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Synthesis and Properties of (Aminomethyl)nickel Complexes. [{Li(OEt$_2$)}$_2$Ni(CH$_2$NC$_5$H$_{10}$)$_4$]: The First Structurally Characterized Homoleptic Aminomethyl Complex of a Transition Metal

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$\mathrm{Bu_3SnCH_2NR_2}$ ($\mathrm{R_2N = Me_2N, C_5H_{10}N, Ph_2N}$) react with BuLi to give $\mathrm{R_2NCH_2Li{\cdot}}x\mathrm{thf}$ (**1a**, $\mathrm{R_2N = Me_2N}$, $x = 0$; **1b**, $\mathrm{R_2N = C_5H_{10}N}$, $x = 0$; **1c**, $\mathrm{R_2N = Ph_2N}$, $x = 1$). **1a** and **1b** react with nickel halide−phosphine adducts to give very air-sensitive homoleptic aminomethyl complexes of nickel [{Li(OEt$_2$)}$_2$Ni(CH$_2$NR$_2$)$_4$] (**2a**, $\mathrm{R_2N = Me_2N}$; **2b**, $\mathrm{R_2N = C_5H_{10}N}$), which have been characterized analytically and spectroscopically by NMR. **2** is diamagnetic, is thermally very stable [T_{dec} 90−115 °C (**2a**), 95−110 °C (**2b**)], and reacts with water and alcohols to give R$_2$NMe. The crystal structure of **2b** (space group $P2_1/c$; $R = 0.0656$) exhibits a molecular C_i symmetry. There is a planar NiC$_4$ unit [d(Ni−C) 2.023(4), 2.032(4) Å] and a nearly trigonal planar coordination of Li at R$_2$*N* and Et$_2$*O* as well as Li contacts to nickel [d(Li−Ni) 2.592(2) Å] and to carbon atoms R$_2$N*C*H$_2$Ni of the piperidinomethyl ligands [d(Li−C) 2.166(7), 2.312(8) Å].

Introduction

Organometallic compounds with functionalized methyl ligands $\mathrm{L}_x\mathrm{M{-}CH_2YR}_n$ (Y = heteroatom; R = alkyl, aryl, H; L = ligand) cover a wide range of stability, structure, and reactivity. There is a great variety of these compounds, and a classification is useful into compounds with (i) neutral, coordinatively saturated heteroatomic centers (e.g. $\mathrm{R}_n\mathrm{YCH_2 = Me_3SiCH_2}$), (ii) neutral, Lewis-basic heteroatomic centers (e.g. $\mathrm{R}_n\mathrm{YCH_2 = ClCH_2}$), and (iii) cationic heteroatomic centers (e.g. $\mathrm{R}_n\mathrm{YCH_2 = Me_3P^+CH_2}$). Compounds ii are of special interest because the Lewis-basic heteroatom is in many cases highly reactive, opening up the possibility of entirely new structures (e.g. η^2-coordination) and reactions (e.g. carbenoid reactivity).[2]

Homoleptic[3] derivatives of transition metals are especially useful for study. There are no other ligands L which influence stability, structure, and reactivity. Types i and iii homoleptic (trimethylsilyl)methyl[4] and phosphorus ylide complexes,[5] respectively, of many transition metals have been well characterized. In case of type ii, a complete series of homoleptic piperidinomethyl complexes of 3d elements[6] have been synthesized. Here we are reporting investigations of homoleptic (aminomethyl)nickel complexes.

Results

According to Peterson[7] $\mathrm{Bu_3SnCH_2NR_2}$ (Bu = n-C$_4$H$_9$) reacts with BuLi to give (aminomethyl)lithium compounds **1** (cf. eq 1), which was proved by reactions with ketones/aldehydes to give aminomethylated alcohols. We isolated **1a** and **1b** as colorless pyrophoric powders. Complex **1c** crystallizes as a thf adduct in the form of well-shaped yellow crystals. Compounds **1** were characterized by microanalysis and NMR spectroscopy (cf. Table 1). The methylene proton shifts indicate a higher electron density in **1a** and **1b** than in **1c**.

$$\mathrm{Bu_3SnCH_2NR_2 + BuLi \xrightarrow[-\,Bu_4Sn]{hexane\ (thf)} R_2NCH_2Li{\cdot}}x\,\mathrm{thf} \qquad (1)$$

1a - c

	1a	**1b**	**1c**
R$_2$N	Me$_2$N	C$_5$H$_{10}$N	Ph$_2$N
x	0	0	1

Nickel halide−phosphine complexes react with ((dialkylamino)methyl)lithium complexes **1a** and **1b** in ether as solvent to give dilithium tetrakis((dialkylamino)methyl)nickelate complexes **2** (cf. eq 2).

$$\mathrm{NiX_2\,2\,PR'_3 + 4\,R_2NCH_2Li \xrightarrow[-\,2\,LiX;\ -\,2\,PR'_3]{ether} [\{Li(OEt_2)\}_2Ni(CH_2NR_2)_4]} \qquad (2)$$

2a, b

	2a	**2b**
R$_2$N	Me$_2$N	C$_5$H$_{10}$N

Complexes **2a** and **2b** form highly oxygen- and moisture-sensitive yellow crystals which are soluble in most aprotic solvents, among them n-hexane.

In principle, a wide variation of $\mathrm{NiX_2{\cdot}2\,PR'_3}$ (X = Br, Cl; R′ = Me, Bu, Ph) is possible at reaction temperatures between −30 and −78 °C. The synthesis of **2a** should start from a nickel chloride−phosphine adduct because LiCl can be easily separated by filtration from the highly soluble **2a**. Complex **2b** is

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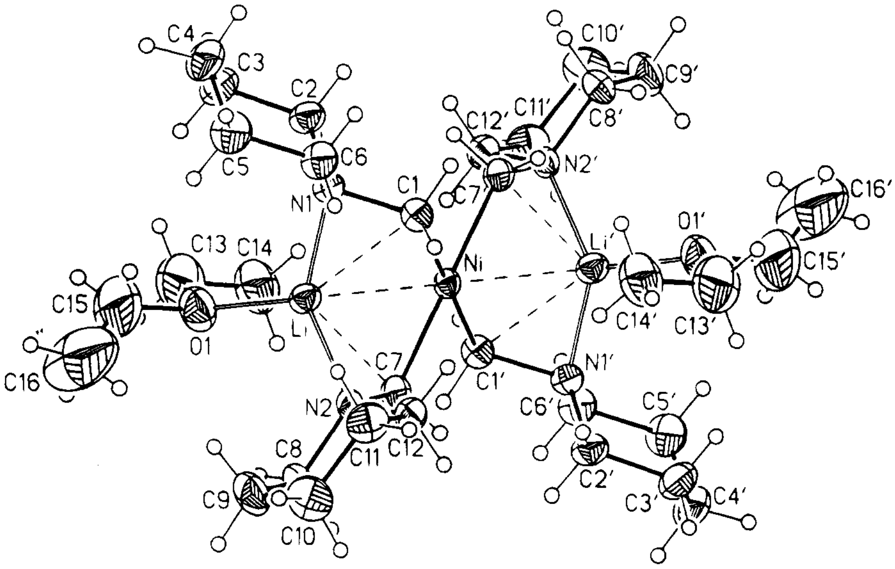

Figure 1. ORTEP drawing of the molecular structure of [{Li(OEt$_2$)}$_2$Ni(CH$_2$NC$_5$H$_{10}$)$_4$] (**2b**) in crystal form. Except for H atoms, 30% thermal ellipsoids are shown. The molecule posseses crystallographically imposed inversion symmetry (C_i); symmetry-related atoms are indicated with a prime.

Table 1. ^{1}H (300 MHz) and ^{13}C (75 MHz) Chemical Shifts (in ppm) of (Aminomethyl)lithium Compounds (**1a**, **1b** in THF-d_8 and **1c** in C$_6$D$_6$ as Solvent)

	^{1}H		^{13}C	
	$\delta(CH_2)$	$\delta(H_R)$	$\delta(CH_2)$	$\delta(C_R)$
Me$_2$NCH$_2$Li (**1a**)	0.94	2.15	57.0	53.9
C$_5$H$_{10}$NCH$_2$Li (**1b**)	0.98	1.29−2.23	55.9	63.4, 28.5, 25.2
Ph$_2$NCH$_2$Li·thf (**1c**)[a]	2.59	6.98−7.82	46.1	155.4, 118.9, 129.1, 121.2

[a] THF: 1.44 (quint), 3.58 (tr) (^{1}H) and 68.1, 25.4 (^{13}C).

Table 2. ^{1}H (300 MHz) and ^{13}C (75 MHz) Chemical Shifts (in ppm) of (Aminomethyl)nickel Complexes **2a** and **2b** in THF-d_8 as Solvent

	^{1}H		^{13}C	
	$\delta(CH_2)$	$\delta(H_R)$	$\delta(CH_2)$	$\delta(C_R)$
[{Li(OEt$_2$)}$_2$Ni(CH$_2$NMe$_2$)$_4$] (**2a**)[a]	1.32	2.10	61.4[c]	51.5[d]
[{Li(OEt$_2$)}$_2$Ni(CH$_2$NC$_5$H$_{10}$)$_4$] (**2b**)[b]	1.39	1.32−2.15	59.0	60.2, 28.1, 25.4

[a] Ether: 1.07 (tripl), 3.34 (quart) (^{1}H) and 15.6, 66.3 (^{13}C). [b] Ether: 1.11 (tripl), 3.38 (quart) (^{1}H) and 15.7, 66.3 (^{13}C). [c] Coupled spectrum: tripl (^1J(H,C) = 120.5 Hz). [d] Coupled spectrum: quart (^1J(H,C) = 131.7 Hz).

Table 3. Selected Bond Distances (Å) and Angles (deg) for [{Li(OEt$_2$)}$_2$Ni(CH$_2$NC$_5$H$_{10}$)$_4$] (**2b**)[a]

Ni−C1	2.023(4)	Ni−C7	2.032(4)
C1−N1	1.518(5)	C7−N2	1.513(4)
Li−N1	1.974(8)	Li−N2	2.021(7)
Ni−Li	2.592(6)	Li−O	2.021(8)
Li−C1	2.312(8)	Li−C7	2.166(7)
N1−C2	1.477(5)	N1−C6	1.476(5)
N2−C8	1.478(5)	N2−C12	1.474(5)
C1−Ni−C7	96.1(2)	C1−Ni−C7′	83.9(2)
Ni−C1−N1	122.2(3)	Ni−C7−N2	126.0(3)
C1−N1−Li	81.8(3)	C7−N2−Li	74.0(3)
C1−N1−C2	109.6(3)	C1−N1−C6	111.4(3)
C2−N1−C6	108.9(3)	C7−N2−C8	111.8(3)
C7−N2−C12	109.1(3)	C8−N2−C12	107.9(3)
N1−Li−N2	121.7(4)	N1−Li−O	116.7(3)
N2−Li−O	116.8(4)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

somewhat less soluble; thus nickel bromide−phosphine adducts are suitable as starting materials, also. Both **2a** and **2b** have been recrystallized from ether.

Complex **1c** under similar reaction conditions does not give the corresponding homoleptic tetrakis((diphenylamino)methyl)nickel complex from NiCl$_2$·2PR′$_3$.

The complexes [{Li(OEt$_2$)}$_2$Ni(CH$_2$NR$_2$)$_4$] (**2a**,**b**) have been characterized by microanalysis (cf. Experimental Section) and NMR spectroscopy (cf. Table 2). The nickel complexes are diamagnetic in accordance with a square planar low-spin d^8 nickel(II) complex

$$\textbf{2a}:\ \chi_g(295\ \text{K}) = -0.67 \times 10^{-6}\ \text{cm}^3/\text{g}\ (\mu_{\text{eff}} = 0.22\ \mu_B)$$

$$\textbf{2b}:\ \chi_g(298\ \text{K}) = -0.61 \times 10^{-6}\ \text{cm}^3/\text{g}\ (\mu_{\text{eff}} = 0.33\ \mu_B)$$

Complexes **2a** and **2b** react with alcohols and water to give trimethylamine and *N*-methylpiperidine, respectively. Complex **2b** also reacts with LiAlH$_4$ to give *N*-methylpiperidine. Dimercury(I) dichloride is the main product in the reaction of **2b** with HgCl$_2$. Diethyl ether is strongly coordinated to **2b**. An exchange was not observed with TMED (tetramethylethylenediamine) or DABCO (1,4-diazabicyclo[2.2.2]octane) with **2b** at room temperature.

The nickel complexes are thermally very stable. They melt at 90−115 °C (**2a**) and 95−110 °C (**2b**) with decomposition. Similar decomposition temperatures have been found in complexes of the type [Li$_2$NiR$_4$(thf)$_x$] [129−130 °C (R = Me, x = 2); 102−103 °C (R = Ph, x = 4); 90 °C (R = C≡CPh, x = 4)],[8] the first complexes of the type [Li$_2$NiR$_4$], and in [Li$_2$Ni(C$_4$H$_8$)$_2$(OEt$_2$)] (C$_4$H$_8$ = 1,4-butanediyl) (105 °C).[9]

The molecular structure of **2b** (C_i symmetry) is shown in Figure 1, and selected bond distances and angles are compiled in Table 3. The piperidinomethyl ligands are η^1-coordinated at nickel with a planar arrangement of the four methylene C atoms. These atoms (C1, C1′, C7, C7′) and Ni define a plane exactly. The two nitrogen atoms N2 and N2′ are nearly placed within this plane too (deviation 0.035(3) Å). The other two

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Table 4. Crystallographic Data for the Structural Analysis of [{$Li(OEt_2)$}$_2Ni(CH_2NC_5H_{10})_4$] (**2b**)

chem formula $C_{32}H_{68}Li_2N_4O_2Ni$	space group $P2_1/c$ (No. 14)
fw 613.49	$T = -98$ °C
$a = 9.533(3)$ Å	$\lambda = 0.710\,69$ Å
$b = 17.932(6)$ Å	$\varrho_{calcd} = 1.180$ g/cm^3
$c = 10.975(4)$ Å	$\mu = 1.06$ mm^{-1}
$\beta = 102.08(3)$°	$R^a = 0.0656$
$V = 1834.7(1.0)$ Å^3	$R_w{}^b = 0.0784$
$Z = 2$	

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = (\sum w||F_o| - |F_c||^2/\sum|F_o|^2)^{1/2}$ ($w^{-1} = (\sigma^2(F_o) + 0.0024F_o{}^2)$.

nitrogen atoms N1 and N1′ are placed at 1.227(3) Å beneath and above this plane, respectively. The Ni−C bond lengths d(Ni−C1) = 2.023(4) Å and d(Ni−C7) = 2.032(4) Å are typical for complexes with NiC_4 units such as a nickelacyclopentane complex and nickel phosphorus ylide complexes (1.978−2.032 Å).[9b,10]

The three donors (n-EPD: N1, N2, O1) around lithium are in a nearly trigonal planar arrangement. The sum of angles around Li amounts to 355.2°, and the distance between Li and the N1−N2−O plane is 0.255(7) Å. Furthermore, Li comes into contact with two methylene carbon atoms and with the nickel atom. The Li−C bond lengths d(Li−C7) = 2.166(7) Å and d(Li−C1) = 2.312(8) Å are in the range for alkyllithium compounds.[11] One of them (d(Li−C7) = 2.166(7) Å) is shorter than in $[MeLi]_4$ (2.28 Å).[12] The Li−Ni−Li unit is linear, intersecting the NiC_4 plane with an angle of 34.1°. Considering the sum of covalent (2.50 Å) and van der Waals radii (3.40 Å), the Ni−Li separation of 2.592(2) Å indicates a metal−metal interaction. d(Ni−Li) = 2.592(2) Å is only slightly longer than d(Ni−Li) = 2.561 Å in $[Li_2Ni(Me_2NCH_2CH{=}CHCH_2NMe_2)]$.[13b] On the other hand, there are complexes with Li−Ni−Li fragments in which d(Ni−Li) is considerably shorter: [{$Li(thf)_2$}$Ni(C_4H_8)_2$], 2.389(4) Å;[9b] [{Li(tmed)}$_2$Ni(norbornene)$_2$], 2.381 Å;[13c] [{Li(tmed)}$_2$Ni(CDT)], 2.39 Å.[13a]

Considering the lithium contacts to nitrogen, oxygen, carbon, and nickel, a position of high electron density is obviously occupied by lithium. As a consequence, lithium is coordinated outside the NiC_4 plane ($d(Li/NiC_4)$ = 1.454(6) Å) and the angles C1−Ni−C7 are widened in comparison to C1−Ni−C7′: 96.1(2) vs 83.9(2)°.

The results demonstrate that the lone electron pair of nitrogen in aminomethyl ligands is strongly involved in lithium coordination. This fact and the absence of β-hydrogen atoms seem to be important for the relatively high thermal stability not only for the nickel complexes **2** but also for other piperidinomethyl complexes of 3d elements.[6]

Experimental Section

Materials and General Procedures. All reactions and manipulations were carried out under purified argon using Schlenk techniques. Diethyl ether and tetrahydrofuran were dried and distilled from sodium benzophenone ketyl under argon. A 15% solution of BuLi in hexane was obtained from Fluka. Nickel halide−phosphine complexes[14] and the (aminomethyl)tin compounds[7] were prepared according to the literature. NMR spectra were recorded on a Varian Gemini-300 (^{1}H, ^{13}C) by using the protio impurities and the ^{13}C resonances of the deuterated solvents as references for ^{1}H and ^{13}C NMR spectroscopy, respectively. The nickel and lithium contents were determined by complexometry and by AES, respectively. The nitrogen content was determined in the microanalytical laboratory of Martin-Luther-Universität.

Table 5. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for [{$Li(OEt_2)$}$_2Ni(CH_2NC_5H_{10})_4$] (**2b**)[a]

	x	y	z	U(eq)[a]
Ni	0	0	0	28(1)
N1	851(3)	−723(2)	2625(3)	34(1)
N2	2169(3)	1000(2)	1900(3)	31(1)
O1	4023(3)	−624(2)	1677(3)	64(1)
Li	2173(8)	−127(3)	1853(7)	35(2)
C1	-262(4)	−277(2)	1725(3)	34(1)
C2	771(5)	−1515(2)	2247(4)	42(1)
C3	1854(5)	−1998(3)	3109(4)	55(2)
C4	1686(6)	−1940(3)	4450(5)	65(2)
C5	1721(6)	−1114(3)	4840(4)	59(2)
C6	622(5)	−669(3)	3911(4)	45(1)
C7	1532(4)	786(2)	565(3)	37(1)
C8	3559(4)	1387(2)	2013(4)	44(1)
C9	4207(5)	1600(3)	3350(5)	59(2)
C10	3200(6)	2082(3)	3913(5)	67(2)
C11	1731(5)	1707(3)	3721(5)	54(2)
C12	1178(4)	1510(2)	2353(4)	42(1)
C13	4244(7)	−1165(4)	781(8)	100(3)
C14	3221(6)	−1045(4)	-392(5)	78(2)
C15	5108(11)	−743(6)	2854(11)	171(6)
C16	5999(16)	−377(7)	3302(11)	194(7)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Synthesis of 1a and 1b. To a stirred solution of $Bu_3SnCH_2NR_2$ ($NR_2 = NMe_2$, NC_5H_{10}) (50.0 mmol) in hexane (15 mL) was added an equimolar amount of a solution of BuLi in hexane (0 °C). A colorless precipitate formed immediately. This was filtered out, washed with hexane, and vacuum dried (70−95%). Anal. Calcd for **1a**: Li, 10.68. Found: Li, 10.47. Calcd for **1b**: Li, 6.60; N, 13.33. Found: Li, 6.49; N, 13.76.

Synthesis of 1c. To a stirred solution of BuLi (17.0 mmol) in hexane was added dropwise a solution of $Bu_3SnCH_2NPh_2$ (8.5 g, 17.0 mmol) in hexane (10 mL) and tetrahydrofuran (5 mL). After 20 min of stirring at 0 °C, yellow crystals of **1c** formed, which were filtered out, washed with cold hexane, and vacuum dried (2.9 g, 65%). Complex **1c** was recrystallized from tetrahydrofuran/hexane. Anal. Calcd for **1c**: Li, 2.66; N, 5.36. Found: Li, 2.58; N, 5.29.

Synthesis of 2a. To a stirred suspension of **1a** (4.0 g, 60.0 mmol) in diethyl ether (40 mL) was added dropwise a solution of $NiCl_2{\cdot}2\,PBu_3$ (8.3 g, 15.0 mmol) in ether (50 mL) at −30 °C. Stirring was continued for 2 h at −20 °C. The precipitated LiCl was filtered out and the orange filtrate concentrated under oil-pump vacuum down to 30 mL. At −78 °C the precipitated yellow crystals of **2a** were filtered out and vacuum dried (4.1 g, 58%). The product was recrystallized from diethyl ether. Anal. Calcd. for **2a**: Li, 3.06; Ni, 12.95. Found: Li, 3.03; Ni, 12.67.

Synthesis of 2b. To a stirred suspension of **1b** (3.4 g, 30.0 mmol) in diethyl ether (25 mL) was added dropwise a solution

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of $NiBr_2 \cdot 2\ PBu_3$ (4.7 g, 7.5 mmol) in diethyl ether (25 mL) at −78 °C. After being stirred at −40 °C for 3 h, the orange solution was concentrated under oil-pump vacuum at −20 °C down to 30 mL. The precipitated yellow crystals of **2b** were filtered out and vacuum dried. The product was recrystallized from ether (1.65 g, 36%). Anal. Calcd for **2b**: Li, 2.26; Ni, 9.57; N, 9.13. Found: Li, 2.12; Ni, 9.49; N, 9.00.

Crystallographic Studies. A crystal of $[\{Li(OEt_2)\}_2Ni(CH_2NC_5H_{10})_4]$ (**2b**), grown from diethyl ether, was selected (0.62 × 0.43 × 0.27 mm^3) and mounted on a Nicolet R3m/V diffractometer. Unit cell parameters were determined from diffractometer angles of 50 reflections ($20 \leq 2\theta \leq 25°$) and refined by least-squares methods. Intensities were collected with graphite-monochromatized Mo Kα radiation, using the ω-scan technique. The intensities of 3516 reflections were measured in the range $3 \leq 2\theta \leq 50°$, resulting in 3203 unique reflections, 2573 of which were assumed as observed ($F_o \geq 4\sigma(F)$; $F(000) = 692$ e). The crystallographic data, conditions used for the intensity data collections, and some features of the structure are listed in Table 4.

The structure was solved by Patterson syntheses and refined by full-matrix least-squares methods on F, with the SHELXTL-Plus computer program.[15] The final R factor was 0.0656 (R_w = 0.0784) for all observed reflections. The number of parameters refined was 190. All atoms except hydrogen atoms were assigned anisotropic thermal parameters. H atoms were introduced in the structure factor calculations by their computed coordinates with isotropic temperature factors as riding atoms. Maximum and minimum peaks in the final difference synthesis were 0.90 and −0.47 e Å^{-3}, respectively. Atomic coordinates and equivalent isotropic displacement coefficients except those for hydrogen atoms are given in Table 5.

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Supplementary Material Available: Complete bond lengths and bond angles (Table S1), anisotropic displacement coefficients (Table S2), and coordinates and isotropic displacement coefficients of H atoms (Table S3) (3 pages). Ordering information is given on any current masthead page.

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(15) SHELTX-Plus, Version 4.2/Iris, a complete software package for solving, refining and displaying crystal structures, Siemens Co., 1991.