A low-coordinate nickel(II) hydride complex and its reactivity†

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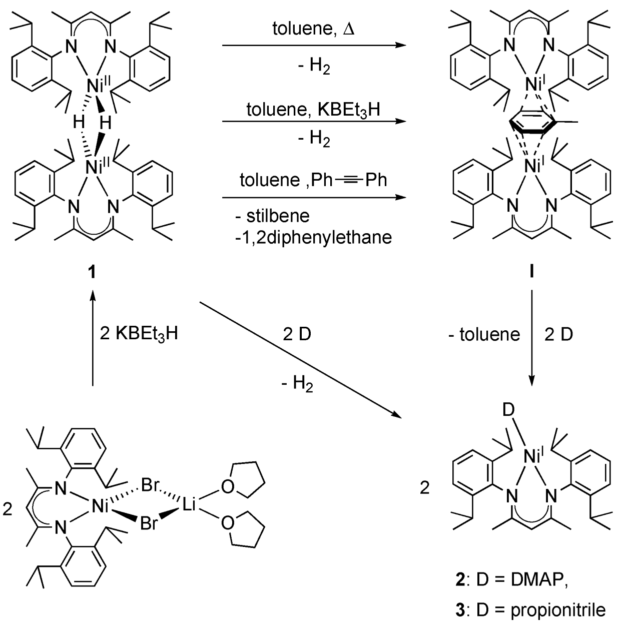
The preparation of a novel dinuclear nickel(II) hydride complex and its reactivity that often leads to nickel(I) compounds is described.

There is a lot of interest in low-coordinate transition metal complexes as they are often highly reactive: their flexibility in exogenous ligand binding accounts for a high diversity of conversions within the coordination sphere of the metal, if this contains a reactive unit to start from. In this respect metal-hydride entities are particularly interesting, first, because their behaviour depends a lot on the residual ligand sphere and secondly as they are capable of initiating the most different transformations. A lot of fascinating chemistry is found for the combination of hydride ligands with nickel: this ranges from the activation of H_2 by Raney nickel,[1] *via* elementary steps within the SHOP process[2,3] to hydrogenase enzymes where hydride bridges between nickel and iron are proposed to be central to the reactivity.[4]

Here we describe a low-coordinate dinuclear nickel(II) complex that contains hydride bridges.

The β-diketiminato ligand has proved a very versatile ligand in the past, both in main group and transition metal chemistry,[5] as (i) it can be used to prepare coordinatively unsaturated complexes, (ii) it stabilises high as well as low oxidation states, and (iii) often its complexes show interesting reactivities.[6] Hence we chose this ligand system—that had already allowed for the isolation of low-valent iron-hydride complexes[7]—for our investigation concerning low-valent nickel hydrides.

For this purpose we have employed $LNi(\mu\text{-}Br)_2Li(thf)_2$—where L is the bulky β-diketiminato ligand shown in Scheme 1—for a reaction with $KBEt_3H$. Appropriate work-up led to the isolation of dark green crystals in 36% yield, and the X-ray‡ crystal structure revealed the product to have a dimeric constitution, $[LNiH]_2$, **1**, in the solid state. The nickel atoms are bridged by two hydride ligands which were located in the Fourier difference map (Scheme 1, Fig. 1). The distance between the nickel centers was found to be 2.3939(6) Å. Similarly as in other LNi complexes the N–Ni bond lengths are between 1.912(2) and 1.935(2) Å and the N–Ni–N chelate bite angles amount to 94.93(8) and 93.90(9)°.[8] As described for the analogous iron hydride complex the β-diketiminato-Ni rings in **1** twist into a distorted boat form caused by steric hindrance within the dimer. Therefore the N–Ni(1)–N plane is located at an angle of 30.9(3)° with respect to the C–C–C plane of the β-diketiminato ligand backbone.



Scheme 1 Synthesis and reactivity of **1**; D = donor.

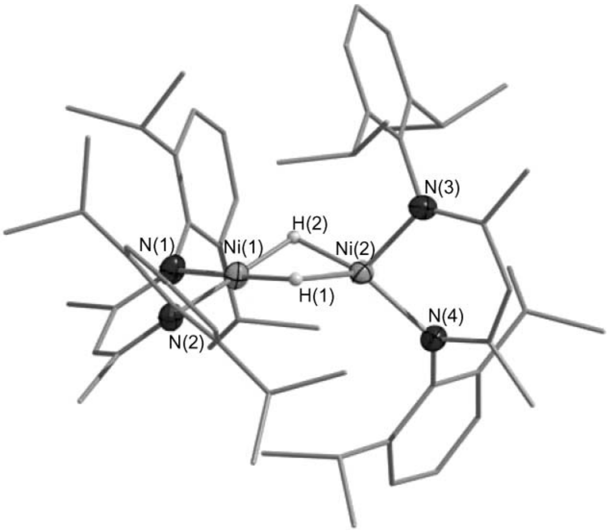


Fig. 1 Molecular structure of $[LNi(\mu\text{-}H)]_2$ **1**. Solvent molecules and hydrogen atoms apart from the bridging hydrides are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni(1)–Ni(2) 2.3939(6), Ni(1)–N(1) 1.912(2), Ni(1)–N(2) 1.9125(18), Ni(2)–N(3) 1.922(2), Ni(2)–N(4) 1.935(2); N(1)–Ni(1)–N(2) 94.93(8), N(3)–Ni(2)–N(4) 93.90(9).

The magnetic moment of **1** in the solid state at r.t. amounts to 3.05 μ_B per complex which is lower than the spin-only value expected for two uncoupled high-spin Ni(II) ions (4.00 μ_B for

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$g = 2.00$), which points to an antiferromagnetic coupling. **1** is EPR silent in frozen toluene solutions at 77 K.

The results of spectroscopic studies did not provide any evidence that on dissolution **1** enters into an equilibrium with a monomeric form: a ^{1}H-NMR spectrum of **1** dissolved in toluene-d_8 recorded at 80 °C did not show a further set of signals as compared to the r.t. spectrum. However, it turned out that on heating the complex slowly decomposes to give the known nickel(I) complex (LNi)$_2$(μ-η^3:η^3-C$_6$H$_5$Me), **I**,[9] which could unambiguously be identified by ^{1}H NMR spectroscopy, as well as H$_2$ (see Scheme 1). To clarify how the LNi(I) species formed in course of the reductive elimination of H$_2$ behaves, if no stabilising ligand (like toluene) is present in solution, **1** was also heated in hexane solution. Formation of a nickel mirror was observed then, and the solution obtained contains protonated ligand LH beside other unidentified (paramagnetic) products.

In order to see whether the dimer **1** can be broken up into monomers *via* the addition of external potential ligands, it was treated with nitrogen donors, D. Reaction with both 4-dimethylaminopyridine and propionitrile led to the reductive elimination of H$_2$ to give the T-shaped Ni(I) complexes LNiD (D = 4-dimethylaminopyridine (4-DMAP), **2**, and propionitrile, **3**), that can also be obtained by treating (LNi)$_2$(μ-η^3:η^3-C$_6$H$_5$Me) with D (see Scheme 1, for H$_2$ detection see electronic supplementary information, ESI†).

The molecular structure of **3** as revealed by single crystal X-ray crystallography‡ is shown in Fig. 2. Due to the asymmetric coordination of the propionitrile ligand the distances between the N atoms belonging to the β-diketiminato ligand and the Ni ion (Ni(1)–N(1) 1.861(2) and Ni(1)–N(2) 1.928(2) Å) and also the N(1)–Ni(1)–N(3) and N(2)–Ni(1)–N(3) angles (157.86(10) and 104.50(10)°) differ significantly. Strong σ donation of the nitrile ligand expresses itself by a Ni–N bond length of 1.857(3) Å. Altogether the geometry of **3** is in good agreement with other three coordinate Ni(I) β-diketiminato complexes described in the literature.[9,10]

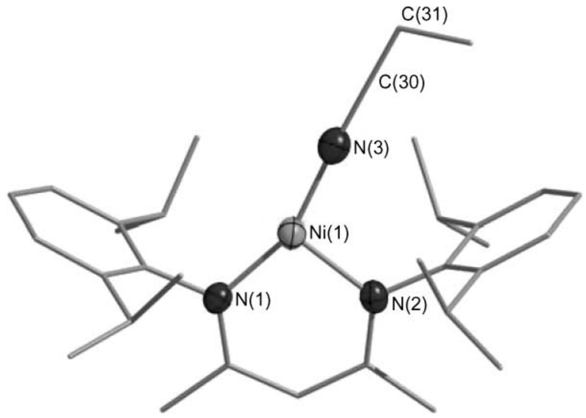

Fig. 2 Crystal structure of LNiNCEt **3**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni(1)–N(1) 1.861(2), Ni(1)–N(2) 1.928(2), Ni(1)–N(3) 1.857(3), N(3)–C(30) 1.149(4); N(1)–Ni(1)–N(2) 97.58(10), N(1)–Ni(1)–N(3) 157.86(10), N(2)–Ni(1)–N(3) 104.50(10), Ni(1)–N(3)–C(30) 177.5(3), N(3)–C(30)–C(31) 179.0(4).

Reductive elimination of dihydrogen on addition of ligands has been recently reported for an iron analogue[7d] and in one instance it has been observed for a nickel hydride complex bearing diphosphane ligands, too.[11] Remarkably, **1** exhibits this reactivity even in contact with B–H units, as we suspected noticing that employing excessive KBEt$_3$H for its synthesis leads to significantly decreased yields: Subsequently, independent experiments proved that indeed treatment of **1** with KBEt$_3$H in toluene leads to the known complex **I** and H$_2$.

The reactions of **1** with donors D must proceed through a mechanism where D binds to the metal first before H$_2$ loss occurs, as **1** is stable at r.t. in solution and under vacuum.

1 is stable in contact with potential π-ligands like diphenylacetylene. However on warming to 80 °C it transfers hydrogen onto the triple bond to give *cis*- and *trans*- diphenylethylene as well as diphenylethane (in 35%, 7% and 12% yield, respectively) as revealed by GC-MS and ^{1}H NMR spectroscopy. A further product is (in toluene) **I**. As PhCCPh does not react with H$_2$, we assume that H$_2$ is transferred directly from **1** to this substrate. There was no indication of an intermediate insertion of PhCCPh into one of the Ni–H bonds that would lead to a Ni–C(Ph)=C(Ph)H species as observed for corresponding iron complexes.[7a,d]

In conclusion we have shown that the first isolable low-coordinate nickel hydride complex readily eliminates H$_2$ in contact with external donors (or on heating) which leads to nickel(I) complexes. Alternatively, H$_2$ can be transferred to unsaturated substrates. Future research will now for instance address its reactivity towards oxidants (which might reveal interesting insights concerning the behaviour of [NiFe] hydrogenases that are O$_2$ sensitive) or towards iron hydrides in order to prepare [NiFe] hydrogenase mimics.

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Notes and references

‡ *Crystal data* for **1**·OEt$_2$: C$_{62}$H$_{94}$N$_4$Ni$_2$O, M = 1028.83, monoclinic, a = 11.5933(13), b = 18.187(2), c = 28.265(4) Å, β = 98.742(15)°, V = 5890.4(12) Å^3, T = 180(2) K, space group $P2_1/c$, Z = 4, μ(Mo-K$_\alpha$) = 0.681 mm^{-1}, 31426 reflections measured, 10624 unique (R_{int} = 0.0486), R_1 = 0.0380 ($I > 2\sigma(I)$), wR_2 = 0.0788 (all data). For **3**: C$_{32}$H$_{46}$N$_3$Ni, M = 531.43, triclinic, a = 8.812(2), b = 9.1249(16), c = 19.980(4) Å, α = 87.59(2), β = 80.83(3), γ = 73.63(3)°; V = 1521.7(5) Å^3, T = 180(2) K, space group P-1, Z = 2, μ(Mo-K$_\alpha$) = 0. 661 mm^{-1}, 15879 reflections measured, 5185 unique (R_{int} = 0.0601), R_1 = 0.0523 ($I > 2\sigma(I)$), wR_2 = 0.1365 (all data).

1 R. J. Kokes and P. H. Emmett, *J. Am. Chem. Soc.*, 1959, **81**, 5032–5037.
2 W. Keim, A. Behr, B. Limbäcker and C. Krüger, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 503; W. Keim, R. Appel, S. Gruppe and F. Knoch, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1012–1013; K. Nomura, *Recent Res. Dev. Pure Appl. Chem.*, 1998, **2**, 473–513; D. Vogt, in *Aqueous-Phase Organometallic Chemistry*, ed. B. Cornils and W. A. Herrmann, Wiley-VCH, Weinheim, 1998, p. 541.
3 E. Kogut, A. Zeller, T. H. Warren and T. Strassner, *J. Am. Chem. Soc.*, 2004, **126**, 11984–11994.
4 M. Brecht, M. van Gastel, T. Buhrke, B. Friedrich and W. Lubitz, *J. Am. Chem. Soc.*, 2003, **125**, 13075–13083; C. Mealli and T. B. Rauchfuss,

Angew. Chem., 2007, **119**, 9100–9102; C. Mealli and T. B. Rauchfuss, *Angew. Chem., Int. Ed.*, 2007, **46**, 8942–8944.

5 L. Bourget-Merle, M. F. Lappert and J. R. Severn, *Chem. Rev.*, 2002, **102**, 3031–3065.

6 (*a*) Y.-C. Tsai, P.-Y. Wang, S.-A. Chen and J.-M. Chen, *J. Am. Chem. Soc.*, 2007, **129**, 8066–8067; W. H. Monillas, G. P. A. Yap, L. A. MacAdams and K. H. Theopold, *J. Am. Chem. Soc.*, 2007, **129**, 8090–8091; (*b*) J. M. Smith, R. L. Lachicotte, K. A. Pittard, T. R. Cundari, G. Lukat-Rodgers, K. R. Rodgers and P. L. Holland, *J. Am. Chem. Soc.*, 2001, **123**, 9222–9223; (*c*) G. Bai and D. W. Stephan, *Angew. Chem.*, 2007, **119**, 1888–1891; (*d*) N. W. Aboelella, E. A. Lewis, A. M. Reynolds, W. W. Brennessel, C. J. Cramer and W. B. Tolman, *J. Am. Chem. Soc.*, 2002, **124**, 10660–10661; D. J. E. Spencer, N. W. Aboelella, A. M. Reynolds, P. L. Holland and W. B. Tolman, *J. Am. Chem. Soc.*, 2002, **124**, 2108–2109.

7 (*a*) J. M. Smith, R. J. Lachicotte and P. L. Holland, *J. Am. Chem. Soc.*, 2003, **125**, 15752–15753; (*b*) J. Vela, J. M. Smith, Y. Yu, N. A. Ketterer, C. J. Flaschenriem, R. J. Lachicotte and P. L. Holland, *J. Am. Chem. Soc.*, 2005, **127**, 7857–7870; (*c*) A. R. Sadique, E. A. Gregory, W. W. Brennessel and P. L. Holland, *J. Am. Chem. Soc.*, 2007, **129**, 8112–8121; (*d*) Y. Yu, A. R. Sadique, J. M. Smith, T. R. Dugan, R. E. Cowley, W. W. Brennessel, C. J. Flaschenriem, E. Bill, T. R. Cundari and P. L. Holland, *J. Am. Chem. Soc.*, 2008, **130**, 6624–6638.

8 N. A. Eckert, E. M. Bones, R. J. Lachicotte and P. L. Holland, *Inorg. Chem.*, 2003, **42**, 1720–1725.

9 G. Bai, P. Wei and D. W. Stephan, *Organometallics*, 2005, **24**, 5901–5908.

10 E. Kogut, H. L. Wiencko, L. Zhang, D. E. Cordeau and T. H. Warren, *J. Am. Chem. Soc.*, 2005, **127**, 11248–11249.

11 K. Jonas and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 312–313.