563	0.880/0.745	0.821/0.802	
Scan	ω and ψ	ω and ψ	ω and ψ	
2θ range [°]	3.5–51.9	6.8–54.2	5.9–57.2	
Measured reflections	15298	87231	13028	
Unique reflections	5672	13166	3647	
Obsd. reflections ^[a]	4501	9307	5505	
Refined parameters	345	1006	281	
<i>wR2</i> (all data) ^[b]	0.0888	0.1278	0.1783	
<i>R1</i> (obs. data) ^[c]	0.0332	0.0482	0.0550	
ρ _{fin} (max./min.) [e Å ⁻³]	0.564/–0.657	0.812/–0.687	0.987/–1.979	
Weighting scheme ^[d]	<i>k</i> = 0.0425/ <i>l</i> = 4.4217	<i>k</i> = 0.0415/ <i>l</i> = 16.7211	<i>k</i> = 0.1003/ <i>l</i> = 1.1743	
Abs. struct. parameter	–	–	–	

[a] With $F_o \geq 4\sigma(F)$. [b] $wR2 = (\{\Sigma[w(F_o^2 - F_c^2)^2]\}/\{\Sigma[w(F_o^2)^2]\})^{0.5}$. [c] $R1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$ for $F_o > 4\sigma(F)$. [d] $w = 1/[\sigma^2(F_o^2) + (k \cdot P)^2 + l \cdot P]$ and $P = (F_o^2 + 2F_c^2)/3$.

NMR (400 MHz, [D₄]methanol, 25 °C, TMS): δ = 8.16 (t, $^3J_{\text{H,H}}$ = 7.3 Hz, 1 H, H^3), 7.83 (d, $^3J_{\text{H,H}}$ = 7.3 Hz, 1 H, H^4), 7.81 (d, $^3J_{\text{H,H}}$ = 7.3 Hz, 1 H, H^2), 2.39–1.90 (2 × m, 4 H, $\text{CH}_2^{7,10}$), 2.28 (s, 2 H, CH_2^{15}), 1.87 (s, 3 H, CH_3^{13}), 1.81 (s, 6 H, $\text{CH}_3^{18,19}$), 1.72–1.65 (m, 6 H, $\text{PCH}_3^{8,11}$), 1.59–1.53 (m, 6 H, $\text{PCH}_3^{9,12}$), 0.74–0.69 (m, 6 H, $\text{PCH}_3^{16,17}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.64 MHz, [D₄]methanol, 25 °C, TMS): δ = 168.52 (s, 1 C, C^1), 167.97 (s, 1 C, C^5), 143.09 (s, 1 C, C^3), 124.86 (s, 1 C, C^2), 123.79 (s, 1 C, C^4), 43.58 (s, 1 C, C^6), 42.75 (s, 1 C, C^{14}), 38.68 (m, 1 C, C^{15}), 38.24 (m, 2 C, $\text{C}^{7,10}$), 32.52 (s, 2 C, $\text{C}^{18,19}$), 31.16 (s, 1 C, C^{13}), 15.44 (m, 2 C, $\text{PCH}_3^{16,17}$), 14.38 (m, 4 C, $\text{PCH}_3^{8,9,11,12}$) ppm. $^{19}\text{F}\{^1\text{H}\}$ NMR (188.31 MHz, [D₄]methanol, 25 °C, CFCl_3): δ = –147.92 (s, 4 F, BF_4^-) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (80.95 MHz, [D₄]methanol, 25 °C, 85% H_3PO_4): δ = 3.00 (d, $^2J_{\text{P,P}}$ = 83.6 Hz, 2 P, $\text{P}^{2,1}$), –0.90 (t, $^2J_{\text{P,P}}$ = 83.6 Hz, 1 P, P^3) ppm.

X-ray Crystallography for Compounds 3, 4, 5, 7, 9, 14, 15 and 16: Colourless single crystals of “pyBr₄” (3) formed upon keeping the oily product under oil pump vacuum for three weeks. Red single crystals of [(py{PMe₂}₄)Ni](ClO₄)₂·CHCl₃ (4·CHCl₃) were obtained within 10 d by isothermal diffusion of diethyl ether into a saturated solution of the reaction product in chloroform. Red crystals of [(py{PMe₂}₄)Ni](BF₄)₂·MeOH (5·MeOH) and green crystals of [(py{PMe₂}₄)Co](BF₄)₂·MeOH (7·MeOH) were similarly obtained by isothermal diffusion of diethyl ether into a saturated solution of the reaction product in methanol within a few days. Violet blocks of [(py{PMe₂}₂{OPMe₂}₂{CH₃CN}₃)Co]₂Co(BF₄)₆·2CH₃CN (9·2CH₃CN) formed after a solution of the reaction product in acetonitrile had been saturated hot and subsequently cooled to 2 °C. Single crystals of [(py{PMe₂}₃CH₃CN)Ni](BF₄)₂ (yellow, 14), [(py{PMe₂}₃CH₃CONH₂)Ni](BF₄)₂ (orange, 15) and [(py{PMe₂}₃Br)Ni](BF₄) (red, 16) were obtained by isothermal diffusion of diethyl ether into an acetonitrile (14 and 15) or a methanol (16) solution. Crystal data for compounds 3, 4·CHCl₃, 5·MeOH, 9·2CH₃CN, 14, 15 and 16 are given in Table 4, and selected distances and angles are listed in Tables 1–3. Structures are presented in Figures 1–8. Compounds 4, 5 and 7 are isostructural. Intensity data for 4·CHCl₃ and 14 were collected on a Stoe Stadi 4 diffractometer; data for 5·MeOH, 7·MeOH and 9·2CH₃CN were collected on a SMART CCD diffractometer; data for 15 were collected on a Bruker-Nonius KappaCCD diffractometer and data for 3 and 16 on a Oxford Diffraction Xcalibur S Sapphire diffractometer using Mo- K_α radiation (λ = 0.71073 Å, graphite monochromator) in all cases. The structures were solved by direct methods using SHELXS-97^[13] or SIR 97^[14] and were refined on F^2 using SHELXL-97.^[15] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions using a riding model. SADABS^[16] was used to perform area detector scaling absorption corrections, as applicable (Table 4). The absolute structure in non-centrosymmetric space groups was determined with SHELXL-97 according to Flack.^[13] The geometrical features of the structures were analysed using the DIAMOND programme.^[17]

CCDC-608569 (for 3), -608571 (for 4·CHCl₃), -608566 (for 5·MeOH), -608567 (for 7·MeOH), -608568 (for 9·2CH₃CN), -608564 (for 14), -608565 (for 15) and -608570 (for 16) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

Financial support of this work by the Deutsche Forschungsgemeinschaft (SPP 1118) is gratefully acknowledged. We are indebted to Dr. Ziemer (Humboldt-Universität zu Berlin) for the structural characterisation of compounds 4 and 14.

- [1] a) *Applied Homogeneous Catalysis with Organometallic Compounds*, vol. 1 (Eds.: B. Cornils, W. A. Herrmann), VCH, Weinheim, 1996; b) G. W. Parshall, S. D. Ittel, *Homogeneous Catalysis*, 2nd ed., Wiley, New York, 1992.
- [2] M. E. van der Bloom, D. Milstein, *Chem. Rev.* **2003**, 103, 1759.
- [3] A. Grohmann, *Adv. Inorg. Chem.* **2004**, 56, 179.
- [4] C. Zimmermann, F. W. Heinemann, A. Grohmann, *Eur. J. Inorg. Chem.* **2005**, 3506.
- [5] S. W. Kohl, F. W. Heinemann, M. Hummert, W. Bauer, A. Grohmann, *Chem. Eur. J.* **2006**, 12, 4313.
- [6] H. H. Karsch, A. Appelt, *Z. Naturforsch., Teil B* **1983**, 38, 1399.
- [7] P. Klaboe, B. Klewe, K. Martinsen, C. J. Nielsen, D. L. Powell, D. J. Stubbles, *J. Mol. Struct.* **1986**, 140, 1.
- [8] C. Dietz, F. W. Heinemann, J. Kuhnigk, C. Krüger, M. Gerdan, A. X. Trautwein, A. Grohmann, *Eur. J. Inorg. Chem.* **1998**, 1041.
- [9] S. Berger, S. Braun, H.-O. Kalinowski, *NMR-Spektroskopie von Nichtmetallen*, vol. 3, ^{31}P -NMR-Spektroskopie, Thieme, Stuttgart, 1993, p. 53.
- [10] K. Heinze, G. Huttner, L. Zsolnai, *Chem. Ber./Recueil* **1997**, 130, 1393.
- [11] G. Socrates, *Infrared Characteristic Group Frequencies*, 2nd ed., Wiley, New York, 1994.
- [12] E. C. Constable, *Metals and Ligand Reactivity*, VCH, Weinheim, 1996, p. 65.
- [13] G. M. Sheldrick, *SHELXS-97 Program for the Solution of Crystal Structures*, University of Göttingen, Germany, 1990.
- [14] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, 32, 115.
- [15] G. M. Sheldrick, *SHELXL-97 Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, 1997.
- [16] H. D. Flack, *Acta Crystallogr., Sect. A* **1983**, 39, 876; G. Bernardinelli, H. D. Flack, *Acta Crystallogr., Sect. A* **1985**, 41, 500.
- [17] G. M. Sheldrick, *SADABS Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Germany, 1996.

Received: June 7, 2006

Published Online: August 10, 2006