ARTICLE

Evaluating a dispersion of sodium in sodium chloride for the synthesis of low-valent nickel complexes

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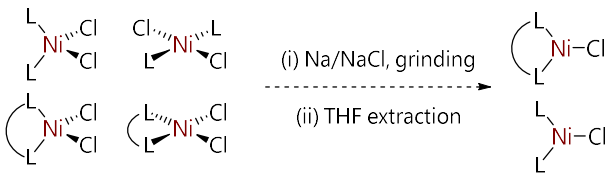
The use of a sodium in sodium chloride dispersion is systematically evaluated for the synthesis of nickel(0) and nickel(I) complexes from readily-prepared nickel(II) precursors. A variety of complexes with phosphine and bipyridine-type ligands were accessed, although some reactions were found to produce mixtures of nickel(0) and nickel(I), and yields were highly variable. Several new nickel(I) complexes were obtained, and these were characterised using techniques including NMR spectroscopy, EPR spectroscopy, and single crystal X-ray diffraction analysis.

Introduction

Nickel catalysis for organic synthesis is an area that is currently under intensive study by many groups[1] and, like any other transition metal-mediated reaction, developments in organic synthesis rely on a fundamental understanding of the underlying organometallic chemistry. This is often accompanied by, and indeed informs, the development of robust and convenient (pre-)catalyst systems. The ideal pre-catalyst is one that is stable for long periods of storage in a standard laboratory, but that rapidly releases an active catalyst that can mediate the reaction(s) of interest. The fluidity with which nickel can change oxidation state, and the accessibility of a range of oxidation states through single electron changes both enables exciting new chemistry[2-5] but presents significant challenges for the study and understanding of nickel catalysis. There is a clear need for the full exploration of the coordination chemistry and reactivity of nickel(0), nickel(I), and nickel(II) complexes with a diverse range of ligand frameworks.

The vast majority of nickel sources for catalytic reactions are either nickel(0) or nickel(II); [Ni(COD)$_2$] is typically the favoured nickel(0) source, but [Ni(alkene)$_3$] and [Ni(COD)(DQ)] complexes present alternatives that overcome the poor solid-state stability of [Ni(COD)$_2$] (DQ = duroquinone).[6-8] For nickel(II), favoured precursors include [Ni(acac)$_2$], or halides of nickel with or without coordinated water or ethereal ligands (e.g. [NiCl$_2$(DME)]) (DME = 1,2-dimethoxyethane). A number of convenient (pre-)catalysts are available with ancillary ligands coordinated in the desired ratio to nickel (typically 1:1 or 2:1); these include [Ni(Ar)X(PR$_3$)$_2$][9] and [Ni(allyl)Cl(NHC)][10, 11] complexes in the case of nickel(II), and [Ni(η^2-arene)(L)][12, 13] and [Ni(NHC)(η^2-olefin)$_2$] complexes[14, 15] for nickel(0). However, there is a dearth of convenient nickel(I) precursors, although recent advances have been made in this area with the discovery of [Ni(COD)(OPh*)] (Ph* = 2,4,6-tri*tert*-butylphenyl).[16] In addition, there are relatively few examples of well-defined nickel (pre-)catalysts with bipyridine-type ligands. The developing mechanistic landscape of nickel catalysis continues to implicate nickel(I) complexes as either species that are off-cycle and poorly active,[17, 18] complexes that are competent for catalysis *via* a Ni^{I}/Ni^{III} manifold,[19] or the true active species in catalysis;[20-23] the exact role of nickel(I) in a particular reaction is not easy to determine, and is a function of ligand and substrate structure.

As part of our ongoing efforts to understand the mechanisms of nickel-catalysed reactions, we sought a general method to access a diverse range of low valent nickel complexes with different supporting ancillary ligands, so that we might carefully evaluate their reactivity and their competence (or lack thereof) in catalytic reactions. In doing so, we wished to avoid the use of nickel(0) precursors, and particularly [Ni(COD)$_2$], so that we can avoid the well-known drawbacks of this compound. Here, we document our findings in the use of a sodium in sodium chloride dispersion[24] to access nickel(I) and nickel(0) complexes from well-defined nickel(II) halide precursors which can be readily prepared from inexpensive NiCl$_2$·6H$_2$O or [NiCl$_2$(DME)] (Scheme 1).



Scheme 1. Aims of this work.

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Results and Discussion

Nickel/Phosphine Complexes

A number of nickel(I) halide complexes of phosphines have been prepared previously, including [NiX(PEt_3)$_3$],[25] [NiX(P*i*-Pr_3)$_2$],[26] [NiX(dppf)],[17, 18, 27] and [Ni(X)(*t*-BuXantPhos)].[28] Typical methods of preparation can include the reduction of nickel(II) complexes or the comproportionation of nickel(0) and nickel(II) species.

The corresponding nickel(II) chloride complexes for most phosphine ligands – of both mono- and bidentate types – are readily prepared from $NiCl_2.6H_2O$ or [$NiCl_2$(DME)].[9] The required nickel(II) precursors were therefore typically synthesised in ethanol (from $NiCl_2.6H_2O$) or in THF (from [$NiCl_2$(DME)]); the latter method avoids the potential for traces of protic solvent to interfere with the stoichiometry of the sodium reducing agent, which would then lead to sodium alkoxide complexes that might also react with the nickel(I) or nickel(II) complexes present in the reaction mixture.

Reduction reactions were conducted as follows; detailed synthetic procedures can be found in the experimental section at the end of the manuscript. These reactions were carried out under argon in a glovebox. The nickel(II) precursor and 0.95 equivalents of sodium (dispersed in sodium chloride at 5% *w*/*w*) were weighed out and then ground together (see Scheme 1); THF was then added to extract the product(s), and the solution was filtered to remove sodium chloride. The nickel(II) precursor complexes tend to be rather poorly soluble in most solvents (including arenes and ethers) which helps to facilitate the recovery of the nickel(I) and nickel(II) products. Evaporation of the solvents provided the product(s) in solid form. These products were then analysed by methods including NMR and EPR spectroscopy and, where suitable crystals could be grown, single crystal X-ray diffraction analysis.

Table 1 lists the phosphine-ligated complexes that were studied and the results of the reduction experiments. The complexes studied including those with phosphine ligands that are monodentate (PMe_3, P*n*-Bu_3, PPh_3, PCy_3) and bidentate (dppm, dppe, dppp, dppb, dppf, XantPhos, dcpe) and which cover a wide range of steric and electronic character. (dppm = bis(diphenylphosphino)methane; dppe = 1,2-bis(di-phenylphosphino)ethane; dppp = 1,3-bis(diphenylphosphino)-propane; dppb = 1,4-bis(diphenylphosphino)butane; dppf = 1,1'-bis(diphenylphosphino)ferrocene; XantPhos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene; dcpe = 1,2-bis(dicyclohexylphosphino)ethane).

The complexes with dppf and PPh_3 ligands give low to moderate yields of the corresponding monomeric nickel(I) complexes. [NiCl(dppf)][17, 18, 27] and [NiCl(PPh_3)$_3$][29, 30] have been reported previously. In the case of [NiCl(dppf)], EPR spectra obtained during this work match those previously reported for this species (g_{iso} = 2.171; A_{iso} = 66 x 10^{-4} cm^{-1}) (Figure 1(a)).[18, 27] For the triphenylphosphine complexes, EPR data suggested that the product was [NiCl(PPh_3)$_3$] (g_{iso} = 2.196, A_{iso} = 58 x 10^{-4} cm^{-1}) (Figure 1(b)), and NMR data also matched this species.[29]

The complexes with monomeric trialkylphosphine ligands PMe_3 and PCy_3 did not provide any nickel(I) complexes, even though [NiCl(PCy_3)$_2$] has been reported previously using methods including reduction by sodium sand;[31, 32] we note that these nickel(II) complexes are often very poorly soluble, and so this may mean that this method is simply not appropriate for these types of complexes. The reduction of [$NiCl_2$(PMe_3)$_2$] produced some [Ni(PMe_3)$_4$].[33] [$NiCl_2$(P*n*-Bu_3)] is an oil, and is very soluble in all organic solvents. The reduction reactions of this complex produced some nickel(I), which is proposed to be [NiCl(P*n*-Bu_3)$_2$] on the basis of EPR data (Figure 1 (c)). This sample was contaminated with an unidentified diamagnetic compound (δ_P = 42.2 ppm) which is neither [$NiCl_2$(P*n*-Bu_3)$_2$] (δ_P = -2.3 ppm) nor free P(*n*-Bu)$_3$ (δ_P = -32.1 ppm). Control experiments were conducted where [Ni(COD)$_2$] was combined with 3 or 11 equiv. P(*n*-Bu)$_3$; the former sample exhibits a sharp singlet at δ_P = 11.3 ppm ($\omega_{1/2}$ = 5 Hz), while the latter spectrum contains signals at 11.3 ppm, -3.3 ppm ($\omega_{1/2}$ = 133 Hz), and -32.1 ppm (P(*n*-Bu)$_3$) in a *ca.* 3:2:21 ratio. The unidentified species is therefore not likely to be a nickel(0) complex.

The complexes with bidentate 1,*n*-bis(diphenylphosphino)alkane ligands gave mixtures of nickel(0) and nickel(I) products, with the exception of [$NiCl_2$(dppm)] which did not give a tractable product.

The reduction of [$NiCl_2$(dppe)] gave two species. [Ni(dppe)$_2$] (δ_P = 44.1 ppm, *c.f* lit. 44.7 ppm)[34] is a known complex that forms very readily in reactions between nickel(0) sources and dppe[35] or in reduction reactions of [$NiCl_2$(dppe)];[36] this must

Table 1. Outcomes of reactions in which [$NiCl_2$(PR_3)$_2$] complexes are reduced by a 5% *w*/*w* dispersion of sodium in sodium chloride and then extracted using THF (nd = not determined)

Entry	Substrate	Synthesis Solvent	Yield	Product(s)
1	[$NiCl_2$(PMe_3)$_2$]	THF	nd	Unidentified diamagnetic compound
2	[$NiCl_2$(P*n*-Bu_3)$_2$]	EtOH	nd	[NiCl(P*n*-Bu_3)$_2$] plus an unidentified diamagnetic compound[a]
3	[$NiCl_2$(PPh_3)$_2$]	EtOH	63%	[NiCl(PPh_3)$_3$]
5	[$NiCl_2$(PCy_3)$_2$]	EtOH	nd	No tractable product
6	[$NiCl_2$(dppm)]	THF	nd	No tractable product
7	[$NiCl_2$(dppe)]	THF	nd	[NiCl(dppe)], [Ni(dppe)$_2$]
8	[$NiCl_2$(dppp)]	THF	nd	[NiCl(dppp)], [Ni(dppp)$_2$]
9	[$NiCl_2$(dppf)]	THF	45%	[NiCl(dppf)]
10	[$NiCl_2$(XantPhos)]	THF	56%	[NiCl(XantPhos)]
12	[$NiCl_2$(dcpe)	THF	5%	[NiCl(dcpe)]

(a) [$NiCl_2$(P*n*-Bu_3)] is an oil, and is much more soluble in most organic solvents than the other nickel(II) precursor complexes. (b) Tetrahedral geometry obtained from reaction in ethanol. (c) Square planar geometry obtained by recrystallisation from DCM.

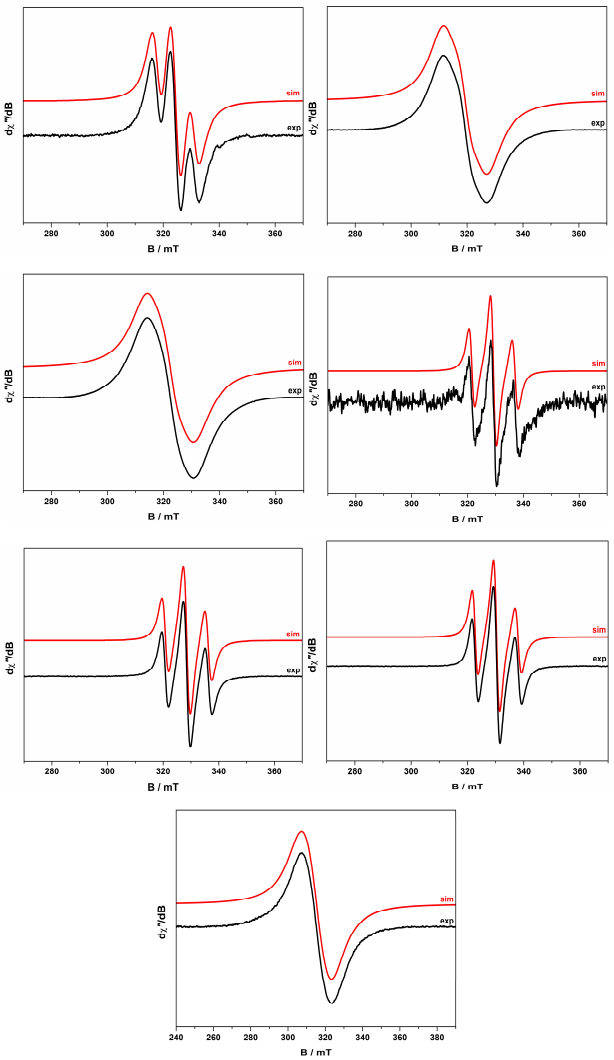

Figure 1. X-band EPR spectra for reaction products in THF solution at 293 K; full details can be found in the Supporting Information. (a) [NiCl(dppf)] (g_{iso} = 2.1713; A_{iso} = 66 × 10^{-4} cm^{-1}). (b) [NiCl(PPh_3)$_2$] (g_{iso} = 2.1956; A_{iso} = 58 × 10^{-4} cm^{-1}). (c) [NiCl(P*n*-Bu_3)$_2$] (g_{iso} = 2.1844; A_{iso} = 61 × 10^{-4} cm^{-1}). (d) [NiCl(dppe)] (g_{iso} = 2.1418; A_{iso} = 77 × 10^{-4} cm^{-1}). (e) [NiCl(dppp)] (g_{iso} = 2.1418; A_{iso} = 58 × 10^{-4} cm^{-1}). (f) [NiCl(dcpe)] (g_{iso} = 2.1292; A_{iso} = 76 × 10^{-4} cm^{-1}). (g) [NiCl(XantPhos)] (g_{iso} = 2.2207; A_{iso} = 54 x 10^{-4} cm^{-1}).

have arisen from the inadvertent two electron reduction of the starting material. The second product was a nickel(I) complex that is tentatively assigned as [NiCl(dppe)] on the basis of EPR data (Figure 1(d)). Analogously to the dppe example, the reduction of [$NiCl_2$(dppp)] returned a mixture of [NiCl(dppp)] (from EPR data, Figure 1(e)) and [Ni(dppp)$_2$] (δ_P = 13.4 ppm *c.f.* lit. 12.7 ppm).[34]

[NiCl(dcpe)] is a new complex, and was characterised by NMR spectroscopy, EPR spectroscopy (g_{iso} = 2.129) (Figure 1(f)), and single crystal X-ray diffraction analysis (Figure 2). This displays a trigonal planar geometry; presumably the steric bulk of the cyclohexyl groups prevents the formation of a chloride-bridged dimeric structure.

The reduction of [$NiCl_2$(XantPhos)] afforded [NiCl(XantPhos)], as judged by EPR spectroscopy (Figure 1(g)); [NiBr(*t*-BuXantPhos)] has been reported previously.[28]

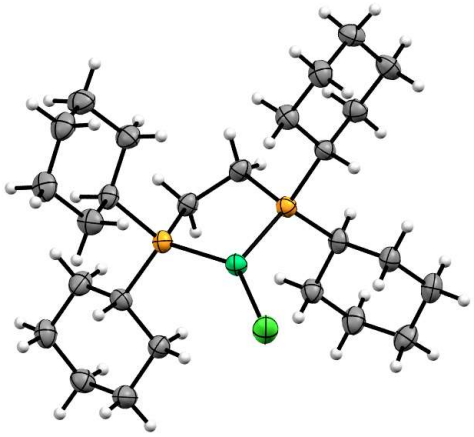

Figure 2. Molecular structure of [NiCl(dcpe)] as determined from single crystal X-ray diffraction analysis.

Nickel/Nitrogen Ligand Complexes

Following studies of the phosphine complexes, a series of [$NiCl_2$(L)] complexes were exposed to the sodium dispersion, where L is a bidentate bipyridine or phenanthroline ligand. We had previously attempted to synthesise [NiCl(L)] complexes with this ligand type through comproportionation between nickel(0) and nickel(II) without success; however, Somerville *et al.* have recently reported the synthesis of [NiCl(2,9-mes_2phen)] and [NiCl(2,9-*n*-Bu_2bphen)] *via* a comproportionation route (2,9-mes_2phen = 2,9-di(mesityl)phenanthroline; 2,9-*n*-Bu_2bphen = 2,9-di(*n*-butyl)-4,7-diphenylphenanthroline).

The required nickel(II) complexes are prone to coordinating molecules of water, and so these were prepared from [$NiCl_2$(DME)] in anhydrous solvent: either DME, THF, or a 9/1 *v*/*v* THF/DME mixture.

Table 2 lists the complexes that were exposed to the sodium in sodium chloride dispersion, and summarises the outcomes of the reactions. [$NiCl_2$(TMEDA)], [$NiCl_2$(PMDETA)], and [$NiCl_2$($py)_4$] were also exposed to the reaction conditions in the hopes of preparing a nickel(I) species that might serve as a useful precursor to a range of complexes, but no tractable complexes were obtained; it is suspected that any species that did form decomposed rapidly. The reduction of [$NiCl_2$(bpy)] produced very low yields of a product that yielded no EPR signal; it is not clear at this stage whether this means that no nickel(I) product was formed, that the nickel(I) product is unstable, or that the product is a ferromagnetically-coupled dimer.

Table 2. Outcomes of reactions in which [$NiCl_2$(L)] complexes are reduced by a dispersion of 3% *w*/*w* sodium in sodium chloride (L = bipyridine or phenanthroline ligand)

Entry	Complex	Yield	Product(s)
1	[$NiCl_2$(bpy)]	2%	See text
2	[$NiCl_2$(dtbpy)]	8%	[Ni(μ-Cl)(dtbpy)]$_2$
3	[$NiCl_2$(dmbpy)]	21%	[NiCl(dmbpy)]
4	[$NiCl_2$(phen)]	2%	[Ni(phen)]$_3$·2THF
5	[$NiCl_2$(neoc)]	3%	[NiCl(neoc)]

The reduction of [$NiCl_2$(dtbpy)] formed the known S = 1 dimer in a low yield, as confirmed by comparison of the paramagnetic ^{1}H NMR spectrum with that reported previously.[37] This species is known to be EPR-silent.

In contrast, the reduction of [$NiCl_2$(dmbpy)] produced a low but tractable yield of monomeric complex [NiCl(dmbpy)]. This is one of the smallest [NiCl(L)] complexes of a bidentate nitrogen ligand that has been prepared. The formation of a dimeric species is likely to be disfavoured by the steric impact of the methyl groups, while the strict 1:1 ligand:metal stoichiometry in the precursor may have allowed the formation of a [Ni(L)$_2$][X] structure[37, 38] to be avoided. The molecular structure of this complex was obtained *via* X-ray diffraction analysis of a single crystal (Figure 3). This confirmed the flat, trigonal-planar structure of the monomeric nickel(I) product. EPR data for this species were consistent with an *S* = ½ monomer (g_{iso} = 2.213) (Figure 4(a)). Other species of this type have been characterised, but these typically bear much larger substituents at the positions 2 and 9 of a more rigid phenanthroline ligand (g_{iso} = 2.221 for [NiCl(2,9-mes$_2$phen)]; 2.217 for [NiCl(2,9-*n*Bu$_2$bphen)].[23]

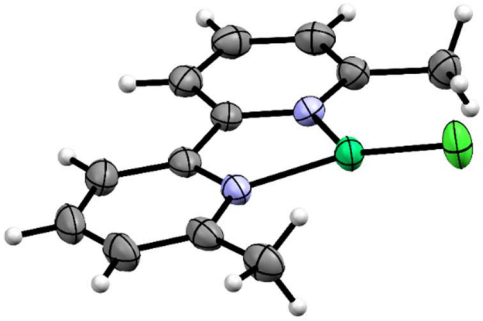

Figure 3. Molecular structure of [NiCl(dmbpy)] as determined from single crystal X-ray diffraction analysis.

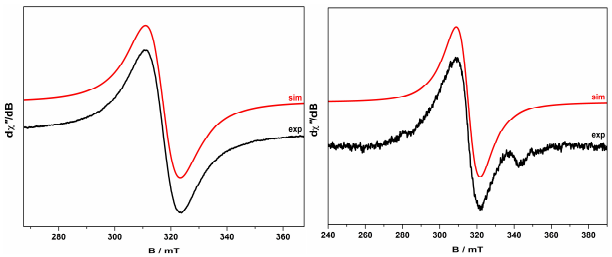

Figure 4. X-band EPR spectra for reaction products in THF solution at 293 K; full details can be found in the Supporting Information. (a) [NiCl(dmbpy)] (g_{iso} = 2.213). (b) [NiCl(neoc)] (g_{iso} = 2.221).

The reduction of [$NiCl_2$(neoc)] gave a species that was consistent with [NiCl(neoc)] as judged by EPR spectroscopy (g_{iso} = 2.221) (Figure 4(b)) (neoc = neocuprionine, 2,9-dimethylphenanthroline); given the structural similarity between neocuprionine and 6,6'-dimethylbipyridine and the lack of excess ligand it is reasonable that a monomeric complex is formed, but [Ni(neoc)$_2$][X] complexes have also been reported (g_{iso} = 2.228) from two different synthetic routes from either [Ni(neoc)$_2$] or neoc-Ni complex plus additional neoc.[37, 38]

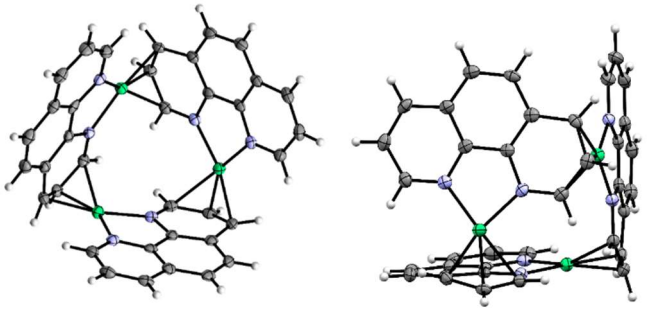

Figure 5. Molecular structure of [NiCl(phen)$_3$] as determined from single crystal X-ray diffraction analysis (left), and an alternative view, showing the perturbation of the phenanthroline ligand from planarity (right); two atoms of THF solvent are omitted for clarity.

A small amount of a trimeric structure was obtained when [$NiCl_2$(phen)] was exposed to the reducing agent (phen = phenanthroline). In this cyclic trimer, each nickel atom is coordinated to the nitrogen atoms of one phenanthroline ligand and appears to be η^3-coordinated to another phenanthroline ligand (Figure 5); the oxidation state of nickel is not entirely clear. It does not appear to be nickel(0), otherwise η^2- or η^6-coordination of a planar arene would be expected, such as in the case of all other unsupported nickel(0)-arene complexes found in the Cambridge Structural Database:[39] nickel complexes with a single NHC or phosphine ligand favour [Ni(η^6-arene)(L)] geometries,[12, 13] while complexes with two monodentate phosphine ligands or one bidentate phosphine ligand favour η^2-coordination,[40] even with heteroarenes.[41] The structure in Figure 5 differs from [Ni(μ-κ^2(N,N):η^2-2,6-mes$_2$phen)]$_n$ (n = 3,4),[23] where each nickel centre coordinates C5 and C6 in an η^2-mode rather than C2,C3,C4 in an η^3-mode as observed here.

Conclusions

We have evaluated the use of a sodium in sodium chloride dispersion for the reduction of nickel(II) complexes, with the aim of developing a robust and general method for the selective formation of nickel(I) species. It is apparent from the range of outcomes and often low yields that this methodology does not meet the initial aims of the work. However, several new complexes have been prepared and characterised, building upon recent investigations of nickel(I) complexes that may be relevant to catalysis.[42]

We should note several general observations from this work. The variable solubility of the nickel(II) precursors presents a challenge in many cases; while the procedure involves a grinding step, it is apparent that the reduction itself most likely takes place on the addition of solvent. Most nickel(II) dichloride complexes are relatively poorly soluble in THF solvent, and so this can lead to two-electron reduction taking place if the nickel(I) intermediate is more soluble. This is most apparent in the case of the dppe and dppp complexes, where the product was a mixture of nickel(0) and nickel(II). The procedure appeared to be more selective for nickel complexes with nitrogen ligands, but the low yields mean that this procedure is unlikely to be an efficient method for the synthesis of these complexes on scales greater than a millimole or so.

Experimental

General

Materials. All solvents were obtained commercially and used as supplied, unless otherwise stated. Anhydrous THF was obtained from an Innovative Technologies PureSolv system (< 10 ppm H_2O) and degassed by freeze-pump-thaw. Anhydrous 1,2-dimethoxyethane (DME) was obtained commercially. Ethanol was degassed by sparging with nitrogen. [$NiCl_2$(DME)] was prepared using the literature procedure.[43]

NMR Spectroscopy. NMR spectroscopy was carried out using a Bruker AV3-400 spectrometer equipped with a liquid nitrogen Prodigy cryoprobe or a Bruker AV3-400Nano spectrometer equipped with a BBFO-*z*-ATMA probe. Chemical shifts (^{1}H) were internally referenced to the residual solvent signal.[44] Coupling constants are reported in Hertz.

X-ray Crystallography. Single crystal x-ray diffraction data for [NiCl(dcpe)] and [NiCl(dmbpy)] were measured with an Oxford Diffraction Gemini S instrument while data for [Ni_3(phen)$_3$].2THF were measured with a Rigaku Synergy-i instrument. All used Cu Kα(λ = 1.54184 Å) radiation. Data collection and processing used CrysalisPro software.{NOTE:CrysalisPro (Rigaku Oxford Diffraction,2019)} The structures were refined to convergence on F2 using all independent reflections and the program SHELXL-2018 as implemented within WinGX.{Sheldrick, 2015 #19426}{Farrugia, 2012 #19427} The non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in idealised positions and refined in riding modes. Selected crystallographic data and refinement parameters are presented in the Supporting Information. CCDC deposition numbers CCDC 2104986 to 2104988 contain the full supplementary crystallographic data for this paper in cif format. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

EPR Spectroscopy. EPR spectroscopic analyses were conducted using a Bruker ELEXSYS E500 spectrometer, and simulations were performed using Bruker Xsophe software.[46]

Synthesis of Nickel(II) Phosphine Complexes

General. Nickel(II) dichloride complexes of mono- and bidentate phosphines were typically prepared from $NiCl_2.6H_2O$ or [$NiCl_2$(DME) in degassed ethanol according to the published method.[9] Data are reported here for complexes where a deviation from the published procedure was used or where the complex has not been reported previously.

***trans*-[$NiCl_2$(P*n*-Bu_3)$_2$]**. Synthesised as a red crystalline solid by precipitation from a saturated ethanol solution using distilled water. 80% yield. **^{1}H NMR** (400 MHz, C_6D_6): δ_H 1.80-1.45 (m, 36H, CH_2), 0.93 (t, *J* = 6.7 Hz, CH_3). **^{31}P{^{1}H} NMR** (161 MHz, C_6D_6): -2.3 (s).

***trans*-[$NiCl_2$(PPh_3)$_2$]**. Synthesised as a red crystalline solid (99% recovery) by slurrying the tetrahedral form in DCM for 1 h, followed by vacuum filtration.

[$NiCl_2$(dcpe)].[47, 48] Synthesised as a paramagnetic orange powder from $NiCl_2$(DME) and dcpe using the general procedure but in THF rather than ethanol. 94% yield.

***trans*-[$NiCl_2$(PMe_3)$_2$]**. [$NiCl_2$(DME)] was suspended in anhydrous THF under a nitrogen atmosphere, and a toluene solution of trimethylphosphine was added. The reaction volume was decreased *in vacuo* and then hexane was added to precipitate a red crystalline solid. >99% yield. **^{1}H NMR** (400 MHz, C_6D_6): δ_H 0.97 (s, 18 H). **^{31}P{^{1}H} NMR** (161 MHz, C_6D_6): δ_P -8.5 (br s).

Synthesis of Nickel(II) Complexes of Nitrogen Ligands

Method A. [$NiCl_2$(DME)] and 1 equiv. of a bidentate polypyridyl ligand (L) were weighed into a vial, anhydrous DME (10 mL per mmol of Ni) was added, and the mixture was sonicated at room temperature for 45 minutes. The precipitate was isolated *via* vacuum filtration and washed with anhydrous DME (2x 10 mL) and diethyl ether (1x 10 mL) before drying under vacuum. The material was then stored in the glovebox.

Method B. [$NiCl_2$(DME)] and 1 equiv. of a bidentate polypyridyl ligand (L) were weighed into a vial, anhydrous THF or 9/1 *v*/*v* THF/DME (10 mL per mmol of Ni) was added, and the mixture was stirred at room temperature overnight. The precipitate was isolated *via* vacuum filtration and washed with anhydrous DME (1x 10 mL) and diethyl ether (2x 10 mL) before drying in the oven. The material was then stored in the glovebox.

[$NiCl_2$(dtbpy)]. Obtained as a pale blue-green powder using Method A (88%).

[$NiCl_2$(bpy)]. Obtained as a green powder using Method B (76%).

[$NiCl_2$(dmbpy)]. Obtained as a pink-red powder using Method B (83%).

[$NiCl_2$(phen)]. Obtained as a green powder using Method B (69%).

[$NiCl_2$(neoc)]. Obtained as an orange-yellow powder using Method B (84%).

Reduction of Nickel(II) Complexes

Method C. In an argon-filled glovebox, sodium dispersion (200 mg, 5.4% *w*/*w*, 0.475 mmol) was added to a 14 mL vial equipped with a large magnetic stirrer bar and 0.5 mmol of the nickel(II) complex. The vial was closed and the reactions were stirred at 300 rpm in the absence of solvent for 24 h. THF (10 – 12 mL) was added to suspend the material. The solution was passed through a syringe filter, and the vial and filter were washed with further THF (10 – 12 mL). The filtrate was transferred to a Schlenk flask, removed from the glovebox, and attached to a Schlenk line (also under argon). The solution was evaporated to dryness. The resulting solids were returned to the glovebox.

Reduction of [$NiCl_2$(PCy_3)$_2$]. Isolated 45 mg of an unidentified red solid.

Reduction of [$NiCl_2$(PMe_3)$_2$]. Isolated 85 mg of an unidentified diamagnetic purple-red solid. **^{1}H NMR** (400 MHz, C_6D_6): δ_H 1.15 (s), 0.94 (br s). **^{31}P{^{1}H} NMR** (161 MHz, C_6D_6): δ_P -21.6 (s).

Reduction of [$NiCl_2$(P*n*-$Bu)_3$]. Isolated 79 mg of a low-melting red solid, which comprises a mixture of [NiCl(P*n*-Bu_3)$_2$] (from EPR analysis) and an unidentified diamagnetic species. **^{1}H NMR**

(400 MHz, C_6D_6): δ_H 1.90 – 0.75 (m). **$^{31}P\{^1H\}$ NMR** (161 MHz, C_6D_6): δ_P 42.2 (s).

Reduction of [$NiCl_2(PPh_3)_2$]. Isolated 185 mg of [$NiCl(PPh_3)_2$] (63%). NMR data are consistent with the reported ^1H NMR spectrum of [$NiCl_2(PPh_3)_3$].

Reduction of [$NiCl_2$(dppm)]. Isolated 10 mg on a purple solid. The use of a modified method in which the THF suspension was stirred for a further hour increased the yield to 44 mg of a purple-black solid, but NMR analysis indicated the presence of several species. EPR analysis indicated no nickel(I) products.

Reduction of [$NiCl_2$(dppe)]. Isolated 44 mg of a blue-black solid, which comprises a mixture of [NiCl(dppe)] (from EPR analysis) and [$Ni(dppe)_2$] (from NMR analysis). **^1H NMR** (400 MHz, C_6D_6): δ_H 7.46 (br s, 16H), 6.94 (br s, 24H), 2.11 (t, J = 6 Hz, 8H). **$^{31}P\{^1H\}$ NMR** (161 MHz, C_6D_6): δ_P 44.1 (s).

Reduction of [$NiCl_2$(dppp)]. Isolated 80 mg of a blue-black solid, which comprises a mixture of [NiCl(dppp)] (from EPR analysis) and [$Ni(dppp)_2$] (from ^{31}P NMR analysis). **$^{31}P\{^1H\}$ NMR** (161 MHz, C_6D_6): δ_P 13.3 (s).

Reduction of [$NiCl_2$(dcpe)]. Isolated 12 mg of a yellow-orange powder, which is assigned as [NiCl(dcpe)] on the basis of EPR and single crystal X-ray diffraction analysis.

Reduction of [$NiCl_2$(XantPhos)]. Isolated 180 mg of an orange-brown powder, which was assigned as [NiCl(XantPhos)] on the basis of EPR spectroscopic analysis (56%).

Reduction of [$NiCl_2$(dppf)]. Isolated 144 mg of a dark orange powder (45%). Assigned as [NiCl(dppf)] based on EPR and NMR spectroscopy data, compared to literature data.[27]

Reduction of [$NiCl_2$(bpy)]. Isolated < 5 mg of material.

Reduction of [$NiCl_2$(dmbpy)]. Isolated 57 mg of a blue-green solid (21%). Assigned as [NiCl(dmbpy)] based on EPR spectroscopy and single crystal X-ray diffraction.

Reduction of [$NiCl_2$(dtbpy)]. Isolated 30 mg of a grey-green solid (8%). Assigned as [$Ni(\mu\text{-}Cl)(dtbpy)]_2$ by comparison of the NMR data with the literature.[37]

Reduction of [$NiCl_2$(phen)]. Isolated < 5 mg of material.

Reduction of [$NiCl_2$(neoc)]. Isolated 8 mg of material (3%). Assigned as [NiCl(neoc)] based on EPR spectroscopic data.

Author Contributions

ELBJH: conceptualisation, data curation, formal analysis, investigation, methodology, writing – original draft, writing – review & editing. ARK: data curation, formal analysis, investigation, resources. SS: data curation, formal analysis, investigation, resources, visualisation. DJN: conceptualisation, funding acquisition, project administration, resources, supervision, writing – original draft, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

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