

COMMUNICATION

Facile Synthesis of a Nickel(0) Phosphine Complex at Ambient Temperature

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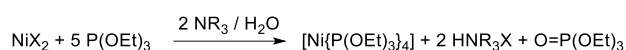
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The reaction of the bis(methoxy)-2-pyridyl-phosphine (MeO)₂P(2-py) (1) with [Ni(MeCN)₆](BF₄)₂ leads to the unexpected single-step reduction of Ni^{II} and the formation of a tetrahedral nickel(0) complex [(MeO)₂P(2-py-H)]₂[(MeO)₂P(2-py)]₂Ni(BF₄)₂ (2). The redox activity is probably induced by the decomposition of the tetrafluoroborate anion; NMR spectroscopic studies point towards a fluoride-assisted oxidation of the 2-pyridyl-phosphine ligand, with associated reduction of the metal.

In the past two decades, there has been increasing interest in the use of homogeneous nickel catalysts in a broad range of organic transformations, such as C–H bond activation, Heck coupling, and the reductive- and cross-coupling reactions of halo-alkanes.¹ One obvious motivation is the low cost of nickel compared to more commonly used palladium and platinum catalysts in Group 10. However, the atomic characteristics of nickel itself, being smaller, more electronegative and harder (based on the hard and soft acids and bases principle) than the 4d/5d elements, also gives it distinctly different reactivity, for example, facile oxidative addition and β-migratory insertion as well as the potential for radical reaction pathways. Most nickel-based catalytic systems involve Ni^{II}/Ni⁰ reaction cycles, with Ni⁰ species being the active catalytic species. Although Ni^{II} precatalysts can be employed, stable Ni⁰ catalysts or precatalysts such as the ubiquitous [Ni(COD)₂] (COD = 1,5-cyclooctadiene) feature strongly in this area,^{2–11} and the development of new Ni⁰ species for selective organic transformations is a growing field of research.¹²

Commonly, tetracoordinate nickel(0) complexes of the type [NiL₄] (L = trialkyl-, triaryl-, alkyl-aryl-phosphines) have been synthesised from labile Ni⁰ precursors, such as [Ni(COD)₂] or [Ni(CO)₂(COD)].¹³ However, the use of these very reactive and unstable nickel(0) species can be avoided using *in situ* reduction of a nickel(II) precursor, such as NiCl₂ or [NiX₂L₂] (X = Cl, Br, L = phosphine), with Zn,¹⁴ Na,¹³ NaBH₄¹⁵ or KC₈¹⁶ in the presence of a phosphine. The use of such strong reducing agents can be avoided in a number of phosphine-mediated reduction reactions. For example, nickel(II) halides are reduced by triethyl phosphite, P(OEt)₃, in the presence of an amine and water to the tetrakis(triethylphosphite)nickel(0) complex, together with the corresponding ammonium salt and phosphine oxide (Scheme 1).^{17,18} This reaction can also proceed thermally using triethyl phosphite alone,¹⁹ although the mechanism is poorly understood.



Scheme 1. Reduction of nickel(II) halides in the presence of a triethyl phosphite, an amine and water (X = Cl, Br, I, R = H, Me).

A further development in this area has been the F⁻-induced reduction of Pd^{II} to Pd⁰ in the presence of phosphines, a reaction which occurs *via* oxidation of the phosphines to difluorophosphoranes, R₃PF₂.^{20–23} A related mechanism is thought to be involved in the reaction of [Pd(MeCN)₄](BF₄)₂ with dppp [propane-1,3-diylbis(diphenylphosphane)], in which the BF₄⁻ anion acts as the F⁻ source to give the Pd⁰ complex [Pd(dppp)₂]. However, attempts to extend this reaction to nickel were not successful.²⁰ The tetrafluoroborate anion, which has previously been shown to be a suitable fluoride source for transition metal complexes,^{24,25} was identified as the fluoride source in the case of the Pd^{II} to Pd⁰ reduction reaction. Relevant to the current work, the activity of BF₄⁻ as a source of F⁻ in transition metal chemistry is strongly influenced by the presence of a Lewis base, which is involved in the decomposition of the metal BF₄⁻ species formed initially (presumably by the formation of an adduct of BF₃).

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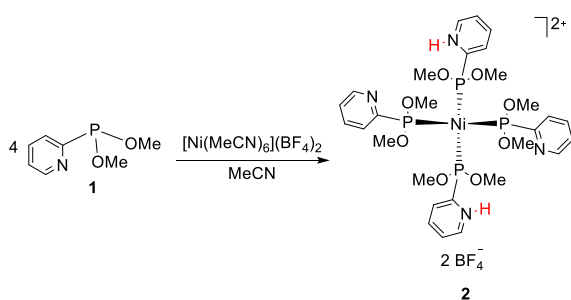
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As part of a broader research program on the development of main group element-bridged 2-pyridyl ligands, we recently explored the synthesis and coordination chemistry of unsymmetrical phosphines of the type $(RO)_xP(2-py)_{3-x}$ ($2-py = 2-pyridyl$; $x = 1, 2$) with a range of transition metal ions.^{26,27} Although ligands such as $(PhO)_2P(2-py)$ can coordinate to transition metals intact, here we show that interaction of the closely related ligand $(MeO)_2P(2-py)$ (**1**) with $[Ni(MeCN)_6](BF_4)_2$ at room temperature leads to the reduction of Ni^{II} to Ni^0 . Our studies indicate that this involves the BF_4^- anion and is, to our knowledge, the first example of an F^- -mediated reduction of Ni^{II} to Ni^0 .

The reaction of $[Ni(MeCN)_6](BF_4)_2$ with bis(methoxy)-2-pyridyl-phosphine $(MeO)_2P(2-py)$ (**1**)²⁷ in acetonitrile under nitrogen produces a dark orange/brown solution. Crystallisation of the brown reaction residue from MeOH produces a crop of dark red crystals of the Ni^0 complex $[Ni(1)_2(1-H)_2](BF_4)_2$ (**2**) in 37 % yield (Scheme 2), which is isolated as the solvate **2**·MeOH. Using the related ligand $P(6-Me-2-py)_3$ or the more closely related ligands $(Me_2N)_2P(2-py)$ and $(MeO)P(2-py)_2$ in place of phosphine **1** does not result in the corresponding $Ni(0)$ complexes, suggesting that characteristics like the Lewis acidity and the σ -donor/ π -acceptor character are key to the reactivity of **1**.²⁸ The importance of the Lewis acidity of the P centre in particular can be related to the proposed mechanism involved, and it is noteworthy that being the most Lewis acidic phosphine we have explored fluorination of the P-atom of **1** would produce the most stable intermediate (**A**, Scheme 3).



Scheme 2. Reaction of bis(methoxy)-2-pyridyl-phosphine (**1**) with nickel(II), affording the nickel(0) complex **2**.

The solid-state structure of the dicationic Ni^0 complex of **2** is shown in Figure 1 (present in the crystalline solvate **2**·MeOH obtained from MeOH). Within the complex, the nickel centre is tetrahedrally coordinated *via* the phosphorus bridgehead atoms of four ligand molecules **1**, with Ni–P bond lengths of 2.1006(6)–2.1234(7) Å. Similar Ni–P bond lengths have been found in previously reported tetrahedral nickel(0) phosphine complexes.^{29,30} A slight distortion of the tetrahedral coordination geometry is observed, with the P–Ni–P bond angles being in the range 106.16(2)–111.63(2)°. This appears to be largely a consequence of the protonation of two of the pyridyl-N atoms, which form strong intramolecular N–H...N hydrogen bonds with the unprotonated pyridyl-N atoms on opposite sides of the cation ($N\cdots N$ 2.647(3)–2.688(3) Å, $N_{py}-H\cdots N_{py}$ 1.76(3)–1.80(3) Å). Similar, short intramolecular N...N

distances have been found in bis(4-methylpyridine)hydrogen tetraphenylborate (2.608 Å).³¹

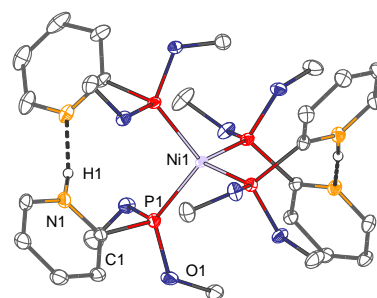


Figure 1. Structure of the dication $\{[(MeO)_2P(2-py-H)]_2[(MeO)_2P(2-py)]_2Ni\}(BF_4)_2 \cdot MeOH$ (**2**·MeOH). Hydrogen atoms, BF_4^- counterions and the MeOH molecule are omitted for clarity. Displacement ellipsoids are drawn at the 30 % probability level. Selected bond lengths (Å) and angles (°): Ni–P 2.1006(6)–2.1234(7), P–O 1.597(2)–1.659(2), P–C_{py} 1.837(2)–1.857(2), $N_{py}-H$ 1.76(3), 1.80(3), $N_{py}-N_{py}$ 2.647(3), 2.688(3), P–Ni–P 106.12(2)–111.25(2), O–P–O 104.18(8)–106.7(1), O–P–C_{py} 92.45(9)–103.25(9).

The expected diamagnetic character of **2** is shown in the ³¹P and ¹H NMR spectra of the complex at room temperature in CD₃CN, which both contain sharp resonances (Figures S4 and S5). Unfortunately, the signals of the N–H protons in **2** are too broad to be observed in the ¹H NMR spectrum, despite the use of various solvents and solvent combinations and a wide NMR screening window. However, the solid-state IR spectrum shows a broad N–H band at 1900–2250 cm⁻¹ (Figure S9) consistent with the presence of a strong $N_{py}-H\cdots N_{py}$ H-bond which causes weakening of the N–H bond involved.³² Similar N–H bond weakening has also been found in related $N_{py}-H\cdots N_{py}$ systems,³³ such as in the dimer of $[(4-benzoylpyridine)_2H]$ (1955 cm⁻¹).³⁴ For comparison, the O–H stretching vibration for MeOH in the solvate **2**·MeOH is observed as a broad band at 3400 cm⁻¹. Negative-ion HR-MS analysis of crystalline **2** shows a major peak for $[2+BF_4]^-$ (1005.1412 Da, calcd. 1005.1400 Da), adding further support for the presence of the protonated pyridyl groups in **2** (Figure S10). A downfield shift of the ³¹P{¹H} NMR signal to 154.5 ppm (CD₃CN) is observed upon complexation of the phosphine ligand in **2** (free ligand: 150.0 ppm, CDCl₃).

In order to clarify the reduction mechanism, *in situ* NMR spectroscopic investigations were carried out (Figure 2). One of the key questions in this regard is whether a fluoride-assisted redox reaction is a possible reaction pathway, similar to that observed in the formation of Pd⁰ phosphine complexes.^{20–22} The ³¹P{¹H} NMR spectrum of the reaction mixture of bis(methoxy)-2-pyridyl-phosphine (**1**) and $[Ni(MeCN)_6](BF_4)_2$ in CD₃CN after 30 mins at room temperature is shown in Figure 2a. No further splitting of the observed resonances is seen in the proton-coupled ³¹P NMR spectrum, excluding the presence of P–H-containing by-products. The main signal at δ 154.5 ppm is due to the nickel(0) complex **2** (a singlet resonance being observed in the ³¹P{¹H} NMR spectrum presumably due to the rapid exchange of the N–H protons between the N-atoms in the N–H...N H-bonds). Other resonances for P-containing species are also present which indicate that a number of other transformations of ligand **1** have also taken place. The broadening of some of these resonances may be due to the presence of residual paramagnetic Ni^{II} and makes any assignment of the by-products difficult.

One potentially significant observation is the broad resonance at *ca.* 15 ppm, which is typical of P^V phosphine oxide derivatives.^{35–37} However, test reactions of **1** with ambient air or water show that both lead to the exclusive formation of the secondary phosphine oxide (MeO)P(O)H(2-py) (³¹P NMR δ 24.6 ppm, ¹J_{PH} = 581.6 Hz). Since this species is entirely absent in the reaction mixture, adventitious water- or O₂-induced P^{III} → P^V redox reaction¹⁷ is unlikely to be responsible for the formation of **2**.

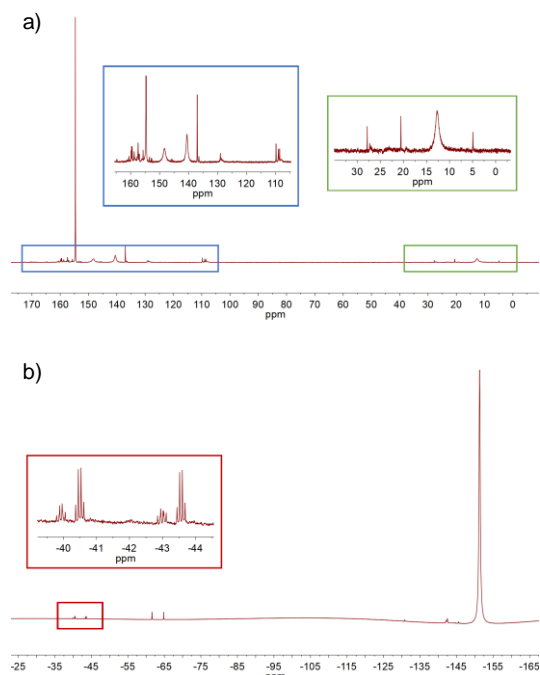
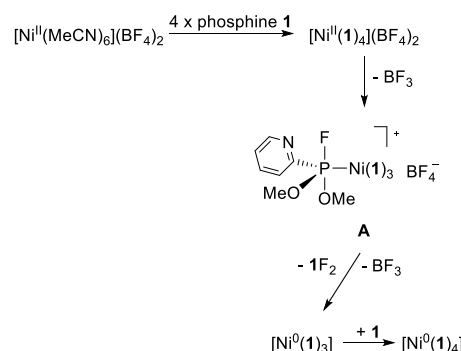


Figure 2. a) *In-situ* ³¹P{¹H} NMR (CD₃CN, 161.99 MHz) spectrum and b) *in-situ* ¹⁹F{¹H} NMR (CD₃CN, 376.49 MHz) spectrum of the reaction mixture of **1** and [Ni(MeCN)₆](BF₄)₂ in CD₃CN at room temperature.

The ¹⁹F{¹H} NMR spectrum of the reaction mixture is shown in Figure 2b. The proton-coupled ¹⁹F NMR spectrum is identical. The main signal, a singlet at δ –151.9 ppm, can be attributed to the tetrafluoroborate anions of the nickel(0) complex **2**. Additionally, two, closely-related low-intensity doublets of (binomial) quartets (δ –41.4 and –41.9 ppm) are seen. Both signals comprise one large coupling constant of 1155.8 Hz, which is in the typical range for a one-bond P–F scalar coupling,³⁸ and smaller coupling constants of 35.0 and 30.9 Hz, which presumably arise from the long-range coupling to three magnetically-equivalent P atoms. The possible origin of these signals could be nickel complexes with fluorinated and unfluorinated ligand molecules, *e.g.*, the Ni⁰ complex [(1F)Ni(1)₃][–] (species **A**, Scheme 3). In addition, a doublet at –63.2 ppm with a coupling constant of 1203.2 Hz is also observed, which again indicates the presence of a P–F moiety. Traces of other F-containing species in the region of –130 to –150 ppm show no distinct splitting. Although none of these species can be unambiguously identified on this basis, the NMR spectroscopic data provide a strong indication (*i.e.*, the presence of a P^V resonance and P–F-containing by-products) that the formation of **2** involves a fluoride-induced redox process, involving the decomposition of the BF₄[–] anion, related to that observed previously for Pd^{II}. Further support for this conclusion comes

from the *in situ* NMR spectroscopic study of the reaction of NiCl₂ in place of [Ni(MeCN)₆](BF₄)₂ (in thf), which showed no apparent formation of **2**.

Based on previous studies of the formation of Pd⁰ complexes and on the basis of the spectroscopic evidence, a tentative mechanism for the formation of **2** is shown in Scheme 3. In this process, the decomposition of the BF₄[–] anion into BF₃ and F[–] is most likely to be driven thermodynamically by the formation of strong P–F bonds and by the potential formation of a BF₃ adduct with the Lewis basic 2-pyridyl groups of **1**. The nucleophilic attack of F[–] on to the Ni(II)-bonded phosphine leads to the formation of intermediate **A**, which contains a hypervalent [(MeO)₂(2-py)PF][–] P^{III} anion (Scheme 3). A two-electron transfer from P to Ni then yields the nickel(0) complex **2** and 1F⁺ (and subsequently 1F₂). The existence of the 1F⁺ cation was confirmed in a separate NMR experiment in which the phosphine ligand was reacted with NFSI (N-fluorobenzenesulfonimide) in MeCN (1:1, ³¹P{¹H} δ 9.0 ppm, ¹J_{PF} = 1055.3 Hz). The difluorophosphorane 1F₂ could not be synthesised *via* this route.



Scheme 3: A possible pathway to the formation Ni⁰ using the phosphine ligand **1**.

Our studies have not allowed us to identify unequivocally the proton source which is ultimately responsible for the formation of the [(MeO)₂P(2-py-H)]₂{(MeO)₂P(2-py)}₂Ni²⁺ cation. However, this is likely to be the CH₃CN solvent itself, and it has been shown previously that C–H activation of MeCN can occur in the presence of zero-valent nickel bis(dialkylphosphino)ethane fragments.^{39–41} It can be noted in this regard that **2** is formed in the reaction mixture *before* crystallisation from MeOH (Figure 2a) so that this is not the proton source. Complex **2** can, however, also be obtained using MeOH as the reaction solvent, albeit in lower (27%) isolated crystalline yield. The complex is again not formed in this case using NiCl₂.

In summary, an unexpected *in situ* reduction of Ni^{III} → Ni⁰ is observed in the reaction of bis(methoxy)-2-pyridyl-phosphine **1** with [Ni(MeCN)₆](BF₄)₂. This synthetic strategy allows the isolation of a phosphine Ni⁰ tetrakis-phosphine complex without the addition of any external reducing agent or the use of a labile Ni⁰ precursor, providing a very convenient one-step route to reactive nickel(0) complexes. Our results support a mechanism involving fluoride-assisted oxidation of the phosphorus atom caused by the decomposition of the tetrafluoroborate anion. Complex **2** not only provides a potential Ni⁰ reagent for homogeneous catalysis, but is also of

interest in the field of electro-catalysts, as it possesses a non-coordinating pendant amine functionality in the secondary coordination sphere of the ligand backbone.^{42–45}

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Conflicts of interest

There are no conflicts to declare.

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