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Notes

Synthesis and Structures of 9-Nickelafluorenyllithium Complexes

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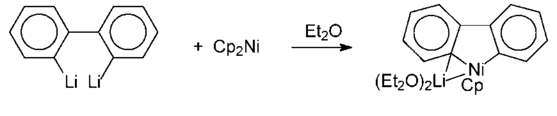
*Summary: A novel lithium biphenyl-2,2′-diyl(cyclopentadienyl)nickelate compound (9-nickelafluorenyllithium complex), (η^2-(1-(η^5-cyclopentadienyl))-1-nickelafluorenyl)lithium(diethyl ether)$_2$ (**1**), was prepared in the reaction between 2,2′-dilithiobiphenyl and nickelocene in diethyl ether. Compound **1** was transformed to other 9-nickelafluorenyllithium compounds, [(1-(η^5-cyclopentadienyl))-1-nickelafluorenyl][lithium(dimethoxyethane)$_3$] (**2**) and (η^5-(1-(η^5-cyclopentadienyl))-1-nickelafluorenyl)lithium(dimethoxyethane) (**3**), whose crystal and molecular structures were determined by single-crystal X-ray analysis.*

Introduction

While the crystal structure of the first fluorenyllithium complex was published over 35 years ago[1] and the structures of other complexes (with oxygen-containing ligands bonded to the lithium) during the last 10 years,[2] only few examples of analogues of fluorenyllithium or fluorenyl-alkali metal complexes containing main group elements have been reported so far.[3] Similarly, 2,2′-biphenyldiyl−transition metal complexes are still scarce. Following a first report on Cp$_2$Ti(biph)[4] (biph = 2,2′-biphenyldiyl), some related neutral complexes were reported for other transition metals.[5] There are examples of complexes in which the nickel atom is bonded to the biphenyl ligand as well as to phosphine[6] or carbene ligands.[7] The only known anionic compounds containing a metallafluorenyl ring are complexes of zirconium[8] with two [Li(THF)$_4$][CpZr(biph)$_2$], three [Li(THF)$_4$]$_2$[Zr(biph)$_3$], and four biphenyl ligands [Li-Et$_2$O]$_4$[Zr(biph)$_4$]. We report here the synthesis and characterization of the first 9-nickelafluorenyllithium complexes that belong to the family of the 2,2′-biphenyldiyl−transition metal compounds.

Results and Discussion

The reaction of 2,2′-dilithiobiphenyl with nickelocene in diethyl ether at 20 °C for several days afforded a dark brown solution, from which transparent orange crystals of **1** separated at −15 °C (eq 1). Drying the crystals under vacuum turned the solid into a yellow powder, which was not soluble again in diethyl ether. This change made **1** difficult to handle.



(1)

1

The molecular structure of **1** is presented in Figure 1. Crystal data, data collection, and refinement parameters are given in Table 3. Complex **1** is the first example of the lithium biphenyl-2,2′-diyl(cyclopentadienyl)nickelate compounds. It may also be called 9-nickelafluorenyllithium. The compound crystallizes in an orthorhombic crystal system. Two diethyl ether molecules are coordinated to the lithium atom. The molecule contains an almost planar five-membered nickelacycle for which the maximum deviation from the mean plane defined by the C1, C2, C7, C8, and Ni atoms is 0.0160 Å for C8, which is much less

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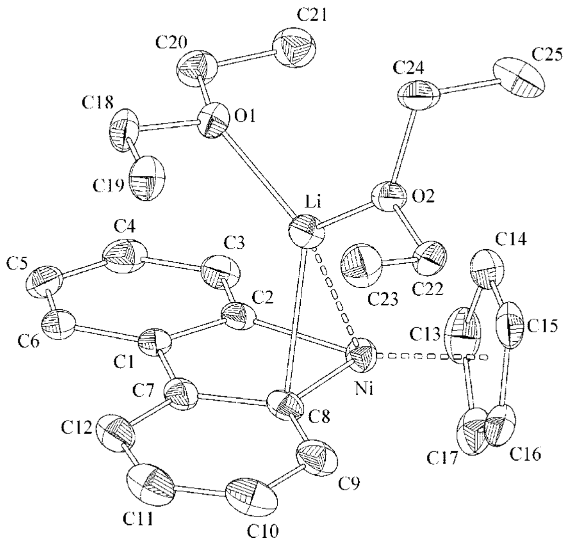

Figure 1. ORTEP view of the molecular structure of **1** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Selected interatomic distances [Å] and angles [deg]: Ni−C2 1.894(3), Ni−C8 1.889(3), Ni−Li 2.513(5), C1−C2 1.422(4), C1−C7 1.466(4), C7−C8 1.432(4), Li−C8 2.402(5); C2−Ni−C8 84.8(1).

than in fluorenyllithium diethyl ether complex (C9, 0.1 Å).[2b] The average length of the Ni−C2 and Ni−C8 bonds is 1.89 Å, which is in the range of nickel−carbon single bonds and similar to the distances in the other complex containing the nickelafluorenyl ring.[9] The angle between the centroid (C1, C2, C7, C8)−midpoint (Ni, C8)−Li is 80.5°. The Li−C8 (2.402(5) Å) bond length is in the range of single bonds, while other interatomic distances (Li−C1 (3.05 Å), Li−C2 (2.85 Å), and Li−C7 (2.83 Å)) are longer than lithium−carbon single bonds.[2b,2d] The interatomic distance between lithium and nickel is 2.513(5) Å. Jonas and Krüger[10] and Brauer et al.[11] reported Ni−Li single bonds shorter than 2.4 Å. On the other hand, Steinborn et al.[12] wrote that a nickel−lithium distance of 2.59 Å, considering that the sum of the van der Waals radii is 2.50 Å, indicates metal−metal interaction. On this basis we may conclude that there is at least moderate interaction between the lithium and nickel atoms in **1**. Thus the lithium atom interacts with two members of the nickelacyclic ring (C8 and Ni), which is similar to a fluorenyllithium diethyl ether complex.[2b]

The behavior of 9-nickelafluorenyllithium in different solvents was investigated. In the present experiments DME, THF, and TMEDA were used (DME = 1,2-dimethoxyethane, TMEDA = *N,N,N'N'*-tetramethylethylenediamine).

Complexes **2**, **4**, and **5** were obtained by adding DME, THF, and TMEDA, respectively, to the ethereal solution of **1**. In the case of **2** and **5** a yellow precipitate was formed. Compound **4** was isolated as a black solid by removing solvents from its solution. Complexes **2** and **4** are easily soluble in toluene and only slightly soluble in hexane or diethyl ether, while complex **5** is very poorly soluble in toluene but very soluble in THF. Compound **2** upon addition of THF gives complex **4**. The structure of complex **4** proposed in Scheme 2 is based on its ^{1}H NMR spectrum in benzene solution, which suggests that four THF molecules are coordinated to one lithium atom. Thus far we have not been able to grow crystals of **4** suitable for an X-ray structure determination.

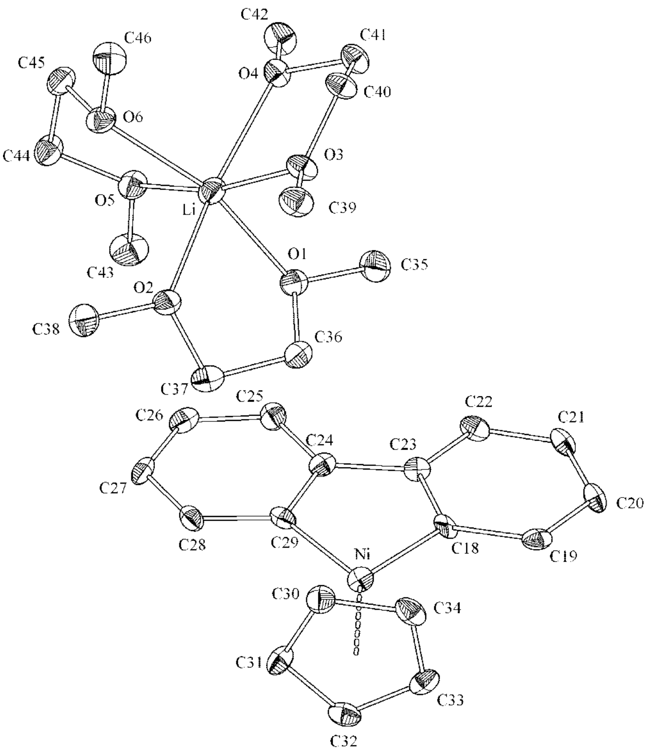

Figure 2. ORTEP view of the molecular structure of **2** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Selected interatomic distances [Å] and angles [deg] for molecules **A** and **B**: Ni−C18 1.880(6) 1.863(6), Ni−C29 1.885(6) 1.890(6), C18−C23 1.426(7) 1.408(8), C23−C24 1.466(7) 1.462(7), C24−C29 1.415(7) 1.409(8), C18−Ni−C29 84.3(2) 84.0(3).

We tried to synthesize compounds **2** and **4** directly from dilithiobiphenyl and nickelocene in DME and THF, respectively. We succeeded in synthesis of **4** in THF (90% yield), while no reaction occurred between dilithiobiphenyl and nickelocene in dimethoxyethane.

Crystals of **2** appropriate for X-ray measurements were obtained from DME solution. The molecular structure of **2** is presented in Figure 2. Crystal data, data collection, and refinement parameters are given in Table 3. The compound crystallizes in the monoclinic crystal system. There are two independent molecules of **2** (**A** and **B**) in an asymmetric unit cell. There is also one molecule of dimethoxyethane per two molecules of **2**. Complex **2** represents a solvent-separated ion pair that is similar to the fluorenyllithium(diglyme)$_2$ complex.[2c] Each lithium cation of **2** is bonded to three DME molecules, and the average lithium−nickel distance is 6.50 Å. The Ni atom in the anion is a part of an almost flat nickelafluorene ring.

Complex **3** was obtained by drying compound **2**. When complex **2** is dried under vacuum, it reversibly loses 2 DME to give **3** (eq 2). We have recorded the solid-state ^{1}H and ^{13}C NMR spectra of **2** and **3** and found the chemical shifts to be almost identical to those in the solution spectra of **2** and **3**.

Crystals of **3** appropriate for X-ray measurements were obtained from hexane/toluene solution. The molecular structure of **3** is presented in Figure 3. Crystal data, data collection, and refinement parameters are given in Table 3. The compound crystallizes in the monoclinic crystal system. There are two independent molecules (**A** and **B**) in an asymmetric unit cell.

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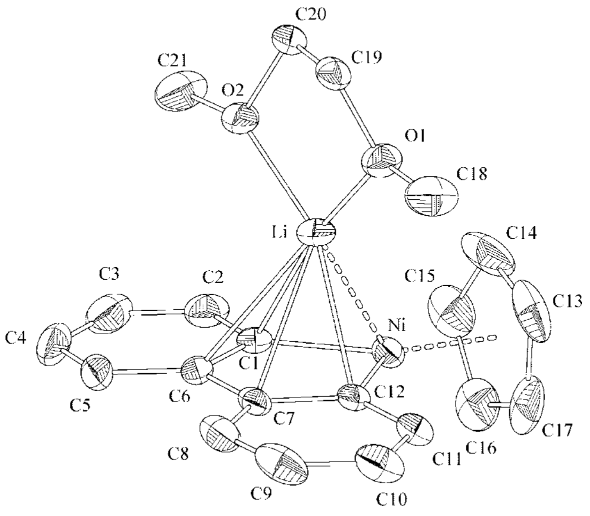

Figure 3. ORTEP view of the molecular structure of **3** showing atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Selected interatomic distances [Å] and angles [deg] for molecules **A** and **B**: Ni−C1 1.897(3) 1.892(2), Ni−C12 1.885(2) 1.896(2), Ni−Li 2.510(4) 2.563(4), Li−C1 2.535(5) 2.411(5), Li−C6 2.660(5) 2.495(4), Li−C7 2.550(5) 2.450(4), Li−C12 2.375(5) 2.385(5); C1−Ni−C12 84.8(1) 84.5(1).

Table 1. Comparison of Chemical Shifts of Corresponding Protons in ^{1}H NMR Spectra of Complexes 1, 2, 3, 4, and 5 and ^{7}Li Spectra of 2, 3, and 4 (butyllithium solution in benzene used as the external reference)[b]

	Ph[a]				Cp	solvent		^{7}Li
1	7.45 (d)	7.26 (d)	6.79 (t)	6.52 (t)	5.20 (s)	unknown	unknown	
2	7.76 (d)	7.51 (d)	7.08 (t)	6.82 (t)	5.55 (s)	3.11 (s)	2.98 (s)	−4.67
3	7.75 (d)	7.56 (d)	7.09 (t)	6.84 (t)	5.52 (s)	2.47 (s)	2.26 (s)	−3.50
4	7.71 (d)	7.50 (d)	7.07 (t)	6.82 (t)	5.53 (s)	3.18 (m)	1.23 (m)	−3.63
5	7.19 (d)	6.90 (d)	6.43 (t)	6.20 (t)	5.03 (s)	2.24 (s)	2.09 (s)	

[a] Spectrum of **1** was measured in diethyl ether with addition of 10% of C_6D_6; spectra of **2**, **3**, and **4** were measured in C_6D_6; spectrum of **5** was measured in d_8-THF. [b] All coupling constants for protons of phenyl groups equal $^3J = 7.2$ Hz.

Table 2. Comparison of Chemical Shifts of Corresponding Carbon Atoms in ^{13}C NMR Spectra of Complexes 2, 3, 4, and 5[a]

	Ph						Cp	solvent	
2	168.22	154.66	145.34	123.06	122.00	120.30	90.36	71.62	58.73
3	166.79	154.65	145.47	123.28	122.42	120.42	90.39	69.55	59.00
4	166.85	154.63	145.37	123.35	122.44	120.37	90.37	67.95	25.48
5	174.42	158.52	143.13	121.25	119.13	117.77	89.67	58.65	46.14

[a] Spectra of **2**, **3**, and **4** were measured in C_6D_6; spectrum of **5** was measured in d_8-THF.

The lithium atom interacts with five members of the nickelacyclic ring, which is similar to the fluorenyllithium−DME complex.[2e] The lithium−nickel distance is 2.510(4) Å in molecule **A** and 2.563(4) Å in molecule **B**. Similarly to **1**, such distances may indicate at least moderate metal−metal interaction. The average distance between the lithium atom and four carbon atoms from the nickelacyclic ring (C1, C6, C7, C12) is 2.44 Å in molecule **B**. In molecule **A** this value equals 2.53 Å but is still within the range of the single Li−C bond length.[13]

In conclusion, we have described the synthesis of the first lithium biphenyl-2,2′-diyl(cyclopentadienyl)nickelate compounds (9-nickelafluorenyllithium complexes), the first metallafluorenyllithium complexes possessing a transition metal in the heterocyclic ring. Their structures are analogous to the structures of the appropriate fluorenyllithium complexes. We are now investigating their reactivity especially as precursors of nickelafluorenyl−metal compounds.

Experimental Section

All reactions were carried out in an atmosphere of dry argon or nitrogen using Schlenk tube techniques. Solvents were dried by conventional methods. ^{1}H and ^{13}C NMR spectra were measured on a Varian Mercury 400BB instrument. Solid-state NMR spectra were recorded on a Varian 700 MHz spectrometer. 2,2′-Dibromobiphenyl was synthesized according to the literature methods.[14] Crystallographic data for the structural analysis of **1**, **2**, and **3** have been deposited with the Cambridge Crystallographic Data Centre, Nos. CCDC 650794−650796. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (fax + 44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Synthesis of Compound 1. 2,2′-Dibromobiphenyl (4.00 g, 12.8 mmol) and 150 mL of hexane were placed in a Schlenk flask. Then 25.6 mmol of *n*-butyllithium (solution in heptane) was added at room temperature. The reaction was carried out for 4 days. The white precipitate of 2,2′-dilithiobiphenyl was washed three times with hexane (to remove bromobutane) and dried under vacuum. Then 200 mL of diethyl ether and 2.35 g (12.5 mmol) of nickelocene were added to the Schlenk flask. The reaction was carried out for 3 days at room temperature. Then the precipitate was allowed to settle and the clear solution of **1** was transferred to another Schlenk flask. Crystals appropriate for X-ray analysis were grown from diethyl ether solution at −15 °C.

Crystal Structure Determination of 1. The crystal was sealed in a glass capillary under a nitrogen stream. X-ray data were collected on a Nonius KappaCCD diffractometer. Data were collected with subsequent φ and ω scans (132 frames, rotation per frame 2°, exposure per frame 60 s). The diffractometer control program was Collect,[15] unit cell parameters and data reduction were obtained with Denzo and Scalepak,[16] and the structure was solved by direct methods with SHELXS-97[17] and refined on F^2 by full-matrix least-squares with SHELXL-97.[18] All hydrogen atoms were placed in calculated positions and refined using a riding model.

Synthesis of Compounds 2 and 3. A 20 mL amount of dimethoxyethane was added to a solution of **1** in diethyl ether, and an orange precipitate was formed. Solvents were removed under vacuum, and the solid residue was dissolved in 30 mL of warm dimethoxyethane. Red crystals of **2** were obtained after cooling the solution to −15 °C. Drying of **2** under vacuum at approximately 50 °C afforded **3** in the form of a yellow powder, 3.29 g (8.8 mmol, 69% yield refers to the 2,2′-dibromobiphenyl used in synthesis of **1**). Complex **3** crystallized as orange needles from a mixture of hexane and toluene. Anal. Calcd for $C_{31}H_{48}LiNiO_7$ (**2**·(1/2DME)): C, 62.23; H, 8.09. Found: C, 60.97; H, 8.60. Results of the analysis are probably due to the impossibility of fine drying of the compound. Prolonged drying causes stepwise loss of coordinated DME with formation of **3**. Anal. Calcd for **3**, $C_{21}H_{23}LiNiO_2$: C, 67.61; H, 6.21. Found: C, 66.93; H, 6.47.

Crystal Structure Determination of 2 and 3. The structures were solved and refined using the programs SHELXS-97[17] and SHELXL-97,[18] respectively.

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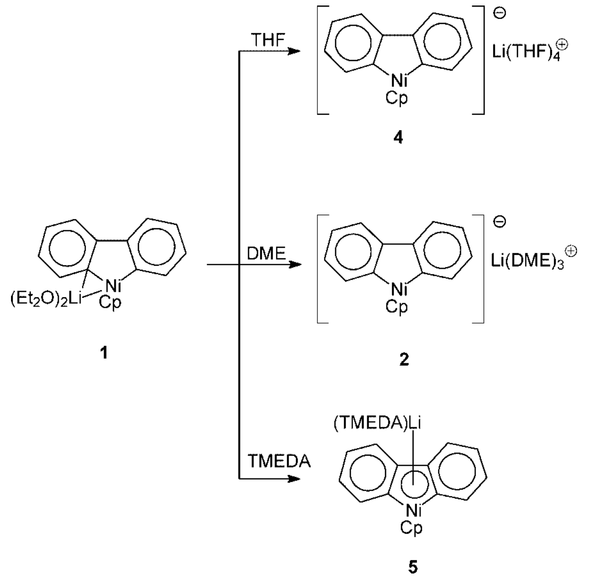
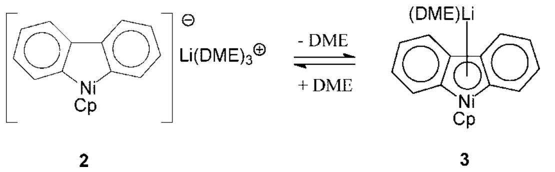
Table 3. Crystal Data and Structure Refinement Parameters

	1	2	3
empirical formula	C_{25} H_{33} Li Ni O_2	C_{31} H_{48} Li Ni O_7	C_{42} H_{46} Li_2 Ni_2 O_4
cryst size (mm)	0.6 × 0.4 × 0.3	0.15 × 0.10 × 0.05	0.30 × 0.17 × 0.09
cryst syst	orthorhombic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
unit cell dimens	$a = 9.8482(3)$ Å $b = 14.5816(4)$ Å $c = 15.6829(5)$ Å	$a = 31.21(3)$ Å $b = 11.851(7)$ Å $c = 17.44(2)$ Å $\beta = 98.85(3)°$	$a = 16.5651(5)$ Å $b = 14.5732(5)$ Å $c = 17.3587(3)$ Å $\beta = 116.770(2)°$
volume	2252.1 (1) Å^3	6374(10) Å^3	3741.4(2) Å^3
Z	4	8	4
fw	431.16	598.34	746.09
density (calcd)	1.272 Mg·m^{-3}	1.247 Mg·m^{-3}	1.325 Mg·m^{-3}
temperature (K)	120(2)	100(2)	150(2)
absorption coeff	0.878 mm^{-1}	0.651 mm^{-1}	1.046 mm^{-1}
$F(000)$	920	2568	1568
radiation	Mo Kα (λ = 0.71073 Å, graphite monochromator)		
θ range for data collection	2.95−27.47°	2.92−25.00°	2.98−27.49°
scan type	ϕ and $\omega-2\theta$	ϕ and $\omega-2\theta$	ϕ and $\omega-2\theta$
index ranges	$-12 \le h \le 12$, $-18 \le k \le 18$, $-20 \le l \le 20$	$-37 \le h \le 36$, $-14 \le k \le 0$, $0 \le l \le 20$	$-21 \le h \le 21$, $-18 \le k \le 18$, $-21 \le l \le 22$
no. of reflns collected /unique	19 720/5015 [$R_i = 0.068$]	47 962/10 745 [$R_{int} = 0.115$]	61 625/8525 [$R_{int} = 0.0552$]
refinement method	full-matrix least-squares on F^2		
no. of data/restraints/params	5015/0/266	10 745/0/735	8525/0/456
goodness-of-fit on F^2	1.03	0.93	0.99
final R indices [$I > 2\sigma(I)$]			
$R_1 = \sum(F_o - F_c)/\sum F_o$	$R_1 = 0.043$	$R_1 = 0.062$	$R_1 = 0.041$
$wR_2 = \{\sum[w(F_o^2 - Fc^2)^2]/\sum[w(F_o^2)^2]\}^{1/2\,a}$	$wR_2 = 0.073$	$wR_2 = 0.133$	$wR_2 = 0.094$
R indices (all data)	$R_1 = 0.060$; $wR_2 = 0.076$	$R_1 = 0.172$; $wR_2 = 0.175$	$R_1 = 0.084$; $wR_2 = 0.103$
largest difference peak and hole	0.278 and −0.405 e·Å^{-3}	0.699 and −0.825 e·Å^{-3}	0.544 and −0.494 e·Å^{-3}

[a] Weighting scheme (where $P = (F_o^2 + 2F_c^2)/3$): For **1**: $w^{-1} = \sigma^2(F_o^2) + (0.0211P)^2 + 1.2076P$. For **2**: $w^{-1} = \sigma^2(F_o^2) + (0.0785P)^2 + 0.0000P$. For **3**: $w^{-1} = \sigma^2(F_o^2) + (0.0534P)^2 + 0.0000P$.

Scheme 1. Reactions of Complex 1 with THF, DME, and TMEDA



 (2)

Synthesis of Compound 4. A 10 mL amount of THF was added to the solution of **1** in diethyl ether, and the mixture was stirred for 1 h. Solvents were removed under reduced pressure. Compound **4** was obtained as a brown solid.

To determine the yield of **4**, 0.29 g (0.78 mmol) of **3** was dissolved in 10 mL of toluene, and 10 mL of THF was added. The mixture was stirred for 15 min. The solvents were removed, and the solid was washed two times with hexane; 0.42 g (0.74 mmol) of **4** was isolated (95%). Anal. Calcd for **4** $C_{33}H_{45}LiNiO_4$: C, 69.37; H, 7.94. Found: C, 68.97; H, 8.16.

Synthesis of Compound 5. A 10 mL amount of TMEDA was added to the solution of **1** in diethyl ether, and a yellow precipitate of **5** was formed. It was washed several times with hexane and dried under vacuum.

To determine the yield of **5**, 0.24 g (0.65 mmol) of **3** was dissolved in 10 mL of toluene, and 10 mL of TMEDA was added. The mixture was stirred for 15 min. The solvents were removed, and the solid was washed two times with hexane; 0.25 g (0.63 mmol) of **5** was isolated (97%). Anal. Calcd for **5**, $C_{23}H_{29}LiN_2Ni$: C, 69.21; H, 7.32. Found: C, 68.74; H, 7.51.

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Supporting Information Available: CIF files giving X-ray crystallographic data for the structure determinations of **1**, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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