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Notes

Solvent-Free Dinickelate $[Ni\{[CH_2N(Me)]_2CH_2\}Li_2]_2$ with a Li_4Ni_2 Cluster Core via Nucleophilic Aminomethylation

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*Summary: The doubly lithiated aminal bis(lithiomethyl-(methylamino))methane, $[LiCH_2N(Me)]_2CH_2$, reacts with bis(trimethylphosphine)nickel dichloride in diethyl ether to give the solvent-free dinickelate $[Ni\{[CH_2N(Me)]_2CH_2\}Li_2]_2$ (**1**) in good yield. The molecular structure of **1** has been studied by X-ray-crystallography.*

Introduction

Metallacyclic nickel compounds have attracted much interest in the last two decades due to their structural features, thermal behavior, and reactivity.[1] Within the group of alkanediyl compounds, metallacyclic “ate” complexes represent a class of their own. The organometallic cyclic “ate”-type compounds $Li_2M(C_4H_8)_n(solv)_x$ (M = Ti, Zr, $n = 3$; M = Fe, $n = 2$; solv = Et_2O, THF, TMEDA; $x = 1-6$) of zirconium,[2] titanium,[3] and iron[4] as well as the nickel(II) complexes $[Li_2Ni(C_4H_8)_2(solv)_n]$ (solv = Et_2O, THF, TMEDA; $n = 2$) have been described,[5,6] but solvent-free examples are not known. Solvent-free “ate” metallacycles are only obtained in cases of internal charge compensation, as for example in $\{[Me_2P(CH_2)_2]_2Ni\}_2$.[7] With the aim of synthesizing new metallaheterocyclic “ate” complexes via nucleophilic aminomethylation,[8] we included nickel for the aforementioned reasons. Some rare examples of nucleophilic aminomethylations at nickel centers are known. The α-lithiated methylamines Me_2NCH_2Li and $C_5H_{10}NCH_2Li$ were reacted with phosphine-substituted nickel halides $(R_3P)_2NiX_2$ (R = Me, *n*-Bu; X = Cl, Br).[9,10] In both cases the dilithium tetrakis[(dialkylamino)methyl]-nickelate complexes $[\{Li(OEt_2)\}_2Ni(CH_2NMe_2)_4]$[9] (**I**) and $[\{Li(OEt_2)\}_2Ni\{CH_2N(C_5H_{10})_2\}_4]$[10] (**II**) were obtained under elimination of the phosphine ligands. Again, solvent-free examples have not been described. First attempts in reacting $(Me_3P)_2NiCl_2$ and the doubly metalated aminal $[(LiCH_2NMe)_2CH_2]$[8] in a ratio of 1:1 in order to obtain a nickelaheterocyclic complex with retention of the phosphine substituents failed. A considerable amount of $Ni(PMe_3)_4$ has been isolated instead. This observation corresponds to attempts to obtain the metallacyclic compound $(Ph_3P)_2Ni(C_4H_8)$, which cannot be synthesized by reacting $(Ph_3P)_2NiX_2$ (X = Cl, Br) and α,δ-lithiated *n*-butane.[6] A nickelaheterocycle was obtained, however, when 2 equiv of the lithiated compound was used. Phosphine-substituted nickel(II) chloride and 2 equiv of $[(LiCH_2NMe)_2CH_2]$ affords the dimeric nickelate complex $[Ni\{[CH_2N(Me)]_2CH_2\}Li_2]_2$ (**1**), which is free of donor solvent and characterized by X-ray structure determination as well as by spectroscopic means (NMR, CI-MS). The isolated complex represents an example of a Li_4Ni_2 cluster core.

Results and Discussion

According to eq 1 reaction of 2 equiv of the doubly lithiated aminal $[(LiCH_2NMe)_2CH_2]$ with 1 equiv of $(PMe_3)_2NiCl_2$ in diethyl ether at −78 to −30 °C afforded compound **1** in 84% yield.

$$2\ (Me_3P)_2NiCl_2 + 4\ [LiCH_2N(R)]_2CH_2 \xrightarrow[\substack{-78°C/-30°C \\ -4\ PMe_3 \\ -4\ LiCl}]{Et_2O} \underset{\mathbf{1}}{[Ni(\{CH_2N(R)\}_2CH_2)_2Li_2]_2} \quad (1)$$

The yellow crystals obtained are extremely air sensitive and were suitable for X-ray analysis. The molecular structure of **1** is shown in Figure 1 including the atom-labeling scheme and selected bond distances and angles.

A perpendicular arrangement of two spirocyclic nickelate units is the basic structural motif of this molecule. Two double-metalated bis(methylamino)methylene - chelating ligands form six-membered metallacycles with a nickel spiro center of an approximately planar arrangement of the four methylene C atoms. The sum of angles around Nil and Ni2 amount to 357.2° and 357.1°,

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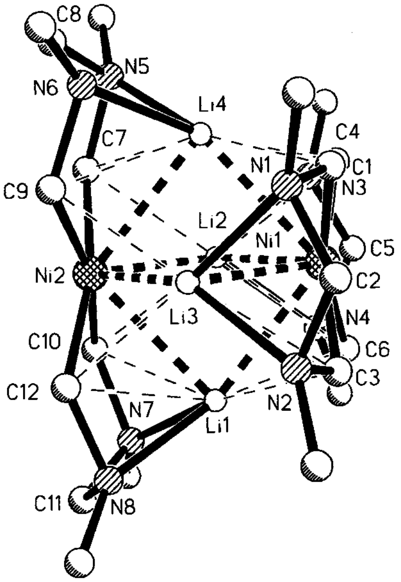

Figure 1. Molecular structure of $[Ni\{[CH_2N(Me)]_2CH_2\}_2Li_2]_2$ (**1**). Selected distances of Li(1) and Ni(1) (Å): Ni(1)−Li(1) 2.542(5); Ni(1)−Li(2) 2.569(5); Ni(1)−Li(3) 2.593(5); Ni(1)−Li(4) 2.541(5); Ni(1)−C(1) 1.976(3); Ni(1)−C(3) 1.989(3); Ni(1)−C(4) 1.987(3); Ni(1)−C(6) 1.980(3); Li(1)−Ni(2) 2.580(5); Li(1)−C(3) 2.428(6); Li(1)−C(6) 2.347(6); Li(1)−C(10) 2.489(6); Li(1)−C(11) 2.505(6); Li(1)−C(12) 2.429(6); Li(1)−N(2) 3.268; Li(1)−N(4) 3.105; Li(1)−N(7) 2.080(6); Li(1)−N(8) 2.040(6); Li(1)−Li(2) 2.687(7); Li(1)−Li(3) 2.752(7). Selected bond angles between the lithium atoms (deg): Li(2)−Li(1)−Li(3) 89.8; Li(1)−Li(2)−Li(4) 89.8; Li(1)−Li(3)−Li(4) 90.8; Li(1)−Li(4)−Li(3) 89.5.

respectively. In comparison to other compounds with a planar NiC_4 unit, e.g., the metallacyclopentane complex $[\{Li(THF)_2\}_2Ni(C_4H_8)_2]^5$ (**III**) (1.998 and 2.001 Å) and the (aminomethyl)nickel complexes $[\{Li(OEt_2)\}_2Ni(CH_2NMe_2)_4]$ (**I**) (2.028 and 2.037 Å) and $[\{Li(OEt_2)\}_2Ni(CH_2NC_5H_{10})_4]$ (**II**) (2.023 and 2.032 Å), the Ni−C distances in **1** (1.974(3)−1.989(3) Å) are slightly decreased. Two of these NiC_4 dianionic units are closely held together mainly via four lithium atoms which compensate for the negative charge and are generating a neutral, trans-octahedral cluster of two nickel and four lithium atoms within a perpendicular framework of four dimetalated tetramethyl aminals. The two nickel atoms slightly approach each other as indicated by their slight deviation from a planar geometry, which is particularly remarkable, since all four Ni−C bonds of an individual cluster constituent are eclipsed to that of the other part. Nevertheless, the Ni···Ni distance (3.364 Å) is too large for any substantial bonding relationship.

The four lithium atoms form an almost rectangular plane which is sandwiched by the two nickelate units and coplanar to their two sets of four carbanionic C atoms. Each of these lithium atoms, as exemplified by lithium atom 1 (Figure 2), not only is coordinated by two nitrogen donors (Lil−N7 (2.080(6) Å), Lil−N8 (2.040(6); two “long” distances, Lil−N2 (3.268 Å), Li1−N4 (3.105 Å), remain without the range of consideration) and by four methylen carbon atoms (Li1−C10 (2.489(6) Å), Li1−C12 (2.429(6) Å), Li1−C3 (2.428(6) Å), Lil−C6 (2.347(6) Å)) but also shows contacts to the two nickel atoms (2.542(5) and 2.580(5) Å) and even to two of the other lithium atoms (2.687(7) and 2.752(7) Å).

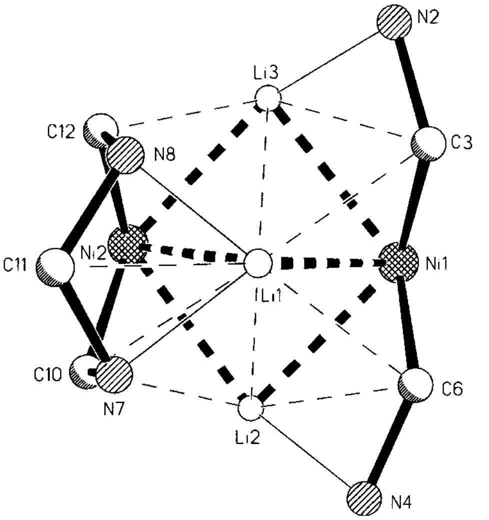

Figure 2. Atomic contacts of Li(1) in $[Ni\{[CH_2N(Me)]_2CH_2\}_2Li_2]_2$ (**1**).

Although the majority of these distances are slightly shorter in the complexes **I** and **II** (**I**, Li−N/Li−C 1.975 Å/2.248 Å mean; **II**, Li−N/Li−C 1.998 Å/2.239 Å mean), in the light of the bridging functionality of the lithium atoms in **1** and the thus drastically enhanced number of contacts, the same trends seem to apply for **1** and **I**/**II**. There is one important exception: The high “coordination number” of the lithium atoms in **1** renders an additional solvent coordination obsolete, in marked contrast to **I** and **II**.

In line with the X-ray results the mass spectrum of the crystalline material shows a base peak at *m*/*z* 544, the molecular mass of $[Ni\{[CH_2N(Me)]_2CH_2\}_2Li_2]_2$ (**1**). A minor amount (<5%) of the reduced nickel(0) species $(Me_3P)_4Ni$ was identified as the main constituent of the noncrystalline viscous liquid, separated from the ether extract by means of ^1H-, ^{13}C-, and $\{^1H\}^{31}P$ NMR spectroscopy. The presumed oxidation product $[(CH_2N(Me)]_2CH_2$ was not detected, however. The ^1H NMR spectrum of **1** indicates diastereotopic $NiCH_2N$ methylene protons at $\delta = 0.70$ and 2.70 ($^2J_{H-H} = 13.0$ Hz). Accordingly, an AB pattern can be observed for the NCH_2N methylene protons at $\delta H_A = 2.17$ and $\delta H_B = 3.12$ ($^2J_{H-H} = 6.5$ Hz). The protons of all aminomethyl groups give rise to a single resonance at $\delta = 2.13$. The ^1H NMR spectra of **1** at −80 to +80 °C indicate no temperature dependence. The $\{^1H\}^{13}C$ NMR spectrum of **1** exhibits three single resonances at $\delta = 49.53$, 53.00, and 85.07, which can be attributed to the aminomethyl, aminomethylene, and diaminomethylene carbon atoms, respectively. A singlet was observed in the ^7Li NMR spectrum at $\delta = 0.20$. All these spectral data are consistent with the preservation of the solid-state structure of the dinuclear nickel-“ate” complex **1** in solution.

Some reactions provide additional information about the nature of **1**. Reaction of **1** with carbon monoxide at −78 °C in toluene occurred spontaneously, as judged from the rapid color change (see Experimental Section) and afforded predominantly the lithium salt of the red polynuclear $[Ni_5(CO)_9]^{2-}$ dianion,[11] which is insoluble in pentane and toluene, but soluble in THF.

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$$\underset{\mathbf{1}}{[Ni\{[CH_2N(Me)]_2CH_2\}_2Li_2]_2} + CO \xrightarrow[-78°C]{\text{toluene}} Li_2Ni_5(CO)_{12} \text{ (+ ox. product)} \quad (2)$$

Its formation might be rationalized by analogy with the system $Li_2\overline{Ni(CH_2CH_2CH_2C}H_2)_2(Et_2O)/CO$.[6] Removal of lithium from **1** by 12-crown-4 was not feasible. Under forcing conditions (excess crown ether, toluene, 6 days, 40 °C) only some minor decomposition with nickel precipitation was observed, as it is also observed on prolonged storage of solid **1** at room temperature; 90% of **1** was recovered. Corresponding oxidation products (nitrogen-containing organic compounds) could not yet be identified. At −20 °C, solid **1** can be stored for months.

Conclusions

A first example of a solvent-free, cluster-type tetralithium dinickelate, synthesized via nucleophilic aminomethylation, is described. The four lithium atoms in a planar arrangement function as a "glue" to hold together two dianionic, spirocyclic nickelate centers. In turn, the lithium atoms gain a high number of more or less weak contacts and balance the overall charge to neutral. Obviously, the double-metalated aminal ligand can play a valuable role in the synthesis of novel metallacycles in the near future. Respective work is in progress.

Experimental Section

General procedures are detailed elsewhere.[12] Standard high-vacuum-line techniques were used. $(PMe_3)_2NiCl_2$[13] and solvent-free $\{[LiCH_2N(Me)]_2CH_2\}$[8] were synthezised according to literature procedures.

The elemental analyses were performed by Microanalytisches Labor der TU Muenchen. Chemical-ionization (CI) mass spectra were obtained with a Varian MAT 311A spectrometer. The ^1H NMR data were collected on a JEOL JNM-GX400 (399.65 MHz), and the ^{13}C NMR data on a JEOL JNM-GX270 spectrometer (270.05 MHz). ^1H and ^{13}C NMR chemical shifts (δ) are referenced to the internal residual proton or natural abundance ^{13}C resonances of the deuterated solvent relative to TMS ($\delta = 0$). The ^7Li NMR data were collected on a JEOL JNM-LAMBDA 400 (155.40 MHz ^7Li). The chemical shifts δ(^7Li) are reported relative to a solution of LiCl (20%) in D_2O (external). All measurements were carried out at 25 °C in C_6D_6. Exceptions are given separately. All chemical shifts are reported in parts per million (ppm) and coupling constants J in hertz. IR data were collected on a Nicolet 5DX FT-IR spectrometer.

Preparation of $[Ni\{[CH_2N(Me)]_2CH_2\}_2Li_2]_2$ (1). Bis(lithiomethyl(methylamino))methane $\{[LiCH_2N(Me)]_2CH_2\}$ (0.90 g, 7.89 mmol) was dissolved in 30 mL of diethyl ether, and the solution was cooled to −78 °C. Under stirring, 30 mL of an ethereal solution of $(PMe_3)_2NiCl_2$ (1.11 g, 3.95 mmol) was added within 5 min at −78 °C. Stirring was continued for 3 h at −30 °C. During this time, the color of the solution turned from dark red to yellow, and precipitation of LiCl could be observed. After filtration the amount of solvent was reduced to 20 mL. Cooling at 0 °C afforded yellow crystals of **1** suitable for X-ray analysis (1.80 g, 84%), dec 87−90 °C. CI-MS [*m*/*e* %]: 544 (11) [M^+], 258 (100) [$Ni\{[CH_2N(CH_3)]_2CH_2\}_2^+$]. ^1H NMR: δ 0.70 (d, $^2J = 13.0$, 8H, NCH_2Ni), 2.13 (s, 24H, NCH_3), 2.17 (d,$^2J = 6.5$, 4H, NCH_2N), 2.70 (d,$^2J = 13.0$, 8H, NCH_2Ni), 3.12 (d,$^2J = 6.5$, 4H, NCH_2N). $\{^1H\}^{13}C$ NMR: δ 85.07 (s, NCH_2N). 53.00 (s br, NCH_2Ni), 49.53 (s, NCH_3). ^7Li NMR: δ 0.20 (s). Anal. Calcd for $C_{20}H_{48}N_8Ni_2Li_4$: C, 44.01; H, 8.86; N, 20.53; Ni, 21.51; Li, 5.09. Found: C, 44.58; H, 8.38; N, 19.57; Ni, 21.96; Li, 5.38.

Reaction of $[Ni\{[CH_2N(Me)]_2CH_2\}_2Li_2]_2$ (1) with CO. A solution of 0.49 g (0.90 mmol) of **1** in 20 mL of toluene at −78 °C was stirred under an atmosphere of purified carbon monoxide (specif. N4.7). A fast uptake of CO was indicated by a color change of the solution from light yellow to dark red. After 2 h at room temperature the solvent was removed and an extraction of the residue was performed consecutively with pentane, toluene, and THF. A red crystalline solid (0.19 g), insoluble in pentane and toluene, was obtained after the extraction with THF. IR (Nujol) vs (CO): 1991(s) cm^{-1}, 1930(w, sh) cm^{-1}, 1817(m) cm^{-1}.

X-ray Measurement. The single crystal was sealed in a thin-walled capillary and mounted on a four-circle diffractometer CAD4 (Fa. ENRAF−NONIUS) with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). All data were collected at low temperatures (−88 °C). The structure was solved by direct methods with the software package SHELXTL PC[13] and refined with the program SHELXL-93.[14] All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the hydrogen atom positions. Further details can be obtained from the Cambridge Crystallographic Data Center under the following CCDC number: 118947.

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Supporting Information Available: Text giving tables of atomic coordinates and isotropic thermal parameters, complete bond lengths, and thermal parameters for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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