High-Oxidation-State Ni Complex

A Pseudotetrahedral, High-Oxidation-State Organonickel Compound: Synthesis and Structure of Bromotris(1-norbornyl)nickel(IV)**

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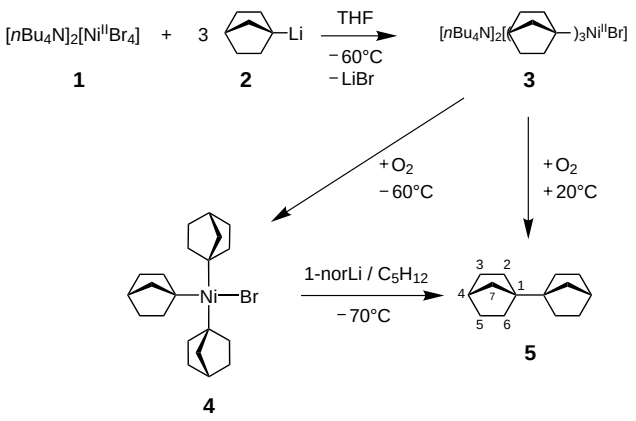
The organometallic chemistry of late transition metals in high oxidation states has been of considerable interest because of its relevance to certain catalytic reactions.[1–4] Organonickel compounds in the formal oxidation state +4 have been obtained by the oxidation of decamethylnickelocene[5] and in a trinickelacarborane complex.[6] The first examples of octahedral diorganonickel(IV) compounds containing σ-bonded methyl and acylphenolato ligands were reported only recently.[7] The occurrence of tetracoordinate organonickel(IV) intermediates has been proposed in some cases,[8] but there are no previous reports of the isolation of a tetrahedral nickel(IV) compound containing σ-bonded organic ligands. Herein we report the preparation of a tris(1-norbornyl)nickelate(II) complex and its oxidation, which results in the formation of a diamagnetic pseudotetrahedral triorganonickel(IV) compound. The tetrakis(1-norbornyl) compounds of the first-row metals, with the exception of nickel, are rare examples of high oxidation state homoleptic transition-metal alkyl complexes with extraordinarily high stability.[9]

Previously, we prepared several 1-norbonyl complexes of Ni^{II}, which include the nickelate(II) salt $Li[CpNi(1\text{-nor})_2]$ ($Cp = C_5H_5$), starting from nickelocene.[10] For the preparation of the tris(1-norbornyl)nickel(II) complex anion we now started from the pale blue compound $[n\mathrm{Bu_4N}]_2[Ni^{II}Br_4]$ (**1**). The reaction of **1** with three equivalents of 1-norbornyllithium (**2**) in THF at −60 °C gave a blue-green solution of the anionic complex **3** (Scheme 1). The reaction with four equivalents of **2** also produced **3** and not the tetrakis(1-norbonyl)nickel(II) complex, as was demonstrated by a subsequent transformation. Note that all previously reported nickel complexes of the type $Li_2[Ni^{II}R_4]$ are yellow.[11] Complex **3** could not be isolated because it decomposed during removal of the solvent, but it could be characterized by NMR spectroscopy after preparation in [D_8]THF (Table 1). A solution of **3** in THF can be handled at room temperature for 1 h without decomposition. By following analogous procedures reported in the literature,[12] complex **3** was oxidized at −60 °C by bubbling air through this THF solution. The resulting nickel(IV) complex **4** was isolated by pentane extraction and crystallization as a red-brown crystalline solid. Compound **4** is stable in air for several days. On heating, it decomposes at 131–133 °C without melting. Conversely, decomposition of **4** occurs rapidly in solution, as shown by the NMR spectra of one-hour-old solutions which indicated the presence of small quantities of dinorbornane. In the mass spectrum (EI-MS), only dinorbornane was detected, formed as a result of an elimination reaction. The high stability of the complex can be attributed to the strong σ-bond-donor capability of the 1-norbornyl group, which provides the necessary electron density for stabilizing the formal +4 oxidation state. The strong electron-donating ability of the 1-norbonyl ligand was demonstrated in a previous investigation.[13] In addition, the electron-donating ability of the bromo ligand can also contribute to the stabilization of the coordinatively and electronically unsaturated complex **4**.[14]



Scheme 1. Preparation of **4** by air oxidation of **3**.

Interestingly, when the oxidation of **3** was carried out at room temperature, only dinorbornane (**5**) could be isolated.[15] A similar elimination reaction was observed in the reaction of iodine with $Li_2[NiMe_4]\cdot 2\,THF$ and $Li_2[NiPh_4]\cdot 4\,THF$.[8a,11a] The formation of dinorbornane also occurred during attempts to exchange the bromine atom in **4** with a 1-norbornyl group by treating **4** with **2** in pentane at −70 °C (Scheme 1). Consequently, it seems unlikely that tetrakis(1-norbornyl)nickel(IV) can be prepared by this method.

Complexes **3** and **4** were characterized by NMR spectroscopy (Table 1). For the nickel(II) complex **3** the ^{13}C resonance signal of the coordinating carbon atom is shifted up field, and

Table 1: ^{13}C NMR spectroscopy chemical shift values of **3** and **4**.[a]

Compound	C-1	C-2,6	C-3,5	C-4	C-7
$[n\mathrm{Bu_4N}]_2[Ni^{II}(1\text{-nor})_3Br]$ (**3**)	20.19	35.65	30.39	34.49	44.79
$[Ni^{IV}(1\text{-nor})_3Br]$ (**4**)	68.79	35.99	31.58	32.83	45.69

[a] Chemical shifts δ (in ppm relative to TMS) measured in [D_8]THF, at 75.5 MHz, for numbering of C atoms, see **5** in Scheme 1.

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its chemical shift is comparable with those of related nickel(II) complexes.[10,11c] The ^{13}C resonance signal of the coordinating bridgehead C atom in **4** is shifted down field, which is in agreement with the trend observed for the corresponding Ti^{IV},[16a] Fe^{IV},[16b] and Co^{V}[17] compounds.[18] The remaining sharp resonance signals, which are not shifted from their normal positions, indicate the diamagnetic nature of **4**. In addition, EPR measurements showed that **4** is diamagnetic in the temperature range 77–298 K.

To support the spectroscopic and chemical evidence for the nickel(IV) complex **4**, an X-ray crystallographic analysis was carried out. The Ni atom is four-coordinate with almost tetrahedral geometry, but the tetrahedron is stretched in the direction of the Br atom, so that the C-Ni-C angles are all significantly smaller than the normal tetrahedral angle, while the Br-Ni-C angles are correspondingly larger (Figure 1).

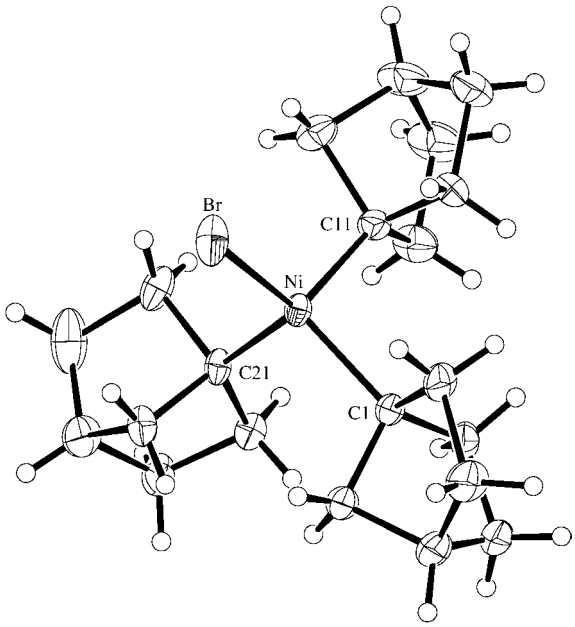

Figure 1. ORTEP plot of the structure of compound **4** (thermal ellipsoids set at 50% probability). Selected bond lengths [Å] and angles [°]: Ni–Br 2.3858(5), Ni–C1 1.931(3), Ni–C11 1.931(3), Ni–C21 1.937(3); Br-Ni-C1 123.84(10), Br-Ni-C11 116.08(10), Br-Ni-C21 113.36(9), C1-Ni-C11 98.18(14), C1-Ni-C21 100.14(13), C11-Ni-C21 101.83(14).

Furthermore, there are 15 C···H and H···H intramolecular contacts that are 0.10–0.31 Å shorter than the sum of the van der Waals radii of the relevant atoms. In contrast, there are no unusually short intramolecular contacts involving the Br atom. The ligand-field requirements of a true tetrahedrally coordinated nickel(IV) atom are inconsistent with the measured diamagnetism of the compound. However, the distortions of the tetrahedron correspond to lowering of symmetry from T_d to C_{3v}, which splits the energies of the t_2 orbitals and produces one orbital of lower energy. In the pseudotetrahedral arrangement of **4**, the observed lowering of symmetry evidently splits the orbital energies sufficiently to allow pairing of all six d electrons, which leads to the observed diamagnetism.

In conclusion, we have prepared and structurally characterized a pseudotetrahedral organonickel compound in the formal oxidation state +4. Being diamagnetic it seems to be the first low-spin tetracoordinate organonickel compound with d^6 configuration. This and the remarkable stability of the new compound are consistent with the ability of the 1-norbornyl ligand to stabilize metals in high oxidation states.

Experimental Section

All operations were carried out by using standard Schlenk techniques under an Ar atmosphere. The solvents were prepared free of oxygen and moisture by standard methods. The starting compounds **1**[19] and **2**[16c] were prepared according to literature procedures.

3 in [D_8]THF: Three equivalents of **2** (0.0404 g, 0.40 mmol) were added to a suspension of **1** (0.1103 g, 0.13 mmol) in [D_8]THF (1 mL) at −60 °C, and the mixture was stirred for 1 h at this temperature and then insoluble material was removed by filtration. For NMR spectroscopy investigations, 0.6 mL of the solution of **3** in [D_8]THF was transferred into a NMR tube.

4: Three equivalents of **2** (0.16 g, 1.56 mmol) were added to a suspension of **1** (0.43 g, 0.50 mmol) in THF (15 mL) at −60 °C, and the mixture was stirred for 1 h at this temperature and then insoluble material was removed by filtration. Dry air was bubbled through the blue-green solution for 1 min, the mixture was allowed to warm to room temperature, and all volatile materials were removed. The residue was extracted with pentane, and insoluble material was removed by filtration. After concentration, the solution was cooled to −20 °C and the crystalline solid collected by filtration to give a brown solid, which was recrystallized three times from pentane/Et_2O to give 0.115 g (55%) of **4** as red-brown crystals. Crystals for crystallographic analysis were obtained from pentane/Et_2O by slow evaporation of the solvents.

Data for **4**: decomposition at 131–133 °C; elemental analysis (%) calcd: C 59.48, H 7.84, Br 18.84, Ni 13.84; found: C 59.25, H 7.97, Br 18.53, Ni 13.50.

Crystal data for **4**: crystals from pentane/Et_2O; $C_{21}H_{33}BrNi$, $M_r = 424.10$; orthorhombic, space group *Pbca*, $a = 17.1432(2)$, $b = 12.0680(1)$, $c = 18.5311(3)$ Å, $V = 3833.79(8)$ Å^3, $Z = 8$, $\rho = 1.469$ g cm^{-3}, crystal dimensions: $0.03 \times 0.20 \times 0.30$ mm, $T = -113$ °C, Nonius Kappa CCD diffractometer, graphite-monochromated $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\mu = 3.102$ mm^{-1}, $2\theta_{max} = 55°$, 102373 measured reflections of which 4391 were unique and 3531 had $I > 2\sigma(I)$. The intensities were corrected for Lorentzian and polarization effects, as well as for absorption.[20] The structure was solved by direct methods using SHELXS97[21a] and refined on F^2 by full-matrix least-squares methods using SHELXL97.[21b] The H atoms were placed in geometrically calculated positions and were allowed to ride on their parent atom with $U_{iso}(H) = 1.2\,U_{eq}(C)$. The refinement of 208 parameters using 4390 reflections gave $R(F) = 0.0430$ ($I > 2\sigma(I)$ data), $Rw(F^2) = 0.1025$ (all data), GOF on F^2 1.061, $\Delta\rho_{max} = 0.85$ e Å^{-3}. CCDC-185226 (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[1] M. Ohff, A. Ohff, M. E. van der Boom, D. Milstein, *J. Am. Chem. Soc.* **1997**, *119*, 11687.

[2] a) S. Stahl, J. A. Labinger, J. E. Bercaw, *Angew. Chem.* **1998**, *110*, 2298; *Angew. Chem. Int. Ed.* **1998**, *37*, 2180; b) R. J. Puddephatt, *Angew. Chem.* **2002**, *114*, 271; *Angew. Chem. Int. Ed.* **2002**, *41*, 261.

[3] a) S. B. Duckett, R. N. Perutz, *Organometallics* **1992**, *11*, 90; b) K. Ezbiansky, P. I. Djurovich, M. LaForest, D. J. Sinning, R. Zayes, D. H. Berry, *Organometallics* **1998**, *17*, 1455.

[4] a) M. Brookhart, B. E. Grant, *J. Am. Chem. Soc.* **1993**, *115*, 2151; b) M. Brookhart, B. E. Grant, C. P. Lenges, M. H. Prosenc, P. S. White, *Angew. Chem.* **2000**, *112*, 1742; *Angew. Chem. Int. Ed.* **2000**, *39*, 1676.

[5] U. Kölle, F. Khouzami, H. Leuken, *Chem. Ber.* **1982**, *115*, 1178.

[6] C. G. Salentine, C. E. Strouse, M. F. Hawthorne, *J. Am. Chem. Soc.* **1976**, *98*, 841.

[7] a) H.-F. Klein, A. Bickelhaupt, T. Jung, G. Cordier, *Organometallics* **1994**, *13*, 2557; b) H.-F. Klein, A. Bickelhaupt, M. Lemke, H. Sun, A. Brand, T. Jung, C. Röhr, U. Flörke, H.-J. Haupt, *Organometallics* **1997**, *16*, 668; c) H.-F. Klein, X. Li, H. Sun, R. Beck, U. Flörke, H.-J. Haupt, *Inorg. Chim. Acta* **2000**, *298*, 63.

[8] a) M. F. Semmelhack, P. M. Helquist, L. D. Jones, *J. Am. Chem. Soc.* **1971**, *93*, 5908; b) R. Taube, D. Steinborn, H. Drevs, P. N. Chuong, N. Stransky, J. Langlotz, *Z. Chem.* **1988**, *28*, 381.

[9] B. K. Bower, H. G. Tennent, *J. Am. Chem. Soc.* **1972**, *94*, 2512.

[10] a) H. Lehmkuhl, V. Dimitrov, *J. Organomet. Chem.* **1996**, *519*, 69; b) H. Lehmkuhl, V. Dimitrov, *J. Organomet. Chem.* **1996**, *519*, 83; c) H. Lehmkuhl, V. Dimitrov, unpublished results.

[11] a) R. Taube, G. Honymus, *Angew. Chem.* **1975**, *87*, 291; *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 261; b) H.-O. Frölich, B. Hipler, B. Hofmann, *J. Organomet. Chem.* **1992**, *430*, 133; c) H.-O. Frölich, R. Wyrwa, H. Görls, *J. Organomet. Chem.* **1992**, *441*, 169; d) D. Steinborn, F. Becke, R. Boese, *Inorg. Chem.* **1995**, *34*, 2625.

[12] a) The complex $Li[Cr^{III}Mes_4]\cdot 4THF$ was oxidized in air to $[Cr^{IV}Mes_4]$ (Mes = 2,4,6-trimethylphenyl): W. Seidel, I. Bürger, *Z. Anorg. Allg. Chem.* **1976**, *426*, 155; b) $[Mo^{IV}Mes_4]$ was prepared by air oxidation of $Li[Mo^{III}Mes_4]\cdot 4THF$: W. Seidel, I. Bürger, *J. Organomet. Chem.* **1979**, *171*, C45.

[13] The donor influence of the 1-norbornyl ligand was determined by ^{13}C NMR spectroscopy investigations on (1-nor)Hg compounds and comparison with the data of other alkyl ligands: V. Dimitrov, K.-H. Thiele, R. Radeglia, *Z. Anorg. Allg. Chem.* **1983**, *503*, 177; see also ref. [8b].

[14] K. Fagnou, M. Lautens, *Angew. Chem.* **2002**, *114*, 26; *Angew. Chem. Int. Ed.* **2002**, *41*, 26.

[15] Data of **5**: a) ^{13}C NMR (300 MHz, $[D_8]$THF, 20 °C, TMS): $\delta =$ 51.05 (C-1), 40.79 (C-7), 37.94 (C-4), 32.73 (C-2,6), 31.49 ppm (C-3,5); MS (70 eV): *m*/*z* (%): 190 (40) [M^+], 161 (100); elemental analysis (%) calcd: C 88.35, H 11.65; found: C 88.11, H 11.78; b) The crystal structure of **5** was also determined and will be published elsewhere.

[16] a) V. Dimitrov, K.-H. Thiele, D. Schenke, *Z. Anorg. Allg. Chem.* **1985**, *527*, 85; b) K.-H. Thiele, V. Dimitrov, D. Schenke, A. Krüger, A. Rusina, *Wiss. Z. Tech. Hochsch. "Carl Schorlemmer" Leuna-Merseburg* **1986**, *28*, 197; c) V. Dimitrov, K.-H. Thiele, A. Zschunke, *Z. Anorg. Allg. Chem.* **1982**, *494*, 144.

[17] E. K. Byrne, K. H. Theopold, *J. Am. Chem. Soc.* **1989**, *111*, 3887.

[18] The preparation of tetrakis(1-camphenyl) compounds of Ti^{IV}, Zr^{IV},and Hf^{IV} has been described; the ^{13}C NMR data are comparable with those of the corresponding tetrakis(1-norbornyl) derivatives: D. Schenke, K.-H. Thiele, *J. Organomet. Chem.* **1990**, *382*, 109.

[19] H. Lehmkuhl, K. Mehler, G. Hauschild, *Chem. Ber.* **1983**, *116*, 438.

[20] R. H. Blessing, *Acta Crystallogr. Sect. A* **1995**, *51*, 33.

[21] a) G. M. Sheldrick, SHELXS97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany), **1997**; b) G. M. Sheldrick, SHELXL97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany), **1997**.

