

Selective Phosphoramidite Cleavage as a Route to Novel Chiral and Achiral Pentacoordinated Nickel(II) PNP Pincer Complexes

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Treatment of $\text{NiBr}_2(\text{DME})$ ($\text{DME} = 1,2\text{-dimethoxyethane}$) or anhydrous NiBr_2 with 2 equiv. of PNP pincer ligands featuring phosphoramidites in CH_2Cl_2 yields the novel neutral pentacoordinate complexes $[\text{Ni}(\text{PNP})\{\kappa^1(\text{P})\text{-R}_2\text{P=O}\}\text{Br}]$. Over the course of this reaction the P–N bonds of the phosphoramidite units of one PNP ligand are selectively cleaved due to hydrolysis affording an anionic $\kappa^1\text{-(P)}$ -coordinated phosphin-

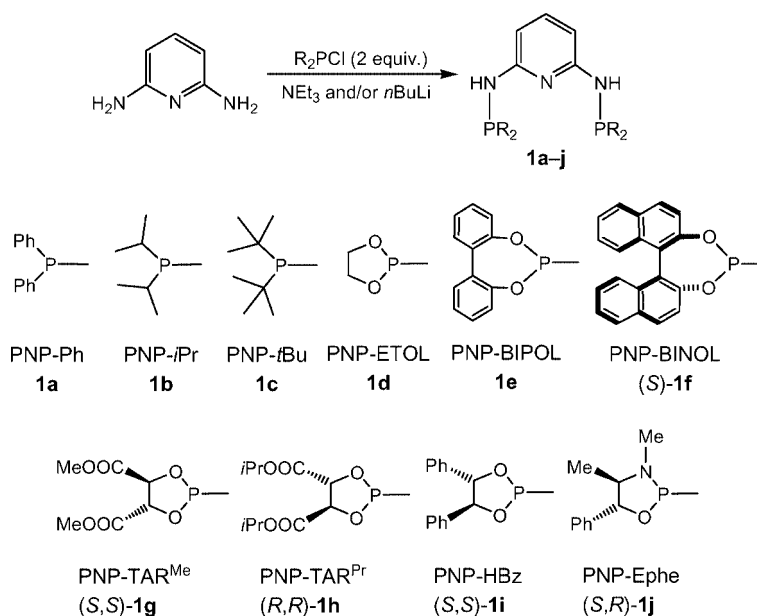
ite ligand $[\text{R}_2\text{P=O}]^-$, while a second PNP ligand remains intact and is coordinated in a $\kappa^3\text{-(P,N,P)}$ fashion. The X-ray structure of one $[\text{Ni}(\text{PNP})\{\kappa^1(\text{P})\text{-PR}_2\text{=O}\}\text{Br}]$ complex has been determined.

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Introduction

Tridentate PNP ligands in which the central pyridine-based ring donor contains $-\text{CH}_2\text{PR}_2$ substituents in the two *ortho* positions are widely utilized ligands in transition metal chemistry (e.g., Fe, Ru, Rh, Ir, Pd, Pt).^[1–10] We have

recently designed an alternative and versatile modular approach for the high-yield synthesis of a new generation of tridentate PNP pincer-type ligands based on 2,6-diaminopyridine and R_2PCL . The latter may contain both bulky and/or electron-rich dialkylphosphanes as well as various



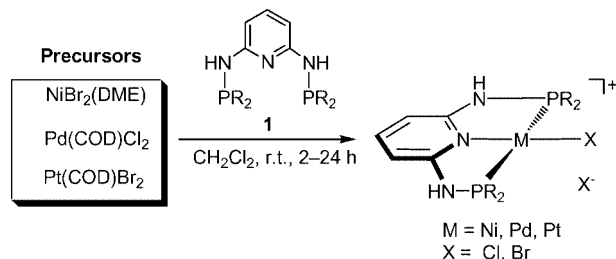
Scheme 1.

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P–O bond containing achiral and chiral phosphite units derived from diols or amino alcohols (Scheme 1).^[11] With this synthetic route it is possible to modify both electronic, steric, and stereochemical parameters of the PNP ligands in a simple and straightforward manner avoiding tedious multi-step syntheses and expensive starting materials.

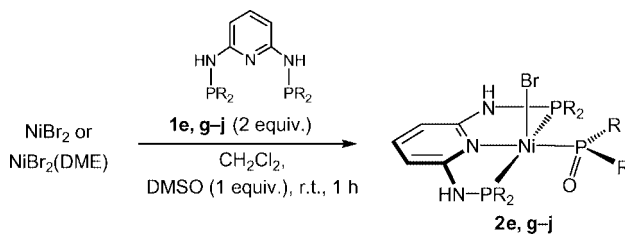
Several of these new PNP ligands have recently been successfully applied to the synthesis of square-planar Ni^{II} , Pd^{II} , and Pt^{II} PNP complexes as shown in Scheme 2.^[11] While in the case of palladium and platinum there were no limitations as to the nature of the PNP ligands, surprisingly with nickel the synthesis of square-planar PNP complexes was limited to the alkyl- and aryl-substituted phosphane ligands **1a–c**, which lack P–O bonds. In the particular case of phosphite ligands hydrolysis of the P–N bond(s) took place presumably because of the presence of small amounts of water in the solvents leading to the formation of decomposition products. It has to be noted that indeed in some instances $\text{P}^{\text{III}}\text{–N}$ bonds turned out to be sensitive towards acid- or base-catalyzed hydrolysis during complexation reactions.^[12] In this paper we utilize one such decomposition pathway as a selective high-yield synthetic route to obtain novel pentacoordinated Ni PNP complexes featuring chiral and achiral PNP ligands together with $\kappa^1\text{-(P)}$ -coordinated phosphinite ligands $\text{R}_2\text{P=O}^-$.



Scheme 2.

Results and Discussion

Treatment of $\text{NiBr}_2(\text{DME})$ ($\text{DME} = 1,2\text{-dimethoxyethane}$)^[13] with 1 equiv. of the PNP ligands **1e**, (*S,S*)-**1g**, (*R,R*)-**1h**, (*S,S*)-**1i**, and (*S,R*)-**1j** (see Scheme 1) in CH_2Cl_2 at room temperature for 16 h afforded the novel neutral pentacoordinate complexes $[\text{Ni}(\text{PNP})\{\kappa^1(\text{P})\text{-PR}_2=\text{O}\}\text{Br}]$ (**2e,g–j**) (Scheme 3). The isolated yields were typically less than 50%. There was no evidence for the formation of other products such as square-planar complexes of the type $[\text{Ni}(\text{PNP})\text{Br}]\text{Br}$. The isolated yields of **2e,g–j** could be significantly improved up to 89% when $\text{NiBr}_2(\text{DME})$ was treated with ≥ 1.5 equiv. of PNP ligand in CH_2Cl_2 as the solvent for 16 h. The same reaction took place if anhydrous NiBr_2 was treated with 2 equiv. of the respective PNP ligands in CH_2Cl_2 in the presence of 1 equiv. of DMSO (or DMF). The addition of these solvents resulted in immediate dissolution of the otherwise insoluble nickel precursor accompanied by a color change of the solution from colorless to bright orange indicating the formation of **2e,g–j**. It has to be emphasized that DMSO does not participate in the reaction as an oxygen-transfer agent but merely increases the solubility of the stated materials. Under these conditions the reaction time could be reduced to 1 h.



Scheme 3.

All complexes have been characterized by a combination of elemental analysis and ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Most diagnostic is the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum exhibiting an A_2X pattern with a doublet in the range of $\delta = 116\text{--}147$ ppm, assignable to the intact PNP ligand, and a triplet in the range of $\delta = 74\text{--}87$ ppm, assignable to the $\kappa^1\text{-(P)}$ -coordinated phosphinite ligand $\text{R}_2\text{P=O}^-$. The J_{PP} coupling constant ranges from 90 to 115 Hz.

In order to unequivocally establish the ligand arrangement around the metal center, the structure of **2i** (in the form of **2i**·MeOH) has been determined by X-ray crystallography. A structural view is depicted in Figure 1 with selected bond lengths and angles given in the caption. The nickel atom exhibits a square-pyramidal coordination with the Br atom in the apical position. The diphenylphosphinite ligand is clearly coordinated through the lone-pair at the P atom rather than through the oxygen lone-pairs. The PNP ligand is coordinated in the typical meridional $\kappa^3\text{-(P,N,P)}$ fashion. Nickel pentacoordination is rare in organometallic chemistry and only about 9% of all complexes adopt this coordination number of which about half belong to the trigonal-bipyramidal and the rest to the square-pyramidal type (Cambridge Structural Data base, CSD, version 5.27, release 2006).^[14] Only one compound was found in this database with a square-pyramidal $\text{Ni}(\text{PNP})(\text{P})\text{Br}$ coordination, however, with the Br atom in the basal and the N atom in the apical position.^[15] Another example with a coordination related to **2i**·MeOH is dibromo{bis[2-(diphenylphosphanyl)ethyl]amine}nickel(II)^[16] having a $\text{Ni}(\text{PNP})\text{Br}_2$ square pyramid with a basal Ni–Br bond of 2.33 Å and an apical Ni–Br bond of 2.70 Å, whereas in **2i**·MeOH the latter measures 2.54 Å on average for the two independent complexes.

Over the course of this reaction, the P–N bonds of one PNP ligand were selectively cleaved to afford a complex with one anionic phosphinite ligand $\text{PR}_2=\text{O}^-$ and one intact $\kappa^3\text{-(P,N,P)}$ -coordinated PNP ligand. Only a few examples of mononuclear complexes with a single $\text{PR}_2=\text{O}^-$ ligand are reported in the literature including $[\text{RuCP}\{\text{C}(\text{CH}_2\text{Ph})\text{-NHPh}\}(\text{PPh}_2\text{NHPh})\{\kappa^1(\text{P})\text{-PPh}_2=\text{O}\}]$,^[17] $[\text{Pt}(\text{PPh}_3)(\text{Ph})\text{-(NC-9-anthracenyl)}\{\kappa^1(\text{P})\text{-PPh}_2=\text{O}\}]$,^[18] and $\text{HNEt}_3\text{-}[\text{W}(\text{CO})_5\{\kappa^1(\text{P})\text{-PPh}_2=\text{O}\}]$.^[19] However, in many cases phosphinite ligands are found in conjunction with the corresponding phosphinous acids PR_2OH to form $\text{R}_2\text{P=O}\cdots\text{H}\cdots\text{O}=\text{PR}_2$ moieties with very strong and almost symmetric hydrogen bonds of $\text{O}\cdots\text{O}$ distances as low as 2.40 Å.^[20–22]

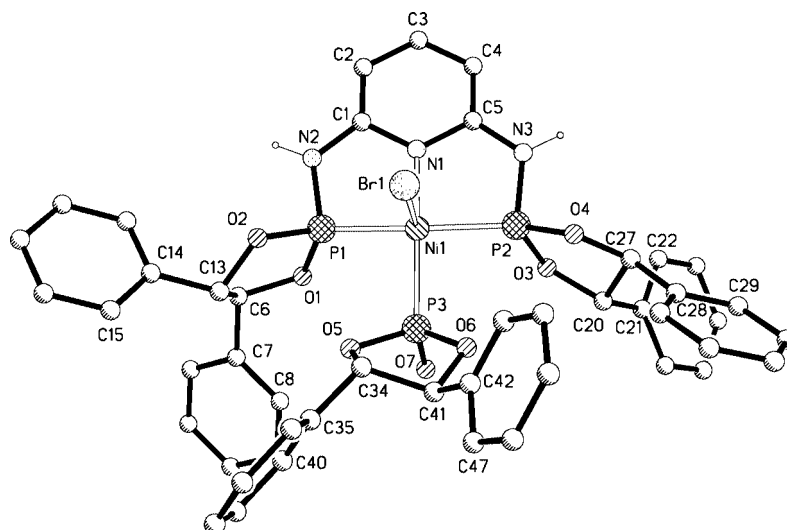


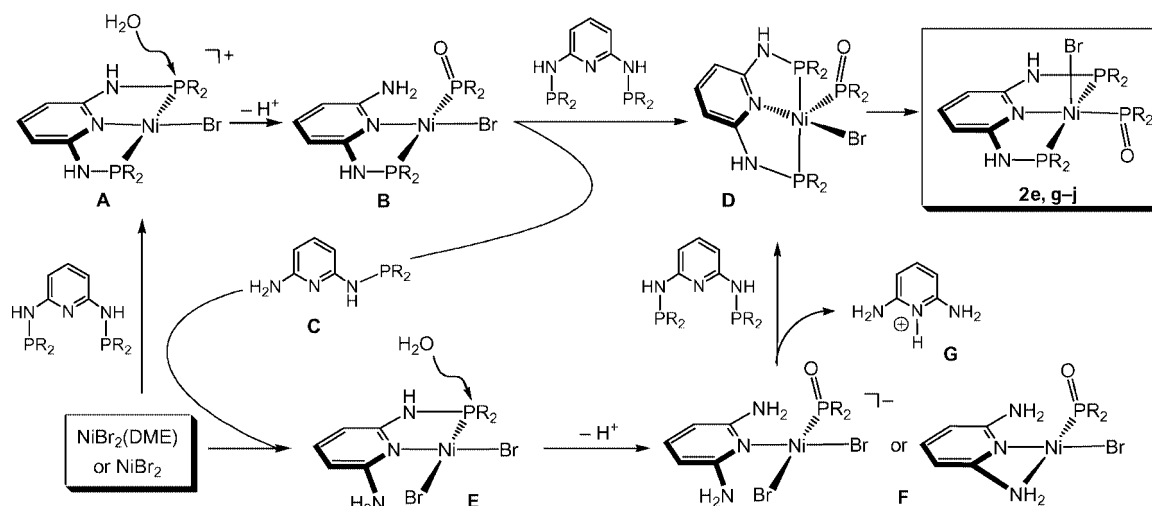
Figure 1. Structural view of $[\text{Ni}(\text{PNP-HBz})\{\kappa^1(\text{P})\text{-HBz-P=O}\}\text{Br}]$ (**2i-CH₃OH**) (second independent Ni complex, C-bonded H atoms and CH₃OH omitted for clarity). Selected bond lengths [Å] and bond angles [°]: Ni(1)–N(1) 1.913(8), Ni(1)–P(1) 2.144(3), Ni(1)–P(2) 2.114(3), Ni(1)–P(3) 2.132(6), Ni(1)–Br(1) 2.535(4); P(1)–Ni(1)–P(2) 157.6(3), N(1)–Ni(1)–P(3) 163.6(4), Br(1)–Ni(1)–N(1) 97.1(4), Br(1)–Ni(1)–P(1) 98.7(2), Br(1)–Ni(1)–P(2) 101.8(2), Br(1)–Ni(1)–P(3) 99.2(2).

A proposed and plausible mechanism for the formation of **2e,g-j** supported by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic studies is depicted in Scheme 4. NMR monitoring of the reaction of $\text{NiBr}_2(\text{DME})$ with varying amounts of PNP-BIPOL (**1e**) ranging from 0.8 to 4 equiv. in CD_2Cl_2 revealed in all cases the formation of an intermediate species that exhibits a characteristic A_2X pattern in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum with a doublet centered at $\delta = 145.7$ ppm and a triplet centered at $\delta = 122.4$ ppm ($J_{\text{PP}} = 109.8$ Hz). This pattern is consistent with a square-pyramidal five-coordinate species **D** where, in contrast to the final product **2e**, the phosphinite ligand is coordinated in the apical position and the Br atom in a basal position. This intermediate isomerizes at room temperature within 16 h to afford quantitatively the final product **2e** exhibiting a doublet centered at $\delta = 145.8$ ppm and a triplet centered at $\delta = 95.4$ ppm ($J_{\text{PP}} = 104.2$ Hz). Surprisingly, in all cases there was no evidence for the formation of any additional phosphorus-containing species as a result of PNP decomposition. In fact, if $\text{NiBr}_2(\text{DME})$ was treated with 0.8 equiv. of **1e**, complex **2e** was cleanly formed after 16 h but the conversion was not quantitative and substantial amounts of the unreacted poorly soluble nickel precursor remained in the NMR tube. If $\text{NiBr}_2(\text{DME})$ was treated with 1.5 equiv. of **1e**, complete consumption of both $\text{NiBr}_2(\text{DME})$ and **1e** took place, while with an excess of **1e** (>1.5 equiv.) $\text{NiBr}_2(\text{DME})$ was completely converted to afford **2e** but unreacted PNP ligand was still present. In the course of all these experiments a white precipitate was formed, which was removed by filtration. Upon dissolution in CD_3CN this compound was unequivocally identified as the 2,6-diaminopyridinium salt **G** giving rise to signals at $\delta = 7.46$ (t, $J = 7.5$ Hz, 1 H, H^5) and 5.92 (d, $J = 7.5$ Hz, 2 H, $\text{H}^{3,4}$) ppm and broad signals at $\delta = 13.4$ (1 H, pyN-H) and 7.2 (4 H, NH_2) ppm, which is in agreement with an authentic sample^[23] of the 2,6-diaminopyridinium cation [cf. the three $\text{p}K_{\text{a}}$ values of 2,6-di-

aminopyridine are 2.16 and 2.90 (NH_2 protonation), and 7.22 (protonation of the pyridine nitrogen atom)].^[24]

In line with the observed stoichiometry (2 equiv. of nickel salt requires 3 equiv. of PNP ligand for quantitative conversion), despite the absence of other detectable intermediates, the reaction may be initiated by the formation of the cationic square-planar $[\text{Ni}(\text{PNP})\text{Br}]^+$ complex **A**. Nucleophilic attack of water at one of the two electrophilic phosphorus atoms of the coordinated PNP ligand leads to P–N bond cleavage affording **B**. This compound reacts readily with another PNP ligand to afford **D**. Thereby the monophosphanylated 2,6-diaminopyridine ligand **C** is released, which in turn reacts with $\text{NiBr}_2(\text{DME})$ to give complex **E** adopting either a square-planar or tetrahedral geometry. The latter reacts again with water to give **F**. The 2,6-diaminopyridine ligand is readily replaced by the tridentate PNP ligand to yield **D** with concomitant release of 2,6-diaminopyridine in the form of its pyridinium cation **G**.

Additional evidence for intermediate **B** comes from the fact that a similar square-planar palladium chloride complex, viz. $[\text{Pd}\{\kappa^2(\text{P,N})\text{-NH}_2\text{-PN-BIPOL}\}\{\kappa^1(\text{P})\text{-BIPOL-P=O}\}\text{Cl}]$ (**4**), was obtained during an attempt to obtain crystals of $[\text{Pd}(\text{PNP-BIPOL})\text{Cl}]\text{Cl}$ (**3**) (Scheme 5). Small amounts of pale-yellow crystals of **4** were repeatedly formed by slow solvent evaporation of a DMF solution of **3** at room temperature over a period of 10 d. The molecular structure of this compound (in the form of **4-DMF**) is shown in Figure 2 with selected bond lengths and angles reported in the caption. The Pd center adopts a distorted square-planar geometry defined by two phosphorus atoms, the central nitrogen atom of the PNP ligand, and a chlorine atom. The PdNP_2Cl coordination deviates significantly from planarity most likely because of a short intramolecular contact between C(28)H and Cl (Figure 1). Moreover, there is a stabilizing short intramolecular hydrogen bond $\text{N}(3)\text{-H}\cdots\text{Cl}$ with $\text{N}\cdots\text{Cl} = 3.15$ Å. It has to be mentioned



Scheme 4.

that structurally related “one-armed” pincer-type platinum complexes have been reported recently.^[25]



Scheme 5.

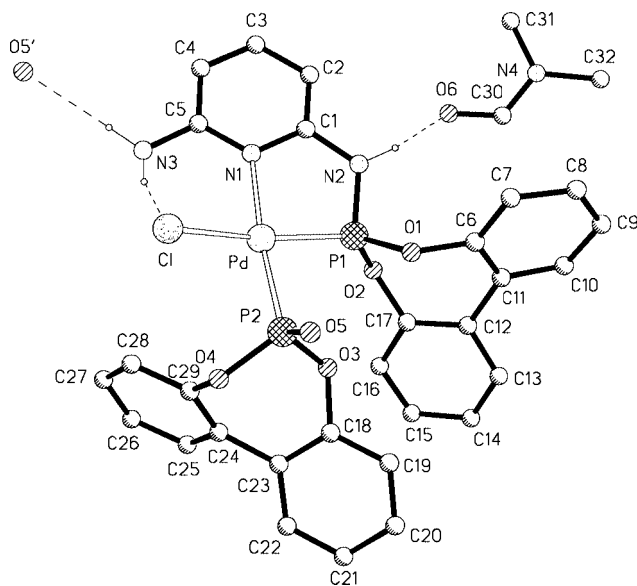


Figure 2. Structural view of $[\text{Pd}\{\kappa^2(\text{P},\text{N})\text{-NH}_2\text{-PN-BIPOL}\}\{\kappa^1(\text{P})\text{-BIPOL-P=O}\}\text{Cl}]\cdot\text{DMF}$ (**4**·DMF) (C-bonded H atoms omitted for clarity). Selected bond lengths [Å] and bond angles [°]: Pd–N(1) 2.171(2), Pd–P(1) 2.1787(5), Pd–P(2) 2.2276(6), Pd–Cl 2.3505(5); P(1)–Pd–P(2) 91.78(2), Cl–Pd–P(2) 86.76(2), N(1)–Pd–P(2) 173.51(5), Cl–Pd–P(1) 165.39(2).

Finally, it has to be noted that phosphoramidite PNP ligands are very stable in CH_2Cl_2 and comparatively stable also in neat DMSO. In the case of PNP-BIPOL (**1e**) about 50% decomposition is observed at room temperature after

16 h leading to the formation of several intractable materials giving rise to signals in the range of $\delta = 6\text{--}20$ ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum [cf. BIPOL- $\text{P}(\text{OH})=\text{O}$, a possible decomposition product, gives rise to a signal at $\delta = 5.71$ ppm].^[26]

Experimental Section

General: All manipulations were performed under argon by using Schlenk techniques. The solvents were purified according to standard procedures. The starting materials (4*S*,5*S*)-2-chloro-4,5-diphenyl-1,3,2-dioxaphospholane,^[27] (4*S*,5*R*)-2-chloro-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine,^[28] PNP-BIPOL (**1e**), PNP-TAR^{Me} (**1g**), PNP-TAR^{Pr} (**1h**), and $[\text{Pd}(\text{PNP-BIPOL})\text{Cl}]\text{Cl}$ (**3**) were prepared according to literature procedures.^[11] The deuterated solvents were purchased from Aldrich and dried with molecular sieves (4 Å). ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded with a Bruker AVANCE-250 spectrometer and were referenced to SiMe_4 and H_3PO_4 (85%), respectively. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR signal assignments were confirmed by ^1H -COSY, 135-DEPT, and HMQC(^1H - ^{13}C) experiments.

***N,N'*-Bis[(4*S*,5*S*)-4,5-diphenyl-1,3,2-dioxaphospholan-2-yl]-2,6-diaminopyridine (PNP-HBz) (**1i**):** (4*S*,5*S*)-2-Chloro-4,5-diphenyl-1,3,2-dioxaphospholane (500 mg, 1.8 mmol) was dissolved in toluene (5 mL) and added to a mixture of 2,6-diaminopyridine (98 mg, 0.9 mmol) and triethylamine (0.25 mL, 1.8 mmol) dissolved in toluene (15 mL). The reaction mixture was stirred at 80 °C for 16 h and insoluble materials were removed by filtration. After removal of the solvent under reduced pressure, **1i** was obtained in an analytically pure form as a white solid. Yield: 363 mg (68%). $\text{C}_{33}\text{H}_{29}\text{N}_3\text{O}_4\text{P}_2$ (593.56): calcd. C 66.78, H 4.92, N 7.08; found C 66.81, H 4.89, N 7.15. ^1H NMR (CDCl_3 , 20 °C): $\delta = 7.38\text{--}7.11$ (m, 21 H, Ph and py^4), 6.43 (d, $J = 8.0$ Hz, 2 H, $\text{py}^{3,5}$), 6.05 (d, $J = 8.2$ Hz, 2 H, NH), 5.24–5.15 (m, 2 H, CH), 5.00–4.81 (m, 2 H, CH) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 20 °C): $\delta = 157.6$ ($\text{py}^{2,6}$), 140.2 (py^4), 136.5 (Ph^1), 129.0 ($\text{Ph}^{2,6}$), 128.5 (Ph^4), 126.7 ($\text{Ph}^{3,5}$), 100.7 ($\text{py}^{3,5}$), 87.2 (CH) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 20 °C): $\delta = 130.0$ ppm.

***N,N'*-Bis[(4*S*,5*R*)-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidin-2-yl]-2,6-diaminopyridine (PNP-Ephe) (**1j**):** This ligand was prepared analogously to **1i** with (4*S*,5*R*)-2-chloro-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine (500 mg, 2.2 mmol), 2,6-diami-

nopyridine (118 mg, 1.1 mmol), and triethylamine (0.30 mL, 2.2 mmol). Yield: 283 mg (52%). $C_{25}H_{31}N_5O_2P_2$ (495.50): calcd. C 60.60, H 6.31, N 14.13; found C 60.54, H 6.42, N 14.25. 1H NMR ($CDCl_3$, 20 °C): δ = 7.37–7.15 (m, 13 H, Ph, $py^{3,5}$ and py^4), 5.86 (d, J = 7.8 Hz, 2 H, NH), 4.71–4.60 (m, 2 H, $CHPh$), 3.77–3.60 (m, 2 H, $CHCH_3$), 2.84–2.63 (m, 6 H, NCH_3), 0.84–0.63 (m, 6 H, $CHCH_3$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ = 157.0 ($py^{2,6}$), 140.1 (py^4), 139.6 (Ph¹), 128.5 (Ph^{2,6}), 126.8 (Ph⁴), 125.8 (Ph^{3,5}), 99.7 ($py^{3,5}$), 81.7 ($CHPh$), 60.2 ($CHCH_3$), 29.1 (NCH_3), 14.6 ($CHCH_3$) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ = 119.0 ppm.

[Ni(PNP-BIPOL){ $\kappa^1(P)$ -BIPOL- $P=O$ }Br] (2e): $NiBr_2$ (150 mg, 0.46 mmol) was suspended in a solution of **1e** (500 mg, 0.93 mmol) in CH_2Cl_2 (5 mL). Upon addition of DMSO (33 μ L, 0.46 mmol), the solution turned deep orange. The mixture was stirred at room temperature for 1 h and the volume of the solution was reduced under vacuum. The orange product was precipitated with Et_2O and dried under vacuum. Yield: 371 mg (89%). $C_{41}H_{29}BrN_3NiO_7P_3$ (907.23): calcd. C 54.28, H 3.22, N 4.63; found C 54.24, H 3.16, N 3.35. 1H NMR ($[D_6]DMSO$, 20 °C): δ = 7.33–7.09 (m, 20 H, Ph), 6.93–6.88 (m, 4 H, Ph), 6.70 (t, J = 7.3 Hz, 1 H, py^4), 6.36 (d, J = 7.3 Hz, 2 H, $py^{3,5}$), 5.80 (d, J = 8.0 Hz, 2 H, NH) ppm. $^{13}C\{^1H\}$ NMR ($[D_6]DMSO$, 20 °C): δ = 155.1 (Ph), 154.3 ($py^{2,6}$), 142.2 (py^4), 132.3–124.4 (Ph), 100.8 ($py^{3,5}$) ppm. $^{31}P\{^1H\}$ NMR ($[D_6]DMSO$, 20 °C): δ = 147.7 (d, J = 98.6 Hz, BIPOL-PNP), 86.6 (t, J = 98.6 Hz, BIPOL-PO) ppm.

[Ni(PNP-TAR^{Me}){ $\kappa^1(P)$ -TAR^{Me}- $P=O$ }Br] (2g): This complex was prepared analogously to **2e** with $NiBr_2$ (205 mg, 0.94 mmol), **1g** (980 mg, 1.87 mmol), and DMSO (68 μ L, 0.94 mmol) as the starting materials. Yield: 672 mg (81%). $C_{35}H_{53}BrN_3NiO_9P_3$ (1051.35): calcd. C 39.99, H 5.08, N 4.00; found C 40.09, H 5.00, N 4.10. 1H NMR ($[D_6]DMSO$, 20 °C): δ = 7.44 (t, J = 8.0 Hz, 1 H, py^4), 6.40 (d, J = 8.0 Hz, 2 H, $py^{3,5}$), 5.83 (d, J = 8.3 Hz, 2 H, NH), 5.03–4.89 (m, 4 H, CH), 4.80–4.61 (m, 2 H, CH), 1.23–1.14 (m, 18 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($[D_6]DMSO$, 20 °C): δ = 170.2 (CO), 166.3 (CO), 159.6 ($py^{2,6}$), 142.1 (py^4), 100.8 ($py^{3,5}$), 95.1 (CH), 76.7 (CH), 45.9 (CH_3), 45.3 (CH_3) ppm. $^{31}P\{^1H\}$ NMR ($[D_6]DMSO$, 20 °C): δ = 146.2 (d, J = 104.2 Hz, TAR^{Me}-PNP), 85.3 (t, J = 104.2 Hz, TAR^{Me}-P=O) ppm.

[Ni(PNP-TAR^{Pr}){ $\kappa^1(P)$ -TAR^{Pr}-PO}Br] (2h): This complex was prepared analogously to **2e** with $NiBr_2$ (290 mg, 1.33 mmol), **1h** (1.6 g, 2.7 mmol), and DMSO (96 μ L, 1.33 mmol) as the starting materials. Yield: 979 mg (70%). $C_{23}H_{29}BrN_3NiO_9P_3$ (883.03): calcd. C 31.28, H 3.31, N 4.76; found C 31.21, H 3.40, N 4.66. 1H NMR ($[D_6]DMSO$, 20 °C): δ = 7.42 (t, J = 7.8 Hz, 1 H, py^4), 6.41 (d, J = 7.8 Hz, 2 H, $py^{3,5}$), 5.81 (d, J = 8.2 Hz, 2 H, NH), 5.06–4.40 [m, 12 H, CH and $CH(CH_3)_2$], 1.23–1.12 (m, 36 H, $[CH(CH_3)_2]$) ppm. $^{13}C\{^1H\}$ NMR ($[D_6]DMSO$, 20 °C): δ = 170.2 (CO), 168.3 (CO), 159.8 ($py^{2,6}$), 145.1 (py^4), 100.8 ($py^{3,5}$), 95.2 (CH), 80.0 (CH), 69.1 $[CH(CH_3)_2]$, 68.8 $[CH(CH_3)_2]$, 21.9 $[CH(CH_3)_2]$, 21.7 $[CH(CH_3)_2]$ ppm. $^{31}P\{^1H\}$ NMR ($[D_6]DMSO$, 20 °C): δ = 146.1 (d, J = 100.8 Hz, TAR^{Pr}-PNP), 85.5 (t, J = 100.8 Hz, TAR^{Pr}-P=O) ppm.

[Ni(PNP-HBz){ $\kappa^1(P)$ -HBz- $P=O$ }Br] (2i): This complex was prepared analogously to **2e** with $NiBr_2$ (54 mg, 0.24 mmol), **1i** (300 mg, 0.49 mmol), and DMSO (18 μ L, 0.24 mmol) as the starting materials. Yield: 132 mg (55%). $C_{47}H_{41}BrN_3NiO_7P_3$ (991.39): calcd. C 56.94, H 4.17, N 4.24; found C 57.04, H 4.19, N 4.31. 1H NMR ($[D_6]DMSO$, 20 °C): δ = 7.29–7.00 (m, 33 H, Ph, py^4 and $py^{3,5}$), 5.70 (d, J = 8.0 Hz, 2 H, NH), 5.24–4.90 (m, 6 H, CH) ppm. $^{13}C\{^1H\}$ NMR ($[D_6]DMSO$, 20 °C): δ = 152.6 ($py^{2,6}$), 144.3 (Ph), 142.5 (py^4), 130.1–127.3 (Ph), 98.8 ($py^{3,5}$), 95.1 (CH), 87.0 (CH) ppm. $^{31}P\{^1H\}$ NMR ($[D_6]DMSO$, 20 °C): δ = 143.4 (d, J = 107.2 Hz, PNP-HBz), 87.8 (t, J = 107.2 Hz, HBz-P=O) ppm.

[Ni(PNP-Ephe){ $\kappa^1(P)$ -Ephe- $P=O$ }Br] (2j): This complex was prepared analogously to **2e** with $NiBr_2$ (175 mg, 0.40 mmol), **1j** (400 mg, 0.80 mmol), and DMSO (29 μ L, 0.40 mmol) as the starting materials. Yield: 213 mg (63%). $C_{35}H_{44}BrN_6NiO_4P_3$ (844.31): calcd. C 49.79, H 5.25, N 9.95; found C 49.69, H 5.09, N 10.05. 1H NMR ($[D_6]DMSO$, 20 °C): δ = 7.40–7.02 (m, 18 H, Ph, py^4 and $py^{3,5}$), 5.60 (s, 2 H, NH), 4.90–4.74 (m, 3 H, $CHPh$), 3.64–3.47 (m, 3 H, $CHCH_3$), 3.22–3.11 (m, 9 H, NCH_3), 0.94–0.72 (m, 9 H, $CHCH_3$) ppm. $^{13}C\{^1H\}$ NMR ($[D_6]DMSO$, 20 °C): δ = 155.7 ($py^{2,6}$), 143.9 (py^4), 141.3 (Ph), 128.6–126.1 (Ph), 99.7 ($py^{3,5}$), 84.5 ($CHPh$), 81.6 ($CHPh$), 65.2 ($CHCH_3$), 59.2 ($CHCH_3$), 30.9 (NCH_3), 28.8 (NCH_3), 15.5 ($CHCH_3$), 9.5 ($CHCH_3$) ppm. $^{31}P\{^1H\}$ NMR ($[D_6]DMSO$, 20 °C): δ = 116.8 (d, J = 114.1 Hz, PNP-Ephe), 74.5 (t, J = 114.1 Hz, Ephe-P=O) ppm.

X-ray Structure Determination: Crystals of **2i** were obtained as **2i**· CH_3OH from diethyl ether diffusion into a saturated CH_3OH solution of **2i**. Crystals of **4** were obtained as **4**·DMF by slow concentration of a DMF solution. X-ray data were collected with a Bruker Smart APEX CCD area detector diffractometer using graphite-monochromated Mo- K_α radiation (λ = 0.71073 Å) and 0.3° ω -scan frames. Corrections for absorption, $\lambda/2$ effects, and crystal decay were applied.^[29] The structures were solved by direct methods using the program SHELXS97.^[30] Structure refinement on F^2 was carried out with the program SHELXL97.^[27] Non-hydrogen atoms were refined anisotropically (for **2i**·MeOH isotropically for C, N, and O atoms). Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they are bonded, except for N -bound hydrogen atoms, which were refined in x,y,z if permitted by data quality. Salient crystallographic data are: **2i**· CH_3OH : $C_{48}H_{45}BrN_3NiO_8P_3$, M_r = 1023.40 g mol⁻¹, orthorhombic, space group $P2_12_12_1$, a = 15.043(12), b = 19.159(12), c = 33.21(3) Å, V = 9572(12) Å³, Z = 8, μ = 1.396 mm⁻¹, T = 173 K. 11282 independent reflections, reflections were collected up to θ_{max} = 23.1°; final R indices: R_1 = 0.131 [5725 reflections with $I > 2\sigma(I)$], wR_1 = 0.365 (all data). All available crystals were thin and bent blades (<0.03 mm), giving broad reflection profiles and poor intensities. Therefore, anisotropic displacement parameters were used only for Ni, Br, and P, and the phenyl rings were refined as idealized rigid groups. Despite the relatively large R values, the structure is sound and hydrogen bonding as well as absolute structure [Flack absolute structure parameter = 0.00(3)] could safely be clarified. The asymmetric unit of the structure contains two independent Ni complexes and methanol molecules mutually linked through hydrogen bonds with $N-H$ and $O-H$ as donors and the Br and phosphinite O atoms as acceptors. Only one of the two independent Ni complexes is shown in Figure 1. **4**·DMF: $C_{32}H_{29}ClN_4O_6P_2Pd$, M_r = 769.38 g mol⁻¹, monoclinic, space group $P2_1/c$, a = 9.4778(4), b = 13.7127(6), c = 24.2252(10) Å, β = 94.642(1)°, V = 3138.1(2) Å³, Z = 4, μ = 0.831 mm⁻¹, T = 173 K. 9147 independent reflections, reflections were collected up to θ_{max} = 30.0°; final R indices: R_1 = 0.0330 [7211 reflections with $I > 2\sigma(I)$], wR_1 = 0.0768 (all data). A view of the molecular structure with all hydrogen bonds is shown in Figure 2. CCDC-608245 (**2i**· CH_3OH) and -608246 (**4**·DMF) 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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