SYNTHESIS AND CHARACTERIZATION OF Ni(II) AND Pd(II) COMPLEXES BEARING ACHIRAL AND CHIRAL BIDENTATE AMINOPHOSPHINE LIGANDS

David BENITO-GARAGORRI[a1], Kurt MEREITER[b] and Karl KIRCHNER[a2,*]

[a] *Institute of Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt 9, A-1060 Vienna, Austria; e-mail:* [1] *garagorri@ioc.tuwien.ac.at,* [2] *kkirch@mail.zserv.tuwien.ac.at*

[b] *Institute of Chemical Technologies and Analytics, Vienna University of Technology, Getreidemarkt 9, A-1060 Vienna, Austria; e-mail: kmereite@mail.zserv.tuwien.ac.at*

Received March 1, 2007
Accepted April 11, 2007

Dedicated to Dr Karel Mach on the occasion of his 70th birthday in recognition of his contributions to the area of organometallic chemistry.

The synthesis of a range of achiral and chiral bidentate aminophosphine ligands and their complexes with nickel(II) and palladium(II) has been investigated. The ligands and the complexes have been characterized by NMR spectroscopy, and X-ray structures of representative compounds have been determined. In addition, DFT calculations have been performed to investigate different geometries of the nickel(II) complexes in the solid state and in solution.
Keywords: Aminophosphines; Nickel; Palladium; Allyl complexes; DFT calculations.

The coordination chemistry of pyridylphosphine ligands has been extensively studied[1]. Most research in this area has been focused on the chemistry of 2-(diphenylphosphino)pyridine, which can act as a bidentate ligand containing both hard (nitrogen) and soft (phosphorus) donor atoms. However, chelate complexes with this ligand are unstable because of ring strain, and other ligand systems containing the same donor groups with organic spacers between the phosphorus and the pyridine nitrogen atom have been reported, including $Ph_2PCH(R)py$ (R = H [2], CH_2OEt [3], PPh_2 [4]) and $Ph_2PCH_2CH_2py$ [5].

Surprisingly, considering the ease of phosphine–nitrogen bond forming reactions, there are only few examples of PN ligands in which the phosphine and the pyridine rings are separated by amino groups[6]. We have recently reported a new class of tridentate PNP and PCP pincer ligands in which an amine acts as spacer between the aromatic ring and the phos-

Collect. Czech. Chem. Commun. 2007, Vol. 72, No. 4, pp. 527–540

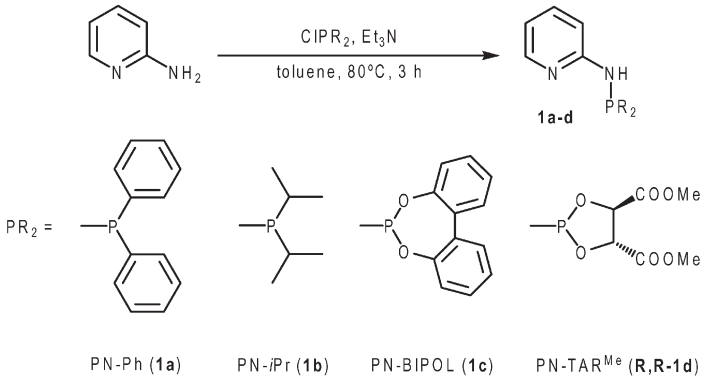
doi:10.1135/cccc20070527

phines[7]. In these ligands, their steric, electronic and stereochemical properties can be easily modulated by using different phosphine substituents. In this article we apply the same synthetic methodology to the preparation of several bidentate PN ligands which contain aryl- and alkylphosphines as well as different P–O bond containing achiral and chiral phosphine units. Furthermore, these ligands have been applied to the synthesis of several Ni(II) and Pd(II) complexes.

RESULTS AND DISCUSSION

Ligands

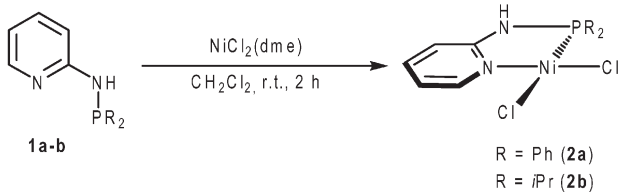
Similarly to the known ligand 2-[(diphenylphosphino)amino]pyridine (PN-Ph; **1a**)[6e], the new PN ligands **1b**–**1d** were prepared in 88–95% yields by treatment of 2-aminopyridine with 1 equivalent of the respective chlorophosphine or chlorophosphite in the presence of a base (NEt_3) (Scheme 1). The reactions were carried out in toluene at 80 °C for 3 h. The ligands **1a**–**1d** were isolated as air-stable solids or oils and were characterized by ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopics. Most diagnostic are the $^{31}P\{^1H\}$ NMR spectra, which exhibit a single resonance in the range between 27.5 (**1a**) and 147.3 ppm (**1c**). In the ^1H NMR spectra, the NH protons of **1a**–**1d** give rise to a broadened singlet between 4.94 and 6.60 ppm. All other resonances are unremarkable and are not discussed here.



SCHEME 1

Nickel(II) Complexes

The tetracoordinated nickel(II) complexes $[NiCl_2(PN\text{-}Ph)]$ (**2a**) and $[NiCl_2(PN\text{-}i\text{Pr})]$ (**2b**) were prepared in 86 and 92% yields, respectively, by reacting equimolar amounts of $[NiCl_2(dme)]$ and of the ligands **1a**, **1b** in CH_2Cl_2 at room temperature for 2 h (Scheme 2). Complexes **2a**, **2b** are paramagnetic and give rise to very broad signals in the ^1H NMR spectra indicating a tetrahedral coordination geometry around the metal center in solution. No signals could be observed in the $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra. This observation is in agreement with the findings reported by Braunstein et al.[8] with similar nickel(II)-PN complexes.



SCHEME 2

The solid-state structure of **2b** was determined by X-ray diffraction. A view of the molecular structure is shown in Fig. 1 with selected bond lengths and angles given in the caption. The nickel(II) center in **2b** shows a slightly dis-

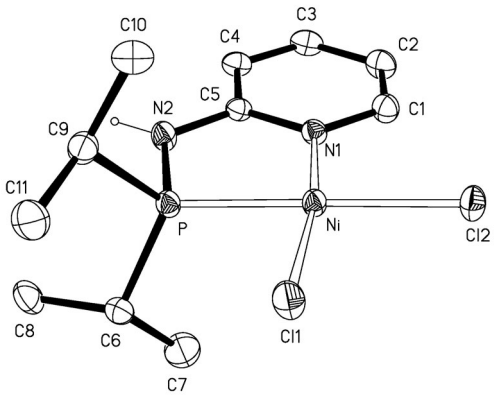


FIG. 1

Structure view of **2b** showing atomic displacement ellipsoids drawn at 40% probability level. C-bonded hydrogen atoms are omitted for clarity. Selected bond lengths (in Å) and angles (in °): P–N2 1.6839(11), Ni–N1 1.9259(10), Ni–P 2.1209(4), Ni–Cl1 2.1710(4), Ni–Cl2 2.2359(3); N1–Ni–P 86.55(3), N1–Ni–Cl2 95.74(3), P–Ni–Cl1 84.34(2), Cl1–Ni–Cl2 93.39(2)

torted square-planar geometry. This result is surprising in view of the paramagnetic nature of this complex in solution, but of course solution and solid-state structures need not be identical[9,10], and such differences between the geometry in solution and in the solid state have been reported previously for a similar nickel(II)-PN complex[8a]. In agreement with the experimental results, DFT calculations reveal that the tetrahedral geometry is favored over the square-planar one by about 40–60 kJ/mol both in the gas phase and in the solution (CH_2Cl_2 and acetone). The two geometries, i.e. **A** tetrahedral (S = 1) and **B** square-planar (S = 0), and relative energies of the model complexes [$NiCl_2$(PN-Me)] and [$NiCl_2$(PN-Ph)] calculated at the B3LYP level of theory are depicted in Fig. 2.

The Ni–Cl bond distance is about 0.05 Å shorter for the chlorine in the *trans* position to the pyridine nitrogen atom (Ni–Cl1 2.1710(4) Å) than that for the chlorine *trans* to the phosphorus atom (Ni–Cl2 2.2359(3) Å). The ligand bite angle (N1–Ni–P) is 86.55(3)°, which is slightly bigger than that observed in related phosphinopyridine[8a] and phosphinooxazoline[11] nickel(II)-PN complexes. The r.m.s. deviation of the four Ni ligands from perfect planarity is only 0.023 Å. A significant distortion from the exact quadratic geometry is evident from the bond angles at Ni (Fig. 1). The comparatively large bond angle N1–Ni–Cl2 = 95.74(3)° is caused by steric congestion involving the hydrogen of C1 and its short contact to Cl2 (H···Cl = 2.49 Å) although it represents a non-classic hydrogen bond interaction.

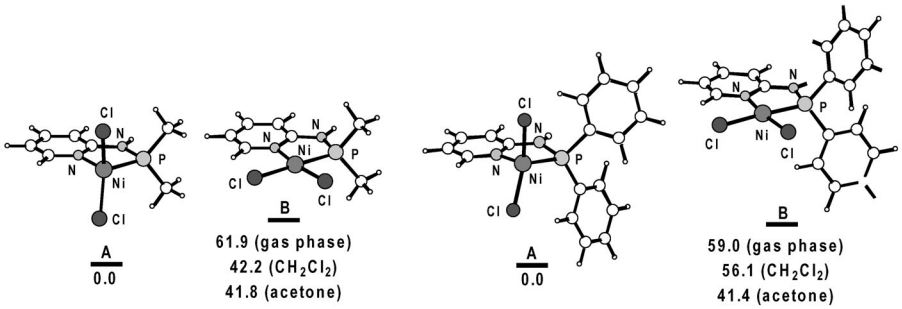
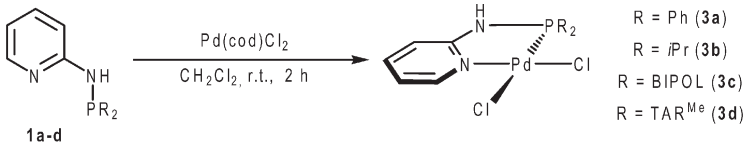


FIG. 2

Optimized geometries and relative energies (in kJ/mol) for the model complexes [$NiCl_2$(PN-Me)] and [$NiCl_2$(PN-Ph)] with tetrahedral (**A**) and square-planar (**B**) geometries calculated at the B3LYP level of theory (Ni sdd; C, N, P, Cl, H 6-31g**)

Palladium(II) Complexes

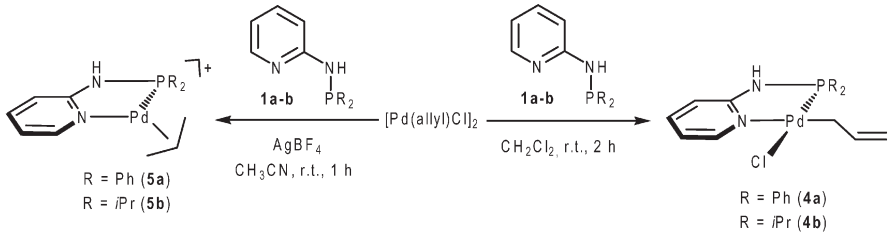
Treatment of 1 equivalent of $[Pd(cod)Cl_2]$ with 1 equivalent of the ligands **1a**–**1d** in CH_2Cl_2 at room temperature for 2 h afforded the neutral PN complexes of the general formula $[PdCl_2(PN)]$ (**3a**–**3d**) cleanly in good isolated yields (74–91%) (Scheme 3). The complexes **3a**–**3d** are thermally robust yellow solids that are air-stable both in the solid state and in solution; their identity was established by ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopies. In the $^{31}P\{^1H\}$ NMR spectra, the complexes show a single resonance at 79.5 (**3a**), 125.7 (**3b**), 109.5 (**3c**) and 118.5 ppm (**3d**). All the other resonances are not remarkable and are not discussed here. It has to be noted that previous reports about the reaction of **1a** with palladium metal precursors indicate that when the reaction is carried out in the $[PdCl_2(cod)]$:**1a** molar ratio 1:2 in refluxing acetone, the cationic species *cis*-[PdCl(Ph-PN-*P*,*N*)-(Ph-PN-*P*)]Cl is obtained, with no evidence for the formation of *trans* bis(PN) or mono(PN) dichloro-Pd(II) complexes[6e].



SCHEME 3

Given the importance of transition metal allyl complexes in catalytic reactions, where they often represent key intermediates[12], we were interested in preparing both η^1- and η^3-allyl palladium(II) complexes with the PN ligands described above. Fully characterized η^1- and η^3-allyl palladium(II) complexes have been previously reported[13]. Thus, the reaction of the dimeric precursor $[Pd(\eta^3\text{-allyl})Cl]_2$ with 2 equivalents of the ligands **1a**, **1b** in CH_2Cl_2 at room temperature for 2 h afforded, upon workup, the Pd(II) η^1-allyl complexes **4a**, **4b** as air-stable yellow solids in moderate to good yields (68–83%) (Scheme 4). Alternatively, treatment of 1 equivalent of $[Pd(\eta^3\text{-allyl})Cl]_2$ with 2 equivalents of $AgBF_4$ in acetonitrile yields the intermediate $[Pd(\eta^3\text{-allyl})(CH_3CN)_2]BF_4$, which on addition of 2 equivalents of the ligands **1a**, **1b** gives the Pd(II) η^3-allyl complexes **5a**, **5b** as air-stable off-white solids in good yields (75–92%) (Scheme 4). The –CH= hydrogen atom in the complexes **4a**, **4b** and **5a**, **5b** gives rise to multiplets between 5.66 (**4b**) and 5.90 ppm (**4a** and **5a**), while the signals of the other allylic protons appear as doublets or multiplets between 3.19 and 4.67 ppm in the case of **4a**, **4b** and between 2.69 and 6.81 ppm for **5a**, **5b**. In the $^{13}C\{^1H\}$

NMR spectra of **4a**, **4b** and **5a**, **5b**, the –CH=, $=CH_2$ and $–CH_2$ carbon atoms appear at about 120, 80 and 45 ppm, respectively. All complexes show a single resonance in the $^{31}P\{^1H\}$ NMR spectrum at 78.4 (**4a**), 115.3 (**4b**), 77.6 (**5a**) and 115.4 ppm (**5b**).



SCHEME 4

The solid-state structures of **5a** and **5b** were determined by X-ray crystallography. Structure views of **5a** and **5b** are shown in Figs 3 and 4 with selected bond lengths and angles given in the captions. The metal center in complexes **5a** and **5b** adopts a distorted square-planar geometry defined by

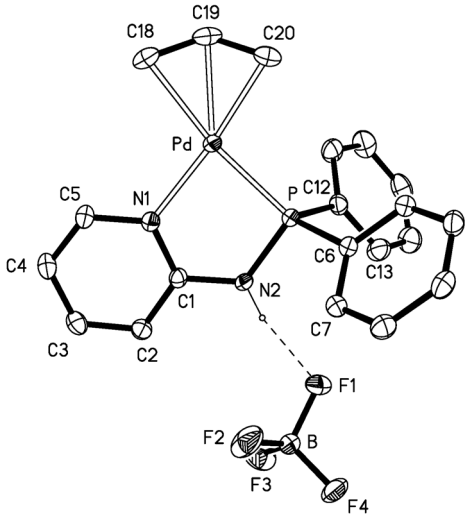


FIG. 3

Structure view of **5a** showing atomic displacement ellipsoids drawn at 50% probability level. C-bonded hydrogen atoms are omitted for clarity. Selected bond lengths (in Å) and angles (in °): Pd–N1 2.0876(14), Pd–P 2.2499(4), P–N2 1.6953(13), Pd–C18 2.199(2), Pd–C19 2.160(2), Pd–C20 2.112(2); N1–Pd–C20 173.34(7), P–Pd–C18 170.89(5), N1–Pd–C19 137.5(2), C18–C19–C20 124.4(2); N2···F1 2.884(2)

the palladium, phosphorus and pyridine nitrogen atoms and by the two lateral carbon atoms of the allyl group. The r.m.s. deviations of these four ligand atoms are 0.003 (**5a**) and 0.021 Å (**5b**). Palladium and the central allyl carbon deviate distinctly from this plane, in the case of **5a** by 0.038 and 0.556 Å, in the case of **5b** by 0.078 and 0.605 Å. The about 0.1 Å longer Pd–C18 and Pd–C14 bonds in complexes **5a** and **5b** compared to Pd–C20 and Pd–C12, respectively, reflect the larger *trans* influence of the phosphorus donor, and have been observed also in oxazoline-based palladium-allyl complexes[14]. The ligand bite angle N1–Pd–P has a value of 83.61(3) and 83.40(6)° for **5a** and **5b**, respectively.

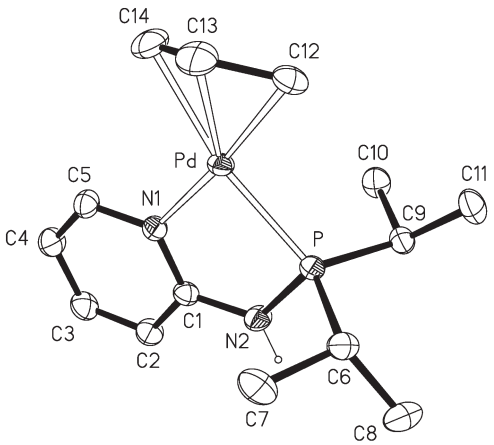


FIG. 4

Structure view of **5b** showing atomic displacement ellipsoids drawn at 50% probability level. BF_4^- anion and C-bonded hydrogen atoms are omitted for clarity. Selected bond lengths (in Å) and angles (in °): Pd–N1 2.110(2), Pd–P 2.2577(6), P–N2 1.694(2), Pd–C12 2.109(2), Pd–C13 2.168(3), Pd–C14 2.222(3); N1–Pd–C12 174.1(1), P1–Pd–C14 168.7(1), N1–Pd–C13 137.4(1), C12–C13–C14 121.57

EXPERIMENTAL

General

All manipulations were performed under inert atmosphere of argon by using Schlenk techniques. The solvents were purified according to standard procedures. The starting materials PPh_2Cl and $PiPr_2Cl$ were purchased from Aldrich and used without further purification. Biphenyl-2,2′-diyl phosphorochloridite[15], dimethyl (4*S*,5*S*)-2-chloro-1,3,2-dioxaphospholane-4,5-dicarboxylate[16], $[PdCl_2(cod)]$ (cod = 1,5-cyclooctadiene)[17], $[Pd(\eta^3\text{-allyl})Cl]_2$ and $[NiCl_2(dme)]$ (dme = 1,2-dimethoxyethane)[18] were prepared according to the literature. The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. ^1H,

$^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were obtained at room temperature (20 °C) on a Bruker AVANCE-250 spectrometer. Chemical shift data (δ, ppm) are referenced to $SiMe_4$ and H_3PO_4 (85%), respectively. Coupling constants, *J*, are given in Hz. ^1H and $^{13}C\{^1H\}$ NMR signal assignments were confirmed by ^1H-COSY, 135-DEPT and HMQC(^1H-^{13}C) experiments.

Syntheses

2-[(N-Diphenylphosphino)amino]pyridine (PN-Ph) (**1a**). PPh_2Cl (9.5 ml, 53.1 mmol) was added dropwise to a solution of 2-aminopyridine (5.0 g, 53.1 mmol) and triethylamine (7.4 ml, 53.1 mmol) in toluene (50 ml) at 0 °C. The mixture was stirred at 80 °C for 3 h, filtered and the solvent was removed under vacuum to give **1a** as a pale yellow solid. Yield 12.9 g (87%). ^1H NMR ($CDCl_3$): 7.93 (d, *J* = 4.6, 1 H, 6-Hpy); 7.51–7.42 (m, 5 H, Ph); 7.36–7.33 (m, 6 H, Ph and 4-Hpy); 7.06 (d, *J* = 8.2, 1 H, 3-Hpy); 6.64 (dd, *J* = 5.2, 6.4, 1 H, 5-Hpy); 5.93 (d, *J* = 8.4, 1 H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 158.7 (d, *J* = 20.7, 2-Hpy); 148.1 (d, *J* = 1.5, 6-Hpy); 139.6 (d, *J* = 11.1, Ph^1); 137.82 (d, *J* = 2.3, 4-Hpy); 131.3 (d, *J* = 20.7, $Ph^{2,6}$); 129.2 (Ph^4); 128.6 (d, *J* = 6.9, $Ph^{3,5}$); 115.0 (5-Hpy); 108.9 (d, *J* = 15.7, 3-Hpy). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 27.5.

2-[(N-Diisopropylphosphino)amino]pyridine (PN-iPr) (**1b**). This ligand has been prepared analogously to **1a** with $PiPr_2Cl$ (8.5 ml, 53.1 mmol), triethylamine (7.4 ml, 53.1 mmol) and 2-aminopyridine (5.0 g, 53.1 mmol) as the starting materials. Yield 10.6 g (95%). ^1H NMR ($CDCl_3$): 8.00 (d, *J* = 3.9, 1 H, 6-Hpy); 7.42 (dt, *J* = 1.5, 2.0, 1 H, 4-Hpy); 7.08 (s, 1 H, 3-Hpy); 6.61 (m, 1 H, 5-Hpy); 4.94 (d, *J* = 10.5, 1 H, NH); 1.77 (m, *J* = 2.3, 7.0, 2 H, C**H**$(CH_3)_2$); 1.09–0.99 (m, 12 H, CH(C**H**$_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 160.7 (d, *J* = 19.6, 2-Hpy); 147.5 (d, *J* = 1.2, 6-Hpy); 137.6 (d, *J* = 2.0, 4-Hpy); 114.1 (5-Hpy); 108.9 (d, *J* = 18.0, 3-Hpy); 26.3 (d, *J* = 11.1, **C**H$(CH_3)_2$); 18.6 (d, *J* = 19.5, CH(**C**H$_3)_2$); 17.0 (d, *J* = 7.7, CH(**C**H$_3)_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 50.1.

2-[(2-Pyridyl)amino]dibenzo[d,f][1,3,2]dioxaphosphepine (PN-BIPOL) (**1c**). This ligand has been prepared analogously to **1a** with biphenyl-2,2′-diyl phosphorochloridite (1.1 g, 4.3 mmol), triethylamine (0.60 ml, 4.3 mmol) and 2-aminopyridine (405 mg, 4.3 mmol) as the starting materials. Yield 1.2 g (92%). ^1H NMR ($CDCl_3$): 8.12 (d, *J* = 5.0, 1 H, 6-Hpy); 7.54–7.47 (m, 3 H, Ph and 4-Hpy); 7.39–7.24 (m, 6 H, Ph); 6.84–6.79 (m, 2 H, 3-Hpy and 5-Hpy); 6.38 (s, 1 H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 155.4 (d, *J* = 16.9, 2-Hpy); 149.6 (d, *J* = 4.2, Ph); 148.3 (6-Hpy); 138.0 (d, *J* = 1.6, 4-Hpy); 131.6 (d, *J* = 3.1, Ph); 129.8 (d, *J* = 1.1, Ph); 129.2 (Ph); 125.3 (Ph); 122.2 (d, *J* = 1.5, Ph); 116.6 (5-Hpy); 110.2 (d, *J* = 11.1, 3-Hpy). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 147.3.

Dimethyl (4S,5S)-2-[(2-pyridyl)amino]-1,3,2-dioxaphospholane-4,5-dicarboxylate (PN-TAR^{Me}) (**1d**). This ligand has been prepared analogously to **1a** with dimethyl (4*S*,5*S*)-2-chloro-1,3,2-dioxaphospholane-4,5-dicarboxylate (1.5 g, 6.1 mmol), triethylamine (0.85 ml, 6.1 mmol) and 2-aminopyridine (577 mg, 6.1 mmol) as the starting materials. Yield 1.6 g (88%). ^1H NMR ($CDCl_3$): 8.14 (d, *J* = 5.0, 1 H, 6-Hpy); 7.48 (m, 1 H, 4-Hpy); 6.80 (m, 1 H, 3-Hpy); 6.70 (d, *J* = 8.2, 5-Hpy); 6.60 (s, 1 H, NH); 5.10 (dd, *J* = 1.6, 5.2, 1 H, CH); 4.84 (dd, *J* = 5.2, 10.0, 1 H, CH); 3.83 (s, 3 H, CH_3); 3.81 (s, 3 H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 171.4 (CO); 169.2 (CO); 155.7 (d, *J* = 20.0, 2-Hpy); 148.0 (6-Hpy); 140.0 (4-Hpy); 116.6 (5-Hpy); 110.3 (d, *J* = 6.9, 3-Hpy); 77.2 (CH); 77.0 (CH); 53.2 (CH_3); 53.1 (CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 142.6.

[$NiCl_2$(PN-Ph)] (**2a**)

1a (91 mg, 0.32 mmol) was added to a suspension of [$NiCl_2$(dme)] (100 mg, 0.32 mmol) in CH_2Cl_2 and the mixture was stirred at room temperature for 2 h The solvent was evaporated under vacuum and the remaining violet solid was washed twice with Et_2O and dried. Yield 108 mg (83%). For $C_{17}H_{15}Cl_2N_2NiP$ (407.9) calculated: 50.06% C, 3.71% H, 6.87% N; found: 50.04% C, 3.77% H, 6.95% N.

[$NiCl_2$(PN-*i*Pr)] (**2b**)

This complex has been prepared analogously to **2a** with **1b** (390 mg, 1.85 mmol) and [$NiCl_2$(dme)] (405 mg, 1.85 mmol) as the starting materials. Yield 490 mg (78%). For $C_{11}H_{19}Cl_2N_2NiP$ (339.9) calculated: 38.87% C, 5.63% H, 8.24% N; found: 38.94% C, 5.57% H, 8.25% N.

[$PdCl_2$(PN-Ph)] (**3a**)

1a (300 mg, 1.1 mmol) was added to a solution of [$PdCl_2$(cod)] (307 mg, 1.1 mmol) in 20 ml CH_2Cl_2 and the mixture was stirred at room temperature for 2 h. The solvent was then removed under vacuum and the remaining yellow solid was washed twice with Et_2O and dried. Yield 420 mg (88%). For $C_{17}H_{15}Cl_2N_2PPd$ (455.6) calculated: 44.82% C, 3.32% H, 6.15% N; found: 44.92% C, 3.27% H, 6.15% N. ^{1}H NMR (CD_2Cl_2): 10.11 (s, 1 H, NH); 9.00 (d, *J* = 5.8, 6-Hpy); 7.90–7.83 (m, 5 H, Ph); 7.71–7.61 (m, 6 H, Ph and 4-Hpy); 7.13 (d, *J* = 8.2, 3-Hpy); 7.03 (t, *J* = 6.5, 5-Hpy). ^{13}C{^{1}H} NMR (CD_2Cl_2): 161.8 (d, *J* = 10.7, 2-Hpy); 148.9 (6-Hpy); 142.1 (4-Hpy); 133.4 (d, *J* = 2.7, Ph); 132.9 (d, *J* = 12.3, $Ph^{2,6}$); 129.6 (d, *J* = 12.3, $Ph^{3,5}$); 128.8 (Ph^4); 116.7 (5-Hpy); 111.7 (d, *J* = 11.5, 3-Hpy). ^{31}P{^{1}H} NMR (CD_2Cl_2): 79.5.

[$PdCl_2$(PN-*i*Pr)] (**3b**)

This complex has been prepared analogously to **3a** with [$PdCl_2$(cod)] (460 mg, 1.6 mmol) and **1b** (340 mg, 1.6 mmol) as the starting materials. Yield 565 mg (91%). For $C_{11}H_{19}Cl_2N_2PPd$ (387.6) calculated: 34.09% C, 4.94% H, 7.23% N; found: 34.00% C, 4.88% H, 7.25% N. ^{1}H NMR (CD_2Cl_2): 8.90 (s, 1 H, NH); 8.83 (d, *J* = 5.2, 1 H, 6-Hpy); 7.84 (t, *J* = 7.8, 1 H, 4-Hpy); 7.07 (d, *J* = 8.2, 1 H, 3-Hpy); 6.95 (t, *J* = 6.4, 1 H, 5-Hpy); 2.47 (m, *J* = 7.1, 2 H, C**H**$(CH_3)_2$); 1.38–1.20 (m, 12 H, CH(C**H**$_3)_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): 163.1 (d, *J* = 7.3, 2-Hpy); 148.5 (6-Hpy); 141.8 (4-Hpy); 116.3 (5-Hpy); 111.1 (d, *J* = 9.2, 3-Hpy); 28.1 (d, *J* = 32.2, **C**H$(CH_3)_2$); 17.8 (d, *J* = 2.0, CH(**C**H$_3)_2$); 16.8 (d, *J* = 2.5, CH(**C**H$_3)_2$). ^{31}P{^{1}H} NMR (CD_2Cl_2): 125.7.

[$PdCl_2$(PN-BIPOL)] (**3c**)

This complex has been prepared analogously to **3a** with [$PdCl_2$(cod)] (92 mg, 0.32 mmol) and **1c** (100 mg, 0.32 mmol) as the starting materials. Yield 112 mg (74%). For $C_{17}H_{13}Cl_2N_2O_2PPd$ (485.6) calculated: 42.05% C, 2.70% H, 5.77% N; found: 42.14% C, 2.67% H, 2.81% N. ^{1}H NMR (CD_2Cl_2): 9.00 (d, *J* = 5.9, 1 H, 6-Hpy); 7.70 (t, *J* = 7.8, 1 H, 4-Hpy); 7.50–7.32 (m, 8 H, Ph); 7.17 (d, *J* = 7.3, 1 H, 3-Hpy); 6.94 (t, *J* = 7.3, 1 H, 5-Hpy); 6.25 (s, 1 H, NH). ^{13}C{^{1}H} NMR (CD_2Cl_2): 155.6 (d, *J* = 22.2, 2-Hpy); 149.3 (Ph); 148.2 (d, *J* = 12.6, 6-Hpy); 141.5 (4-Hpy); 130.2 (Ph); 128.9 (Ph); 127.2 (Ph); 122.5 (d, *J* = 4.2, Ph); 117.9 (Ph); 117.1 (5-Hpy); 111.6 (d, *J* = 12.6, 3-Hpy). ^{31}P{^{1}H} NMR (CD_2Cl_2): 109.5.

[$PdCl_2$(PN-TAR^{Me})] (**3d**)

This complex has been prepared analogously to **3a** with [$PdCl_2$(cod)] (95 mg, 0.33 mmol) and **1d** (100 mg, 0.33 mmol) as the starting materials. Yield 118 mg (75%). For $C_{11}H_{13}Cl_2N_2O_6PPd$ (477.5) calculated: 27.67% C, 2.74% H, 5.87% N; found: 27.64% C, 2.77% H, 5.75% N. ^{1}H NMR (CD_2Cl_2): 9.17 (d, *J* = 6.2, 1 H, 6-Hpy); 7.33 (d, *J* = 8.2, 4-Hpy); 7.06 (t, *J* = 6.5, 1 H, 3-Hpy); 6.78 (t, *J* = 6.5, 1 H, 5-Hpy); 6.27 (s, 1 H, NH); 5.58 (dd, *J* = 4.3, 14.0, 1 H, CH); 5.41 (dd, *J* = 4.3, 13.9, 1 H, CH); 3.92 (s, 3 H, CH_3); 3.86 (s, 3 H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): 168.0 (CO); 166.1 (CO); 149.5 (2-Hpy); 143.8 (6-Hpy); 142.0 (4-Hpy); 117.1 (5-Hpy); 111.7 (d, *J* = 14.6, 3-Hpy); 77.7 (d, *J* = 5, CH); 76.7 (d, *J* = 7.3, CH); 54.0 (CH_3); 53.8 (CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$): 118.5.

[Pd(η^1-allyl)Cl(PN-Ph)] (**4a**)

1a (160 mg, 0.58 mmol) was added to a solution of [Pd(η^3-allyl)Cl]$_2$ (100 mg, 0.28 mmol) in 15 ml CH_2Cl_2 and the mixture was stirred at room temperature for 2 h. The solvent was removed under vacuum and the remaining yellow solid was washed twice with Et_2O and dried. Yield 217 mg (83%). For $C_{20}H_{20}ClN_2PPd$ (461.2) calculated: 52.08% C, 4.37% H, 6.07% N; found: 52.14% C, 4.47% H, 6.15% N. ^{1}H NMR (CD_2Cl_2): 11.21 (s, 1 H, NH); 8.37 (d, *J* = 4.8, 6-Hpy); 7.90–7.74 (m, 6 H, Ph, 3-Hpy and 4-Hpy); 7.49–7.26 (m, 6 H, Ph); 6.69 (t, *J* = 5.8, 5-Hpy); 5.90 (m, *J* = 10.6, CH); 4.67 (bs, 1 H, =CH); 4.06 (bs, 1 H, =CH); 3.32 (bs, 2 H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): 159.4 (d, *J* = 13.1, 2-Hpy); 149.6 (s, 6-Hpy); 137.8 (4-Hpy); 129.9 (d, *J* = 15.5, Ph^{2,6}); 129.4 (d, *J* = 2.5, Ph^4); 129.1 (Ph^1); 126.7 (d, *J* = 12.0, Ph^{3,5}); 122.8 (CH); 113.7 (5-Hpy); 111.8 (d, *J* = 8.1, 3-Hpy); 82.8 (=CH_2); 45.2 (CH_2). ^{31}P{^{1}H} NMR ($CDCl_3$): 78.4

[Pd(η^1-allyl)Cl(PN-*i*Pr)] (**4b**)

This complex has been prepared analogously to **4a** with **1b** (121 mg, 0.58 mmol) and [Pd(η^3-allyl)Cl]$_2$ (100 mg, 0.28 mmol) as the starting materials. Yield 155 mg (68%). For $C_{14}H_{24}ClN_2PPd$ (393.2) calculated: 42.77% C, 6.15% H, 7.12% N; found: 42.74% C, 6.22% H, 7.15% N. ^{1}H NMR (CD_2Cl_2): 10.40 (s, 1 H, NH); 8.23 (bs, 1 H, 6-Hpy); 7.81 (bs, 1 H, 4-Hpy); 7.56 (bs, 1 H, 3-Hpy); 6.65 (bs, 1 H, 5-Hpy); 5.66 (s, 1 H, CH); 4.66 (s, 1 H, =CH); 3.96 (s, 1 H, =CH); 3.19 (s, 2 H, CH_2); 2.56 (s, 2 H, C**H**(CH_3)$_2$); 1.20 (s, 12 H, CH(C**H**$_3$)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): 163.4 (d, *J* = 10.0, 2-Hpy); 152.5 (6-Hpy); 140.1 (4-Hpy); 121.5 (d, *J* = 5.5, CH); 115.5 (5-Hpy); 113.9 (d, *J* = 7.5, 3-Hpy); 82.0 (d, *J* = 29.0, =CH_2); 44.1 (CH_2); 27.5 (d, *J* = 27.4, CH(CH_3)$_2$); 18.1 (CH(CH_3)$_2$). ^{31}P{^{1}H} NMR ($CDCl_3$): 115.3.

[Pd(η^3-allyl)(PN-Ph)](BF_4) (**5a**)

$AgBF_4$ (112 mg, 0.58 mmol) was added to a solution of [Pd(η^3-allyl)Cl]$_2$ (100 mg, 0.28 mmol) in CH_3CN (15 ml) and the mixture was stirred at room temperature in the dark for 15 min. The solution was then filtered under argon, and **1a** (160 mg, 0.58 mmol), dissolved in 5 ml CH_3CN, was added. The mixture was stirred at room temperature for further 30 min, after which the solvent was removed under vacuum and the remaining off-white solid was washed twice with Et_2O and dried. Yield 273 mg (92%). For $C_{20}H_{20}BF_4N_2PPd$ (512.6) calculated: 46.87% C, 3.93% H, 5.47% N; found: 46.92% C, 3.93% H, 5.50% N. ^{1}H NMR (CD_2Cl_2): 8.34 (d, *J* = 5.3, 1 H, 6-Hpy); 8.24 (d, *J* = 4.2, 1 H, NH); 7.65–7.59 (m, 4 H, Ph,

3-Hpy and 4-Hpy); 7.52–7.48 (m, 9 H, Ph and 5-Hpy); 6.79 (t, *J* = 6.4, =CH); 5.90 (m, 1 H, CH); 4.82 (t, *J* = 6.4, 1 H, =CH); 4.13 (d, *J* = 10.1, 1 H, CH_2); 4.08 (d, *J* = 10.1, 1 H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 159.0 (d, *J* = 13.4, 2-Hpy); 150.9 (6-Hpy); 139.4 (4-Hpy); 130.4 (d, *J* = 2.8, $Ph^{2,6}$); 130.1 (Ph^1); 129.8 (Ph^4); 127.5 (d, *J* = 12.4, $Ph^{3,5}$); 120.9 (d, *J* = 5.7, CH); 115.0 (5-Hpy); 111.9 (d, *J* = 7.4, 3-Hpy); 79.6 (d, *J* = 31.4, $=CH_2$); 49.4 (CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 77.6.

[Pd(η^3-allyl)(PN-*i*Pr)](BF_4) (**5b**)

This complex has been prepared analogously to **5a** with $AgBF_4$ (112 mg, 0.58 mmol), $[Pd(\eta^3\text{-allyl})Cl]_2$ (100 mg, 0.28 mmol) and **1b** (121 mg, 0.57 mmol) as the starting materials. Yield 93 mg (75%). For $C_{14}H_{24}BF_4N_2PPd$ (444.5) calculated: 37.83% C, 5.44% H, 6.30% N; found: 37.90% C, 5.51% H, 6.28% N. ^1H NMR (CD_2Cl_2): 8.30 (d, *J* = 4.6, 1 H, NH); 7.63 (d, *J* = 7.0, 1 H, 6-Hpy); 7.39–7.37 (m, 2 H, 3-Hpy and 4-Hpy); 6.76 (t, *J* = 5.3, 5-Hpy); 5.70 (m, *J* = 6.4, 1 H, CH); 4.76 (s, 1 H, =CH); 4.03–3.92 (m, 2 H, CH_2); 2.69–2.42 (m, 3 H, =CH and C**H**$(CH_3)_2$); 1.22–1.14 (m, 12 H, CH(C**H**$_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 162.4 (d, *J* = 10.0, 2-Hpy); 153.0 (6-Hpy); 140.9 (4-Hpy); 121.5 (d, *J* = 5.5, CH); 116.3 (5-Hpy); 113.1 (d, *J* = 7.0, 3-Hpy); 82.2 (d, *J* = 29.4, $=CH_2$); 45.6 (CH_2); 27.6 (d, *J* = 25.9, $CH(CH_3)_2$); 27.2 (d, *J* = 25.9, $CH(CH_3)_2$); 18.2 (d, *J* = 8.0, $CH(CH_3)_2$); 17.3 (d, *J* = 15.0, $CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 115.4.

X-ray Crystallography

X-ray data for **2b** (in the form of a disordered solvate obtained from acetone/diethyl ether), **5a** and **5b** were collected on a Bruker Smart APEX CCD area detector diffractometer using graphite-monochromatized MoKα radiation (λ = 0.71073 Å) and 0.3° ω-scan frames. Corrections for absorption, λ/2 effects, and crystal decay were applied[19]. After structure solution with program SHELXS97 refinement on F^2 was carried out with the program SHELXL97 [20]. Non-hydrogen atoms were refined anisotropically. All H atoms were placed in calculated positions and thereafter treated as riding. The disordered solvent in **2b** was squeezed with program PLATON [21] and it is not contained in chemical formula and quantities derived thereof. A moderate orientation disorder of the allyl group in **5a** was taken into account. Important crystallographic data for **2b**: $C_{11}H_{19}Cl_2N_2NiP$, M_r = 339.86, red block, 0.35 × 0.32 × 0.20 mm, trigonal, space group *R*-3 (No. 148), *a* = 19.4562(6) Å, *c* = 21.4717(12) Å, *V* = 7039.0(5) $Å^3$, *Z* = 18, μ = 1.666 mm^{-1}, *T* = 173 K. 32221 reflections were collected up to θ_{max} = 30.0° and, after applying absorption corrections, merged to 4559 independent data (R_{int} = 0.029), final *R* indices: R_1 = 0.0267 (4066 reflections with $I > 2\sigma(I)$), wR_2 = 0.0715 (all data), 154 parameters; for **5a**: $C_{20}H_{20}BF_4N_2PPd$, M_r = 512.56, colorless prism, 0.45 × 0.25 × 0.24 mm, orthorhombic, space group $P2_12_12_1$ (No. 19), *a* = 9.9980(4) Å, *b* = 12.7834(5) Å, *c* = 15.9105(6) Å, *V* = 2033.50(14) $Å^3$, *Z* = 4, μ = 1.036 mm^{-1}, *T* = 100 K. 24216 reflections were collected up to θ_{max} = 30.06° and, after applying absorption corrections, merged to 5936 independent data (R_{int} = 0.019), final *R* indices: R_1 = 0.0168 (5852 reflections with $I > 2\sigma(I)$), wR_2 = 0.0432 (all data), 266 parameters; for **5b**: $C_{14}H_{24}BF_4N_2PPd$, M_r = 444.53, colorless prism, 0.40 × 0.16 × 0.14 mm, orthorhombic, space group $P2_12_12_1$ (No. 19), *a* = 10.2776(6) Å, *b* = 11.9892(7) Å, *c* = 15.1736(9) Å, *V* = 1869.7(2) $Å^3$, *Z* = 4, μ = 1.112 mm^{-1}, *T* = 100 K. 24084 reflections were collected up to θ_{max} = 30.17° and, after applying absorption corrections, merged to 5516 independent data (R_{int} = 0.043), final *R* indices: R_1 = 0.0279 (5074 reflections with $I > 2\sigma(I)$), wR_2 = 0.0645 (all data), 208 parameters.

Structure views of **2b**, **5a** and **5b** are shown in Figs 1, 3 and 4 with key bond distances and angles reported in the captions. All complexes exhibit N–H···X hydrogen bonds to adjacent Cl or F atoms. CCDC 635593, 635594 and 635595 (for **2b**, **5a** and **5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Computational Details

All calculations were performed using the Gaussian03 software package on the Silicon Graphics Origin 2000 of the Vienna University of Technology[22]. The geometry and energy of the model complexes and the transition states were optimized at the B3LYP level[23] with the Stuttgart/Dresden ECP (SDD) basis set[24] to describe the electrons of the nickel atom. For the C, N, P, Cl and H atoms the 6-31g** basis set was employed[25]. Vibrational analysis was performed to confirm that the structures of the model compounds have no imaginary frequency. All geometries were optimized without symmetry constraints. Solvation effects were evaluated with the DPCM method[26].

Financial support by the "Hochschuljubiläumsfonds der Stadt Wien" is gratefully acknowledged (Project No. H-1024/2004). D. Benito-Garagorri thanks the Basque Government (Eusko Jaurlaritza/ Gobierno Vasco) for a doctoral fellowship.

REFERENCES

1. a) Newkome G. R.: *Chem. Rev.* **1993**, *93*, 2067; b) Zhang Z. Z., Cheng H.: *Coord. Chem. Rev.* **1996**, *147*, 1; c) Espinet P., Soulantica K.: *Coord. Chem. Rev.* **1999**, *193–195*, 499.
2. a) Uhlig E., Schäfer M.: *Z. Anorg. Allg. Chem.* **1968**, *359*, 67; b) Knebel W. J., Angelici R. J.: *Inorg. Chim. Acta* **1973**, *7*, 713; c) Dieck H. T., Hahn G.: *Z. Anorg. Allg. Chem.* **1989**, *577*, 74.
3. a) Alvarez M., Lugan N., Mathieu R. : *J. Chem. Soc., Dalton Trans.* **1994**, 2755; b) Yang H., Alvarez M., Lugan N., Mathieu R.: *J. Chem. Soc., Chem. Commun.* **1995**, 1721.
4. a) Dahlhoff W. V., Dick T. R., Ford G. H., Kelly W. S. J., Nelson M. S.: *J. Chem. Soc. A* **1971**, 3495; b) Anderson M. P., Bruce C. T., Mattson B. M., Pignolet L. H.: *Inorg. Chem.* **1983**, *22*, 3267; c) McNair R. J., Nilsson P. V., Pignolet L. H.: *Inorg. Chem.* **1985**, *24*, 1935; d) Anderson M. P., Mattson B. M., Pignolet L. H.: *Inorg. Chem.* **1983**, *22*, 2644.
5. a) Uhlig E., Maaser M.: *Z. Anorg. Allg. Chem.* **1966**, *334*, 20515; b) Rigo P., Bressan M.: *Inorg. Chem.* **1975**, *14*, 1491; c) Anderson M. P., Casalnuovo A. L., Johnson B. J., Mattson B. M., Mueting A. M., Pignolet L. H.: *Inorg. Chem.* **1988**, *27*, 1649; d) Wang H. H., Casalnuovo A. L., Johnson B. J., Mueting A. M., Pignolet L. H.: *Inorg. Chem.* **1988**, *27*, 325; e) Costella L., Zotto A. D., Mezzetti A., Zangrando E., Rigo P.: *J. Chem. Soc., Dalton Trans.* **1993**, 3001; f) Zotto A. D., Nardin G., Rigo P.: *J. Chem. Soc., Dalton Trans.* **1995**, 3343; g) Casares J. A., Espinet P., Soulantica K.: *Inorg. Chem.* **1997**, *36*, 5251; h) Alonso M. A., Casares J. A., Espinet P., Soulantica K., Charmant J. P. H., Orpen A. G.: *Inorg. Chem.* **2000**, *39*, 705; i) Alonso M. A., Casares J. A., Espinet P., Valles E., Soulantica K.: *Tetrahedron* **2001**, *42*, 5697.

6. a) Seidel W., Scholer H.: *Z. Chem.* **1967**, *11*, 431; b) Schirmer W., Flörke U., Haupt H. J.: *Z. Anorg. Allg. Chem.* **1987**, *545*, 83; c) Schirmer W., Flörke U., Haupt H. J.: *Z. Anorg. Allg. Chem.* **1989**, *574*, 239; d) Brunner H., Weber H.: *Chem. Ber.* **1985**, *118*, 3380; e) Aucott S. M., Slawin A. M. Z., Woolins J. D.: *J. Chem. Soc., Dalton Trans.* **2000**, 2559.
7. a) Benito-Garagorri D., Becker E., Wiedermann J., Lackner W., Pollak M., Mereiter K., Kisala J., Kirchner K.: *Organometallics* **2006**, *25*, 1900; b) Benito-Garagorri D., Bocokic V., Mereiter K., Kirchner K.: *Organometallics* **2006**, *25*, 3817.
8. a) Speiser F., Braunstein P., Saussine L.: *Organometallics* **2004**, *23*, 2625; b) Speiser F., Braunstein P., Saussine L.: *Organometallics* **2004**, *23*, 2633; c) Speiser F., Braunstein P., Saussine L.: *Acc. Chem. Res.* **2005**, *38*, 784.
9. Frömmel T., Peters W., Wunderlich H., Kuchen W.: *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 907.
10. Blanchard S., Neese F., Bothe E., Bill E., Weyhermüller T., Wieghardt K.: *Inorg. Chem.* **2005**, *44*, 3636.
11. Speiser F., Braunstein P., Saussine L., Welter R.: *Organometallics* **2004**, *23*, 2613.
12. a) Consiglio G., Waymouth R. M.: *Chem. Rev.* **1989**, *89*, 257; b) Tsuji J.: *Pure Appl. Chem.* **1989**, *61*, 1673; c) Trost B. M., van Vranken D. L.: *Chem. Rev.* **1996**, *96*, 395; d) Williams J. M. J.: *Adv. Asym. Synth.* **1996**, 299; e) Helmchen G., Pfalz A.: *Acc. Chem. Res.* **2000**, *33*, 336.
13. Braunstein P., Naud F., Dedieu A., Rohmer M.-M., DeCian A., Rettig S. J.: *Organometallics* **2001**, *20*, 2966.
14. a) Braunstein P., Zhang J., Welter R.: *Dalton Trans.* **2003**, 507; b) Zhang J., Braunstein P., Welter R.: *Inorg. Chem.* **2004**, *43*, 4172.
15. a) Tsarev V. N., Kabro A. A., Moieseev S. K., Kalinin V. N., Bondarev O. G., Davankov V. A., Gavrilov K. N.: *Russ. Chem. Bull., Int. Ed.* **2004**, *53*, 814; b) van Rooy A., Kamer P. C. J., van Leeuwen P. W. N. M., Goubitz K., Fraanje J., Veldman N., Spek A.: *Organometallics* **1996**, *15*, 835.
16. Kadyrov R., Heller D., Selke R.: *Tetrahedron: Asymmetry* **1998**, *9*, 329.
17. Drew D., Doyle J. R.: *Inorg. Synth.* **1990**, *28*, 346.
18. Ward L. G. L.: *Inorg. Synth.* **1972**, *13*, 154.
19. Bruker programs: *SMART*, version 5.625; *SAINT*, version 6.54; *SADABS*, version 2.10; *SHELXTL*, version 6.1. Bruker AXS Inc., Madison (WI) **2003**.
20. Sheldrick G. M.: *SHELX97, Program System for Crystal Structure Determination*. University of Göttingen, Göttingen 1997.
21. Spek A. L.: *PLATON, A Multipurpose Crystallographic Tool*. University of Utrecht, Utrecht 2003.
22. Frisch M. J., Trucks G. W., Schlegel H. B., Scuseria G. E., Robb M. A., Cheeseman J. R., Montgomery J. A., Jr., Vreven T., Kudin K. N., Burant J. C., Millam J. M., Iyengar S. S., Tomasi J., Barone V., Mennucci B., Cossi M., Scalmani G., Rega N., Petersson G. A., Nakatsuji H., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Klene M., Li X., Knox J. E., Hratchian H. P., Cross J. B., Bakken V., Adamo C., Jaramillo J., Gomperts R., Stratmann R. E., Yazyev O., Austin A. J., Cammi R., Pomelli C., Ochterski J. W., Ayala P. Y., Morokuma K., Voth G. A., Salvador P., Dannenberg J. J., Zakrzewski V. G., Dapprich S., Daniels A. D., Strain M. C., Farkas O., Malick D. K., Rabuck A. D., Raghavachari K., Foresman J. B., Ortiz J. V., Cui Q., Baboul A. G., Clifford S., Cioslowski J., Stefanov B. B., Liu G., Liashenko A., Piskorz P., Komaromi I., Martin R. L., Fox D. J., Keith T., Al-Laham M. A., Peng C. Y., Nanayakkara A.,

Challacombe M., Gill P. M. W., Johnson B., Chen W., Wong M. W., Gonzalez C., Pople J. A.: *Gaussian 03*, Revision C.02. Gaussian, Inc., Wallingford (CT) 2004.

23. a) Becke A. D.: *J. Chem. Phys.* **1993**, *98*, 5648; b) Miehlich B., Savin A., Stoll H., Preuss H.: *Chem. Phys. Lett.* **1989**, *157*, 200; c) Lee C., Yang W., Parr G.: *Phys. Rev. B: Condens. Matter* **1988**, *37*, 785.
24. a) Haeusermann U., Dolg M., Stoll H., Preuss H.: *Mol. Phys.* **1993**, *78*, 1211; b) Kuechle W., Dolg M., Stoll H., Preuss H.: *J. Chem. Phys.* **1994**, *100*, 7535; c) Leininger T., Nicklass A., Stoll H., Dolg M., Schwerdtfeger P.: *J. Chem. Phys.* **1996**, *105*, 1052.
25. a) McLean A. D., Chandler G. S.: *J. Chem. Phys.* **1980**, *72*, 5639; b) Krishnan R., Binkley J. S., Seeger R., Pople J. A.: *J. Chem. Phys.* **1980**, *72*, 650; c) Wachters A. J. H.: *Chem. Phys.* **1970**, *52*, 1033; d) Hay P. J.: *J. Chem. Phys.* **1977**, *66*, 4377; e) Raghavachari K., Trucks G. W.: *J. Chem. Phys.* **1989**, *91*, 1062; f) Binning R. C., Curtiss L. A.: *J. Comput. Chem.* **1995**, *103*, 6104; g) McGrath M. P., Radom L.: *J. Chem. Phys.* **1991**, *94*, 511.
26. a) Mierts S., Scrocco E., Tomasi J.: *Chem. Phys.* **1981**, *55*, 117; b) Pascual-Ahuir J. L., Silla E., Tomasi J., Bonaccorsi R.: *J. Comput. Chem.* **1987**, *8*, 778; c) Floris F., Tomasi J.: *J. Comput. Chem.* **1989**, *10*, 616; d) Tomasi J., Persico M.: *Chem. Rev.* **1994**, *94*, 2027.