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Dinuclear [RNi(oxam)NiR] Complexes (oxam = N^1,N^2-bis(2-pyridylmethyl)-N^3,N^4-bis(2,4,6-trimethylphenyl)oxalamidinate; R = Me, Ph, C≡CH, C≡CPh): Reactions of the Methyl Complex and Formation of $[Li(THF)]_2Li_2Ni_2Me_8$ and $[Li(THF)]_4Ni_2Me_8$†

Dirk Walther,* Michael Stollenz, and Helmar Görls

Institut für Anorganische und Analytische Chemie der Friedrich-Schiller-Universität Jena, D-07743 Jena, Germany

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The reaction between 1 equiv of $[\{(acac)Ni\}_2(A)]$ and 2 equiv of LiR in THF afforded the binuclear organometallic complexes $[(RNi)_2(A)]$ (A: N^1,N^2-bis(2-pyridylmethyl)-N^3,N^4-bis-(2,4,6-trimethylphenyl)oxalamidinate; **1**: R = Me; **2**: R = Ph). Analogously, **3b** (R = C≡C−H was formed from $[\{(acac)Ni\}_2(A)]$ and sodium acetylide. The reaction of **1** with phenylacetylene resulted in the formation of complex **3a** (R = C≡C−Ph), accompanied by the evolution of methane. Compounds **1**−**3** were characterized by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, and mass spectroscopy. In addition, the molecular structures of **1** and **3b** were determined by X-ray crystallography. The NMR spectra of the complexes showed very simple patterns, thus indicating that only one isomer is present in solution containing a highly symmetrical structure with planar Ni(II) centers. X-ray studies confirmed that two Ni(II) centers are connected via the oxalamidinato bridge A, which coordinates in a tridentate fashion at each Ni atom. The fourth position at the metal center is occupied by the organic groups R. Compound **1** reacts with an excess of LiMe in THF, yielding $[Li(THF)]_2Li_2Ni_2Me_8$ (**5**). Upon recrystallization, the THF-enriched complex $[Li(THF)]_4Ni_2Me_8$ (**6**) was isolated. Both complexes were characterized by X-ray crystallography and ^{1}H/ ^{13}C NMR spectroscopy. Both **5** and **6** are highly symmetrical compounds in which each planar Ni(II) center is surrounded by four methyl groups. The Ni···Ni separations are relatively long (3.167(1) and 3.142(1) Å, respectively), reflecting the absence of a metal−metal bond between those two metal centers. Furthermore, agostic Li−H interactions stabilize the structure in a way similar to that in the corresponding Cr(II) compound $[Li_4(THF)_4Cr_2Me_8]$, in which very short contacts have been found (Cr···Cr distance 1.968(2) Å).

Introduction

In a preliminary paper we described the first homo- and heterobinuclear nickel(II) complexes as well as the first representatives of heterotri- and tetrametallic complexes in which the metal ions are connected via bridging oxalic amidinates ligands ("*oxam*").[1] A series of these complexes containing acetylacetonato ligands as terminating groups have shown the ability to catalyze the oligomerization or polymerization of ethylene in the presence of MAO.

Surprisingly, some of the dinuclear complexes with *oxam* ligands also catalyzed the selective cross coupling between R−X and R′MgX, whereas, according to the generally accepted mechanism of this reaction, the key step of the catalytic cycle is postulated to be the reductive elimination of R−R′, which forms Ni(0).[2] In the case of *oxam*Ni(II) complexes, this reductive elimination of R−R′ is not expected to be energetically favored due to the anionic nature of the *oxam* ligands, which are poor π-acceptor ligands and thus cannot stabilize Ni(0) species.

Since it is likely that di- or oligonuclear organometallic species containing R−Ni units linked by *oxam* bridges are involved in these catalytic reactions, we were interested in investigating the organometallic chemistry of such oligometallic species. We focused on the N^1,N^2-bis(2-pyridylmethyl)-N^3,N^4-bis(2,4,6-trimethylphenyl)oxalamidinate ligand (A), reasoning that this ligand would form dinuclear alkyl-, aryl-, and alkinyl-Ni(II) complexes of the type $[(RNi)_2(A)]$, in which each planar nickel is surrounded by three N donor groups of the *oxam* ligand. This arrangement should inhibit the formation of coordination polymers, which was observed when *oxam* ligands without additional donor groups in

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† This work is dedicated to Prof. Rudi Taube (Halle, Germany) on the occasion of his 70th birthday.

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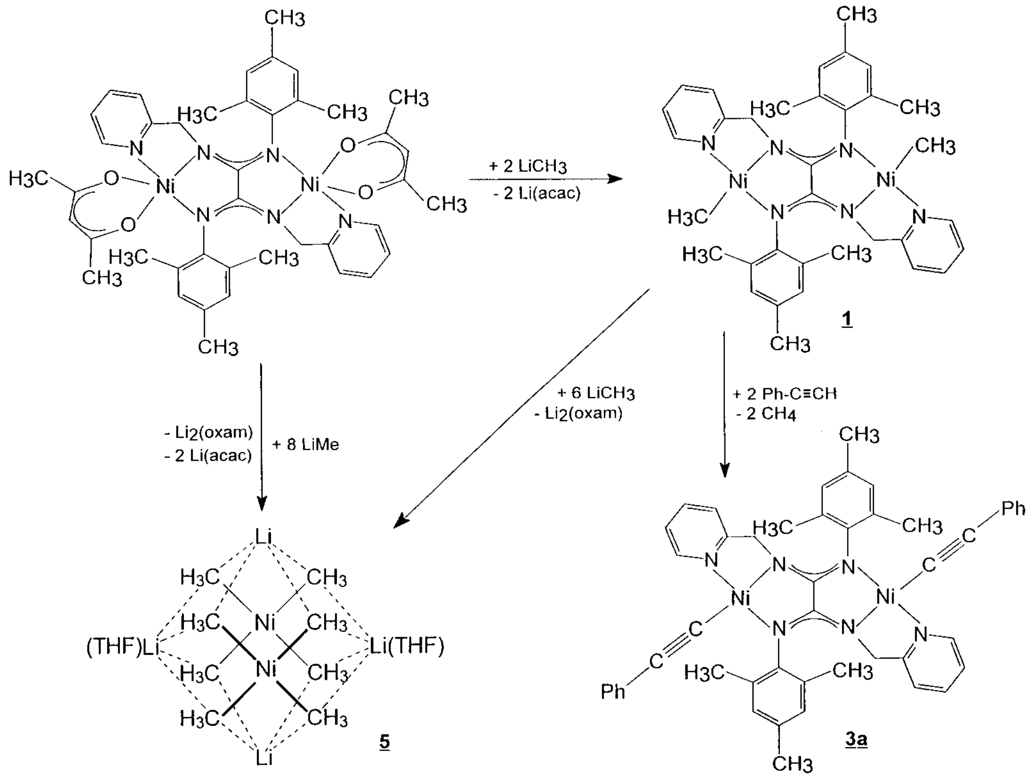
Scheme 1. Formation of the Complexes 1−5



the sidearms were used. Furthermore, lower π-acceptor properties of ligand A compared with *oxam* ligands bearing four aryl substituents at the oxal amidinato moiety should stabilize the Ni−R bonds toward reductive elimination and homolytic splitting to form low-valent nickel.

To the best of our knowledge, di- or oligonuclear σ-organometal complexes bridged by *oxam* ligands have not yet been reported in the literature. In general, very little is known about the organometallic chemistry of *oxam*-based compounds. The first organometallic compound of the type($\{Cp_2Ti\}_2$[*oxam*]) was described by Floriani.[3] Recently, complexes of the type Cp_2Ti(*oxam*)-$Mo(CO)_4$ have been synthesized and structurally characterized by Döring and Beckert.[4] Moreover, coordination compounds containing *oxam* ligands are also relatively rare[5−8] since the ligands tend to form ill-defined coordination polymers.[9]

In this article we describe the synthesis and structures of the first dinuclear organometallic compounds in which an *oxam* ligand acts as bridge between two organometallic R−Ni(II) fragments (R = Me, Ph, HC≡C, PhC≡C) (Scheme 1). Furthermore, we report on some reactions of the methyl complex **1**. Surprisingly, the reaction of **1** with an excess of LiMe results in the displacement of the *oxam* ligand and the formation of the dimeric anionic methyl complexes **5** and **6**, respectively.

Results

Synthesis, Structure, and Reactions of the Complexes 1−3. The reaction of $[\{(acac)Ni\}_2(A)]$[1,28] with $LiCH_3$ in THF at −78 °C (ratio 2:1) resulted in the formation of an orange solution. Upon evaporation of the solvent, dissolution of the residue in toluene, and workup the pure dinuclear methyl nickel(II) compound **1** could be isolated in 56% yield (Scheme 1). Single crystals of **1** were grown from toluene.

The diamagnetic orange complex **1** is readily soluble in toluene or THF and is thermally stable even for several hours in toluene solution at 100 °C. According

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to a DTA measurement, **1** starts to decompose at 274 °C in the solid state. Analysis and a mass spectrum confirmed its composition. In the mass spectrum the dinuclear complex ion $[\{(CH_3)Ni\}_2(oxam)]^+$ ($m/z = 648$) was detected. The ^1H NMR spectrum of **1**, recorded in THF-d_8 at room temperature, showed one singlet of the methyl protons of the Ni-Me group at $\delta = -1.35$ ppm and two singlets for the methyl mesityl groups at $\delta = 2.22$ (*p*-methyl) and 2.43 ppm (*o*-methyl). The relative intensities of these resonances are 1:1:2. In addition to the signals corresponding to the protons of the aromatic rings between 6.65 and 7.85 ppm, the ^1H NMR spectrum shows a singlet of the CH_2 group at 3.62 ppm, which is ascribed to the CH_2 group.

The ^{13}C NMR spectrum in THF-d_8 also showed a very simple pattern. The resonance for the carbon of the Ni-Me groups appeared at $\delta = -7.5$ ppm, and the resonances of the mesityl-Me carbons were found at 19.1 and 21.0 ppm, respectively. Furthermore, the signal for the CH_2 carbon was observed at 53.3 ppm. In addition, 10 resonances in the region of the sp^2-carbons between 121.2 and 168.9 ppm were observed. This is the expected number of signals in this region for a symmetrical structure in solution and corresponds to five signals for the inequivalent aromatic CH groups (121.2, 122.6, 127.6, 136.3, and 149.0 ppm), four signals for the inequivalent quarternary C atoms of the aromatic substituents (133.5, 135.7, 144.4, and 163.1 ppm), and one signal for the equivalent oxalamidinato carbons. We assume that the signal at 168.9 ppm belongs to the latter.

The molecular structure of single crystals isolated from toluene was determined by an X-ray analysis (Figure 1).

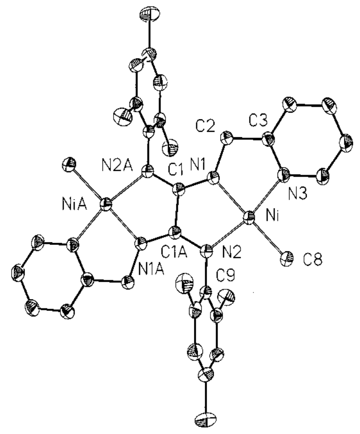

Figure 1. Molecular structure of complex **1**. Selected bond distances (Å) and bond angles (deg): Ni−N1 1.905(2), Ni−N2 1.916(2), Ni−N3 1.912(2), Ni−C8 1.950(3), C1−N1 1.323(3), C1A−N2 1.341(3), C1−C1A 1.506(5), C2−C3 1.514(4), C2−N1 1.459(3), C9−N2 1.435(3), C8−Ni−N1 176.7(1), C8−Ni−N2 96.5(1), C8−Ni−N3 95.7(1), N1−Ni−N2 83.83(9), N1−Ni−N3 84.18(9), N2−Ni−N3 167.38(9), N1A−C1A−N2 133.7(2), N1−C1−C1A 111.9(3), C1−N1−C2 126.8(2), C1A−N2−C9 119.8(2). Symmetry transformations used to generated equivalent atoms: A $-x+1$, $-y+1$, $-z+1$.

The complex consists of a bimetallic centrosymmetric unit in which the *oxam* ligand acts in a bis-chelating fashion to bridge two nickel ions. Each metal ion is in a planar environment created by three N atoms from the bridging ligand and one carbon of the methyl group. The double metallacyclic ring containing the N_2C-CN_2 unit is essentially planar (deviation 0.002 Å). The C−N bonds of the oxalamidinate framework are almost equivalent within experimental error (C1−N1 1.323(3) Å, C1A−N2 1.341(3) Å), indicating a high double-bond character due to a complete electron delocalization over the two CN_2 units. The C1−C1A bond distance of the C_2N_2 unit (1.506(5) Å) is that of a single bond; bond angles around both carbons are typical for sp^2 hybridization.

The two methyl groups coordinated to the Ni centers on the opposite sides of the *oxam* bridge lie trans to each other. The Ni−C bonds (1.950(3) Å) are relatively short compared with the average bond lengths of 2.06 Å for this type of bonding.[10−13] Of particular interest in this connection is the compound $[(Me_3P)NiMe]_2$(oxalate), synthesized and characterized by Klein.[13] In this complex the $[(Ni(CH_3)(PMe_3)]$ fragments are bridged by the oxalate which forms a planar five-membered chelate ring with each nickel atom. Furthermore, the methyl groups lie trans to each other. Remarkably, the Ni−C distance (1.899(4) Å) in this complex is shorter than in **1**.

A search in the Cambridge Data Base showed that numerous X-ray structures of dinuclear complexes containing similar bridging ligands such as bis-imidazolate[14] and bipyrimidine have been published.[15] However, to the best of our knowledge, neither planar Ni complexes nor Ni-σ-organo compounds with these ligands were characterized by X-ray crystallography. In the (μ_2-2,2′-imidazolato)bis(1,4,8,11-tetra-azacyclotetradecane)-dinickel(II) cation containing nickel(II) in an octahedral environment the Ni−N(imidazolate) bonds are much longer (2.192 and 2.150 Å) than those in **1** (1.905(2) and 1.916(2) Å).[16] This is also the case in octahedral dinuclear bispyrimidine nickel complexes.[17]

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The phenyl complex **2** was prepared in a manner similar to that for **1** from 2 equiv of LiPh, dissolved in a cyclohexane/diethyl ether mixture, with 1 equiv of [{(acac)Ni}$_2$(A)] at −78 °C in THF. After workup **2** could be obtained as orange crystals in excellent yields (90%). It is even more thermally stable in the solid state than the corresponding methyl complex **1**. A DTA measurement of single crystals of **2** showed that the decomposition started at 336 °C.

The mass spectrum (molecular ion $m/z = 772$) and NMR spectra also suggest that a dimeric compound similar to **1** is formed. As expected for a symmetric coordination of the dianionic bridging ligand at the Ni(II) ions, two ^{1}H NMR resonances of the two mesityl methyl groups at 2.05 and 2.44 ppm and one singlet for the CH$_2$ protons at 3.62 ppm with the expected intensity ratio of approximately 3:6:2 were observed. The aromatic protons resonate between 6.41 and 7.45 ppm.

In the high-field region of the ^{13}C NMR spectrum (in THF-d_8 at room temperature) two signals for the methyl carbons of the mesityl group at $\delta = 19.4$ and 20.8 ppm as well as one resonance for the CH$_2$ group at $\delta = 53.5$ ppm were observed. These signals appear in the same region as the corresponding signals in compound **1**. Furthermore, 13 ^{13}C signals for the aromatic substituents and one resonance of the equivalent carbons of the oxalamidinato framework were observed for compound **2**. The total number of 17 signals in the ^{13}C spectrum of **2** reflects not only the C_2-symmetry observed in the ligand itself but also the equivalence of the two phenyl groups bonded to each nickel(II) center. This is in agreement with a symmetric structure of the complex in solution depicted in Scheme 1.

Reaction of complex **1** in phenylacetylene at room temperature resulted in the formation of the corresponding phenylacetylide complex **3a** together with the development of methane, which was indicatad by head-space gas chromatography.

The orange acetylide complex **3b** was prepared from sodium acetylide (suspended in xylene and oil) and [{(acac)Ni}$_2$(A)] (ratio 2:1) at −78 °C in THF. After workup, **3b** was obtained in 56% yield. Upon recrystallization from toluene single crystals of **3b**, suitable for an X-ray diffraction analysis, were grown (Figure 2).

NMR studies in THF-d_8 confirm that both complexes **3a** and **3b** have very similar structures in solution. In the ^{1}H NMR spectrum of **3a** the proton signals for the *mesityl methyl* groups were observed at $\delta = 2.24$ and 2.64 ppm. The *methylene* protons resonated at 3.69 ppm. These signals showed the expected intensities of approximately 3:6:2. The corresponding signals in **3b** appeared at 2.20, 2.57, and 3.58 ppm. Additionally, a singlet at $\delta = 0.93$ ppm was found in **3b** that was assigned to the two protons of the two acetylide substituents.

In the high-field region of the ^{13}C NMR spectrum of **3a** three sharp resonances were found at $\delta = 19.5$, 21.0 (*methyl mesityl*), and 54.5 ppm (*methylene*). The corresponding signals in **3b** appeared at 19.5, 21.1, and 54.3 ppm. Furthermore, two signals for the alkynyl carbons (at 103.3 and 106.2 ppm) were observed in the ^{13}C NMR spectum of **3a** (in **3b**, 90.7 and 95.2 ppm).

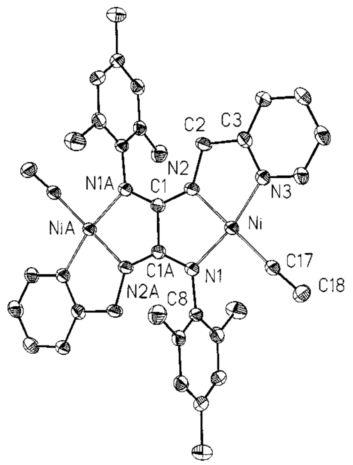


Figure 2. Molecular structure of complex **3b**. Selected bond distances (Å) and bond angles (deg): Ni−N1 1.890(3), Ni−N2 1.872(3), Ni−N3 1.904(4), Ni−C17 1.856(4), C1−N1A 1.326(5), C1−N2 1.319(5), C1−C1A 1.492(8), C2−N2 1.456(5), C2−C3 1.484(6), N1−C8 1.435(5), C17−C18 1.216(6), C18−H18 1.00(6), C17−Ni−N1 95.6(2), C17−Ni−N2 177.5(2), C17−Ni−N3 95.7(2), N1−Ni−N2 84.5(1), N1−Ni−N3 168.6(1), N2−Ni−N3 84.3(1), N1A−C1−N2 133.8(4), C1−N2−C2 127.5(3), C1A−N1−C8 120.3(3), C17−C18−H18 164(4). Symmetry transformations used to generated equivalent atoms: A $-x+1$, $-y+2$, $-z+1$.

The solid-state structure of **3b** is shown in Figure 2. Relevant bond lengths and angles are listed in the figure caption. The coordination environment of the Ni atoms is nearly planar (deviation 0.003 Å), with the alkynyl ligands lying trans to each other. The Ni−C(sp) bond lengths in **3b** are significantly shorter than the Ni−C(sp^3) bond distance in the methyl complex **1** (**1**, 1.950(2); **3b**, 1.890(3) Å).

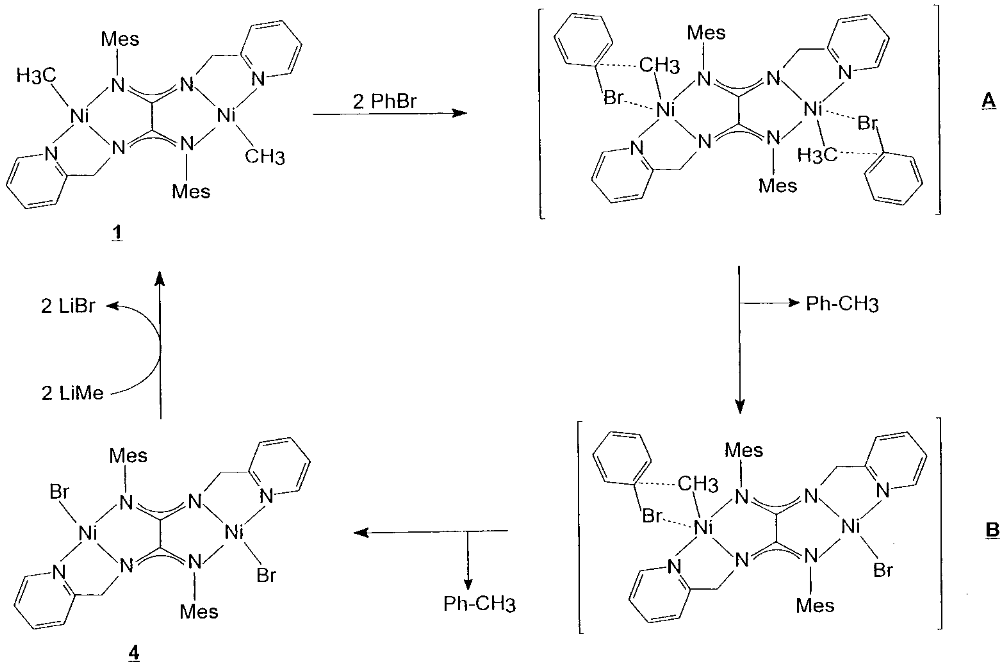
Other relevant bond lengths and angles fall in the range of typical values. Most of them are very close to those of complex **1**; for example the CN bond distances of the oxalamidinato framework are almost equivalent within the experimental error (average distance 1.323 Å) and the C−C bond length corresponds to a single bond (1.492(8) Å).

Single crystals of **3a** were also grown from toluene at −18 °C. Since the compound contains disordered toluene (leading to R1$_{\text{obs}} = 0.110$), only the structure motif will be discussed here, showing without doubt that the solid-state structure of **3a** is similar to that of **3b**. The acetylide ligands in **3a** lie trans to each other, the *oxam* moiety is planar, and the two nickel atoms show planar geometry. This is in agreement with the results of the NMR spectroscopic measurements in solution.

Since dinuclear σ-organo-nickel complexes containing oxam bridges are possibly involved in catalytic cross coupling reactions,[1] we investigated the stoichiometric reaction of **1** with bromobenzene-d_5 to get a deeper insight into the reactivity of both metal centers. Cleavage of the Ni−Me bonds at room temperature in brombenzene-d_5 proceeded slowly to yield toluene-d_5 in reasonable yields (46%). Removing the solvent to dryness followed by extraction of the resulting solid with diethyl ether gave a brown powder (yield ca. 90 wt %). According to its ^{1}H NMR spectrum this product contained the dimeric bromo complex [(BrNi)$_2$A] (**4**) in 80% purity together with an unidentified byproduct.

^{1}H NMR monitoring of this reaction in bromobenzene-d_5 as solvent shows that, in the first step of the reaction,

Scheme 2. Reaction of 1 with Bromobenzene-d_5 to Form 4 and Formation of 1 from 4 and LiMe



a new signal in the methyl region appeared at $\delta = -0.99$ ppm, in addition to the singlet for the methyl groups in the starting compound **1** appearing in bromobenzene-d_5 at lower field (at $\delta = -0.94$ ppm) than in THF-d_8 ($\delta = -1.35$ ppm). The new signal in the methyl region suggests the formation of a mixed bromo-methyl complex as an intermediate (Scheme 2). After 9 days both signals disappeared, and the resonances of the bromo complex **4** appeared in the ^{1}H NMR spectrum together with an unidentified minor product. Furthermore, compound **4** undergoes a clean reaction with 2 equiv of LiMe in THF at −78 °C, resulting in the formation of the dimethyl complex **1** (Scheme 2). From these stoichiometric reactions, we conclude that cross coupling reactions between LiMe and bromobenzene can proceed at *both* Ni(II) centers.

Formation of $[Li(THF)]_2Li_2Ni_2Me_8$ (5) and $[Li(THF)]_4Ni_2Me_8$ (6). To find out if complexes of the type [(R−Ni)$_2$(*oxam*)] are able to form organometallic anionic complexes that, in principle, could play a role as intermediates in catalytic cross coupling reactions,[2a,f] we reacted methyllithium with **1** (ratio 2:1) in THF at −78 °C.

The ^{1}H NMR spectrum of the reaction mixture showed the unreacted complex **1** as main product (ca. 90%). Surprisingly, after keeping the solution at −18 °C for one week a small amount of an *oxam*-free methyl complex of the composition $[Li(THF)]_2Li_2Ni_2Me_8$ (**5**) crystallized from the reaction mixture. Using a 6:1 ratio between LiMe and **1** we could isolate **5** in good yields (69%) crystallizing from toluene as a brown microcrystalline compound. Yellow crystals of the THF-enriched complex $[Li(THF)]_4Ni_2Me_8$ (**6**) were isolated upon recrystallization of **5** from THF instead of toluene. The complexes **5** and **6** are extremely air-sensitive and even pyrophoric. **5** is even more reactive toward traces of air and moisture than **6**. However, in the absence of air, the two complexes are stable at 20 °C in the solid state. Compound **5** could also be obtained by the reaction of 1 equiv of [{(acac)Ni}$_2$(A)] with 8 equiv of LiMe in THF at −78 °C.

NMR measurements of **5** at room temperature in benzene-d_6 clearly show that only one highly symmetrical isomer is present in solution. In addition to the resonances of the coordinated THF (at $\delta = 1.17$ and 3.53 ppm), only one signal for the methyl groups bound to the metal center was observed, which gives rise to a singlet at $\delta = -0.80$ ppm in the ^{1}H NMR spectrum and to a signal at $\delta = -5.3$ ppm in the ^{13}C NMR spectrum. Since also only one signal at $\delta = 2.17$ ppm was observed in the ^{7}Li NMR spectrum of **5** in benzene-d_6, we can assume that the THF ligands coordinated to two of the four Li atoms undergo a rapid exchange at room temperature.

Compared to **5**, compound **6** gives a slightly downfield-shifted singlet for the methyl groups at $\delta = -0.61$ in the ^{1}H NMR spectrum. In contrast, the ^{13}C NMR spectrum shows a high-field-shifted singlet at $\delta = -6.2$ ppm. The integration of the multiplet resonances of coordinated THF ($\delta = 1.25$ and 3.62 ppm) shows the presence of two additional coordinated molecules of THF by comparison with **5**. As expected for a symmetrical structure, only one signal at $\delta = 1.98$ ppm was found in the ^{7}Li NMR spectrum.

Upon recrystallization of **5** from toluene, single crystals were obtained suitable for X-ray crystallographic determination. The crystal structure confirmed the highly symmetrical structure in solution indicated by NMR spectroscopy. Figure 3 shows the dimeric molecular structure with selected bond lengths and angles in the figure caption.

Each nickel ion in **5** is surrounded by four methyl groups in a square-planar geometry. The eight methyl groups of the dimer form a cube. The Ni···Ni separation is relatively long (3.167(1) Å), reflecting the absence of a metal−metal bond between those two metal centers. The two monomeric $NiMe_4$ units are held together by four bridging Li ions. Each Li atom interacts with the

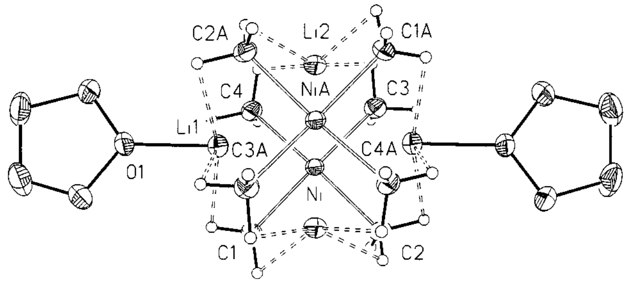


Figure 3. Molecular structure of complex **5**. Selected bond distances (Å) and bond angles (deg): Ni−C1 2.009(2), Ni−C2 2.017(2), Ni−C3 2.016(2), Ni−C4 2.008(2), Li1−C1 2.368(4), Li1−C2A 2.375(4), Li1−C3A 2.388(4), Li1−C4 2.367(4), Li1−O1 1.995(3), Li2−C1A 2.292(4), Li2−C2A 2.359(4), Li2−C3 2.266(4), Li2−C4 2.297(4), C1−Ni−C2 88.92(8), C1−Ni−C3 168.88(9), C1−Ni−C4 90.00(9), C2−Ni−C3 90.76(8), C2−Ni−C4 168.28(9), C3−Ni−C4 88.05(8). Average bond distances (Å) and average bond angles (deg): Li1−H 2.08(3), Li1−C 2.374(4), Li2−H 2.05(3), Li2−C 2.303(4), Ni−C 2.012(2), Li1−H−C 96(2), Li2−H 92(2). Symmetry transformations used to generated equivalent atoms: A $-x+1$, $-y+2$, $-z+1$.

carbon atoms of four methyl groups, forming two Ni1−CH_3−Li−CH_3−Ni2 bonds; however two distinct types of lithium environments are present: Two of the lithium atoms are additionally bound to a THF ligand, while the other two lithium atoms do not coordinate THF.

The C−Li(THF) distances (average 2.374(5) Å) are significantly longer than those of the C−Li bonds (average 2.304 Å). In addition, agostic interactions between one hydrogen atom of a methyl group and Li (Li1−H = 2.08(3) and Li2−H = 2.054(3) Å) are certainly present. The Li−H−C angles confirm this agostic interactions (96(2)° and 95(2)°, respectively).

The solid-state structure of $[Li_4(THF)_4Ni_2Me_8]$ (**6**), determined by an X-ray analysis of single crystals, is very similar to that of **5**. The only remarkable difference is that each lithium in **6** coordinates one THF ligand, leading to four pentavalent lithium atoms. Consequently, all C− Li distances are almost equivalent within experimental error, in contrast to those found in **5**. Figure 4 shows the molecular structure of **6** and shows a list of selected bond distances and angles.

A complex $Li_2[NiMe_4](THF)_2$ of the same analytical composition as **6** which was assumed to be monomeric was obtained by Taube in 1975.[18] Since, however, neither spectroscopic nor X-ray data were determined for this compound, its structure is still unkown. We assume, however, that this complex is probably identical to **6**.

The solid-state structure of **6** is very similar to the structures reported for the corresponding Cr(II), Mo(II), and Re(III) complexes.[20−24] $[Li(THF)]_4Cr_2Me_8$ was first synthesized by Kurras and Otto in the 1960s.[19] An early structural characterization of this compound by an X-ray crystallographic study suggested the existence of a Cr−Cr quadrupole bond.[20] However, a reinvestigation of its structure by Gambarotta has shown that the very short Cr···Cr contact is just the result of favorable geometrical features.[21−22]

The X-ray analyses of both **5** and **6** indicate that the driving force for the stabilization of the dimeric compound is certainly the formation of agostic Li−H bonds between the four Li atoms and the methyl groups. This is in agreement with Gambarotta's conclusion for the corresponding Cr complex. On the other hand, very large Ni···Ni separations were found in both **5** and **6** (3.167(1) and 3.142(1) Å, respectively), in contrast to the very short Cr···Cr distance (1.968(2) Å) in the corresponding Cr complex. This demonstrates that a short M···M contact is no prerequisit for the stabilization of dimeric complexes of the composition $[M_2(Me)_8]^{n-}$. In the analogous Pt complex also a very large M···M separation was found (3.384(1) Å).[25]

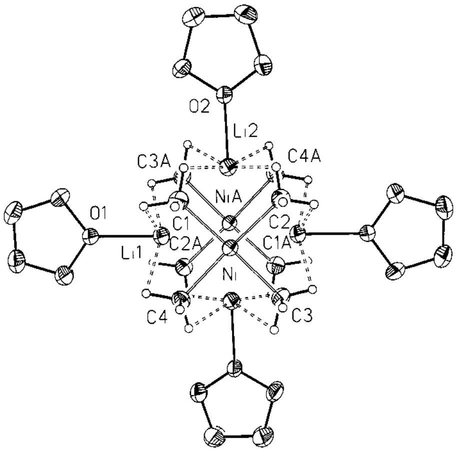


Figure 4. Molecular structure of complex **6**. Selected bond distances (Å) and bond angles (deg): Ni−C1 2.005(5), Ni−C2 2.005(5), Ni−C3 1.994(5), Ni−C4 2.011(5), Li1−C1 2.339(9), Li1−C2A 2.353(9), Li1−C3A 2.364(9), Li1−C4 2.367(9), Li1−O1 2.050(8), Li2−C1 2.339(9), Li2−C2 2.363(9), Li2−C3A 2.358(9), Li2−C4A 2.372(9), Li2−O2 2.075(8), C1−Ni−C2 89.5(2), C1−Ni−C3 166.6(2), C1−Ni−C4 89.6(2), C2−Ni−C3 88.9(2), C2−Ni−C4 167.4(2), C3−Ni−C4 89.0(2). Average bond distances (Å) and average bond angles (deg): Li1−H 2.04(8), Li1−C 2.335(9), Li2−H 2.04(8), Li2−C 2.358(9), Ni−C 2.003(5), Li1−H−C 95(2), Li2−H−C 97(2). Symmetry transformations used to generated equivalent atoms: A $-x$, $-y+1$, $-z+1$.

In summary, we can conclude that the structural principle $[Li_4(solv)_nM_2Me_8]$ is a general stabilizing principle which can be realized not only in organometallic complexes of d-electon-deficient metals (Cr, Mo, or in the case of Re(III) as $[Li_2(solv)_2Re_2Me_8]$) but also in complexes with d-electron-rich metals (such as Ni or Pt).

Conclusions

The planar dinuclear complexes **1**−**3** are the first representatives of σ-organo-nickel compounds bridged by an *oxam*-type ligand. Compound **1** reacts at room temperature with phenylacetylene to form the corresponding phenylacetylide complex **3a.** ^{1}H NMR monitoring of the reaction between **1** and bromobenzene-d_5 results in the formation of the corresponding bromide complex **4** and toluene-d_5 as final products, which indicates that both metal centers react independingly and one after the other. Furthermore, complete displacement of the oxalamidinato ligand in **1** by employing an excess of LiMe leads to the formation of the cluster compounds $[Li(THF)]_2Li_2Ni_2Me_8$ (**5**) and $[Li(THF)]_4Ni_2Me_8$ (**6**), respectively. The solid-state structures of compounds **5** and **6** clearly demonstrate that the driving force for the dimerization of two $Ni(Me)_4$ units lies in the formation of bridges between methyl groups coordinated at different metal centers and Li(THF) fragments. The Ni1−CH_3−Li−CH_3−Ni2 bonds are additionally stabilized by Li−H agostic interactions. These interactions can be considered as a general stabilizing principle for organometallics of the type [$Li_4(solv)_nM_2Me_8$] in which the M···M separations can be very different.

In general, organometallic complexes, described in this paper such as compounds **1**−**3**, may be of considerable interest as starting material for the controlled synthesis of either new organometallic compounds or oligonuclear metal compounds containing adjustable numbers of metal centers. In addition, these complexes can be viewed as models for intermediates in catalytic cross coupling reactions in which the two redox-active metal centers of dinuclear *oxam* complexes are involved.

Experimental Section

General Procedures. All manipulations were carried out by using Schlenk techniques under an atmosphere of argon. Prior to use, tetrahydrofurane, diethyl ether, and toluene were dried over potassium hydroxide and distilled over Na/benzophenone. 2-Aminopicoline, 1.6 M solutions of lithium methyl in diethyl ether, and phenyllithium in cyclohexane/diethyl ether (70:30) (Fluka) were used as received, and phenylacetylene and bromobenzene were distilled prior to use using standard methods. Sodium acetylide was used as a 18 wt % slurry in xylene and oil (95% purity, ABCR).

^1H and ^{13}C spectra were recorded on a Bruker AC 200 F spectrometer (^7Li NMR: Bruker DRX 400). Mass spectra were recorded on a Finnigan MAT SSQ 710. Values for *m/z* are for the most intense peak of the isotope envelope. The measured isotopic pattern for the nickel-containing species is in good agreement with the calculated isotopic pattern using the program ICIS (version 8.2.1, Finnigan). Elemental analyses were performed with Leco CHNS-932. Since both **5** and **6** are extremely reactive and pyrophoric, C, H analyses could not be carried out. Ni analyses were obtained by titration of a solution in dilute hydrochloric acid with 0.01 M EDTA using murexid as indicator. Li analyses were performed by atomic absorption spectroscopy. For **5**, only the Li:Ni ratio was determined since the substance started to decompose after 2 min when it was dried by oil pump vacuum at room temperature.

The ligand *N,N′*-bis(2-pyridylmethyl)-1,2-bis(2,4,6-trimethylphenylimino)ethane-1,2-diamine (H_2A) was prepared according to described methods;[26,27] the complex [{(acac)Ni}$_2$(A)] was obtained following the procedure described in refs 1 and 28.

Complex 1. A solution of [{(acac)Ni}$_2$(A)] (4.049 g, 4.95 mmol) in THF (170 mL) was stirred at −78 °C. LiMe (6.4 mL, 10.24 mmol), dissolved in diethyl ether, was added dropwise. After stirring the solution at room temperature overnight, the solvent was removed in vacuo. The residue was extraxted with toluene (170 mL). The extract was filtered, and the residue was washed with toluene (50 mL). The clear orange solution was concentrated under vacuum (ca. 10 mL), and diethyl ether (80 mL) was added. An orange precipitate was formed. After keeping it at −18 °C overnight, the precipitate was filtered off, washed with diethyl ether (25 mL), and dried under vacuum (5 h) at room temperature. An orange solid was obtained. Yield: 1.866 g (56%) of **1**. Recrystallization from toluene and standing overnight at −18 °C yielded orange crystals of **1**, including 0.3 mol toluene per mol complex (determined by NMR spectroscopy). Anal. Calcd for $C_{34}H_{40}N_6Ni_2\cdot 0.3C_7H_8$: C, 63.97; H, 6.31; N, 12.40; Ni, 17.32. Found: C, 63.62; H, 6.01; N, 12.06; Ni, 17.16. ^1H NMR (200 MHz, THF-d_8): δ −1.35 [s, 6 H, CH_3, *Ni*−*CH*$_3$], 2.22 [s, 6 H, CH_3, *mes para*], 2.43 [s, 12 H, CH_3, *mes ortho*], 3.62 [s, 4 H, CH_2], 6.65 [d ($^3J_{HH}$ = 7.9 Hz), 2 H, CH, *3-pyridyl*], 6.71 [s, 4 H, CH, *mes meta*], 6.93 [t ($^3J_{HH}$ = 6.4 Hz), 2 H, CH, *5-pyridyl*], 7.52 [t ($^3J_{HH}$ = 7.7 Hz), 2 H, CH, *4-pyridyl*], 7.85 [d ($^3J_{HH}$ = 5.8 Hz), 2 H, CH, *6-pyridyl*]. Signals for the toluene included in the complex: 2.32 [s, ca. 1 H, CH_3, according to 0.3 *toluene* per dimeric unit], 7.07−7.22 [m, CH, *toluene*]. ^{13}C NMR (50 MHz, THF-d_8): δ −7.5 [CH_3, *Ni*−*CH*$_3$], 19.1 [CH_3, *mes ortho*], 21.0 [CH_3, *mes para*], 53.3 [CH_2], 121.2 [CH, *3-pyridyl*], 122.6 [CH, *5-pyridyl*], 127.6 [CH, *mes meta*], 133.5, 135.7 [C], 136.3 [CH, *4-pyridyl*], 144.4 [C], 149.0 [CH, *6-pyridyl*], 163.1, 168.9[C]. MS (DEI): *m/z* (rel intensity, %) 648 [M$^+$, 25], 633 [(M − CH_3)$^+$, 77], 618 [(M − 2CH_3)$^+$, 83].

Single crystals of **1** containing two molecules of noncoordinated toluene per dimeric unit suitable for an X-ray analysis were grown from toluene at −18 °C.

Complex 2. The compound was prepared as a yellow solid analogously to **1** from [{(acac)Ni}$_2$(A)] (0.578 g, 0.71 mmol) using LiPh in a mixture of 70:30 cyclohexane/diethyl ether (0.9 mL, 1.44 mmol). Yield: 0.495 g (90%). The dried complex contained 0.3 mol of toluene per dimeric unit, determined by ^1H NMR spectroscopy. Anal. Calcd for $C_{44}H_{44}N_6Ni_2\cdot 0.3\ C_7H_8$: C, 69.05; H, 5.83; N, 10.48, Ni, 14.64. Found: C, 69.37; H, 5.79; N, 10.24; Ni, 14.74. ^1H NMR (200 MHz, THF-d_8): δ 2.05 [s, 6 H, CH_3, *mes para*], 2.44 [s, 12 H, CH_3, *mes ortho*], 3.62 [s, 4 H, CH_2], 6.41 [s, 4 H, CH, *mes meta*], 6.42−6.46 [m, 6 H, CH, *phenyl meta*, *para*], 6.64−6.71 [m, 4 H, *3,5-pyridyl*], 7.05 [d ($^3J_{HH}$ = 5.7 Hz), 2 H, CH, *6-pyridyl*], 7.27 [d ($^3J_{HH}$ = 6.4 Hz), 2 H, CH, *phenyl ortho*], 7.45 [t ($^3J_{HH}$ = 7.6 Hz), 2 H, CH, *4-pyridyl*]. Signals for the toluene included in the complex: 2.32 [s, ca. 1 H, CH_3, according to 0.3 *toluene* per dimeric unit], 7.07−7.22 [m, CH, *toluene*]. ^{13}C NMR (50 MHz, THF-d_8): δ 19.4 [CH_3, *mes ortho*], 20.8 [CH_3, *mes para*], 53.5 [CH_2], 121.1 [CH, *pyridyl*], 121.8 [CH, *phenyl*], 122.6 [CH, *pyridyl*], 124.9 [CH, *phenyl*], 127.3 [CH, *mes meta*], 133.4 [C], 134.9 [C], 136.9 [CH, *4-pyridyl*], 137.1 [CH, *phenyl ortho*], 144.2 [C], 152.0 [CH, *6-pyridyl*], 162.0, 163.8, 168.4 [C]. MS (DEI): *m/z* (rel intensity, %) 772 [M$^+$, 4], 695 [(M − Ph)$^+$, 1], 618 [(M − 2Ph)$^+$, 1].

Complex 3a. Complex **1** (0.381 g, 0.56 mmol) was dissolved in phenylacetylene (30 mL) and stirred at room temperature for 1 week. After removing the solvent in vacuo, the solid was washed with *n*-heptane and dried in vacuo. Complex **3a** was obtained as an orange microcrystalline solid. Yield: 0.287 g (62%). Anal. Calcd for $C_{48}H_{44}N_6Ni_2$: C, 70.11; H, 5.39; N, 10.22; Ni, 14.28. Found: C, 70.25; H, 5.42; N, 9.98; Ni, 14.19. ^1H NMR (200 MHz, THF-d_8): δ 2.24 [s, 6 H, CH_3, *mes para*], 2.64 [s, 12 H, CH_3, *mes ortho*], 3.69 [s, 4 H, CH_2], 6.63−6.66 [m, 2 H, CH, *3-pyridyl*], 6.74 [s, 4 H, CH, *mes meta*], 6.77−7.09 [m, 12 H, CH, *phenyl*, *5-pyridyl*], 7.63 [t ($^3J_{HH}$ = 7.7 Hz), 2 H, CH, *4-pyridyl*], 8.87 [d ($^3J_{HH}$ = 5.9 Hz), 2 H, CH, *6-pyridyl*]. ^{13}C NMR (50 MHz, THF-d_8): δ 19.5 [CH_3, *mes ortho*], 21.0 [CH_3, *mes para*], 54.5 [CH_2], 103.3 [C, *alkyne*],106.2 [C, *alkyne*], 121.1 [CH, *3-pyridyl*], 123.0 [CH, *5-pyridyl*], 124.7, 127.6, 127.8 [CH, *mes meta*, *phenyl*], 129.7 [C], 132.0 [CH *mes meta*, *phenyl*], 134.3, 135.5 [C], 138.3 [CH, *4-pyridyl*], 144.6 [C], 153.8 [CH, *6-pyridyl*], 164.5, 167.4 [C]. MS (DEI): *m/z* (rel intensity, %) 820 [M$^+$, 2], 718 [(M − *phenylacetylide*)$^+$, 100], 618 [(M − 2 *phenylacetylide*)$^+$, 4].

Single crystals of **3a** containing four noncoordinated molecules of toluene per dimeric unit suitable for an X-ray analysis were grown from toluene at −18 °C.

Complex 3b. A solution of [{(acac)Ni}$_2$(A)] (0.987 g, 1.21 mmol) in THF (150 mL) was stirred at −78 °C. Sodium acetylide (0.119 g, 2.48 mmol), suspended in oil and xylene, was added dropwise. After stirring the suspension at room temperature overnight, the solvent was removed in vacuo. Then toluene (150 mL) was added. The precipitate was filtered and washed twice with toluene (50 mL). After concentrating the solution to 2 mL, diethyl ether (40 mL) was added. **3b** crystallized as an orange compound. It was filtered off, washed twice with diethyl ether (20 mL), and dried in vacuo. Yield: 0.454 g (56%). Anal. Calcd for $C_{36}H_{36}N_6Ni_2$: C, 64.53; H, 5.42; N, 12.54; Ni, 17.52. Found: C, 64.38; H, 5.59; N, 11.98; Ni, 17.64. ^{1}H NMR (200 MHz, THF-d_8): δ 0.93 [s, 2 H, *alkyne*], 2.20 [s, 6 H, CH$_3$, *mes para*], 2.57 [s, 12 H, CH$_3$, *mes ortho*], 3.58 [s, 4 H, CH$_2$], 6.65 [s, 4 H, CH, *mes meta*], 6.72 [d ($^3J_{HH}$ = 7.9 Hz), 2 H, CH, *3-pyridyl*], 6.97 [t ($^3J_{HH}$ = 5.9 Hz), 2 H, CH, *5-pyridyl*], 7.58 [t ($^3J_{HH}$ = 7.5 Hz), 2 H, CH, *4-pyridyl*], 8.85 [d ($^3J_{HH}$ = 5.9 Hz), 2 H, CH, *6-pyridyl*]. ^{13}C NMR (50 MHz, THF-d_8): δ 19.5 [CH$_3$, *mes ortho*], 21.1 [CH$_3$, *mes para*], 54.3 [CH$_2$], 90.7 [C, *alkyne*], 95.2 [C, *alkyne*], 121.0 [CH, *3-pyridyl*], 122.8 [CH, *5-pyridyl*], 125.9 [CH, *mes meta*], 134.1, 135.4 [C], 138.1 [CH, *4-pyridyl*], 144.5 [C], 153.8 [CH, *6-pyridyl*], 164.4, 167.4 [C]. MS (neg. DCI/H$_2$O): *m/z* (rel intensity, %) 668 [M$^+$, 100], 643 [(M − *acetylide*)$^+$, 2].

Single crystals of **3b** containing two molecules of toluene per dimeric unit suitable for an X-ray analysis were grown from toluene at −18 °C.

Complex 4. This compound was obtained by reacting perdeuterated bromobenzene-d_5 with **1** in bromobenzene-d_5 in an NMR tube (9 days at room temperature) and characterized by comparison with an authentic sample (prepared from 1 equiv of Li$_2$A and 2 equiv of (Ph$_3$P)$_2$NiBr$_2$ in THF[28]) via ^{1}H NMR spectroscopy. ^{1}H NMR (200 MHz, bromobenzene-d_5): δ 2.10 [s, 6 H, CH$_3$, *mes para*], 2.80 [s, 12 H, CH$_3$, *mes ortho*], 3.39 [s, 4 H, CH$_2$], 5.74−5.79 [m, 2 H, CH, *3-pyridyl*], 6.16−6.23 [m, 2 H, CH, *5-pyridyl*], 6.65 [m, 6 H, CH, *mes meta*, *4-pyridyl*], 8.66−8.69 [m, 2 H, CH, *6-pyridyl*]. ^{1}H NMR (200 MHz, benzene-d_6): δ 2.13 [s, 6 H, CH$_3$, *mes para*], 2.92 [s, 12 H, CH$_3$, *mes ortho*], 3.36 [s, 4 H, CH$_2$], 5.20−5.25 [m, 2 H, CH, *3-pyridyl*], 5.78−5.86 [m, 2 H, CH, *5-pyridyl*], 6.14 [t ($^3J_{HH}$ = 7.9 Hz), 2 H, CH, *4-pyridyl*], 6.71 [s, 4 H, CH, *mes meta*], 8.92 [d ($^3J_{HH}$ = 5.9 Hz), 2 H, CH, *6-pyridyl*]. MS (DEI): *m/z* (rel intensity, %) 776 [M$^+$, 0.07], 697 [(M − *Br*)$^+$, 0.13], 618 [(M − *2Br*)$^+$, 0.06], 560 [(M − *Ni* − *2Br*)$^+$, 3.68].

Upon evaporation of the solvent the reaction mixture was extracted with diethyl ether. The remaining residue (yield ca. 90 wt %) contained **4** in 80% purity, together with an unidentified byproduct.

Complex 5. To a stirred solution of **1** (0.333 g, 0.49 mmol) in THF (60 mL) was added dropwise LiMe, dissolved in diethyl ether (2.0 mL, 3.20 mmol), at −78 °C. The reaction mixture was stirred for 24 h and allowed to warm to room temperature. Then the reaction mixture was filtered. The residue was washed with toluene (2 × 15 mL). Concentrating the solution to 5 mL and standing for 1 week gave brown crystals. They were washed with toluene (2 mL) and pentane (5 mL) and dried in vacuo for 2 min. Yield: 0.139 g (69%). Anal. Calcd for C$_{16}$H$_{40}$Li$_4$Ni$_2$O$_2$: Molar ratio Li:Ni = 4.0:2.0. Found: Li:Ni = 4.1:2.0. ^{1}H NMR (200 MHz, benzene-d_6): δ −0.80 [s, 24 H, CH$_3$], 1.17 [m, 8 H, CH$_2$], 3.53 [m, 8 H, CH$_2$]. ^{13}C NMR (50 MHz, benzene-d_6): δ −5.3 [CH$_3$], 25.2 [CH$_2$], 68.4 [CH$_2$]. ^{7}Li NMR (156 MHz, benzene-d_6): δ 2.17.

Single crystals of **5**, suitable for an X-ray analysis, were isolated upon recrystallization from toluene at −18 °C. The reaction to form **5** can also be carried out using 1 equiv of [{(acac)Ni}$_2$(A)] as starting material, which was reacted with 8 equiv of LiMe following the above procedure.

Complex 6. Complex **5** was recrystallized from THF. After keeping the solution overnight at −20 °C yellow crystals of **6** were isolated. Yield: 60%. Anal. Calcd for C$_{24}$H$_{56}$Li$_4$Ni$_2$O$_4$: Li, 5.01; Ni, 21.20. Found: Li, 5.43; Ni, 21.63. ^{1}H NMR (200 MHz, benzene-d_6): δ −0.61 [s, 24 H, CH$_3$], 1.25 [m,16 H, CH$_2$], 3.62 [m, 16 H, CH$_2$]. ^{13}C NMR (50 MHz, benzene-d_6): δ −6.2 [CH$_3$], 25.4 [CH$_2$], 68.2 [CH$_2$]. ^{7}Li NMR (156 MHz, benzene-d_6): δ 1.98.

X-ray Crystallography. The intensity data for the compound **3b** were collected on a Nonius CAD4 diffractometer and for the other compounds on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz and polarization effects, but not for absorption.[29−31] The structures were solved by direct methods (SHELXS[32]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97[33]). For the acetylide group of **3b**, the whole compound **5** and for the methyl groups of **6** the hydrogen atoms were located by difference Fourier synthesis and refined isotropically. The hydrogen atoms of the other structures and for the THF molecules of **5** were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[29] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations. The toluene molecules of **3a** and **3b** are disordered. The disorder could be solved. Due to the high *R* value in the case of **3a** (R1$_{obs}$ = 0.110), the crystallographic data of **3a** will not be published here. Additional information is given in ref 35.

Crystal Data for 1:[34] C$_{34}$H$_{40}$N$_6$Ni$_2$·2C$_7$H$_8$, fw = 834.41 g mol^{-1}, brown prism, size 0.19 × 0.12 × 0.10 mm^3, triclinic, space group $P\bar{1}$, a = 8.3999(3) Å, b = 11.7368(5) Å, c = 13.0598(6) Å, α = 103.617(2)°, β = 107.802(2)°, γ = 108.26(2)°, V = 1083.18(8) Å^3, T = −90 °C, Z = 1, ρ_{calcd} = 1.279 g cm^{-3}, μ(Mo Kα) = 9.09 cm^{-1}, F(000) = 442, 7206 reflections in h(−10/10), k(−15/13), l(−16/16), measured in the range 3.35° ≤ θ ≤ 27.47°, completeness θ_{max} = 96.4%, 4774 independent reflections, R_{int} = 0.020, 4274 reflections with $F_o > 4\sigma(F_o)$, 223 parameters, 0 restraints, R1$_{obs}$ = 0.050, wR$^2_{obs}$ = 0.141, R1$_{all}$ = 0.057, wR$^2_{all}$ = 0.147, GOOF = 1.012, largest difference peak and hole 0.836/−0.534 e Å^{-3}.

Crystal Data for 3b:[34] C$_{36}$H$_{36}$N$_6$Ni$_2$·4C$_7$H$_8$, fw = 1038.66 g mol^{-1}, brown prism, size 0.18 × 0.16 × 0.12 mm^3, monoclinic, space group $P2_1/c$, a = 11.019(2) Å, b = 12.329(2) Å, c = 20.850(3) Å, β = 103.69(2)°, V = 2752.1(8) Å^3, T = −90 °C, Z = 2, ρ_{calcd} = 1.253 gcm^{-3}, μ(Mo Kα) = 7.29 cm^{-1}, F(000) = 1100, 5844 reflections in h(−13/13), k(−15/0), l(−26/0), measured in the range 2.42° ≤ θ ≤ 27.42°, completeness θ_{max} = 90.9%, 5694 independent reflections, R_{int} = 0.019, 3876 reflections with $F_o > 4\sigma(F_o)$, 287 parameters, 0 restraints, R1$_{obs}$ = 0.062, wR$^2_{obs}$ = 0.1763, R1$_{all}$ = 0.114, wR$^2_{all}$ = 0.203, GOOF = 1.039, largest difference peak and hole 1.605/−0.777 e Å^{-3}.

Crystal Data for 5:[34] C$_{16}$H$_{40}$Li$_4$Ni$_2$O$_2$, fw = 409.66 g mol^{-1}, brown prism, size 0.18 × 0.16 × 0.12 mm^3, triclinic, space group $P\bar{1}$, a = 6.9022(3) Å, b = 8.4718(5) Å, c = 10.1497(6) Å, α = 110.586(3)°, β = 97.200(3)°, γ = 97.684(3)°, V = 541.02(5) Å^3, T = −90 °C, Z = 1, ρ_{calcd} = 1.257 g cm^{-3}, μ(Mo Kα) = 17.42 cm^{-1}, F(000) = 220, 3645 reflections in h(−8/8), k(−9/10), l(−12/13), measured in the range 3.03° ≤ θ ≤ 27.47°, completeness θ_{max} = 97.7%, 2404 independent reflections, R_{int} = 0.022, 2211 reflections with $F_o > 4\sigma(F_o)$, 189 parameters, 0 restraints, R1$_{obs}$ = 0.027, wR$^2_{obs}$ = 0.082, R1$_{all}$ = 0.031, wR$^2_{all}$ = 0.086, GOOF = 1.015, largest difference peak and hole 0.375/−0.405 e Å^{-3}.

Crystal Data for 6:[34] C$_{24}$H$_{56}$Li$_4$Ni$_2$O$_4$, fw = 553.87 g mol^{-1}, yellow prism, size 0.20 × 0.18 × 0.12 mm^3, triclinic, space group $P\bar{1}$, a = 8.5892(8) Å, b = 8.9512(8) Å, c = 11.0999(9) Å, α = 111.184(6)°, β = 107.343(8)°, γ = 91.881(7)°, V = 750.0(1) Å^3, T = −90 °C, Z = 1, ρ_{calcd} = 1.226 g cm^{-3}, μ(Mo Kα) = 12.79 cm^{-1}, F(000) = 300, 4990 reflections in h(−10/11), k(−10/11), l(−14/14), measured in the range 3.77° ≤ θ ≤ 27.53°, completeness θ_{max} = 95.6%, 3311 independent reflections, R_{int} = 0.032, 2963 reflections with $F_o > 4\sigma(F_o)$, 202 parameters, 0

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(29) *MOLEN*, An Interactive Structure Solution Procedure; Enraf-Nonius: Delft, The Netherlands, 1990.

(30) *COLLECT*, Data Collection Software; Nonius B.V., Netherlands, 1998.

(31) Otwinowski, Z.; Minor W. Processing of X-ray Diffraction Data Collected in Oscillation Mode. In *Methods in Enzymology*, Vol. 276, Macromolecular Crystallography, Part A; Carter, C. W., Sweet, R. M., Eds.; Academic Press: San Diego, 1997; pp 307−326.

(32) Sheldrick, G. M. *Acta Crystallogr. Sect. A* **1990**, *46*, 467−473.

(33) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Germany, 1993.

(34) Further details of the crystal structure investigations are available on request from the director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1 EZ, on quoting the depository number CCSD-150911 (**1**), CCSD-164309 (**3b**), CCSD-150913 (**5**), and CCSD-150914 (**6**), the names of the authors, and the journal citation.

(35) CCSD-150912 (**3a**) (private communication).

restraints, $R1_{obs} = 0.086$, $wR^2_{obs} = 0.143$, $R1_{all} = 0.101$, $wR^2_{all} = 0.148$, GOOF = 1.188, largest difference peak and hole 0.706/−0.730 e Å^{-3}.

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Supporting Information Available: X-ray structural information for complexes **1**, **3**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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