A Tetraphosphane Imine Ligand Which Enforces Square-Pyramidal Coordination

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Dedicated to Professor Herbert Schumann on the occasion of his 70th birthday

The tetrapodal pentadentate NP_4 ligand 2,6-$C_5H_3N[CMe(CH_2PPh_2)_2]_2$, which is readily prepared from the reaction of the corresponding tetrabromide with $KPPh_2$, forms mononuclear complexes with nickel(II) and cobalt(II). In the case of nickel(II), the coordination mode adopted by the ligand is sensitive to the nature of the counterion: Use of $NiCl_2$ gives a chloro complex as one of the products, which, as determined by X-ray crystallography, has a central ion coordinated by three phosphane and one chloro substituent in a distorted square planar fashion; by contrast, the reaction with $Ni(BF_4)_2$ gives a complex of approximate square-pyramidal geometry as the only product, in which all five atoms of

the NP_4 set are coordinated to the nickel ion, despite the steric bulk of the eight phenyl substituents. The same type of complex is obtained with $Co(BF_4)_2$ and $Co(ClO_4)_2$. Attempts to increase the coordination number of either complex beyond 5 have been unsuccessful. In particular, the cobalt(II) complex (17 valence electrons) is practically inert to reagents such as O_2, NO, NO^+, I_2, Cl_2 or H_2. Full spectroscopic details for the complexes, as well as X-ray structure analyses, are reported.

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Introduction

Chelating phosphane ligands are widely employed in catalysis and organic synthesis.[1,2] The vast majority of applications in homogeneous catalysis requires bidentate ligands (e.g., in asymmetric hydrogenation).[3] Owing to the necessity for "labile" donors and/or vacant coordination sites in molecular catalysts, ligands of higher denticity such as tridentate $H_3CC(CH_2PPh_2)_3$, "triphos", or tetradentate $P(CH_2CH_2PPh_2)_3$, "pp3", are less prone to give catalytically active species, although specialised applications in the "heterogenisation" of homogeneous catalysts do make use of the increased thermal and kinetic complex stability that such ligands impart.[4] Complexes of polypodal phosphane ligands show a rich coordination and reaction chemistry in their own right, however. This is because of the increasing electron-richness of the metal centre, which is a direct consequence of the increasing number of aryl-, or, better still, alkylphosphane donors. It is in this context that we have begun to extend our study of tetrapodal pentadentate li-

gands[5] to include tetraphosphane imine ligands. We recently described the C_{2v}-symmetrical NP_4 ligand 2,6-bis{2-(diphenylphosphanyl)-1-[(diphenylphosphanyl)methyl]-1-methylethyl}pyridine ("py{PPh_2}_4", **1**).[6] The present contribution summarises coordination chemistry aspects of this ligand with respect to nickel(II) and cobalt(II).
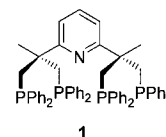

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Results and Discussion

Coordination Behaviour of py{PPh₂}₄ Towards Nickel(II)

A red-brown solid was obtained from the reaction of equimolar amounts of py{PPh_2}_4 and $NiCl_2·6H_2O$ in refluxing acetonitrile (cf. Experimental Section). Recrystallisation from methanol in the presence of $NaPF_6$ produced a microcrystalline purple material. Structural analysis using a single crystal from this batch revealed a chiral (*) 16 valence electron chloro complex (**2**) with a tetracoordinate nickel(II) centre. The tetraphosphane acts as a tridentate chelator, one diphenylphosphanyl unit and the pyridine nitrogen atom remaining uncoordinated [Equation (1)]. The

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complex is also detected in the mass spectrum of the purple material, where it gives rise to a peak at $m/z = 1022$ ($\{[(py\{PPh_2\}_4)NiCl]\}^+$, 20%).

(1)
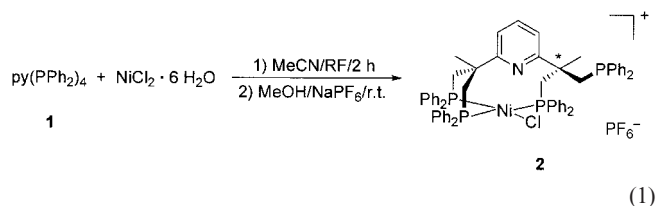
It should be noted, however, that the percentage of carbon in the solid analyses is consistently too low to be acceptable for pure compound **2**, $C_{61}H_{57}ClF_6NNiP_5$ (1167.14), which requires C 62.78, H 4.92, N 1.20%; a typical analysis is C 56.12, H 4.72, N 1.31%. This indicates that a mixture of products (of different solubilities) is formed, and that the major part of the material may in fact be the bis(hexafluorophosphate) salt, which requires C 57.39, H 4.50, N 1.10%. The ^1H, ^{13}C, and ^{31}P NMR spectroscopic data do suggest a highly symmetrical species and are virtually identical to the spectra obtained for the bis(tetrafluoroborate) salt **3** (below).

Apparently, the coordination mode adopted by the ligand is determined by the reaction conditions (solvent, coordinating ability of the counterion); this is evident from the outcome of an overall similar reaction, between stoichiometric amounts of py$\{PPh_2\}_4$ and Ni(BF$_4$)$_2$·6H$_2$O in a methanol/dichloromethane mixed solvent (1:1). In this case, there is only one product, which contains the tetraphosphane as a pentadentate capping ligand. The 18 valence electron complex $[(py\{PPh_2\}_4)Ni](BF_4)_2$ (**3**), which forms as purple-brown microcrystals in 50% yield [Equation (2)], has the nickel(II) ion in a distorted square-pyramidal coordination environment. In the mass spectrum, the cation appears at $m/z = 987$ ($\{[(py\{PPh_2\}4)Ni]\}^+$, 75%).

(2)
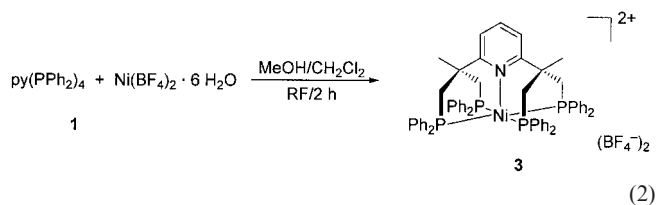
Compound **3** is readily soluble in acetonitrile and chloroform, and sparingly soluble in methanol. In the IR spectrum (KBr), the band at 1435 cm^{-1} attributed to the P–Ph stretching vibration is second in intensity only to the band diagnostic of BF$_4^-$ (1060 cm^{-1}). Compared to the IR spectroscopic data for uncoordinated py$\{PPh_2\}_4$, $\nu_{P–Ph}$ (str) does not shift upon coordination.[6] Complex **3** is diamagnetic and gives well-resolved NMR spectra at room temperature. The ^{19}F spectrum has a singlet at $\delta = -149.5$ ppm (in CD$_2$Cl$_2$), which is due to tetrafluoroborate. In the ^{31}P spectrum, there are two triplets for the diphenylphosphanyl groups at $\delta = 18.7$ ppm and -10.9 ppm (A$_2$B$_2$ system). This

spin system indicates similar geometries of the cation both in solution and in the solid state, with distortion of diametrically opposed Ni–P bonds from a square-planar towards a tetrahedral arrangement (cf. discussion of the X-ray structure, below). High symmetry in solution is also evident from the ^1H and ^{13}C NMR spectra. The pyridine protons give rise to a triplet ($\delta = 8.74$ ppm) and a doublet ($\delta = 8.39$ ppm) in a 1:2 intensity ratio (AB$_2$ system). Several multiplets between 7.6 ppm and 4.8 ppm are assigned to the diphenylphosphanyl protons. The methylene groups appear as three doublets between 3.3 ppm and 2.3 ppm (equivalent to 2, 2, and 4 protons, respectively), and a singlet at ca. 2.3 ppm accounts for the six methyl protons. In the ^{13}C spectra, there are 12 signals between 169.0 and 123.0 ppm for the aromatic C atoms. One signal each arises from the quaternary ($\delta = 42.3$ ppm) and methyl carbon atoms ($\delta = 29.2$ ppm), whereas the methylene carbon atoms produce two signals at $\delta = 38.9$ ppm and 34.5 ppm, in accordance with the anisochrony observed for the phosphorus atoms.

Molecular Structures of $[(py\{PPh_2\}_4)Ni(Cl)](PF_6)$ and $[(py\{PPh_2\}_4)Ni](BF_4)_2$

Single crystals suitable for X-ray structure determination had the compositions $[(py\{PPh_2\}_4)Ni(Cl)](PF_6)$·MeOH (**2**·MeOH) and $[(py\{PPh_2\}_4)Ni](BF_4)_2$·CH$_2Cl_2$ (**3**·CH$_2$Cl$_2$). Compound **2** is a chiral chloro complex with tridentate coordination of the phosphane ligand (Figure 1); it crystallises as the racemate in the space group $P\bar{1}$. One phosphorus donor and the pyridine nitrogen atom remain uncoordinated [d(Ni1···N11) = 301.6(2) pm]. Selected bond lengths and angles are given in Table 1. The chloro ligand is displaced by 122.1(2) pm from the best plane defined by the nickel ion and the three coordinated P atoms, resulting in a coordination geometry around Ni^{II} which is intermediate between square planar and tetrahedral. The Ni–P and Ni–Cl bond lengths are within the range found for other chloro nickel(II) complexes with polyphosphane ligands.[7]
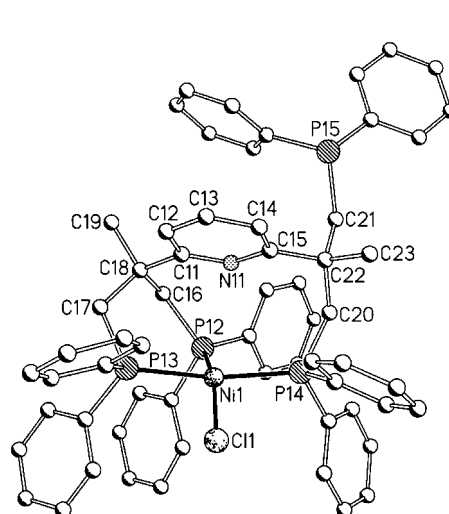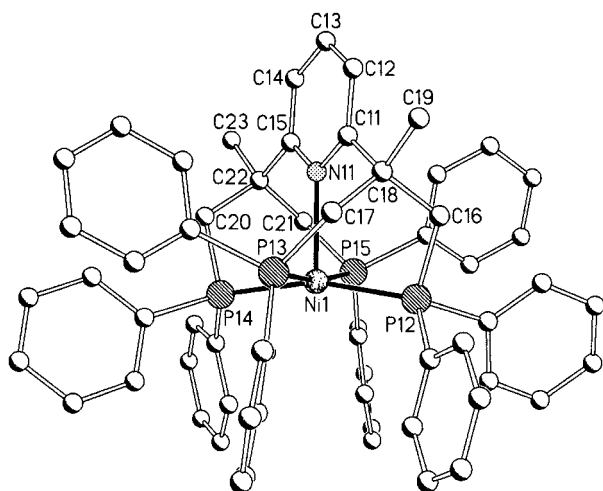

Figure 1. Molecular structure of the cation in the chloro nickel(II) complex **2** (H atoms not shown).

Table 1. Selected bond lengths [pm] and angles [°] in **2**·MeOH (standard deviations in parentheses).

|	
Ni1–P12	220.0(1)
Ni1–P13	226.2(2)
Ni1–P14	223.6(1)
Ni1–Cl1	218.3(1)
P12–Ni1–P13	88.86(4)
P12–Ni1–P14	97.90(4)
P13–Ni1–Cl1	89.33(4)
P14–Ni1–Cl1	89.85(4)
P12–Ni1–Cl1	155.29(4)
P13–Ni1–P14	165.30(4)

Compound **3** crystallises in the space group *Pccn* and contains distorted square-pyramidal coordinated nickel(II). The structure of the complex cation is shown in Figure 2.

Figure 2. Molecular structure of the cation in the nickel(II) complex **3** (H atoms not shown).

The distortion consists in the pairwise displacement of diametrically opposite phosphane donors below (P12–Ni1–P14) and above (P13–Ni1–P15) the best plane defined by the NiP$_4$ unit. All phenyl substituents on P12 and P14 are below this plane, whereas donor atoms P13 and P15 have one phenyl ring above and one below. As a consequence, there are two types of Ni–P bond environments in the solid state, which persist in solution and give rise to an A$_2$B$_2$ spin system in the ^{31}P NMR spectra of **3**. Selected bond lengths and angles of **3** are listed in Table 3. There are no significant differences between the Ni^{II}–P distances in **3** and **2**.

Coordination Behaviour of py{PPh$_2$}$_4$ Towards Cobalt(II)

In view of the results obtained for nickel(II), only cobalt(II) salts with weakly coordinating anions were used. Equimolar amounts of py{PPh$_2$}$_4$ und Co(ClO$_4$)$_2$·6H$_2$O in a methanol/dichloromethane solvent mixture (1:1) produce a red-brown solution from which, upon N$_2$-induced evaporation, [(py{PPh$_2$}$_4$)Co](ClO$_4$)$_2$ (**4**) may be obtained as red-brown microcrystals in moderate yield [25%, Equation (3)]. When Co(BF$_4$)$_2$·6H$_2$O is used, the corresponding tetrafluoroborate salt **5** is formed (52%).

(3)
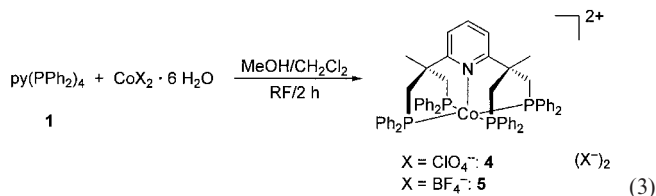
Both compounds are soluble in CH$_2$Cl$_2$ and sparingly soluble in methanol and THF. They are paramagnetic 17-valence-electron complexes of square-pyramidal coordinated cobalt(II), with the parent ion as the base peak in the mass spectra (m/z = 986, [(py{PPh$_2$}$_4$)Co]$^+$, 100%). The IR (KBr) spectra of **5** and the corresponding nickel(II) complex **3** are virtually identical, as expected. The magnetic moment determined for **4** (μ_{eff} = 1.60(3) BM; Gouy balance) corresponds to one unpaired electron, suggesting a low-spin configuration. (This configuration is assumed for the following discussion; given the possibility of experimental error with this technique, however, a reliable assignment of the spin state will require an ESR spectroscopic investigation). The properties of a number of low-spin cobalt(II) complexes of the type [CoL$_2$X]Y (L = bidentate neutral ligand with variable donor set, X = coordinating anion; Y = noncoordinating anion) have been published.[8–10] Meek and coworkers reported the series of complexes [(dppe)$_2$Co^{II}X](SnX$_3$) [X = Cl, Br, I; dppe = 1,2-bis(diphenylphosphanyl)ethane] and also investigated their magnetic behaviour.[11] Depending on the conditions employed (solvent, temperature, mode of crystallisation), the products have either square-pyramidal or trigonal-bipyramidal coordination geometry, but all complexes are low-spin. Magnetic moments vary slightly and are greater under square-pyramidal coordination geometry (μ_{eff} = 2.03–2.14 BM) than under trigonal-bipyramidal geometry (μ_{eff} = 1.89–1.97 BM). For the series of structurally uncharacterised complexes [Co(P$_4$)X](BPh$_4$) (P$_4$ = hexaphenyl-1,4,7,10-tetraphosphadecane, X = Cl, Br, I, NCS), Sacconi and coworkers reported magnetic moments of μ_{eff} = 1.98–2.13 BM.[12] In spite of their different symmetries, both series of complexes have magnetic moments
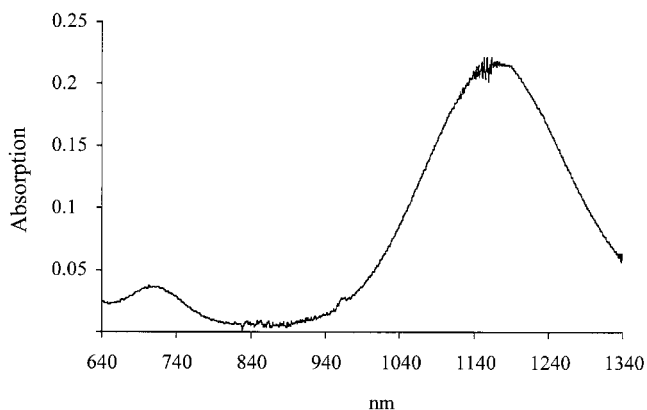
Figure 3. Vis/NIR part of the electronic spectrum of [(py{PPh$_2$}$_4$)Co](ClO$_4$)$_2$ in CH$_2$Cl$_2$ (10^{-3} M) at room temperature.

comparable to a low-spin cobalt(II) complex in an octahedral ligand field ($\mu_{eff} \geq \mu^{s.o.} = 1.73$ BM).[13] By way of comparison, the magnetic moment determined for **4** is smaller by 0.3 to 0.5 BM. The UV/Vis/NIR spectrum of **4** shows two *d-d* transitions at 703 nm (14225 cm^{-1}) and 1166 nm (8576 cm^{-1})(Figure 3).

The ligand field splitting varies with the ligand's position in the spectrochemical series. More weakly coordinating ligands should produce a red shift in the corresponding absorption bands, as has been verified for Sacconi's series, [Co(P$_4$)X](BPh$_4$) (P$_4$ = hexaphenyl-1,4,7,10-tetraphosphadecane, X = Cl, Br, I): Upon going from Cl to I, the two lowest-energy bands shift to lower wavenumbers as shown in Table 2.[12] Assuming square-pyramidal geometry for these complexes in solution, the data obtained for square-pyramidal **4** (Table 2) fit in well, as pyridine is above the halide ions in the spectrochemical series: py > … > Cl > … > Br > I.[13,14]

Table 2. Comparison of the absorption maxima of the two lowest-energy transitions in the solution UV/Vis/NIR spectra of cobalt(II) polyphosphane complexes (see text).

Ionic species	Absorption maximum [cm^{-1}]	Absorption maximum [cm^{-1}]
[(py{PPh$_2$}$_4$)Co]$^{2+[a]}$	8576	14225
[Co(P$_4$)Cl]$^{+[b]}$	8270	10520
[Co(P$_4$)Br]$^{+[b]}$	8000	10000
[Co(P$_4$)I]$^{+[b]}$	7940	9700

[a] In CH$_2$Cl$_2$. [b] In 1,2-dichloroethane.

Preliminary cyclovoltammetric measurements of **4** in CH$_2$Cl$_2$ solution at room temperature (internal standard: ferrocene) show one irreversible wave in the cathodic and one in the anodic region. The cathodic wave (–507 mV) may be assigned to the formation of an 18 valence electron cobalt(I) complex ([(py{PPh$_2$}$_4$)Co]$^+$); the anodic wave, after normalisation on ferrocene, falls outside the voltage range acceptable for CH$_2$Cl$_2$ as a CV solvent (–1800 mV to +1500 mV) and thus has no diagnostic value. Renewed measurements, employing both the perchlorate and the tetrafluoroborate salts, in a range of solvents and at different temperatures are expected to clarify whether a cobalt(III) complex is in fact accessible.

Molecular Structure of [(py{PPh$_2$}$_4$)Co](ClO$_4$)$_2$

The single crystals used for structure determination had the composition [(py{PPh$_2$}$_4$)Co](ClO$_4$)$_2$·0.75CH$_2$Cl$_2$ (**4**·0.75CH$_2$Cl$_2$). For [(py{PPh$_2$}$_4$)Co](BF$_4$)$_2$·MeOH, preliminary data confirm the identical structure of the molecular cation. Compound **4** crystallises in the space group *P*2$_1$/*c*; the structure of its cation is shown in Figure 4. The metal–nitrogen bond in **4** is ca. 8 pm shorter than in the nickel(II) complex **3**, whereas the metal–phosphorus bonds in **4** are 2–5 pm longer than in **3**. Otherwise, there are no significant structural differences between the cations in both complexes. Table 3 lists a comparison of parameters.
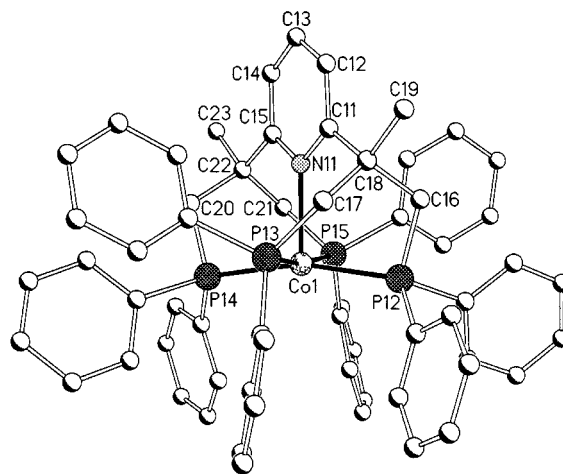

Figure 4. Molecular structure of the cation in the cobalt(II) complex **4** (H atoms not shown).

Table 3. Selected bond lengths [pm] and angles [°] in **3**·CH$_2$Cl$_2$ and **4**·0.75CH$_2$Cl$_2$ (standard deviations in parentheses).

Distance or angle[a]	**3**·CH$_2$Cl$_2$	**4**·0.75CH$_2$Cl$_2$
M–N11	227.8(4)	219.4(3)
M–P12	227.6(2)	232.5(1)
M–P13	223.3(2)	225.1(1)
M–P14	227.4(2)	231.7(1)
M–P15	223.6(2)	225.9(1)
N11–M–P12	98.4(2)	97.65(8)
N11–M–P13	85.2(2)	85.73(8)
N11–M–P14	97.7(2)	97.08(8)
N11–M–P15	85.1(2)	85.40(8)
P12–M–P13	88.21(5)	87.06(3)
P13–M–P14	92.83(6)	93.62(4)
P14–M–P15	88.23(5)	88.46(4)
P15–M–P12	93.42(6)	93.14(4)
P12–M–P14	163.92(5)	165.26(4)
P13–M–P15	170.32(6)	171.07(4)

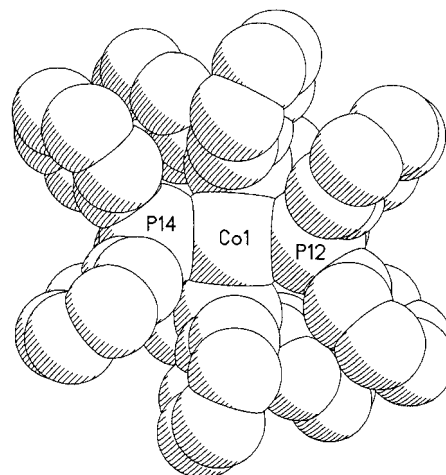[a] **3**: M = Ni1; **4**: M = Co1.

Figure 5. Space-filling model of the cobalt(II) complex **4**, viewed along the Co–N axis.

The Co–P bond lengths in **4** are within the range observed for other low-spin cobalt(II) complexes with polyphosphane ligands.[11] For example, the average Co–P bond length in [(dppe)$_2$CoCl]SnCl$_3$ is, under square-pyramidal coordination geometry, 227.6(2) pm, and 225.8(5) pm in the case of trigonal-bipyramidal coordination. The space-filling representation in Figure 5 shows a vacant potential coordination site, which is surrounded by six phenyl rings of the tetraphosphane ligand in a fencelike manner.

The Cobalt(II) Complexes [(py{PPh$_2$}$_4$)Co](X)$_2$ [X = ClO$_4$, BF$_4$] and Their Reactivity Towards CO, NO, NO$^+$, I$_2$, Cl$_2$ and H$_2$

The square-pyramidal cobalt(II) complexes of the new tetraphosphane ligand are remarkably stable towards oxidation, and can be kept in air for extended periods of time without noticeable decomposition. Attempts to increase the coordination number of the cobalt ion beyond 5 in a directed manner, either by simple coordination or by oxidative addition of a small monodentate ligand, have so far met with no success. In keeping with the electrochemical results, a square-pyramidal coordinated, 16-valence-electron cobalt(III) species does not seem accessible. Treatment with I$_2$ (0.5 equiv., room temperature, 48 h, in THF) reproduces the starting material, whereas the reaction with Cl$_2$ (0.5 equiv., –50 °C, 2 h, CH$_2$Cl$_2$) gives a mixture of products, consisting for the main part of the starting material. Mass spectral features consistent with the formation of the desired chloro complex have a marginal character at best. Whereas the expected steric demand of an iodide or a chloride ligand may preclude its coordination, there is also no indication for the formation of a hydride complex, by oxidative addition of H$_2$ (**4** in CH$_2$Cl$_2$ solution, 40 bar H$_2$ pressure; mixture monitored by ^{1}H NMR after 1, 4 and 10 d; cf. the synthesis of hydridopentacyanocobaltate(III) from pentacyanocobaltate(II) and H$_2$[15,16]). Likewise, treatment of solutions of **4** with CO (1 bar, CH$_2$Cl$_2$, room temperature, 2 h or MeOH, 50 °C, 1 h) or of **5** with NOBF$_4$ (CH$_2$Cl$_2$, room temperature, 48 h) produced no reaction. Only in those cases where solutions of **4** or **5** in CH$_2$Cl$_2$ were treated with equimolar amounts of gaseous NO, IR monitoring of solution samples indicated a significant reaction: two bands, one of intermediate intensity at 1856 cm^{-1} and one strong band at 1802 cm^{-1} appear within 1 h; there are no further spectral changes after extended reaction times (16 h). Whether or not this observation indicates the formation of two distinct NO complexes, or a dinitrosyl complex, is as yet unclear. The formation of N$_2$O [ν_{NN} (str) = 2222 cm^{-1}] with concomitant oxidation of potentially decoordinated phosphane functionalities (a reaction reported to proceed smoothly and quantitatively for free py{PPh$_2$}$_4$ under suitable conditions[6]) is not observed. Both bands (at 1853 and 1797 cm^{-1}) persist with comparable intensity in IR spectra (KBr disc) obtained from the brown solid which remains after evaporation of the solvent. While attempts to obtain single crystals from this material, which would allow structural characterisation, have been unsuccessful, mass spectroscopic data do not rule out the formation of a singly

substituted NO complex: the complex ion, [(py{PPh$_2$}$_4$)-Co]}$^+$, is recorded at m/z = 986 (100%), with a relatively prominent signal at m/z = 1017 (19%); $\Delta(m/z)$ = 31 (fast atom bombardment, matrix: *p*-nitrobenzyl alcohol). Treatment of **4** with NO at 0 °C, however, produced no reaction.

The preparation of ruthenium(II) complexes of the new tetraphosphane ligand will be reported elsewhere. Whereas the phenyl-substituted tetraphosphane ligand **1** may be too sterically encumbered to give complexes with iron(II), such complexes are in fact accessible with the methyl analogue, py(PMe$_2$)$_4$, which we have recently prepared. A study of its coordination behaviour and reactivity is under way.

Conclusions

The new highly symmetrical NP$_4$ ligand 2,6-C$_5$H$_3$N[CMe(CH$_2$PPh$_2$)$_2$]$_2$ forms mononuclear complexes with nickel(II) and cobalt(II), despite the steric bulk of eight phenyl rings on its four phosphorus-substituted "tentacles". The adopted mode of coordination depends on the nature of the counterion: In the case of strongly coordinating chloride, the ligand may in effect be tridentate (P$_3$) whereas, for weakly coordinating anions (BF$_4^-$, ClO$_4^-$), all five donor atoms coordinate to the central ion, to give complexes of approximate square-pyramidal geometry. The cobalt complex is virtually inert with respect to coordination of a sixth monodentate ligand (including dioxygen), owing to a "fence" of phenyl groups shielding the sixth coordination site. The reactivity of these complexes is expected to increase considerably upon the introduction of sterically less demanding and more basic P donors, such as the dimethylphosphanyl residue.

Experimental Section

Unless noted otherwise, all reactions were carried out at room temperature in dried solvents under dry dinitrogen, using standard Schlenk techniques. The tetraphosphane ligand py{PPh$_2$}$_4$ was prepared by literature methods;[6] NiCl$_2$·6H$_2$O, Ni(BF$_4$)$_2$·6H$_2$O, Co(ClO$_4$)$_2$·6H$_2$O and Co(BF$_4$)$_2$·6H$_2$O were purchased from Fluka or Aldrich and used without further purification. IR spectra of solids were measured using KBr disks; solution IR spectra were recorded in CaF$_2$ cuvets, with compensation of solvent absorptions. IR spectra were assigned on the basis of literature data.[17] Magnetic moments of polycrystalline samples were determined on a Gouy balance (Johnson-Matthey) at room temperature, with diamagnetic corrections calculated from Pascal's constants.[18] Spectroscopic data were obtained using the following instruments: IR spectroscopy: Perkin–Elmer 1600 FT IR and 16PC FT IR; mass spectrometry: Varian MAT 212 and Jeol JMS 700; NMR spectroscopy: Jeol FT-NMR JNM-EX 270, Lambda LA 400 und ALPHA 500. Signs of coupling constants in the ^{1}H, ^{13}C, and ^{31}P NMR spectra were not determined. Elemental analyses were carried out with Carlo Erba EA 1106 and 1108 analysers. Cyclic voltammograms were recorded with a PAR 264A potentiostat and a three-electrode cell with a glassy carbon ROTEL working electrode and Pt reference and counter electrode (nBu$_4$NPF$_6$, 10^{-1} mol L^{-1}; internal standard (Cp)$_2$Fe/(Cp)$_2$Fe$^+$; $E_{1/2}$ = +0.4 V vs. NHE[19]).

[(py{PPh$_2$)$_4$)NiCl]PF$_6$ (2): To a solution of py{PPh$_2$}$_4$ (375 mg, 0.400 mmol) in acetonitrile (20 mL) was added solid NiCl$_2$·6H$_2$O (10 mg, 0.40 mmol) in one portion. The resulting reddish-brown suspension was heated to reflux for 30 min, to give a clear solution of the same colour. Stripping of the solvent and drying in vacuo left a red-brown solid, which was dissolved in methanol. Addition of NaPF$_6$ (70 mg, 0.40 mmol) to the warm deep purple solution produced a purple microcrystalline precipitate after 12 h (182 mg). Elemental analysis (CHN) data are consistently too low in carbon. This observation, as well as the fact that the chloroform-soluble fraction gives ^{1}H, {^{1}H}^{13}C, and {^{1}H}^{31}P NMR spectra virtually identical to those of **3**, indicate that a mixture of complexes (with and without coordinated chloride) may have formed (see text). MS (FAB, *p*-NBA): *m/z* (%) = 1022 [(py{PPh$_2$}$_4$)NiCl]$^+$ (20).

[(py{PPh$_2$}$_4$)Ni](BF$_4$)$_2$ (3): The addition of a solution of Ni(BF$_4$)$_2$·6H$_2$O (267 mg, 0.780 mmol) in methanol (20 mL) in one portion to a solution of py{PPh$_2$}$_4$ (724 mg, 0.780 mmol) in dichloromethane (20 mL) instantaneously produced a brown solution, which was heated to reflux for 30 min and subsequently taken to dryness. The obtained purple-brown powder was triturated with n-hexane, separated by filtration, and dried in vacuo. Yield: 465 mg **3**·MeOH (50%). **3**·MeOH: C$_{62}$H$_{61}$B$_2$F$_8$NNiOP$_4$ (1192.37): calcd. C 62.45, H 5.16, N 1.17; found C 62.09, H 5.21, N 0.83. IR (KBr): ṽ = 3048, 1586, 1480, 1435 (str), 1084, 1060, 742, 696, 517 cm^{-1}. MS (FD$^+$, CH$_2$Cl$_2$): *m/z* (%) = 987 (75) [(py{PPh$_2$}$_4$)Ni]$^+$, 1073 (15) {[(py{PPh$_2$}$_4$)Ni]BF$_4$}$^+$. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, room temp.): δ = 8.74 (t, $^2J_{H,H}$ = 8.0 Hz, 1 H, py-H^4), 8.39 (d, $^2J_{H,H}$ = 8.0 Hz, 2 H, py-H^{3,5}), 7.6–4.8 (m, 40 H, overlaid from low to high field: py-H^{3,5}; C$_{ortho}$-H, C$_{ortho}$′-H, C$_{meta}$-H, C$_{meta}$′-H, C$_{para}$-H, C$_{para}$′-H), 3.24 (d, $^2J_{H,H}$ = 7.8 Hz, 2 H, -CH_2-), 3.05 (d, $^2J_{H,H}$ = 7.8 Hz, 2 H, -CH_2-), 2.42 (d, $^2J_{H,H}$ = 7.4 Hz, 4 H, -CH_2-), 2.29 (s, 6 H, -CH_3) ppm. {^{1}H}^{13}C NMR (400 MHz, CD$_2$Cl$_2$, room temp.): δ = 168.3–123.8 (12 signals, 53 C, py-C^4, py-C^{2,6}, py-C^{3,5}, C$_{ipso}$, C$_{ipso}$′, C$_{ortho}$, C$_{ortho}$′, C$_{meta}$, C$_{meta}$′, C$_{para}$, C$_{para}$′), 42.3 (2 C, >C<), 38.8 (2 C, -CH_2-), 34.5 (2 C, -CH_2-), 29.3 (2 C, -CH_3) ppm. {^{1}H}^{19}F

NMR (400 MHz, CD$_2$Cl$_2$, room temp.): δ = –149.5 (s, 4 F, BF_4) ppm. {^{1}H}^{31}P NMR (400 MHz, CDCl$_3$, room temp.): δ = 18.7 (t, $^2J_{P,P}$ = 151 Hz, 2 P, -PPh$_2$), –10.9 (t, $^2J_{P,P}$ = 149.5 Hz, 2 P, -PPh$_2$) ppm.

[(py{PPh$_2$}$_4$)Co](ClO$_4$)$_2$ (4): A solution of py{PPh$_2$}$_4$ (1.10 g, 1.18 mmol) in dichloromethane (20 mL) was slowly added to a stirred solution of Co(ClO$_4$)$_2$·6H$_2$O (430 mg, 1.18 mmol) in methanol (30 mL). In the course of the addition, the colour of the resultant solution changed from pink to brown. After heating to reflux for 30 min, the solution was allowed to cool to room temperature, and its volume reduced in a slow stream of dinitrogen. After 72 h, a red-brown microcrystalline precipitate had formed, which was separated by filtration (G4 frit), washed with Et$_2$O (2×10 mL), and dried in a stream of dinitrogen. Yield: 369 mg **4**·2 MeOH (25%). More product was obtained from the mother liquor after evaporation of the solvent mixture in air. **4**·2MeOH: C$_{63}$H$_{65}$Cl$_2$CoNO$_{10}$P$_4$ (1249.95): calcd. C 60.54, H 5.24, N 1.12; found C 60.31, H 5.37, N 0.94. IR (KBr): ṽ = 3427 (br), 3054 (H–C$_{aryl}$), 2962 (-CH$_3$), 1573, 1483, 1454, 1435 (str, P–Ph), 1262, 1096 (str, br, ClO$_4$$^-$), 803, 742, 694, 623 (ClO$_4$$^-$), 516 cm^{-1}. MS (FAB, *p*-NBA): *m/z* (%) = 986 (100) {[py{PPh$_2$}$_4$]Co}$^+$, 1085 (60) {[py{PPh$_2$}$_4$Co]ClO$_4$}$^+$. μ_{eff} (spin only) = 1.60(3) BM. UV/Vis (10^{-3} mol L^{-1} in CH$_2$Cl$_2$, room temp.): λ (ε) = 1166 nm (218 dm^3 mol^{-1} cm^{-1}), 703 nm (37 dm^3 mol^{-1} cm^{-1}).

[(py{PPh$_2$}$_4$Co](BF$_4$)$_2$ (5): A mixture of solid Co(BF$_4$)$_2$·6H$_2$O (347 mg, 1.02 mmol) and solid py{PPh$_2$}$_4$ (950 mg, 1.02 mmol) was taken up in a methanol/dichloromethane mixture (1:1; 40 mL). The initial pink colour of the solution changed to brown after ca. 5 min. The solution was heated to reflux overnight, allowed to cool to room temperature during several h, taken to dryness in an oil pump vacuum, and the remaining solid triturated with n-hexane, to produce a reddish-tan precipitate, which was filtered (G4 frit), and dried in vacuo. Yield: 751 mg **5** (52%). **5**·4 MeOH: C$_{65}$H$_{73}$B$_2$CoF$_8$NO$_{12}$P$_4$ (1416.73): calcd. C 60.58, H 5.71, N 1.09; found C 60.40, H 5.19, N 0.99. IR (KBr): ṽ = 3446 (br), 1482, 1458, 1436 (str, P–

Table 4. Selected crystallographic data for **2**·MeOH, **3**·CH$_2$Cl$_2$, and **4**·0.75CH$_2$Cl$_2$.

Compound	**2**·MeOH	**3**·CH$_2$Cl$_2$	**4**·0.75CH$_2$Cl$_2$
Molecular formula	C$_{62}$H$_{61}$ClF$_6$NNiOP$_5$	C$_{62}$H$_{59}$B$_2$Cl$_2$F$_8$NNiP$_4$	C$_{61.75}$H$_{58.5}$Cl$_{3.5}$CoNO$_8$P$_4$
M_r [g mol^{-1}]	1199.13	1245.21	1249.48
Crystal size [mm^3]	0.60 × 0.50 × 0.40	0.60 × 0.50 × 0.25	0.60 × 0.55 × 0.45
F (000)	1244	5136	2586
Crystal system	triclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$ (No. 2)	$Pccn$ (No. 56)	$P2_1/c$ (No. 14)
a [pm]	1245.2(2)	4211.3(6)	1260.3(2)
b [pm]	1353.9(2)	1530.7(2)	1982.1(2)
c [pm]	1698.9(3)	1808.0(3)	2390.3(2)
α [°]	92.59(1)	90	90
β [°]	93.10(1)	90	94.30(1)
γ [°]	94.46(1)	90	90
V [nm^3]	2.8478(8)	11.655(3)	5.954(2)
Z	2	8	4
ρ_{calc} [g cm^{-3}]	1.398	1.419	1.394
μ [mm^{-1}]	0.591	0.601	0.608
Temperature [K]	200(2)	210(2)	294(2)
2 Θ range [°]	4.6–54.0	5.8–50.1	6.1–52.8
Measured reflections	14180	12180	14664
Unique reflections	12434	10283	12160
Observed reflections [$I > 2\sigma(I)$]	8327	6180	8750
Refined parameters	719	724	728
wR_2 (all data)	0.1462	0.2004	0.1720
R_1 [$I > 2\sigma(I)$]	0.0572	0.0688	0.0577

Ph), 1060 (BF$_4$), 742, 694 cm^{-1}. MS (FD$^+$, CH$_2$Cl$_2$): m/z (%) = 986 (100) [(py{PPh$_2$}$_4$)Co]$^+$.

X-ray Crystallography of Compounds 2, 3, and 4: Purple single crystals of [(py{PPh$_2$}$_4$)Ni(Cl)]PF$_6$·MeOH (**2·MeOH**) were obtained within 3 d by isothermal diffusion of Et$_2$O into a saturated solution of the reaction product in methanol. Dark red crystalline blocks of [(py{PPh$_2$}$_4$)Ni](BF$_4$)$_2$·CH$_2$Cl$_2$ (**3·CH$_2$Cl$_2$**) were similarly obtained from CH$_2$Cl$_2$/Et$_2$O within 2 d. Red crystals of [(py{PPh$_2$}$_4$)Co](ClO$_4$)$_2$·0.75 CH$_2$Cl$_2$ (**4·0.75 CH$_2$Cl$_2$**) formed within 2 d from a dichloromethane solution whose volume was reduced in a slow stream of dry dinitrogen. Suitable crystals were mounted in glass capillaries. Data sets were obtained on a Siemens P4 diffractometer, using Mo-K_α radiation (λ = 71.073 pm) and the ω-scan technique. The structures of all complexes were solved by direct methods and refined using full-matrix least-squares procedures on F^2 (SHELXTL NT 6.12).[20] All non-hydrogen atoms of all complexes were anisotropically refined. Compound **2** crystallises with one molecule of MeOH per formula unit, which is disordered. Two preferential orientations for the C–O unit were refined, with an occupancy of 0.53(2) (O1, C1) and 0.47(2) (O2, C2), respectively. Compound **3** crystallises with one molecule of CH$_2$Cl$_2$ and compound **4** with ca. 0.75 CH$_2$Cl$_2$ per formula unit. The dichloromethane molecule in **4** is disordered; two preferential positions were determined for one of the chloride atoms, with occupancies refined to 0.53(2) for Cl12 and 0.22(2) for Cl13. Cl13 was only isotropically refined. Treatment of hydrogen atoms: All hydrogen atoms were geometrically positioned and allowed to ride on their carrier atoms during the refinement; their isotropic displacement parameters were tied to those of the adjacent C and O atoms by a factor of 1.2 or 1.5. Crystallographic data are listed in Table 4. CCDC-266966 (**2·MeOH**), CCDC-266967 (**3·CH$_2$Cl$_2$**), and CCDC-266968 (**4·0.75CH$_2$Cl$_2$**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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