Cationic and neutral Ni^{II} complexes containing a non-innocent PNP ligand: formation of alkyl and thiolate species[†]

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The synthesis and characterization of a series of cationic and neutral Ni-complexes with the non-innocent **PNP**^{tBu} pincer ligand is discussed. Starting with the dicationic complex **1**, $[Ni(PNP^{tBu})(NCMe)](BF_4)_2$, a small series of dicationic and monocationic Ni^{II} complexes has been prepared. Substitution with *tert*-butyl isocyanide and azide occurs readily in MeCN solution. IR spectroscopy provided a practical handle to access the formal valence state of the ligand. For the mono-and dicationic *tert*-butyl isocyanide species **3** and **6** the main vibrational bands in the IR spectra were reproduced quantitatively by DFT theoretical calculations, showing good agreement with the experimentally observed Δv upon dearomatization of the **PNP**^{tBu} backbone. Using a selective dearomatization-reprotonation methodology the mononuclear Ni-thiolate species **7** and **8** are cleanly generated and their structures have been determined by X-ray crystal structure determination. Alternatively, starting from the monocationic species [Ni(**PNP**^{tBu})Cl]BF₄, neutral alkyl derivatives are easily available in a two-step procedure, and these species have been spectroscopically characterized.

Introduction

Among the plethora of bulky phosphorus-containing pincer systems applied in coordination and organometallic chemistry during the last decades,1 most are based on a formally monoanionic scaffold upon ligation to a transition metal complex. The 'archetypical' PCP-framework A (with both aliphatic and aromatic core structures) was originally developed by Shaw et al. and then further developed by a number of groups over several decades.² Fryzuk et al. designed the PNP-ligand **B** and elegantly utilized it in N₂-activation chemistry,³ while Caulton et al. have prepared several low-coordinate 14e⁻ species with this particular ligand scaffold as well.⁴ The diphenylamide derived PNP-ligands, structure C, independently prepared by Mayer et al.⁵ and Liang et al.6 and thereafter mainly used by the groups of Ozerov⁷ and Mindiola⁸ are newer examples of meridional monoanionic PNP ligands. Lately, the chemistry of neutral PNP^R-based pincer ligands9 has attracted renewed attention as platform for late transition metal complexes.¹⁰ One special feature of these 2,6lutidine derived systems is their ease of deprotonation of the methylene spacer group (to yield **PN**⁻**P**^R, see Fig. 1), effectively making this a 'non-innocent' class of ligands, as recently explored to great extent and in great detail by Milstein and co-workers, including also analogous PNN derivatives.11



Fig. 1 Generalized structures of representative, monoanionic pincer ligand scaffolds and the class of neutral, non-innocent PNP^R ligands that can undergo deprotonation.

We have applied the neutral (pseudo-)pincer ligand **PNP**^{tBu} to construct a number of Cu¹ complexes wherein the pyridine nitrogen atom exhibits unexpected hemilabile coordination to the Cu-center.¹² We thereafter decided to extent this methodology to Ni and now report on the formation of complex 1, containing a labile MeCN-ligand, that serves as the starting material for a study into the formation of monomeric thiolato-species as well as Ni^{II}-alkyl complexes, by making use of the non-innocent character of the **PNP**^{tBu} backbone.

Results and discussion

Complex 1 is prepared in a straightforward manner by the stoichiometric reaction of $[Ni(NCMe)_4](BF_4)_2$ and **PNP^{rBu}** in MeCN as a deep-yellow crystalline solid. The ³¹P NMR spectrum showed a singlet at δ 69.0, while the presence of the MeCN coligand was corroborated with a triplet at δ 3.03 in the ¹H NMR

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Fig. 2 Displacement ellipsoid plots (50% probability level) of complex **1**, $[Ni(PNP^{tBu})(NCMe)](BF_4)_2$ (left), and complex **2**, $[Ni(PNP^{tBu})(N_3)]BF_4$ (right). Hydrogen atoms and non-coordinated solvent molecules are omitted for clarity. Selected distances (Å) and angles (°) for **1**: $Ni-P_1$ 2.2289(7); $Ni-P_2$ 2.2295(7); $Ni-N_1$ 1.9132(19); $Ni-N_2$ 1.842(2); N_2-C_{24} 1.133(3); P_1-Ni-P_2 173.90(3); P_1-Ni-N_1 87.40(6); P_2-Ni-N_1 86.61(6); P_1-Ni-N_2 92.10(6); P_2-Ni-N_2 93.85(6); N_1-Ni-N_2 177.93(9); $Ni-N_2-C_{24}$ 177.6(2); for **2**: $Ni-P_1$ 2.2043(7); $Ni-P_2$ 2.2038(7); $Ni-N_1$ 1.9179(19); $Ni-N_2$ 1.882(2); N_2-N_3 1.078(3); P_1-Ni-P_2 171.60(3); P_1-Ni-N_1 87.34(6); P_2-Ni-N_1 87.25(6); P_1-Ni-N_2 92.70(7); P_2-Ni-N_2 93.44(7); N_1-Ni-N_2 173.04(10); $Ni-N_2-N_3$ 139.0(2).

spectrum. Recrystallization from MeCN-Et₂O gave yellow plates that were subjected to X-ray crystal structure determination. The molecular structure is shown in Fig. 2 (left). Slightly distorted square planar geometry is observed around the Ni^{II} center, with in-plane coordination of the pyridine fragment, unlike what was observed with Cu^I previously by us.¹² The P₁–Ni–P₂ angle of 173.90(3)° is significantly smaller than for related cationic Pdcomplexes.¹³

Reaction of **1** with one equiv NaN₃ in MeCN (Scheme 1) yielded a burgundy-red solid [Ni(**PNP**^{tBu})(η^1 -N₃)]BF₄ (**2**) in 30 minutes, with IR bands at v 2069, 1601, 1565 cm⁻¹, the former of which is indicative of terminal end-on coordination of the N₃ ligand.¹⁴ These observations were substantiated by X-ray crystal structure determination, as illustrated in Fig. 2 (right), confirming the substitution of the labile MeCN ligand with the monoanionic azido-fragment.

PNP^{tBu}



Scheme 1 Synthesis of complexes 1-6 with ligand PNP^{tBu}

Subtle structural differences are found when comparing the solid-state structures for both compounds, mainly related to the Ni-P and Ni-N₂ distances, which originates from the anionic character of the azido ligand. Rapid substitution of the labile acetonitrile fragment of 1 also occurred with the strong, neutral donor ligand tert-butyl isocyanide to give species 3, even in MeCN solution. The observed ¹H, ³¹P NMR and IR spectroscopic features (δ 1.78 (CN^{tBu}); δ 81.7; v 2188, 1607, 1565 cm⁻¹) indicated full conversion to [Ni(PNP^{tBu})(CN^tBu)](BF₄)₂. In contrast, PMe₃ in MeCN or excess cyclooctene in THF/CH₂Cl₂ failed to displace the MeCN-ligand under identical conditions, suggesting mainly steric control over the substitution. Addition of an excess of the weakly nucleophilic, poorly soluble reagent LiNH₂ to a MeCN-solution of 1 did not lead to reactivity such as observed by Campora, whereby a Ni(PCP)-amido species was selectively formed,15 but the NMR and IR spectroscopic features indicated that selective dearomatization of the neutral PNP ligand, to give the formally monoanionic PN-P derivative, had occurred instead.

A more convenient method to prepare and isolate such a monoamido complex is by reaction of complex 1 with one equiv NaN(SiMe₃)₂ in THF, analogous to other metal complexes with this PNP-ligand system; a color change from yellow to dark redbrown was apparent within minutes for the thus generated complex 4 in solution. A first estimation of the different bond strength of this monoanionic diphosphino-amido ligand was obtained by reaction of complex 2 with the same base, yielding an orangecolored neutral solid with an IR band at v 2055 cm⁻¹, formulated at Ni(PNP^{tBu})(η^1 -N₃) (complex 5), which was not completely characterized. In effect, the IR band for $v_{N=N}$ has shifted by 14 cm⁻¹ upon deprotonation of the PNP-framework, itself evidenced by the presence of a strong band at 1613 cm⁻¹. Similarly, one equiv of tert-butyl isocyanide was added to the in situ generated complex 4 to give a purple solid for complex 6. Coordination via the generated amido-unit was confirmed by the single strong IR band at v 1618 cm⁻¹, whilst the band at v 2164 cm⁻¹ for the isocyanide ligand, compared with 2188 cm⁻¹ for the dicationic analogue 3,

illustrates the increased electron density at the Ni-center and the *trans*-influence of the amido *vs.* pyridine donor.

To support the aforementioned assignments of the observed IR spectroscopic features, we turned to DFT-based analytic calculation of harmonic normal modes. The quantum chemical calculations were all performed at B3LYP/6-31G(d) level using the Gaussian 03 program package.16 To minimize computing time, the tert-butyl substituents on the phosphorus atoms were replaced by methyl groups to yield complex 3' and 6'; this should not drastically alter the electronic properties of the ligand set. Full geometry optimization of species 3 and 6 was performed, followed by analysis of normal vibrational modes, which were computed analytically. It is common, well-accepted practice to apply a scaling factor when comparing theoretical IR data with experimentally observed values; typically the value for this factor varies marginally for different sections of the IR spectral range. For the current computations, the applied scaling factor is 0.95 for the cyanide region (v_{CN} stretch) and 0.97 for the region v_{Nnv} vibrations. After correction with said scaling factors, calculated dicationic complex 3' exhibits bands at v 2188, 1606, 1565 cm⁻¹. The first band originates from the C≡N stretch, while the other two bands relate to the coordinated pyridine ring.¹⁷ For the deprotonated complex 6' those bands were observed at v 2160, 1634, 1540 cm⁻¹. There is a negligible effect of the absolute conformation of the PNP-pincer arms on the absolute values of these vibrations.¹⁸ Even with possible solvent-derived effects for the experimental data and despite the slight alterations on the P-atom substituents, the agreement between experimental and theoretical data is good, both with regards to the absolute values of the relevant vibrations in complexes 3' and 6' as well as concerning the observed Δv shift in the v_{CN} stretch upon dearomatization.

Although complex 4 did not show reactivity towards H_2O or ethanol at room temperature, which is in contrast with related Pt-complexes using a PNN-ligand scaffold,¹⁹ use of more acidic substrates did result in electrophilic substitution of the MeCNligand and reprotonation of the pyridine ring (Scheme 2). This two-step route allows the clean incorporation of functional groups at the Ni-center in combination with the non-innocent PNP scaffold.

As protonation of the dearomatized backbone in effect generates a reactive thiolate fragment that subsequently substitutes the labile MeCN-ligand, this synthetic methodology circumvents the formation of unwanted side-products such as salts, which would be generated *via* a more traditional anion-exchange reaction, that would hamper isolation of the desired product. Thus, addition of one equiv benzylmercaptan to a brownish solution of **4** in MeCN instantaneously led to a color change to deep green. The resulting solid showed a singlet at δ 49.5 in the ³¹P NMR spectrum for complex **7**. Single crystals were obtained from THF-pentane and the resulting molecular structure is displayed in Fig. 3. A green initial solid was also obtained with thiophenol (³¹P NMR: δ 50.0), but although stable as a solid for extended periods of time, this product appeared to be unstable in solution over the course of crystallization in THF/pentane and CH₂Cl₂/hexane, leading to the formation of a brown microcrystalline material which so far has eluded further identification. The intended complex **8** could only be isolated as the minor product from such mixtures as a green crystalline material with identical spectroscopic characteristics as the crude green solid obtained after reaction; the molecular structure is shown in Fig. 4. Similar observations, *i.e.* formation of a green reaction solution and isolation of a crude green solid, could be made from the reaction of **1** with NaSPh in THF.



Fig. 3 Displacement ellipsoid plot (50% probability level) of complex 7 [Ni(**PNP**^{tBu})(SCH₂Ph)]BF₄. Hydrogen atoms and counterion are omitted for clarity. Selected distances (Å) and angles (°): Ni–P₁ 2.2085(6); Ni–P₂ 2.2419(6); Ni–N 1.9655(18); Ni–S 2.2110(6); S–C₂₄ 1.825(3); P₁–Ni–P₂ 169.40(2); P₁–Ni–N 86.70(6); P₂–Ni–N 85.98(6); P₁–Ni–S 88.30(3); P₂–Ni–S 100.10(3); N–Ni–S 169.70(6); Ni–S–C₂₄ 117.86(9).

Sonication of the crude green solid with diethyl ether led to a brown solution and a green precipitate that showed identical spectroscopic features as the isolated complex **8**. Initial tests show that also phenols appear to lead to fast decomposition of the initial green adduct. The structures and mechanism of formation of these apparent decomposition products are currently under investigation.

The chemistry of nickel thiolate complexes attracts increasing interest due to their likely role in biocatalytic systems such as



Scheme 2 Synthesis of complexes 7 and 8 with ligand PNP^{tBu}.



Fig. 4 Displacement ellipsoid plot (50% probability level) of complex **8**, Ni(**PNP**^{tBu})(SPh)]BF₄. Hydrogen atoms and counterion are omitted for clarity. Selected distances (Å) and angles (°): Ni–P₁ 2.2639(5); Ni–P₂ 2.2299(5); Ni–N 1.9534(14); Ni–S 2.1751(5); S–C₂₄ 1.7727(18); P₁–Ni–P₂ 167.399(19); P₁–Ni–N 83.69(4); P₂–Ni–N 85.14(4); P₁–Ni–S 105.043(18); P₂–Ni–S 87.051(17); N–Ni–S 166.11(4); Ni–S–C₂₄ 118.54(6).

NiFe hydrogenase.²⁰ Notwithstanding the inherent instability of the latter complex, both compounds 7 and 8 feature a mononuclear four-coordinate nickel center with a single Ni-thiolate linkage. Such species remain to be quite rare, and only a handful of complexes have been described recently,²¹ most of which feature similar low spin, square planar geometry as is the case in the present complexes 7 and 8. As such, the Ni-S bond lengths fall in the observed range for terminal nickel monothiolate species, at 2.2110(6) Å (for 7) and 2.1751(5) Å (for 8). The slight difference of ~0.06 Å between the two species probably reflects the less-electron donating character of the aromatic scaffold of the thiophenolate ligand. A subtle but significant asymmetry is observed in the Ni-P distances in both 7 and 8, with bond length differences Δd of 0.0334 Å and 0.034 Å, respectively, the shorter Ni–P bond distance being with the phosphine toward which the sulfur-atom is deviating; the latter is implied by the N-Ni-S angles of 169.70(6) and 166.11(4)°, respectively. The origin of this difference in Ni–P bond lengths is uncertain at the moment; steric hindrance from the thiolate with the tert-butyl substituents would most likely argue against the observed trend and it is therefore speculated to be related to an electronic interaction from the thiolate S-atom. Lastly, significant differences exist for the observed interplanar angles between the least-squares planes of the central pyridine ring and the NiL₄ coordination plane, with the following values: complex 1 12.62(10)°; 2 5.66(10)°; 7 8.62(9)°; 8 22.93(7)°. This shows the relatively high degree of flexibility in the PNP-framework and the ease of twisting in the methylene spacer groups to best accommodate the optimal structure for crystallization.

Besides nickel thiolates, nickel alkyl complexes gain increasing importance as these species are inferred as catalytic intermediates for a range of organic transformations, such as hydrovinylation, Heck and Kumada coupling and polymerization reactions. Insight into the directed synthesis and controlled reactivity of such alkyl species might aid the development of more active or selective catalyst systems.

Reaction of NiCl₂(dme) (dme = 1,2-dimethoxyethane) with a stoichiometric amount of PNP^{tBu} and NaBF₄ in CH₂Cl₂ yielded red complex 9 after 16 hours (Scheme 3). Alternatively, complex 9 can be prepared by reaction of NiCl₂(dme) with the transmetallating agent [Ag(PNP^{tBu})]BF4²² in THF-MeCN. Recrystallization from CH₂Cl₂/hexane vielded dark-red blocks that were suitable for X-ray diffraction; the molecular structure (not shown; see Table 1 for details) clearly showed square-planar coordination around Ni, comparable to other complexes discussed here. Subsequent reaction (Scheme 3) with one equiv NaN(SiMe₃)₂ resulted in a color change to green-brown, and the resulting green-brown solid had one strong band at v 1612 cm⁻¹ in the IR spectrum, suggestive of the formation of NiCl(PN⁻P^{tBu}), as two inequivalent phosphorus atoms were observed in the ³¹P NMR spectrum at δ 45.7 and 39.8 in C₆D₆, with a coupling constant ${}^{2}J_{P-P}$ of 293 Hz. In the ¹H NMR spectrum, three signals were present for the protons on the dearomatized pyridine ring at 6.25, 6.03 and 5.12 ppm (in C_6D_6). Moreover, two doublets (intensity ratio 1:2) at 3.22 and 2.27 ppm for the methine and methylene fragments and two doublets (ratio 1:1) at 1.59 and 1.24 ppm (for the tertbutyl groups of inequivalent phosphines) were discernable. With the PNP framework present in its deprotonated version, any further reactivity of complex 10 toward nucleophiles is strictly limited to the Ni^{II} center. In the course of our investigations, Milstein and co-workers disclosed some interesting substitution chemistry of a Pt(PN-N)Cl complex, showing that this species preferentially underwent addition of alkyllithium species, to form anionic compounds of the formula [Pt(PN-N)(R)Cl]Li rather than substitution of the halide co-ligand. Protonation of the dearomatized PN-N backbone yielded neutral Pt(PNN)(R)Clcomplex.19



Scheme 3 Synthesis of complexes 10–13 via sequential dearomatization and selective alkylation.

	1	2	7	8	9
Formula	$\begin{array}{c} [C_{25}H_{46}N_2NiP_2] \ (BF_4)_2 \cdot \\ CH_3CN \end{array}$	$[C_{23}H_{43}N_4NiP_2](BF_4)$	$[C_{30}H_{50}NNiP_2S](BF_4)$	$[C_{29}H_{48}NNiP_2S](BF_4)$	$\left[\mathrm{C}_{23}\mathrm{H}_{43}\mathrm{ClNNiP}_2\right](\mathrm{BF}_4)$
FW	709.96	583.07	664.23	650.20	576.49
Crystal colour	Yellow	Red	Green	Brown	Red
Crystal size/mm ³	$0.30 \times 0.24 \times 0.06$	$0.27 \times 0.18 \times 0.15$	$0.66 \times 0.51 \times 0.12$	$0.51 \times 0.48 \times 0.39$	$0.45 \times 0.36 \times 0.18$
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	<i>P</i> 1̄ (no. 2)	$P2_1/c$ (no. 14)	<i>P</i> 1̄ (no. 2)
a/Å	11.8057(1)	14.9094(2)	8.7077(2)	14.2312(1)	8.3356(1)
b/Å	15.4958(2)	12.4818(2)	11.0192(3)	13.7370(1)	12.2538(1)
c/Å	20.2129(2)	15.5634(2)	17.2498(4)	18.1600(1)	14.6565(2)
$\alpha/^{\circ}$	90	90	94.763(1)	90	73.5826(5)
β/°	112.5118(8)	105.6351(6)	90.893(2)	117.1778(3)	75.8775(6)
$\gamma/^{\circ}$	90	90	101.983(1)	90	87.7751(8)
V/Å ³	3415.96(7)	2789.12(7)	1612.58(7)	3158.21(4)	1391.89(3)
Z	4	4	2	4	2
$D_{\rm x}/{\rm g~cm^{-3}}$	1.380	1.389	1.368	1.367	1.376
$(\sin \theta / \lambda)_{\rm max} / {\rm \AA}^{-1}$	0.65	0.65	0.65	0.65	0.65
Refl. meas./unique	37081/7806	33661/6389	26222/7366	77735/7246	34132/6356
μ/mm^{-1}	0.728	0.857	0.810	0.825	0.947
Abs. corr.	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Abs. corr. range	0.90-0.96	0.83-0.88	0.71-0.91	0.52-0.72	0.60-0.84
Param./restraints	439/285	400/291	374/0	364/0	338/123
$R1/wR2 (I > 2\sigma(I))$	0.0379/0.0926	0.0377/0.0885	0.0434/0.1186	0.0328/0.0839	0.0255/0.0633
<i>R</i> 1/ <i>wR</i> 2/all refl.	0.0595/0.1040	0.0554/0.0975	0.0477/0.1231	0.0407/0.0885	0.0305/0.0659
S	1.112	1.069	1.055	1.032	1.031
Res. density/e Å ⁻³	-0.40/0.45	-0.41/0.69	-1.07/1.97	-0.42/0.71	-0.29/0.50

Table 1Selected crystallographic data for complexes 1, 2, 7, 8 and 9

As the labile, acidic PNP-backbone has already been deactivated, use of strong bases does not result in further deprotonation of a methylene spacer but instead should furnish clean substitution chemistry at the metal center. To probe the subsequent reactivity of the Ni-center, one equiv of PhLi or MeLi was added to a solution of 10 in Et₂O at -40 °C, leading to a color change from green to brown-red upon warming the solution and formation of complexes 11 and 12, respectively. The resulting product was extracted into pentane and characterized by NMR spectroscopy. The deprotonated PN-P^{tBu} backbone remained intact, as evidenced by the three, slightly shifted, signals for the inequivalent protons on the dearomatized pyridine ring in the ¹H NMR spectrum. The protons of the methyl-ligand in 12 were present as a triplet at -0.08 ppm. In the ³¹P NMR spectrum an AB pattern of doublets was observed for the two inequivalent phosphorus atoms at 43.9 and 41.3 ppm for 11 (41.5 and 37.6 ppm for 12) with a coupling constant ${}^{2}J_{P,P}$ of 236 Hz for 11 (250 Hz for 12), slightly smaller than that of the starting material. Future experiments will probe the reactivity of these neutral Ni-alkyl species toward inter alia weak acids, aimed at formation of the corresponding cationic rearomatized pyridyl-based analogues. This will not be trivial, as Ni-alkyl fragments are known to be more labile compared with the heavier Pt-derivatives.

Addition of one equiv LiAlH₄ (1.0 M in Et₂O) to a solution of **10** in Et₂O gave an instantaneous colour change from greenbrown to red and the corresponding red solid exhibited a doublet of doublets at δ –18.4 in the ¹H NMR spectrum (J_{P-H} of 62 and 55 Hz) for the resulting terminal hydride ligand in complex **13**.

Conclusions

In summary, we have described the use of complex 1, $[Ni(PNP^{HBu})(NCMe)](BF_4)_2$ as a versatile building block for the

synthesis of well-defined mononuclear Ni^{II}-species, exemplified by the isolation of rare mononuclear monothiolate complexes 7 and 8. The non-innocent character of the PNP^{(Bu} ligand leads to significant electronic changes, as investigated for the dication 3 and the related monocation 6, both featuring a *tert*-butyl isocyanide co-ligand. DFT calculations reproduced the observed IR spectral features of both complexes and supported our assignment of the deprotonated PN-PtBu ligand as a monoamido fragment. Dearomatization of the PNP^{1Bu} pincer scaffold also provided access to the efficient synthesis of new neutral Ni-complexes with Ph, Me or H as co-ligand, as derived from spectroscopic investigations. We are currently investigating the reactivity of these neutral Ni-complexes (e.g. in Kumada-coupling and other C-C bond forming reactions²³). Also the redox-chemistry of the neutral Ni^{II}-complex 10 with the non-innocent PNP^{tBu} ligand is envisaged to be interesting and might lead to unusual reactivity.24

Experimental

General considerations

Solvents were purified by established procedures and all experiments were carried out using standard Schlenk techniques in flame-dried glassware. Starting materials were purchased from commercial sources and used as received. Microanalyses were performed by the Department of Organic Chemistry at the TU Eindhoven and by Kolbe Laboratories, Mülheim a/d Ruhr. IR spectra (ATR reflectance mode) were recorded with a Nicolet Avatar 360 FT-IR, NMR spectra were recorded on a Varian 200 spectrometer or Varian Mercury 400 spectrometer and calibrated to the residual proton and carbon signals of the solvent (¹H) or external 85% aqueous H₃PO₄ (³¹P{¹H}). [Ni(NCMe)₄](BF₄)₂,²⁵ $\rm NiCl_2(dme)^{26}$ and PNP^{tBu27} were prepared according to literature procedures.

Nickel complex 1, [Ni(PNP^{1Bu})(NCMe)](BF₄)₂. A solution of [Ni(NCMe)₄](BF₄)₂ (350.0 mg, 882.7 µmol) in MeCN (30 mL) was added dropwise to a solution of **PNP^{1Bu}** (349.1 mg, 882.7 µmol) in MeCN (20 mL) by means of a cannula at room temperature. The resultant purplish-blue solution turned yellow within 10 minutes, and was subsequently stirred for 4 h. Filtration and evaporation of solvent *in vacuo* left a yellow solid. Recrystallization from a concentrated acetone solution yielded light-yellow crystalline material in good yield (448.7 mg, 670.9 µmol, 76%). ³¹P-NMR (80.9 MHz, acetone-d₆): δ 69.2 (s). ¹H-NMR (200 MHz, acetone-d₆): δ 8.14 (t, J_1 =8.0 Hz, 1H, *p*-ArH), 7.74 (d, J_1 = 8.0 Hz, 2H, *m*-ArH), 4.26 (vt, 4H, -CH₂), 3.02 (t, J = 2.0 Hz, 3H, NCMe), 1.64 (vt, 36H, ¹Bu). IR (ATR, cm⁻¹): v 1604 (w), 1564 (w). El. Anal. Calcd. for C₂₅H₄₆B₂F₈N₂NiP₂: C, 44.89; H, 6.93; N, 4.19. Found: C, 45.06; H, 6.95; N, 4.41.

Nickel complex 2, [Ni(PNP^{IBu})(N₃)]BF₄. To a solution of 1 (250.0 mg, 373.7 µmol) in MeCN (20 mL) was added NaN₃ (24.3 mg, 373.7 µmol) as a solid at room temperature. The resultant yellow solution turned purple-red within 25 minutes, and was subsequently stirred for 4 h. Evaporation of solvent *in vacuo* left a pink-red crude solid. Extraction into THF and recrystallization by slow diffusion of pentane into a concentrated THF-solution yielded purplish-red single crystals in good yield (143.8 mg, 246.7 mmol, 66%). ³¹P-NMR (80.9 MHz, acetone-d₆): δ 54.1 (s). ¹H-NMR (200 MHz, acetone-d₆): δ 8.02 (t, $J_1 = 7.8$ Hz, 1H, *p*-ArH), 7.59 (d, $J_1 = 7.8$ Hz, 2H, m-ArH), 3.99 (vt, 4H, -CH₂), 1.59 (vt, 36H, ¹Bu). IR (ATR, cm⁻¹): v 2069 (s), 1601 (w), 1565 (w). El. Anal. Calcd. for C₂₃H₄₃BF₄N₄NiP₂: C, 47.38; H, 7.43; N, 9.61. Found: C, 47.54; H, 7.18; N, 9.51.

Nickel complex 3, [Ni(PNP^{1Ba})(CN'Bu)](BF₄)₂. To a solution of 1 (200.0 mg, 299.0 µmol) in MeCN (20 mL) was added 'BuNC (34 µL, 299.0 µmol) *via* microsyringe at room temperature. The resultant yellow solution turned light-yellow within 15 minutes, and was subsequently stirred for 2 h. Evaporation of the solvent *in vacuo* left a cream-yellow solid in good yield (180.7 mg, 254.1 mmol, 85%). ³¹P-NMR (80.9 MHz, acetone-d₆): δ 81.7 (s). ¹H-NMR (200 MHz, acetone-d₆): δ 8.23 (t, $J_1 = 7.6$ Hz, 1H, *p*-ArH), 7.86 (d, $J_1 = 7.6$ Hz, 2H, *m*-ArH), 4.46 (m, 4H, -CH₂), 1.78 (s, 9H, CN'Bu), 1.64 (vt, 36H, 'Bu). IR (ATR, cm⁻¹): v 2188 (m), 1607 (w), 1566 (w). El. Anal. Calcd. for C₂₈H₅₂B₂F₈N₂NiP₂: C, 47.30; H, 7.37; N, 3.94. Found: C, 47.48; H, 7.25; N, 3.85.

Nickel complex 5, Ni(PN⁻P^{(Bu})(N₃). A solution of 2 (175.0 mg, 300.1 µmol) in MeCN (30 mL) was added dropwise to a slurry of NaN(SiMe₃)₂ (55.0 mg, 300.1 mmol) in MeCN (20 mL) by means of a cannula at room temperature. The resultant pink-red solution turned deep-purple within 5 minutes, and was subsequently stirred for 1 h. Filtration and evaporation of solvent left a dark-purple solid that was characterized solely by IR spectroscopy. IR (ATR, cm⁻¹): v 2055 (s), 1613 (w).

Nickel complex 6, $[Ni(PN^-P^{Hbu})(CN^tBu)]BF_4$. A solution of 1 (150.0 mg, 224.2 µmol) in MeCN (30 mL) was added dropwise to a solution of NaN(SiMe₃)₂ (41.1 mg, 224.2 µmol) in MeCN (20 mL) by means of a cannula at room temperature. The resultant light-yellow solution turned deep-purple within 5 minutes, and

was subsequently stirred for 1 h. Filtration and evaporation of solvent *in vacuo* left an off-white solid. Extraction into THF and evaporation of the solvent *in vacuo* yielded a purple-red solid (79.5 mg, 136.8 µmol, 61%). ³¹P-NMR (80.9 MHz, acetone-d₆): δ 79.7 (d, $J_{P,P} = 188$ Hz, 1P), 71.6 (d, $J_{P,P} = 180$ Hz, 1P). ¹H-NMR (200 MHz, acetone-d₆): δ 6.42 (t, $J_1 = 7.4$ Hz, 1H, Py), 6.18 (d, $J_1 = 7.4$ Hz, 1H, Py), 5.55 (d, $J_1 = 7.4$ Hz, 1H, Py), 3.59 (m, 1H, =CH), 3.40 (m, 2H, -CH₂), 1.68 (s, 9H, CN'Bu), 1.54 (d, $J_1 = 9.0$ Hz, 18H, 'Bu), 1.47 (d, $J_1 = 9.0$ Hz, 18H, 'Bu). IR (ATR, cm⁻¹): v 2164 (s), 1618 (m).

Nickel complex 7, [Ni(PNP^{tBu})(SCH₂Ph)]BF₄. A solution of 1 (200.0 mg, 299 µmol) in MeCN (30 mL) was added dropwise to a solution of NaN(SiMe₃)₂ (54.8 mg, 299 µmol) in MeCN (20 mL) via a cannula at room temperature. The resultant yellow solution turned brown within 5 minutes, and was subsequently stirred for 1 h. To this solution was added benzyl mercaptan (35.1 µmL, 299 µmol) via microsyringe. An immediate color change to deep green was apparent. Evaporation of the solvent and extraction into THF gave a green solid after concentrating to dryness that was washed twice with Et₂O (20 mL). Recrystallization by slow diffusion of pentane into a concentrated THF-solution vielded dark-green single crystals (105.3 mg, 158.5 mmol, 53%). ³¹P-NMR (80.9 MHz, acetone-d₆): δ 49.5 (s). ¹H-NMR (200 MHz, acetoned₆): δ 8.02 (t, $J_1 = 7.0$ Hz, 1H, p-ArH), 7.64 (d, $J_1 = 7.0$ Hz, 2H, m-ArH), 7.27 (m, 5H, Ph), 3.97 (m, 4H, -CH₂), 3.45 (s, 2H, CH₂Ph), 1.60 (vt, 36H, ^tBu). IR (ATR, cm⁻¹): v 1603 (w), 1568 (w). El. Anal. Calcd. for C₃₀H₅₀BF₄NNiP₂S: C, 54.25; H, 7.59; N, 2.11. Found: C, 53.83; H, 7.21; N, 1.96.

Nickel complex 8, [Ni(PNP^{tBu})(SPh)]BF₄. A solution of 1 (100.0 mg, 149.5 µmol) in MeCN (30 mL) was added dropwise to a solution of NaN(SiMe₃)₂ (27.4 mg, 149.5 µmol) in MeCN (20 mL) via a cannula at room temperature. The resultant yellow solution changed color to brownish within 5 minutes, and was subsequently stirred for 1h. To this solution was added thiophenol (15.4 µL, 149.5 µmol) via microsyringe. An immediate color change to deep green was apparent. Evaporation of the solvent and extraction into THF gave a green solid after evaporation. This solid was washed with Et₂O (20 mL). Recrystallization by slow diffusion of pentane into a concentrated THF-solution yielded dark-green single crystals as well as brown mother liquor and precipitate. ³¹P-NMR (80.9 MHz, acetone-d₆): δ 50.0 (s). ¹H-NMR (200 MHz, acetone-d₆): δ 8.05 (t, $J_1 = 7.6$ Hz, 1H, *p*-ArH), 7.75 (d, $J_1 =$ 7.0 Hz, 2H, Ph), 7.67 (d, $J_1 = 7.6$ Hz, 2H, *m*-ArH), 7.07 (m, 3H, Ph), 3.99 (m, 4H, -CH₂), 1.47 (vt, 36H, 'Bu). IR (ATR, cm⁻¹): v 1604 (w), 1569 (w). El. Anal. Calcd. for C₂₉H₄₈BF₄NNiP₂S: C, 53.57; H, 7.44; N, 2.15. Found: C, 53.88; H, 7.65; N, 2.31.

Nickel complex 9, [Ni(PNP^{1Bu})Cl]BF₄. A solution of NiCl₂-(dme) (219.7 mg, 1.0 mmol) in CH₂Cl₂ (25 mL) was added to a solution of PNP^{1Bu} (395.5 mg, 1.0 mmol) and NaBF₄ (109.8 mg, 1.0 mmol) in CH₂Cl₂ (50 mL) at room temperature. The solution quickly turned reddish and was thereafter stirred for 16 hours. Filtration and evaporation left a red crude solid. Recrystallization from CH₂Cl₂-hexane yielded orange-red crystals of complex 9 in good yield (386.2 mg, 670 µmol, 67%). ³¹P-NMR (80.9 MHz, acetone-d₆): δ 48.9 (s). ¹H-NMR (200 MHz, acetone-d₆): δ 8.01 (t, $J_1 = 7.6$ Hz, 1H, *p*-ArH), 7.60 (d, $J_1 = 7.6$ Hz, 2H, *m*-ArH), 3.94 (s, 4H, -CH₂), 1.60 (vt, 36H, ¹Bu). IR (ATR, cm⁻¹): v 1604 Published on 16 December 2008. Downloaded by University of Windsor on 26/10/2014 03:51:49.

Nickel complex 10, Ni(PN⁻P^{IBu})Cl. To a solution of 9 (200 mg, 346.9 µmol) in THF (30 mL) was added a solution of NaN(SiMe₃)₂ (63.6 mg, 346.9 µmol) in THF (20 mL) *via* cannula and the solution was left stirring for 4 hours, during which time the color changed from red to deep green-brown. Solvent was removed *in vacuo* and the product extracted with pentane (2 × 25 mL). After filtration, the solvent was evaporated to leave a brown pure solid (147.5 mg, 301.8 µmol, 87%). ³¹P-NMR (162 MHz, C₆D₆): δ 45.7 (d, ²J_{P-P} = 293 Hz), 39.8 (d, ²J_{P-P} = 293 Hz). ¹H-NMR (400 MHz, C₆D₆): δ 6.25 (t, ¹J = 7.2 Hz, 1H, Py), 6.03 (d, ¹J = 7.2 Hz, 1H, Py), 5.10 (d, ¹J = 7.2 Hz, 1H, Py), 3.42 (d, ¹J = 5.2 Hz, 1H, =CH), 2.26 (d, ¹J = 7.2 Hz, 18H, 'Bu). IR (ATR, cm⁻¹): v 1612 (s).

Nickel complex 11, Ni(PN-P^{tBu})(Ph). To a solution of 10 $(125 \text{ mg}, 255.8 \mu \text{mol})$ in Et₂O (30 mL), cooled to -40 °C, was added a solution of PhLi (2.0 M solution in Bu₂O) (128 µL, 255.8 mmol) via microsyringe. The resultant green-brown solution was stirred for 4 hours during which time the solution was slowly warmed to room temperature and a color change to brown-red was observed. After evaporation of the solvent the desired product was extracted into pentane, filtered and then concentrated to dryness to give a brown-red solid (122.1 mg, 230 µmol, 90%). ³¹P-NMR (162 MHz, C_6D_6): δ 43.9 (d, ${}^2J_{P-P} = 236$ Hz), 41.3 (d, ${}^2J_{P-P} = 236$ Hz). ${}^1H-$ NMR (400 MHz, C₆D₆): δ 7.86 (m, 2H, o-PhH), 6.93 (m, 2H, *m*-PhH), 6.78 (m, 1H, *p*-PhH), 6.41 (m, 1H, Py), 6.19 (m, 1H, Py), 5.27 (m, 1H, Py), 3.40 (s, 1H, =CH), 2.55 (m, 2H, -CH₂), 1.32 $(d, {}^{1}J = 8.0 \text{ Hz}, 18\text{H}, {}^{t}\text{Bu}), 0.97 (d, {}^{1}J = 8.0 \text{ Hz}, 18\text{H}, {}^{t}\text{Bu}).$ El. Anal. Calcd. for C₂₉H₄₇NNiP₂: C, 65.68; H, 8.93; N, 2.64. Found: C, 65.12; H, 8.54; N, 2.26.

Nickel complex 12, Ni(PN-PtBu)(Me). To a solution of 10 $(100 \text{ mg}, 204.6 \mu \text{mol})$ in Et₂O (30 mL), cooled to $-40 \degree \text{C}$, was added a solution of MeLi (1.6 M solution in cyclohexane) (127.9 µL, 204.6 µmol) via microsyringe. The resultant green-brown solution was stirred for 4 hours during which time the solution was slowly warmed to room temperature and a color change to brown-red was observed. After evaporation of the solvent the desired product was extracted into pentane, filtered and then concentrated to dryness to give a brown-red solid (83.4 mg, 178.0 µmol, 87%). ³¹P-NMR (162 MHz, C₆D₆): δ 41.5 (d, ²J_{P-P} = 250 Hz), 37.6 (d, ²J_{P-P} = 250 Hz). ¹H-NMR (400 MHz, C_6D_6): δ 6.45 (t, ¹J = 7.4 Hz, 1H, Py), 6.25 (m, ${}^{1}J = 7.4$ Hz, 1H, Py), 5.33 (m, 1H, Py), 3.42 (s, 1H, =CH), 2.50 (d, ${}^{1}J = 8.0$ Hz, 2H, -CH₂), 1.44 (d, ${}^{1}J = 11.2$ Hz, 18H, 'Bu), 1.07 (d, ${}^{1}J = 11.2$ Hz, 18H, 'Bu), -0.08 (t, ${}^{1}J = 8.4$ Hz, 3H, NiCH₃). El. Anal. Calcd. for C₂₄H₄₅NNiP₂: C, 61.56; H, 9.69; N, 2.99. Found: C, 61.05; H, 9.21; N, 2.61.

Nickel complex 13, Ni(PN⁻P^{1Bu})(H). To a solution of 10 (50 mg, 102.3 µmol) in Et₂O (10 mL), cooled to -40 °C, was added a solution of LiAlH₄ (1.0 M solution in THF) (103 µL, 103 µmol) *via* microsyringe. The resultant green-brown solution was stirred for 4 hours during which time the solution was slowly warmed to room temperature and a color change to brown-red was observed. After evaporation of the solvent the desired product was extracted into pentane, filtered and then concentrated to dryness to give a brown-red solid (26.0 mg, 57.3 µmol, 56%). ³¹P-NMR (162 MHz, C₆D₆): δ 76.7 (dd, ²J_{P-P} = 197 Hz, ²J_{P-H} = 52 Hz), 70.6 (dd,

²*J*_{P-P} = 197 Hz, ²*J*_{P-P} = 56 Hz). ¹H-NMR (400 MHz, acetoned₆): δ 6.30 (t, *J* = 7.4 Hz, 1H, Py), 5.95 (d, *J* = 7.4 Hz, 1H, Py), 5.33 (d, *J* = 7.4 Hz, 1H, Py), 3.22 (m, 1H, =CH), 3.07 (m, 2H, -CH₂), 1.32 (vt, 36H, ¹Bu), -18.4 (dd, ²*J*_{P-H} = 62 Hz, ²*J*_{P-H} = 55 Hz, 1H, Ni*H*).

X-Ray crystal structure determinations‡

X-Ray reflections were measured with Mo-K_{α} radiation (λ = 0.71073 Å) on a Nonius Kappa CCD diffractometer with rotating anode at a temperature of 150 K up to a resolution of $(\sin \theta /$ λ)_{max} = 0.65 Å⁻¹. The structures were solved with Direct Methods (program SHELXS-9728) Refinement was performed with SHELXL-97²⁸ against F^2 of all reflections. Non hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were introduced in calculated positions and refined with a riding model. Geometry calculations and checking for higher symmetry was performed with the PLATON program.²⁹ Comments for compound 1: one of the two BF₄ anions was refined with a disorder model. For 2: The BF₄ anion was refined with a disorder model. A slight disorder of the coordinated N₃ anion was not resolved. In 1 and 2 the inadequacy of the BF_4 disorder models lead artificially to slightly too short intermolecular $F \cdots C$ distances of the split F atoms. For 7: The crystal was cracked into two fragments, which was taken into account during the integration of the intensities³⁰ and in the least-squares refinement with SHELXL-97²⁸ using a HKLF5 instruction.³¹ For 9: The BF₄ anion was refined with a disorder model. Further details are given in Table 1.

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