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Synthesis, characterization and application of nickel(II) complexes modified with *N*,*N*′,*N*″-pincer ligands

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ABSTRACT

Different *N*,*N*″-substituted pyridine-2,6-dicarboxamides **1a**–**d** have been synthesized and treated with nickel(II) trifluoromethanesulfonate in the presence of an excess of tetraethylammonium hydroxide to form after double-deprotonation the nickel hydroxido complexes **4a**–**c**. These square planar complexes have been characterized by various techniques, which indicate a tridentate *N*,*N*′,*N*″-coordination mode of the ligands. The other coordination site on the nickel center is occupied by a hydroxido ligand. The reactivity of the complexes was studied in dehalogenation reactions and allows access to square planar nickel chlorido complexes **5a**–**c**. Moreover, by NMR studies it was found that nickel hydroxido complexes as well as chlorido complexes can be converted with diphenylsilane or lithium borohydride to nickel hydrido complexes, which can be seen as a possible catalytic intermediate in reduction chemistry. Based on that, the potential of complexes **4** and **5** were evaluated in the hydrosilylation of ketones to produce alcohols after work-up.

1. Introduction

Catalysis is one of the key methodologies for the development of sustainable, efficient, and selective reactions [1]. In this regard, metal catalysis has been proven to be an outstanding toolbox for such requirements [2]. Especially, the addition of ligands to the metals have a strong influence on the performance of the catalyst; hence the design of new ligands and the study of their coordination chemistry is of importance [3,4]. In this regard, in recent times tridentate pincer-type ligands have been established as useful tool for controlling the catalyst performance [5]. Furthermore, the inexpensiveness, great availability, easy synthesis, high tunability, high flexibility and stability of the ligands should be considered. With respect to these requirements an attractive ligand motif can be precursor **1**, which is simply accessible from commercially available chemicals and easily tunable (Fig. 1). Recently, the coordination chemistry of ligand precursor **1** towards nickel was studied revealing a tridentate pincer-type *N*,*N*′,*N*″-coordination geometry **2** and interesting reactivity of the corresponding complexes have been observed, e.g., activation of small molecules [6]. Moreover, initial investigations on the catalytic abilities have been carried out with this complex class [7]. For instance Ghosh and coworkers demonstrated the usefulness of complexes **2** in cross coupling reactions of C–H bonds or C–Cl bonds with Grignard reagents to create new carbon – carbon bonds.

On the other hand, more recently nickel complexes became attractive catalyst precursors for hydrosilylation reactions and performing a wide range of reductions, e.g., ketones, aldehydes, imines, olefins, alkynes in excellent yields and selectivities [8]. However, so far the catalytic activity of pincer complexes **2** was not evaluated in hydrosilylation reactions. Based on these recent achievements in hydrosilylation and our interest in nickel pincer complexes [9] we became interested in the synthesis and characterization of pincer complexes **2** and their application in hydrosilylation reactions of ketones.

2. Results and discussion

The ligand precursors **1** were synthesized in accordance to literature protocols [6,10]. In more detail, dipicolinic acid **3** was reacted with an excess of thionyl chloride (28 equiv.) under refluxing conditions for 12 h (Scheme 1). Subsequently, the volatiles were removed in vacuum and the residue was dissolved in THF. The solution was added to a mixture of the corresponding aniline (2.0 equiv.) and triethylamine (2.0 equiv.) in THF and stirred for 16 h at room temperature. The mixture was filtered and the solvent was removed in vacuum. The residue was washed with *n*-hex-

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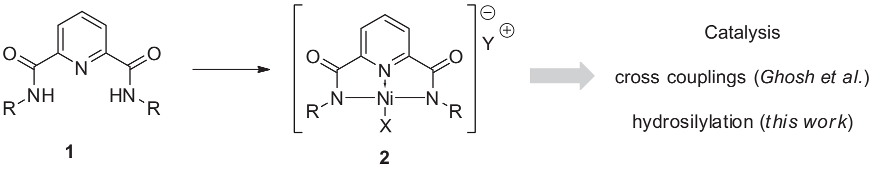
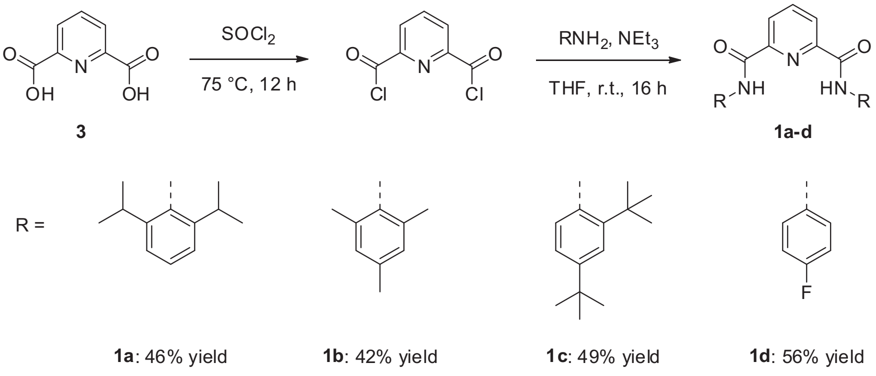


Fig. 1. Nickel complexes modified by *N*,*N*′,*N*″-ligands and application in catalysis.



Scheme 1. Ligand synthesis.

ane and diethyl ether. The colorless residues were dried in vacuum and recrystallized from ethanol or THF in yields of 42–56%.

Crystals suitable for single-crystal X-ray diffraction measurements were grown from ethanol or THF. The solid-state structures of the ligand precursors **1a**, **1c** and **1d** have been characterized by single-crystal X-ray diffraction analysis. The thermal ellipsoid plots, selected bond lengths and angles are shown in Figs. 2–4 and Table 1.

Afterwards the ligand precursors were reacted with nickel(II) trifluoromethanesulfonate ($Ni(OTf)_2$) and tetraethylammonium hydroxide in accordance to literature protocols (Scheme 2) [6]. After 12 h at room temperature the red nickel complexes **4** were isolated in 81–94% yields. Crystals suitable for single-crystal X-ray diffraction measurements were grown from diethylether or ethyl acetate. The solid-state structures of complexes **4a**, **4b** and **4d** have been characterized by single-crystal X-ray diffraction analysis. The thermal ellipsoid plots, selected bond lengths and angles are shown in Figs. 5 and 6, and Table 2. In more detail, the tridentate dianionic ligand (**1**-2H) is coordinated in a *N*,*N*′,*N*″-mode creating two five-membered planar ring system and therefore shielding one site of the metal. In case of complexes **4a** and **4c** the additional coordination site of the square planar nickel complexes are occupied by a hydroxido ligand. Moreover, both anionic complexes are

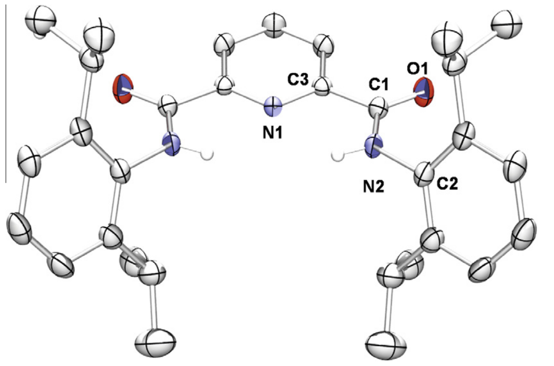


Fig. 2. Molecular structure of ligand precursor **1a**. Thermal ellipsoids are drawn at the 50% probability level. Most hydrogen atoms and one THF molecule are omitted for clarify. Selected bond lengths (Å) and angle (°): C1–O1: 1.229(2), N2–C1: 1.3416(18), N2–C2: 1.438(2), C3–C1–N2: 114.69 (12).

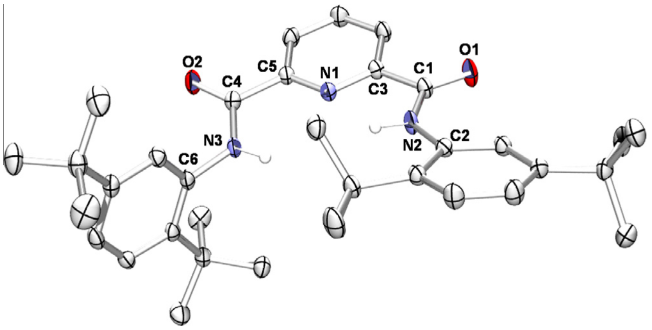


Fig. 3. Molecular structure of ligand precursor **1c**. Thermal ellipsoids are drawn at the 50% probability level. Most hydrogen atoms are omitted for clarify. Selected bond lengths (Å) and angle (°): C1–O1: 1.2152(17), C4–O2: 1.2185(18), N2–C1: 1.3554(19), N2–C2: 1.4141(18), N3–C4: 1.3519(19), N3–C6: 1.4391(18), C3–C1–N2: 111.94(12), C5–C4–N3: 113.84(12).

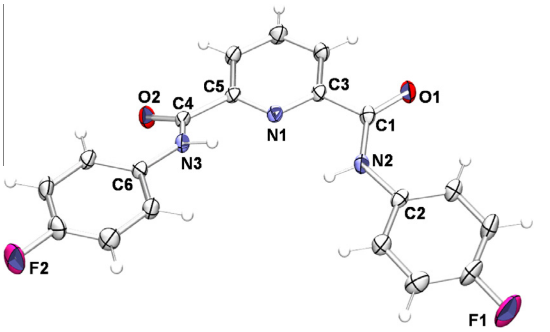


Fig. 4. Molecular structure of ligand precursor **1d**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angle (°): C1–O1: 1.2254(16), C4–O2: 1.2285(16), N2–C1: 1.3469(18), N2–C2: 1.4109(17), N3–C4: 1.3476(17), N3–C6: 1.4147(16), C3–C1–N2: 120.71(12), C5–C4–N3: 120.69(12).

Table 1
Analytical properties of the ligand precursors **1**.

	1a	**1b**	**1c**	**1d**
C1(4)–O1(2) (Å)	1.229(2)	–	1.2152(17)	1.2254(16)
			1.2185(18)	1.2285(18)
N2(3)–C1(4) (Å)	1.3416(18)	–	1.3554(19)	1.3469(18)
			1.4141(18)	1.3476(17)
N2(3)–C2(6) (Å)	1.438(2)	–	1.3519(19)	1.4109(17)
			1.4391(18)	1.4147(16)
C3(5)–C1(4)–N2(3) (°)	114.69(12)	–	111.94(12)	120.71(12)
			113.84(12)	120.69(12)
$^{13}C\{^1H\}$ NMR[a] (C1) (ppm)	162.6	161.7	162.1	162.3[b]
ν (C=O) (cm^{-1})[c]	1666	1680	1699	1666

[a] In $CDCl_3$ at r.t.
[b] In THF-d8 at r.t.
[c] In KBr.

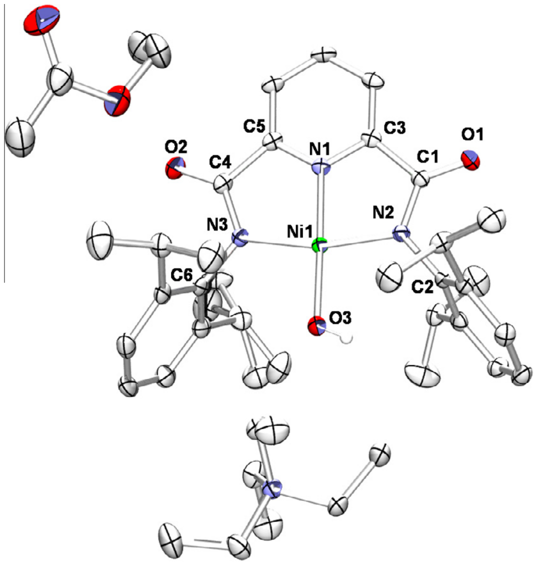


Fig. 5. Molecular structure of complex **4a-EtOAc**. Thermal ellipsoids are drawn at the 50% probability level. Most hydrogen atoms are omitted for clarify. Selected bond lengths (Å) and angle (°): C1–O1: 1.240(3), C4–O2: 1.239(3), N2–C1: 1.347(3), N2–C2: 1.431(3), N3–C4: 1.345(3), N3–C6: 1.429(3), Ni1–O3: 1.8177(16), Ni1–N1: 1.8199(18), Ni1–N2: 1.9125(17), Ni1–N3: 1.9086(18), C3–C1–N2: 110.30(18), C5–C4–N3: 109.97(19), O3–Ni1–N1: 178.08(8), O3–Ni1–N3: 95.49(7), N1–Ni1–N3: 82.85(8), O3–Ni1–N2: 98.58(7), N1–Ni1–N2: 83.06(8), N3–Ni1–N2: 165.89(7).

stabilized by tetraethylammonium cations. Comparing the bond lengths and angles of the ligand precursor **1a** with complex **4a** revealed only minor structural changes. For instances the C=O bond length is only slightly elongated e.g., 1.229(2) for **1a** and 1.239(3)–1.240(3) for **4a** and the C3–C1–N2 angle is reduced, e.g., 114.69(12) for **1a** and 109.97(19)–110.30(18) for **4a**. In contrast to complexes **4a** and **4c** for the reaction of **1d** with $Ni(OTf)_2$ and tetraethylammonium hydroxide as product an octahedral nickel complex was observed by single-crystal X-ray diffraction meas urements (see Supporting information). In more detail, two ligands (**1d**-2H) are coordinated to the metal center in a *N*,*N*′,*N*″-coordination mode.

The diamagnetic complexes **4a**–**c** were investigated by ^1H NMR spectroscopy, showing signals in the range of −4.90 to −5.23 ppm, which could be assigned to the hydroxido ligand (–O*H*). Moreover, the absence of any signals for the N*H* function proves the deprotonation of **1** and the tridentate coordination mode. In case of $^{13}C\{^1H\}$ NMR measurements a shift of the signal for the C1 to lower field was noticed. The effect of coordination on the C=O function was also observed by IR measurements, e.g., the signals were shifted by 56–84 cm^{-1}.

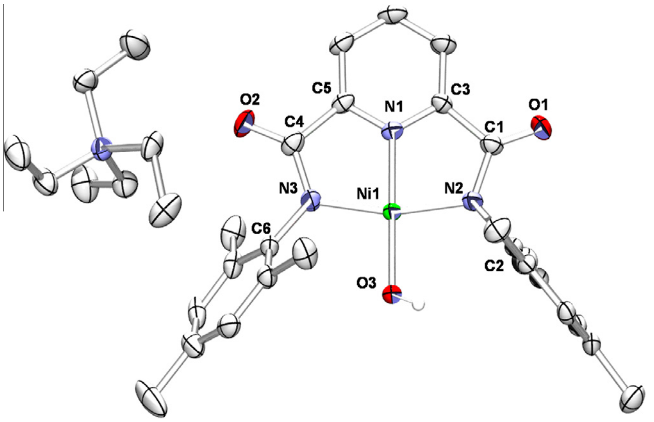


Fig. 6. Molecular structure of complex **4b**. Thermal ellipsoids are drawn at the 50% probability level. Most hydrogen atoms are omitted for clarify. Selected bond lengths (Å) and angle (°): C1–O1: 1.229(3), C4–O2: 1.232(3), N2–C1: 1.349(3), N2–C2: 1.423(3), N3–C4: 1.352(3), N3–C6: 1.418(3), Ni1–O3: 1.825(2), Ni1–N1: 1.822(2), Ni1–N2: 1.923(2), Ni1–N3: 1.903(2), C3–C1–N2: 109.8(2), C5–C4–N3: 109.3(2), O3–Ni1–N1: 176.97(13), O3–Ni1–N3: 97.09(8), N1–Ni1–N3: 82.76(8), O3–Ni1–N2: 97.41(8), N1–Ni1–N2: 82.87(8), N3–Ni1–N2: 165.35(9).

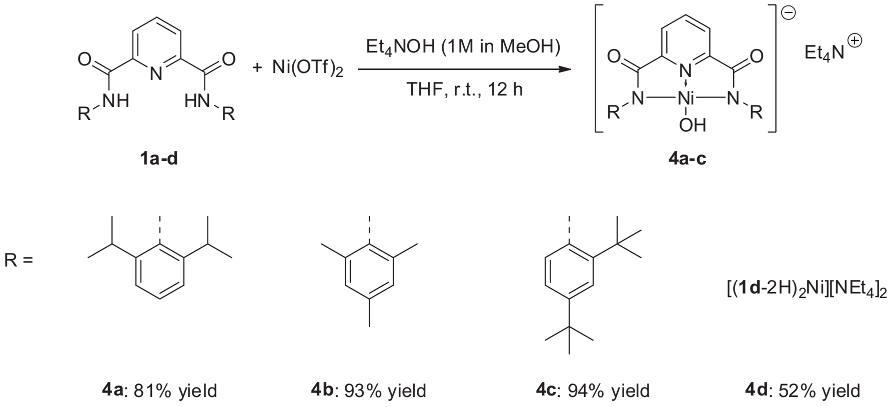
Table 2
Analytical properties of complexes **4**.

	4a	**4b**	**4c**
Ni1–N1 (Å)	1.820(2)	1.822(2)	–
Ni1–N2 (Å)	1.913(2)	1.923(2)	–
Ni1–N3 (Å)	1.9086(18)	1.903(2)	–
Ni1–O3 (Å)	1.818(2)	1.825(2)	–
N1–Ni1–N2 (°)	83.06(8)	82.87(8)	–
N1–Ni1–O3 (°)	178.08(8)	176.97(13)	–
C3(5)–C1(4)–N2(3) (°)	110.30(18)	109.8(2)	–
	109.97(19)	109.3(2)	
^1H NMR (–O*H*) (ppm)	−5.23[a]	−4.90[b]	−5.00[b]
$^{13}C\{^1H\}$ NMR (C1) (ppm)	167.2[a]	168.7[b]	167.5[b]
Δ (C1) (ppm)[c]	4.6	7.0	5.4
ν (C=O) (cm^{-1})[d]	1611	1602	1615
Δ (C=O) (cm^{-1}) [e]	56	79	84

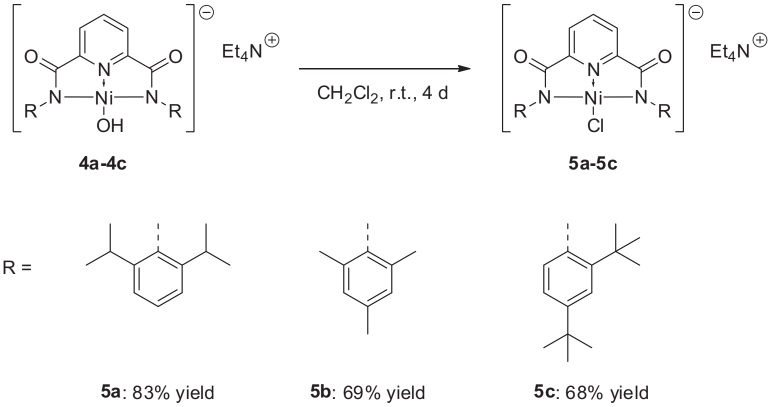
[a] In THF-d8 at r.t.
[b] In CD_2Cl_2 at r.t.
[c] Δ (C1) = δ (C=O-**4**) − δ (C=O-**1**).
[d] In KBr.
[e] Δ (C=O) = ν (C=O-**1**) − ν (C=O-**4**).

Afterwards the nickel hydroxido complexes **4** were converted to nickel chlorido complexes **5** (Scheme 3). In more detail, complexes **4** were dissolved in dichloromethane and stirred for 4 days at room temperature. The complexes **5** were isolated in 68–83% yield. Crystals suitable for single-crystal X-ray diffraction measurements were grown from dichloromethane. The solid-state structures of complexes **5a** and **5b** have been characterized by single-crystal X-ray diffraction analysis. The thermal ellipsoid plots, selected bond lengths and angles are shown in Figs. 7 and 8. In more detail, a similar square planar coordination geometry for complexes **5** with similar bond lengths and angles as found for complexes **4** was observed (Table 3).

After having synthesized a set of nickel(II) complexes attempts were undertaken to convert the nickel(II) hydroxido complexes to nickel(II) hydrido complexes (Scheme 4). In more detail, the nickel(II) hydroxido complex **4b** was reacted with diphenylsilane at low temperature (−70 °C) in THF-d8 [11]. Interestingly, along to the signal for the hydroxido complex (–O*H*) a new signal at −22.5 ppm was observed by ^1H NMR measurements, which can be assigned in accordance to earlier reports as a nickel hydrido complex [11]. After one hour at room temperature the hydroxido



Scheme 2. Synthesis of complexes **4**.



Scheme 3. Synthesis of complexes **5**.

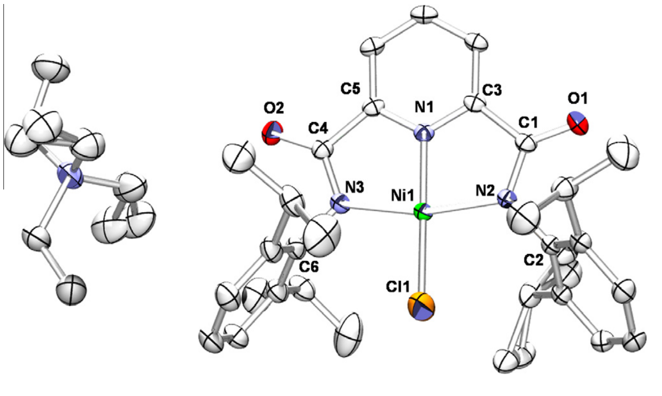


Fig. 7. Molecular structure of complex **5a-H$_2$O**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and a water molecule are omitted for clarify. Selected bond lengths (Å) and angle (°): C1–O1: 1.243(3), C4–O2: 1.244(3), N2–C1: 1.341(3), N2–C2: 1.434(3), N3–C4: 1.341(3), N3–C6: 1.430(3), Ni1–Cl1: 2.1839(10), Ni1–N1: 1.826(2), Ni1–N2: 1.912(2), Ni1–N3: 1.911(2), C3–C1–N2: 110.1(2), C5–C4–N3: 110.4(2), N1–Ni1–Cl1: 175.97(7), Cl1–Ni1–N3: 97.17(7), N1–Ni1–N3: 82.77(9), Cl1–Ni1–N2: 97.59(7), N1–Ni1–N2: 82.44(9), N3–Ni1–N2: 165.21(10).

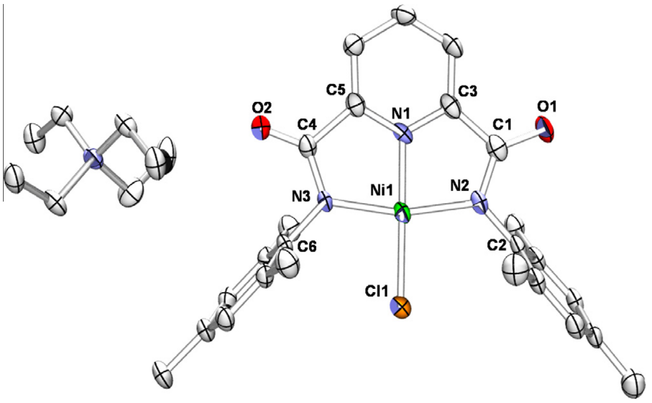


Fig. 8. Molecular structure of complex **5b**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarify. Selected bond lengths (Å) and angle (°): C1–O1: 1.258(7), C4–O2: 1.226(7), N2–C1: 1.339(8), N2–C2: 1.418(8), N3–C4: 1.342(8), N3–C6: 1.425(6), Ni1–Cl1: 2.1850(16), Ni1–N1: 1.837(5), Ni1–N2: 1.912(5), Ni1–N3: 1.911(4), C3–C1–N2: 111.1(5), C5–C4–N3: 110.2(5), Cl1–Ni1–N1: 177.41(16), Cl1–Ni1–N3: 97.07(14), N1–Ni1–N3: 82.4(2), Cl1–Ni1–N2: 97.97(16), N1–Ni1–N2: 82.6(2), N3–Ni1–N2: 165.0(2).

complex was completely converted to the nickel(II) hydrido complex. Attempts to isolate complex **6b** failed so far. In contrast to that complex **4a** was not converted to the corresponding hydrido complex **6a**. Even after heating to 50 °C **6a** was not detected. In case of complex **4c** the hydrido complex **6c** was observed in lower yield compared to **6b** and two sets of signals were monitored. On the other hand, the reaction of the chlorido complexes **5** with diphenylsilane did not lead to the formation of the desired hydrido complexes **6**. However, changing the hydride source to lithium borohydride allows access to **6** in low yields. Interestingly, the formation of hydrido complexes especially with silanes can be useful for hydrosilylation catalysis.

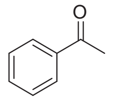
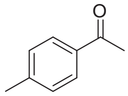
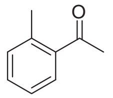
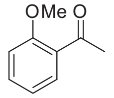
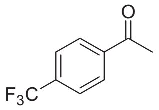
Based on that, the catalytic abilities of complex **4b** were studied in the hydrosilylation of ketones (Table 4). In more detail, 2.5 mol% of **4b** were reacted with diphenylsilane and the corresponding

Table 3
Analytical properties of complexes **5**.

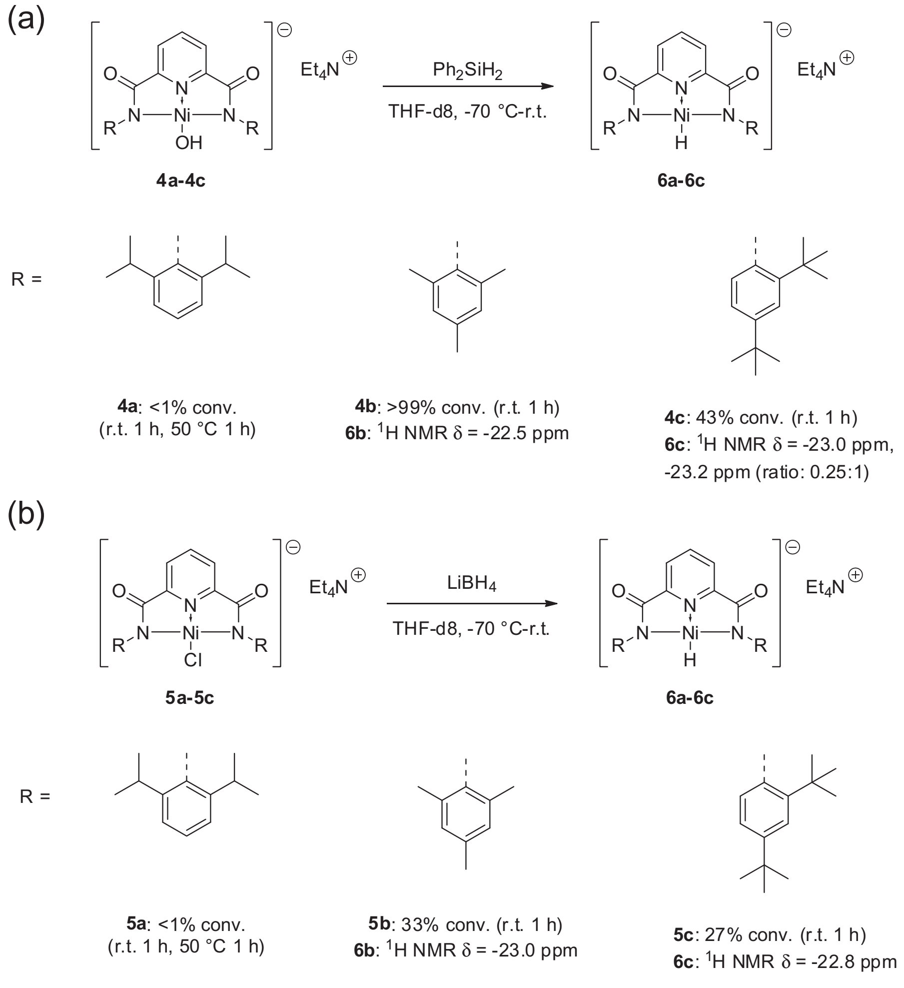
	5a	**5b**	**5c**
Ni1–N1 (Å)	1.826(2)	1.837(5)	–
Ni1–N2 (Å)	1.912(2)	1.912(5)	–
Ni1–N3 (Å)	1.911(2)	1.911(4)	–
Ni1–Cl1 (Å)	2.1839(10)	2.1850(16)	–
N1–Ni1–N2 (°)	82.44(9)	82.6(2)	–
N1–Ni1–Cl1 (°)	175.97(7)	177.41(16)	–
C3(5)–C1(4)–N2(3) (°)	110.1(2) 110.4(2)	111.1(5) 110.2(5)	–
$^{13}C\{^1H\}$ NMR (ppm)[a]	169.5	168.6	169.7
Δ (C1) (ppm)[b]	2.3	−0.1	2.2
Δ (C1) (ppm)[c]	4.6	7.0	7.0
ν (C=O) (cm^{-1})[d]	1616	1615	1632
ν (C=O) (cm^{-1})[e]	5	3	30
Δ (C=O) (cm^{-1})[f]	50	65	67

[a] In CD_2Cl_2 at r.t.
[b] Δ (C1) = δ (C=O-**5**) − δ (C=O-**4**).
[c] Δ (C1) = δ (C=O-**5**) − δ (C=O-**1**).
[d] In KBr.
[e] Δ (C=O) = ν (C=O-**5**) − ν (C=O-**4**).
[f] Δ (C=O) = ν (C=O-**1**) − ν (C=O-**4**).

Table 4
Hydrosilylation of ketones.

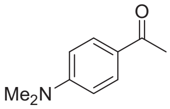
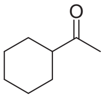
Entry	Substrate	Yield (%) (**4b**)	Yield (%) (**5b**)[a]
1		>99	>99
2		>99	>99
3		<1	<1
4		10	<1
5		>99	>99

ketone at 70 °C for 24 h in THF. Excellent performance was observed for different *p*-substituted acetophenones, while *o*-substitution revealed the formation of the products in low yields, probably due to sterical hindrance. Moreover, no activity was observed in case of dialkyl ketones. On the other hand, similar results were observed for complex **5b**, which was pre-treated with $LiBH_4$.



Scheme 4. Synthesis of hydrido complexes **6**.

Table 4 (*continued*)

Entry	Substrate	Yield (%) (**4b**)	Yield (%) (**5b**)[a]
6		>99	>99
7		<1	<1

Reaction conditions: 2.5 mol% complex **4b** or **5b**, Ph_2SiH_2 (0.75 mmol, 1.5 equiv.), ketone (0.5 mmol), THF (2.0 mL), 70 °C, 24 h. Yield determined by ^1H NMR and GC–MS.

[a] **5b** was pre-treated with LiBH4.

3. Conclusion

In summary, we synthesized and characterized nickel hydroxido complexes **4a**–**c**, which are easily derived from *N*,*N''*-substituted pyridine-2,6-dicarboxamides **1a**–**d**, nickel(II) trifluoromethanesulfonate and tetraethylammonium hydroxide. In more detail, a pincer-type tridentate *N*,*N'*,*N''*-coordination mode of the ligands (**1**-2H) was observed after double deprotonation. The other coordination site on the square planar nickel centre is occupied by a hydroxido ligand. The reactivity of these complexes was examined in dehalogenation reactions to allow access to square planar nickel chlorido complexes **5a**–**c**. Moreover, by NMR studies it was found that nickel hydroxido complexes as well as chlorido complexes can be converted with diphenylsilane or lithium borohydride to nickel hydrido complexes, which can be seen as a possible catalytic intermediate in reduction chemistry. Indeed, complexes **4** and **5** showed activity in the hydrosilylation of ketones to produce alcohols after work-up.

Acknowledgements

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2014.10.003.

References

[1] (a) P.T. Anastas, M.M. Kirchhoff, Acc. Chem. Res. 35 (2002) 686;
(b) P.T. Anastas, M.M. Kirchhoff, T.C. Williamson, Appl. Catal. A 221 (2001) 3;
(c) P.T. Anastas, ChemSusChem 2 (2009) 391.

[2] (a) B. Cornils, W.A. Herrmann, Applied Homogeneous Catalysis with Organometallic Compounds, Wiley-VCH, Weinheim, 1996;
(b) M. Beller, C. Bolm, Transition Metals for Organic Synthesis, Wiley-VCH, Weinheim, 2004;
(c) B. Cornils, W.A. Herrmann, I.T. Horváth, W. Leitner, S. Mecking, H. Olivier-Bourbigou, D. Vogt, Multiphase Homogenous Catalysis, Wiley-VCH, Weinheim, 2005;
(d) A. Behr, Angewandte homogene Katalyse, Wiley-VCH, Weinheim, 2008.

[3] (a) A. Börner, Phosphorus Ligands in Asymmetric Catalysis, Wiley-VCH, Weinheim, 2008;
(b) Q.-L. Zhou, Privileged Chiral Ligands and Catalysts, Wiley-VCH, Weinheim, 2011.

[4] A selection: (a) R.D. Hancock, A.E. Martell, Chem. Rev. 89 (1989) 1875–1914;
(b) A.L. Gavrilova, B. Bosnich, Chem. Rev. 104 (2004) 349–383;
(c) M. Miura, Angew. Chem. 116 (2004) 2251–2253;
(d) Angew. Chem., Int. Ed., 2004, 43, 2201–2203;
(e) P.J. Steel, Acc. Chem. Res. 38 (2005) 243–250;
(f) A.S. Borovik, Acc. Chem. Res. 38 (2005) 54–61.

[5] K.J. Szabó, O.F. Wendt (Eds.), Pincer Ligands, in Pincer and Pincer-Type Complexes: Applications in Organic Synthesis and Catalysis, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2014.

[6] (a) O. Troeppner, D. Huang, R.H. Holm, I. Ivanovic-Burmazovic, Dalton Trans. 43 (2014) 5274;
(b) J. Tehranchi, P.J. Donoghue, C.J. Cramer, W.B. Tolman, Eur. J. Inorg. Chem. (2013) 4077;
(c) X. Zhang, D. Huang, Y.-S. Chen, R.H. Holm, Inorg. Chem. 51 (2012) 11017;
(d) D. Huang, O.V. Makhlynets, L.L. Tan, S.C. Lee, E.V. Rybak-Akimova, R.H. Holm, Inorg. Chem. 50 (2011) 10070;
(e) D. Huang, O.V. Makhlynets, L.L. Tan, S.C. Lee, E.V. Rybak-Akimova, R.H. Holm, Proc. Nat. Ac. Sci. U.S.A 108 (2011) 1222;
(f) Y. Perez, A.L. Johnson, P.R. Raithby, Polyhedron 30 (2011) 284;
(g) D. Huang, R.H. Holm, J. Am. Chem. Soc. 132 (2010) 4693;
(h) S.G. Liu, Y.Z. Li, J.L. Zuo, X.Z. You, Acta Crystallogr., Sect. E 60 (2004) m1153;
(i) Q. Yu, T.E. Baroni, L. Liable-Sands, A.L. Rheingold, A.S. Borovik, Tetrahedron Lett. 39 (1998) 6831;
(j) A.K. Patra, R. Mukherjee, Inorg. Chem. 38 (1999) 1388;
(k) T. Kawamoto, B.S. Hammes, R. Ostrander, A.L. Rheingold, A.S. Borovik, Inorg. Chem. 37 (1998) 3424;
(l) E.K. van den Beuken, A. Meetsma, H. Kooijman, A.L. Spek, B.L. Feringa, Inorg. Chim. Acta 264 (1997) 171;
(m) J.G.H. Du Preez, B.J.A.M. van Brecht, Inorg. Chim. Acta 162 (1989) 49.

[7] (a) Y. Gartia, P. Ramidi, D.E. Jones, S. Pulla, A. Ghosh, Catal. Lett. 144 (2014) 507;
(b) Y. Gartia, A. Biswas, M. Stadler, U.B. Nasini, A. Ghosh, J. Mol. Catal. A: Chem. 363–364 (2012) 322.

[8] See the most recent works and references therein: (a) S.N. MacMillan, H.W. Hill, J.C. Peters, Chem. Sci. 5 (2014) 590–597;
(b) L.P. Bheeter, M. Henrion, M.J. Chetcuti, C. Darcel, V. Ritleng, J.-B. Sortais, Catal. Sci. Technol. 3 (2013) 3111–3116;
(c) L. Gonzalez-Sebastian, M. Flores-Alamo, J.J. Garcia, Organometallics 32 (2013) 7186–7194;
(d) T.M. Porter, G.B. Hall, T.L. Groy, R.J. Trovitch, Dalton Trans. 42 (2013) 14689–14692;
(e) Z.D. Miller, W. Li, T.R. Belderrain, J. Montgomery, J. Am. Chem. Soc. 135 (2013) 15282–15285;
(f) J. Zheng, T. Roisnel, C. Darcel, J.-B. Sortais, ChemCatChem 5 (2013) 2861–2864;
(g) M.L. Lage, S.J. Bader, K. Sa-ei, J. Montgomery, Tetrahedron 69 (2013) 5609–5613;
(h) A. Kuznetsov, Y. Onishi, Y. Inamoto, V. Gevorgyan, Org. Lett. 15 (2013) 2498–2501;
(i) J. Zheng, C. Darcel, J.-B. Sortais, Catal. Sci. Technol. 3 (2013) 81–84.

[9] (a) C.I. Someya, S. Inoue, S. Krackl, E. Irran, S. Enthaler, Eur. J. Inorg. Chem. (2012) 1269;
(b) C.I. Someya, E. Irran, S. Enthaler, Asian J. Org. Chem. 2 (2013) 322;
(c) M. Weidauer, E. Irran, C.I. Someya, M. Haberberger, S. Enthaler, J. Organomet. Chem. 729 (2013) 53;
(d) M. Weidauer, E. Irran, C.I. Someya, S. Enthaler, Asian J. Org. Chem. 2 (2012) 150;
(e) C.I. Someya, E. Irran, S. Enthaler, Inorg. Chim. Acta 2014 (2014), http://dx.doi.org/10.1016/j.ica.2014.05.023;
(f) C.I. Someya, S. Inoue, E. Irran, S. Enthaler, Inorg. Chem. Commun. 44 (2014) 114–118;
(g) C.I. Someya, M. Weidauer, S. Enthaler, Catal. Lett. 143 (2013) 424;
(h) S. Enthaler, M. Weidauer, E. Irran, J.D. Epping, R. Kretschmer, C.I. Someya, J. Organomet. Chem. 745–746 (2013) 262.

[10] (a) B.-L. An, J.-X. Shi, W.-K. Wong, K.-W. Cheah, R.-H. Li, Y.-S. Yang, M.-L. Gong, J. Lumin. 99 (2002) 155;
(b) Y. Yan, W. Zhao, G.V. Bhagavathy, A. Faurie, N.J. Mosey, A. Petitjean, Chem. Commun. 48 (2012) 7829;
(c) T. Lang, A. Guenet, E. Graf, N. Kyritsakas, M.W. Hosseini, Chem. Commun. 46 (2010) 3508;
(d) S.L. Jain, P. Bhattacharyya, H.L. Milton, A.M.Z. Slawin, J.A. Crayston, J.D. Woollins, Dalton Trans. (2004) 862;
(e) N. Kleigrewe, W. Steffen, T. Blömker, G. Kehr, R. Fröhlich, B. Wibbeling, G. Erker, J.-C. Wasilke, G. Wu, G.C. Bazan, J. Am. Chem. Soc. 127 (2005) 13955;
(f) Y. Gartia, A. Biswas, M. Stadler, U.B. Nasini, A. Ghosh, J. Mol. Catal. A: Chem. 363–364 (2012) 322;
(g) J.-C. Wasilke, G. Wu, X. Bu, G. Kehr, G. Erker, Organometallics 24 (2005) 4289.

[11] J. Breitenfeld, R. Scopelliti, X. Hu, Organometallics 31 (2012) 2128.