

Short communication

Lithium Bromide-Induced Structural Changes in a Nickel Bis-Alkoxide Complex

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Abstract

The bis-alkoxide [(DEAMP)₂Ni] (**1**, DEAMP= 1-(diethylamino)-2-methylpropan-2-olate) was found to react with trace amounts of lithium bromide to afford the bis-LiBr adduct **2**, in which the oxygens of the DEAMP ligand coordinate to lithium to form a chiral-at-metal complex. This new complex is five-coordinate at nickel, and contains nickel and oxygen atoms which are all chiral. One diastereomer precipitates from pentane solution. The two lithium ions rigidify the new structure in the solid state by coordinating to the oxygen and bromide atoms.

Keywords: Nickel, coordination chemistry, X-ray crystallography, lithium, mixed-metal alkoxide

1. Introduction

Considering the relatively high price per mole of palladium and platinum, the development of organonickel chemistry remains a priority in contemporary catalysis. Advances in the field of organonickel catalysis will benefit from studies undertaken with well-defined complexes, and methods to prepare new complexes are always in need. Many commonly used or commercially available nickel(II) precursors, however, suffer from extremely low solubility in non-polar and non-halogenated solvents. We were therefore intrigued by the recent report of the preparation of the [(DEAMP)₂Ni] which was used as a molecular precursor for MOCVD of nickel thin films.¹ The authors reported that this precursor sublimates at low temperature and is highly soluble in organic solvents like THF, ether, and toluene. The presence of the bis-alkoxide functionality in **1** suggests that it might also be useful in generating other well-defined nickel complexes of interest to solution-based chemistry. For instance, nickel-oxygen bonds can be transmetalated with organozinc reagents² and are also involved in the formation of esters from well-defined nickel(acyl)(alkoxide) complexes.³ With both the high solubility and heteroatom functionality in mind, we initiated studies directed at obtaining a better understanding of its solution chemistry.

2. Results and Discussion

We explored the synthesis of complex **1** by a new route involving the addition of Li-DEAMP to [(DME)Ni-Br₂] (eq 1). In the end, this route offered no advantages over the published procedure.¹ However, in the course of these studies, we have discovered that pentane extraction of the product is not sufficient to remove all traces of alkali metal salts, and that sublimation is necessary to obtain “salt-free” product. Leaving a pentane extraction of **1**, produced by the route described in eq 1, at –30 °C for weeks led to the selective precipitation of trace amounts of the bis-LiBr adduct **2** (eq 1). Similar coordination by lithium salts were observed in the reaction of the known bis-aminoalkoxide **3** with LiCl in *i*-PrOH to afford the mono-LiCl adduct **4** as described in eq 2.⁴

This new adduct has been characterized by X-ray crystallography (Table 1), and the ORTEP diagram is shown in Figure 1. The coordination number of nickel in this new adduct is five, with one of the bromides remaining in the outer sphere. The lithium atoms in **2** coordinate to the oxygen atoms of the DEAMP ligand, to the bromides, and to extraneous THF molecules which presumably were not fully removed from the reaction mixture before extraction with pentane. The coordination spheres of the two lithium ions are different, with one lithium ion

bridging between two oxygen atoms and the other lithium ion bridging between two bromides. The coordination of the DEAMP ligands significantly changes from starting complex **1**, in which the oxygen and nitrogen atoms were found to be *trans* to each other.¹ One of the lithium atoms bring the two oxygen atoms in more of a *cisoid* conformation, by virtue of chelation, and the structure is further anchored in this position through the chelation of the other lithium to the two bromides.

We have been able to independently prepare **2** by the reaction of sublimed **1** with two equivalents of LiBr in pentane solution containing a few drops of THF solvent. Interestingly, in all cases the crystals of **2** that were obtained were chiral in the solid state and crystallized in the $P2_12_12_1$ space group with the Flack parameter refining to $-0.009(12)$ for the structure shown in Figure 1. Presumably, either one diastereomer (there is chirality at both the metal and oxygen atoms) selectively precipitates from pentane solution, or two crystal forms of this diastereomer are indeed present but only one has thus far been analyzed. Generation of a chiral catalyst from achiral ligands has precedence,⁵ but we are unaware of any examples of the generation of a chiral-at-metal complex upon the addition of a simple metal-halide salt. No significant optical activity was observed in the solution state upon reaction of sublimed **1** with LiBr in THF. Moreover, dissolution of crystallized **2** in THF resulted in a solution bearing no optical activity, signifying that **2** is fluxional in solution.

Table 1. Crystal data and structure refinement parameters for **2**.

Compound	2
chemical formula	$C_{24}H_{52}Br_2Li_2N_2NiO_4$
formula weight	665.08
crystal dimensions (mm)	$0.35 \times 0.22 \times 0.14$
color, habit	orange, prism
crystal system	orthorhombic
wavelength, Å	0.71070
space group, Z	$P2_12_12_1$, 4
a, Å	11.276(11)
b, Å	13.736(13)
c, Å	20.651(20)
α (deg)	90
β (deg)	90
γ (deg)	90
vol, Å ³	3199(5)
σ_{calc} , g cm ⁻³	1.381
temp, K	173
Residuals: R1 [I>2sigma(I)]	0.0464
R indices [all data]	0.0914, 0.1086
goodness of fit	0.899
θ range, deg	1.78–27.49
number of data collected	30110
number of unique data	7212
R_{int}	0.1011

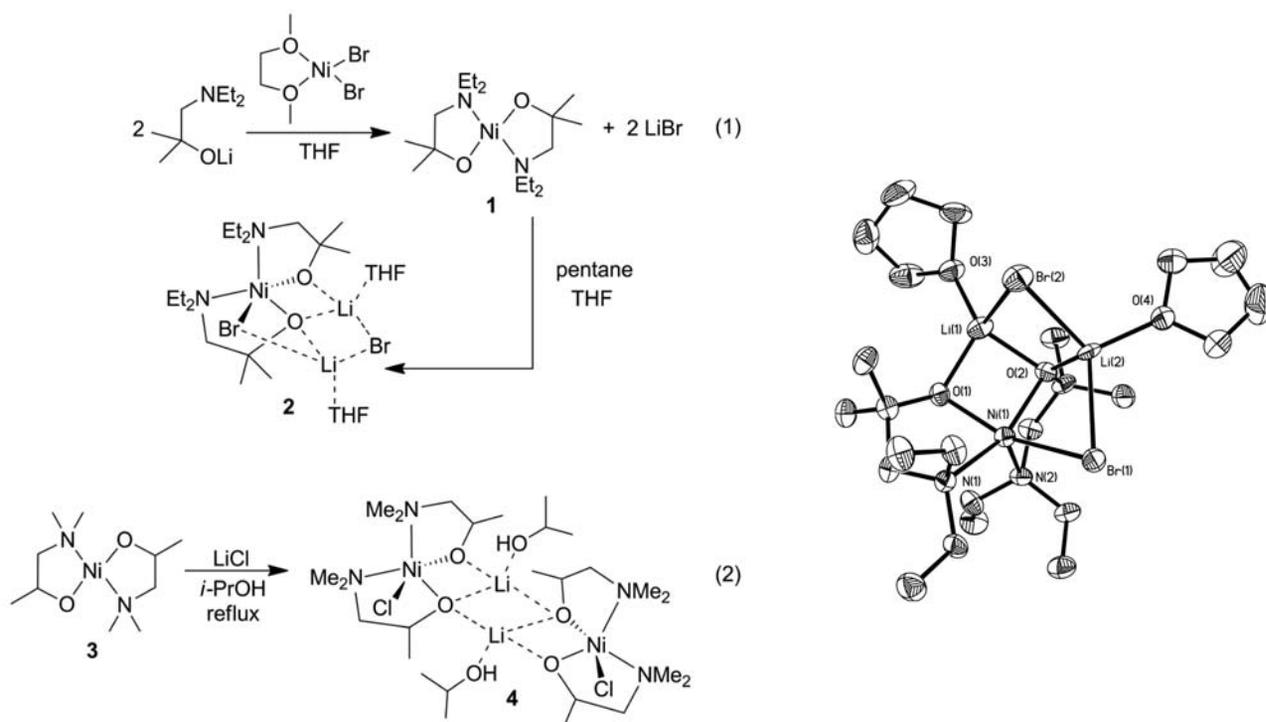


Figure 1. ORTEP diagram of **2**. Ellipsoids shown at 50 %. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Br(1)–Ni(1) 2.562(2); Br(2)–Li(1) 2.591(11); Br(2)–Li(2) 2.550(10); Br(1)–Li(2) 2.612(10); O(1)–Li(1) 1.892(11); Li(1)–O(3) 1.953(11); O(2)–Li(1) 1.966(11); O(4)–Li(2) 1.911(10); Li(2)–O(2) 1.887(11); Ni(1)–O(2) 2.047(4); Ni(1)–O(1) 1.948(4); Ni(1)–N(1) 2.187(5); Ni(1)–N(2) 2.126(5). Selected bond angles (°): O(2)–Ni(1)–O(1) 84.92(16); O(2)–Ni(1)–N(1) 156.23(16); O(1)–Ni(1)–N(1) 82.65(17); O(2)–Ni(1)–N(2) 85.97(17); O(1)–Ni(1)–N(2) 101.83(17); N(1)–Ni(1)–N(2); 116.38(18); O(2)–Ni(1)–Br(1) 88.63(11); O(1)–Ni(1)–Br(1) 153.90(12); N(1)–Ni(1)–Br(1) 93.69(13); N(2)–Ni(1)–Br(1) 102.91(14).

2. Experimental

2. 1. Preparation of Compound 2

Preparation of compound 2: LiBr (40 mg, 0.46 mmol) was added to the suspension of complex **1** (79 mg, 0.23 mmol) in THF 3 mL. This reaction mixture was stirred for 3 days at room temperature to yield an orange brown residue. The volatiles were then removed under the reduced pressure. The residue was dissolved in a minimum amount of THF and then layered with pentane and stored at $-35\text{ }^{\circ}\text{C}$. Orange crystals precipitated, which were washed with cold ($-35\text{ }^{\circ}\text{C}$) pentane, and dried in vacuo to yield the bis-LiBr-THF adduct (96 mg, 63 % yield). Compound **2** is NMR silent. Loss of THF prohibited good elemental analyses: Anal. Calcd (found) for $\text{C}_{24}\text{H}_{52}\text{Br}_2\text{Li}_2\text{N}_2\text{NiO}_4$: C, 43.34 (38.50); H, 7.88 (7.18). Crystallographic data (excluding structure factors) for compound **2** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 828105. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk.

2. 2. X-ray Structure Determination

All measurements were made on a Rigaku Mercury275R CCD (SCX mini) diffractometer using Mo-K α radiation. An orange prism crystal of **2** was covered in Paratone-N oil, mounted on a glass fiber, and cooled to $-100\text{ }^{\circ}\text{C}$ with an Oxford Cryostream 700 cooling unit. The crystal structure was solved by direct methods using SHELXS-97⁶ and refined by full-matrix least-squares procedures on F_o^2 using SHELXL-97.⁷ All non-hydrogen atoms were refined anisotropically. The hydrogen atom positions have been refined using the atom corresponding riding model. One of the coordinated THF molecules show signs of disorder (i.e. a high anisotropic displacement parameters on carbons 18 and 23 of cif file and shorter-than-usual C–C bonds in the ring).

3. Conclusions

[(DEAMP)₂Ni], a pentane-soluble nickel(II) precursor with Lewis basic sites, was found to react with lithium bromide to form a five-coordinate nickel species resulting from the coordination of two lithium bromides and two THF molecules. To our knowledge, this is the first example of the formation of an isolable chiral-at-metal complex upon the addition of a simple metal-halide salt.

4. Acknowledgement

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5. References

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Povzetek

Bis-alkoksid [(DEAMP)₂Ni] (**1**, DEAMP = 1-(dietilamino)-2-metilpropan-2-olat) reagira s sledovi litijevega bromida in tvori bis-LiBr adukt **2**, v katerem so kisikovi atomi DEAMP liganda koordinirani na litij in tvorijo kompleks s kiralnim kovinskim centrom. Koordinacijsko število nikljevega atoma v tem novem kompleksu je pet, nikljev in vsi kisikovi atomi v njem pa so kiralni. Iz raztopine v pentanu izkristalizira samo en diastereomer. Novo strukturo v trdnem stanju stabilizirata dva litijeva iona, ki sta koordinirana na atome kisika in broma.