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Nickel(0) Complexes of Acyclic Polyunsaturated Aza Ligands

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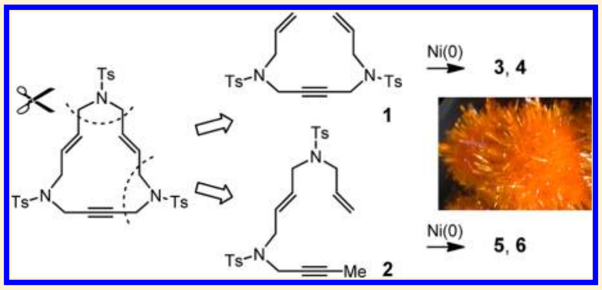
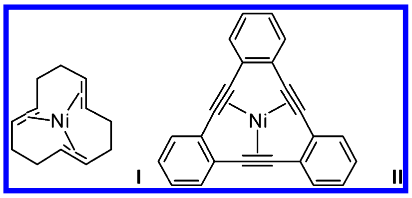
Supporting Information

ABSTRACT: The acyclic 4,9-bis(4-tolylsulfonyl)-4,9-diazadodeca-1,11-dien-6-yne (**1**) and 4,9-bis(4-tolylsulfonyl)-4,9-diazatrideca-1,(*E*)-6-dien-11-yne (**2**), which differ in the sequence of the two ene and one yne functions in the chain, have been reacted with 1 and 2 equiv of Ni(cod)$_2$. The reaction with 1 equiv of Ni(cod)$_2$ affords the mononuclear trigonal-planar nickel(0) complexes **3** and **5**. These react with a further 1 equiv of Ni(cod)$_2$ by addition of a Ni(cod) entity to give the dinuclear derivatives **4** and **6**. While **3** forms a mixture of isomers C_2-**3** and C_s-**3** in solution, C_2-**3** is exclusively present in the crystal, where it is packed in parallel columns. Complex **6** crystallizes as a spherulite. Complexes **3**−**6** have been characterized by NMR and single-crystal X-ray structure analysis, and a detailed conformational analysis is given.

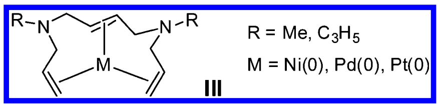


■ INTRODUCTION

It is well established that cyclic polyene or polyyne or mixed polyene/-yne ligands can stabilize transition metals in their zero oxidation state. Classical examples of such complexes are Wilke's trigonal-planar Ni(*t,t,t*-cdt) (**I**; *t,t,t*-cdt = *trans,trans,trans*-1,5,9-cyclododecatriene) and tetrahedral Ni(cod)$_2$ (cod = *cis,cis*-1,5-cyclooctadiene).[1] Ni(*c,c,c*-cdt) and other *c,c,c*-cdt−metal complexes (*c,c,c*-cdt = *cis,cis,cis*-1,5,9-cyclododecatriene) have also been studied in detail.[2] Given that symmetrically structured cod and *t,t,t*-cdt are conveniently obtained by the catalytic cyclodi-[3] and cyclotrimerization[4] of butadiene and that *c,c,c*-cdt can be prepared from *t,t,t*-cdt, the ene functions in these cycloalkenes are congenitally positioned in 1,5-sequences separated by ethano links, and the numbers of ring atoms are multiples of 4. Nickel(0) is also known to be stabilized inside a macrocyclic scaffold of three alkyne moieties, such as planar tribenzocyclyne, as a similar 12-membered ring (**II**), or by dibenzoheterocyclotriynes containing silicon, germanium, or titanium as linking elements between two yne functions, as a predominantly 11-membered or again 12-membered ring.[5]



Cyclicity and C$_2$ bridges between the unsaturated functions are not necessary prerequisites for stabilization of zerovalent metals by such ligands. Pörschke and co-workers[6] have systematically studied the coordination behavior of *acyclic* 1,5-dienes, 1,6-dienes, 1,6-diynes, and 1,6,11-trienes on Ni(0), Pd(0), and Pt(0). An important finding of these investigations is that ligands having 1,6- or 1,6,11-sequences of the olefinic functions are much better suited for coordination to these trigonal-planar metal centers than the corresponding acyclic or cyclic 1,5-dienes and 1,5,9-trienes. A typical metal(0) complex having an acyclic 4,9-diazadodeca-1,6,11-triene ligand is represented by **III**.[6h] In trigonal-planar complexes a chair-type, formally C_s-symmetrical conformation of (1,6-diene)M^0 substructures seems particularly stable. Nevertheless, some tetrahedral (1,6-diene)Ni^0 complexes showing a twist-type, formally C_2-symmetrical conformation have also been reported.[7]



The Roglans group, following the unexpected discovery of a Pd(0)−(*E,E,E*)-1,6,11-triazacyclopentadeca-3,8,13-triene complex,[8] has worked intensively on the synthesis of a series of azamacrocycles with various ring sizes and numbers of C═C and C≡C bonds.[9] These macrocycles have been coordinated to Pd(0), Pt(0), and Ag(I) to afford complexes such as **IV**−**VI**, which contain a 15-membered ring ligand with the ene/yne groups in 1,6,11-sequences.

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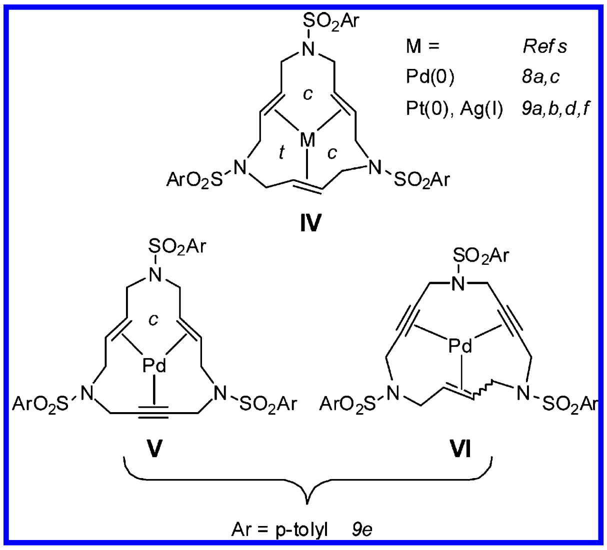


In the case of the cyclo-1,6,11-triene complex **IV**,[9d] the observed isomers have two azapalladacyclohexanic rings in a chair conformation and one ring in a twist conformation, whereas the Pd(0)−cyclo-1,6,11-dienyne **V** and the Pd(0)−cyclo-1,6,11-endiyne **VI** show only chair-type conformations.[9e] These Pd(0) complexes display unprecedented thermal stability, only partially decomposing above 250 °C, which is in sharp contrast to the fact that Pd(*t*,*t*,*t*-cdt) and Pd(*c*,*c*,*c*-cdt) are unknown compounds.

In a recent collaboration we succeeded in synthesizing the Ni(0)−triazacyclopentadeca-3,8,13-triene **VII** and the Ni(0)−triazacyclopentadeca-3,8-dien-13-yne **VIII**, which respectively represent derivatives of **IV** and **V**. Complex **VIII** reacted further with Ni(cod)$_2$ to give dinuclear **IX**.[10] The structure of **VIII** is C_s-symmetrical and resembles a chair, with the 15-membered ring providing the seat, the two SO$_2$-tolyl (tosyl, Ts) groups at NCH$_2$C≡CCH$_2$N representing the front legs, and the other tosyl group forming the back rest (Figure 1). The coordination geometry at Ni is trigonal planar with the C≡C bond and the midpoints of both C=C bonds lying in the plane, but the C=C bonds are twisted by 21° out of the plane about their midpoints. The central azanickelacyclohexanic ring, which in addition to Ni1 involves half of each of the two C=C bonds and their inner ligand section including N2, adopts a chair conformation, with the dihedral angles within the ring ranging between 55 and 69°. The remaining two pseudo-azanickelacyclohexanic rings involving ring sections around N1 (N1*), half of one C=C bond, and half the C≡C bond are equivalent in the crystal and adopt "half-chair" conformations, with dihedral angles in half of the ring being normal at 44−71° and in the other merely 15−37°, due to the fact that C2 (C2*) is constrained to lie in the Ni1,C1,C1* plane.

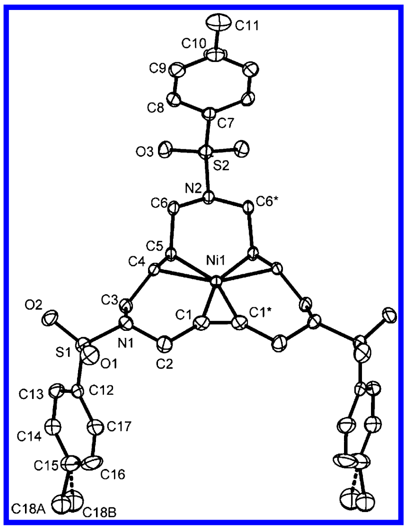
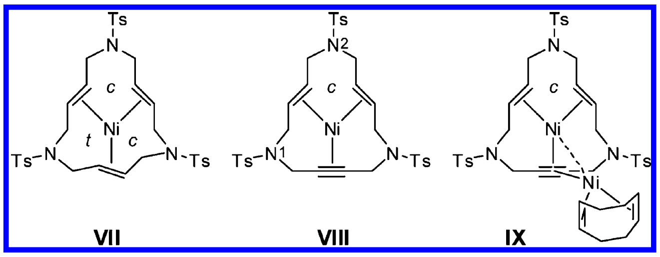
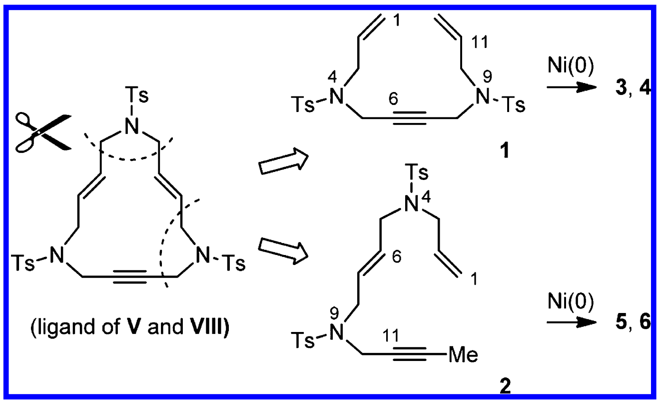


Figure 1. Molecular structure of the Ni(0)−1,6,11-triazacyclopentadeca-(*E*,*E*)-3,8-dien-13-yne complex **VIII** (at the 50% probability level).[10]



The structure of **IX** is derived from that of **VIII** by coordination of a Ni(cod) moiety to the triple bond. In the crystal studied the refined occupancy was only 83.4%. The coordination planes of the two Ni atoms, which each contain the two carbon atoms of the shared C≡C bond, make an angle of 92° to one another, and the metals are at a distance of 2.684(2) Å, indicating a marked d^{10}−d^{10} interaction.[10] The Ni(0) derivative of the cyclopentadeca-1,6,11-endiyne complex **VI** remains hitherto inaccessible.

We subsequently were interested to investigate how the structure and properties of the Ni(0) complexes are affected by replacing the 15-membered 1,6,11-triazacyclopentadeca-(*E*,*E*)-3,8-dien-13-yne ligand in **VIII** and **IX** by acyclic analogues. Formal excision of a CH$_2$−N(Ts)−CH$_2$ unit from this ligand can occur at two different sites, affording after saturation of the chain ends by H or Me either 4,9-bis(tosyl)-4,9-diazadodeca-1,11-dien-6-yne (**1**) or 4,9-bis(tosyl)-4,9-diazatrideca-1,(*E*)-6-dien-11-yne (**2**).

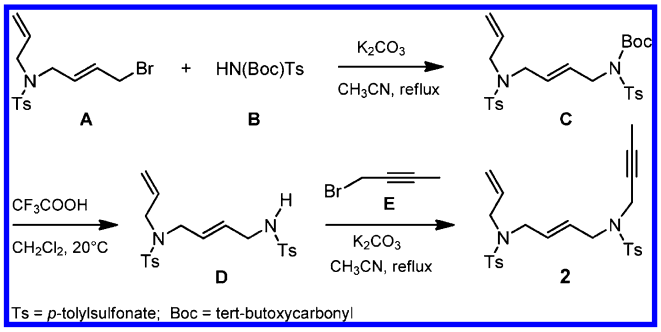


We report here the reaction of **1** and **2** with 1 or 2 equiv of Ni(cod)$_2$ to give the acyclic analogues **3**−**6** of the macrocyclic mono- and dinuclear complexes **VIII** and **IX**. The new Ni(0) complexes have been characterized in detail by NMR and X-ray diffraction analysis, revealing interesting structural properties.

■ RESULTS AND DISCUSSION

Synthesis of the Ligands. While 4,9-bis(tosyl)-4,9-diazadodeca-1,11-dien-6-yne (**1**) is known,[11] 4,9-bis(tosyl)-4,9-diazatrideca-1,(*E*)-6-dien-11-yne (**2**) is new. For the synthesis of **2** (Scheme 1), the aminoallylbutenyl bromide **A**[12] can be

Scheme 1. Synthesis of the 4,9-Diazatrideca-1,(*E*)-6-dien-11-yne 2

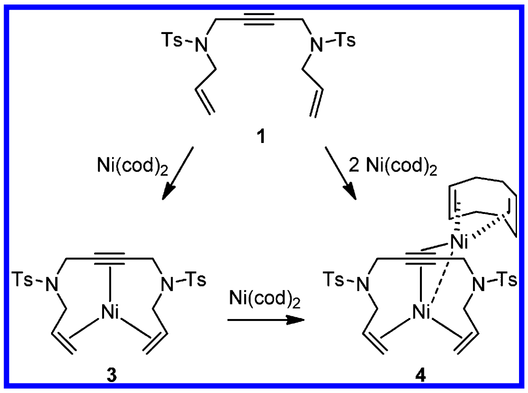


coupled with the Boc-protected sulfonamide **B**[13] to give **C** (Boc = *tert*-butyloxycarbonyl). After elimination of the Boc group, compound **D** can be coupled with 1-bromo-2-butyne (**E**) to yield colorless microcrystals of **2** in 70% overall yield. NMR spectroscopic data of **1** and **2** are contained in Tables 1 and 2. Compounds **1** and **2** are moderately soluble in THF, which appears to be the best solvent.

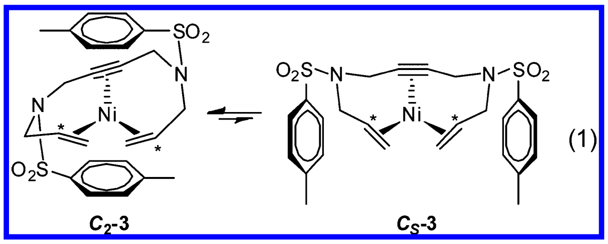
Synthesis of the Nickel(0) Complexes 3 and 4. A yellow solution of Ni(cod)$_2$ in THF reacts with an equimolar amount of **1** by displacement of the cod ligands and formation of complex **3**, in which the Ni atom is coordinated by the acyclic and symmetric 4,9-diazadodeca-1,11-dien-6-yne ligand. The reaction, which involves a slow color change via amber to light yellow, takes about 12 h for completion. Over the course of 1−3 days well-formed yellow crystals of **3** separate from the undisturbed solution in ≥80% yield. When 2 equiv of Ni(cod)$_2$ is used, the color changes to amber, and red crystals of the dinuclear complex **4** are obtained in about 60% yield, again over the course of several days (Scheme 2). This reaction proceeds via **3** as an intermediate, which reacts with the excess of Ni(cod)$_2$ by only partial displacement of cod. These reactions are similar to the formation of the mono- and dinuclear Ni(0)−triazacyclopentadeca-3,8,13-dienyne complexes **VIII** and **IX**. The formation of the dinuclear complex **4** appears to be favored for the acyclic ligand, since occupancy of the second Ni atom in the crystalline solid is 100%. Crystallization of both **3** and **4** is often delayed. While **3** is soluble in THF, **4** once crystallized is insoluble in THF and other solvents, which precludes recording of the NMR spectra of the pure compound.

NMR Spectra of 3. We have learned from the spectra of the M(0)−triazacyclopentadeca-3,8-dien-13-yne complexes **V** (M = Pd)[9e] and **VIII** (M = Ni)[10] that for the C_s-symmetrical azametallacyclohexanic ring, involving the ring section between the two C═C bonds, in the chair conformation, the equatorial protons H*e* of the geminal NCH*e*H*a* protons resonate at low field (δ(H) 4.66), whereas the axial protons H*a* resonate at characteristically higher field (**VIII**: δ(H) 1.32). When the ring adopts the C_2-symmetrical twist conformation, as in Ni(0)−triazacyclopentadeca-3,8,13-triene **VII**, the high-field shift of the axial protons H*a* is less (**VII**: δ(H) 2.84).[10] For the asymmetric pseudo-azametallacyclohexanic rings involving an alkene and an alkyne function in a "half-chair" conformation, the H*a* high-field shift for NCH*e*H*a* connected to the alkene function in the chairlike region is again large (**VIII**: δ(H) 2.00), while that for NCH*e*H*a* connected to the alkyne function in the flat part is small (**VIII**: δ(H) 4.13). The equatorial protons H*e* (δ(H) 4.52−4.66) appear little affected by the conformation of the chelate. These findings are helpful for the discussion of the spectra of **3**, **5**, and **6**.

Scheme 2. Synthesis of Complexes 3 and 4



The ^{1}H and ^{13}C NMR spectra of a solution of **3** in THF-d_8 show two sets of signals in the ratio 1.7:1. Each component gives rise to 10 ^{1}H and 10 ^{13}C NMR signals (Table 1). The signals of the major component can presumably be attributed to the presence of the C_2-symmetrical isomer **C$_2$-3** (as present in the crystal) and the signals of the minor component to the C_s-symmetrical isomer **C$_s$-3**, both components undergoing slow exchange (eq 1). The isomers result from the fact that, on coordination to the metal, the substituted alkene C atoms of the *N*-allyl groups are stereogenic centers (marked with asterisks). Thus, in **C$_2$-3**, the possible diastereomeric forms are either *R,R* or *S,S*, giving rise of a pair of spectroscopically indistinguishable enantiomers, and in the **C$_s$-3** conformation the diastereomeric form is *R,S*, corresponding to the meso form. An exchange between these isomers necessarily requires cleavage of one Ni−alkene bond and recoordination of the alkene by its reverse side. The exchange in solution is consequently slow.



(1)

In agreement with the previous findings, the presumed **C$_s$-3** shows for the two pseudo-azanickelacyclohexanic rings involving alkene and alkyne functions in "half-chair" conformation a marked high-field shift of H3*a* (δ(H) 2.11) in the chairlike alkene part of the ring and only a small high-field shift of H4*a* (δ(H) 4.02) in the flat alkyne part of the ring. For **C$_2$-3** the high-field chemical shift of H3*a* (δ(H) 2.19) in the alkene part of the chelate ring is also normal, and the coupling ^3J(H2,H3*a*) = 10.4 Hz appears. For the alkyne part of the ring the chemical shift difference between H4*e* and H4*a* is larger than is typical (δ(H) 4.70 (H4*e*) and 3.78 (H4*a*)). These observations can be attributed to the unusual boat conformation of the two rings seen in the X-ray structure. Clearly, the boat conformation of the chelate rings in **C$_2$-3** and the "half-chair" conformation of the chelate rings in **C$_s$-3** are of similar stability, since both are present in solution corresponding to the equilibrium of eq 1.

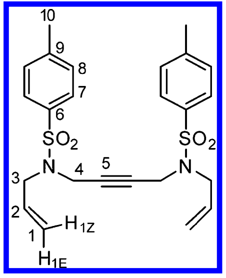
For the alkyne function of the main acyclic isomer, assumed to be **C$_2$-3**, the ^{13}C coordination shift[14] ($\Delta\delta$(C) = 21.3 ppm) is less than that of the minor isomer assumed to be **C$_s$-3**

Table 1. ^{1}H and ^{13}C NMR Data of the 4,9-Diazadodeca-1,11-dien-6-yne **1** and the Isomers of Nickel(0) Complex **3**[a]

				^{1}H NMR						
	H1Z	H1E	H2	H3e	H3a	H4e	H4a	H7	H8	H10
1[b]	5.11 (dd, 16.8, 1.2)	5.18 (dd, 10.4, 1.2)	5.61 (qt, 16.8, 10.4, 6.4)	3.62 (d, 6.4)		3.85 (s)		7.65	7.29	2.42
C_2-**3**[c]	3.35 (m), 2.55 (m)		3.75 (m)	4.60 (d, 13.2)	2.19 (dd, 13.2, 10.4)	4.70 (d, 13.2)	3.78 (d, 13.2)	7.63	7.29	2.38
C_s-**3**[c]	3.47 (m), 2.95 (m)		3.48 (m)	4.60 (d, 13.2)	2.11 (m)	4.62 (d, 13.6)	4.02 (d, 13.6)	7.63	7.25	2.35

					^{13}C NMR					
	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
1[b]	119.8	131.9	49.0	35.8	78.4	136.1	127.7	129.6	143.8	21.6
C_2-**3**[c]	58.5	79.3	48.9	37.6	99.7	134.6	127.8	130.0	144.2	21.6
C_s-**3**[c]	59.3	79.0	48.5	37.4	101.3	134.4	127.8	130.0	144.1	21.5

[a] Solvent CD_2Cl_2. J(H,H) couplings (in hertz) are given in parentheses. Assignment:



[b] Solvent $CDCl_3$. [c] Tentative assignment.

($\Delta\delta$(C) = 22.9 ppm), which is explained by the out-of-plane twist of the triple bond of the former (see the X-ray structure) and hence hindered back-donation from Ni(0). Interestingly, the ^{13}C coordination shift of both isomers is larger than that of the cyclic **VIII** ($\Delta\delta$(C) = 20.1 ppm), suggesting that for both isomers of **3**, containing the flexible acyclic **1**, the Ni(0)−alkyne orbital overlap is better than that in the cyclic **VIII**.

Molecular Structures of 3 and 4. The molecular structures of the mono- and dinuclear complexes **3** and **4**, containing the 4,9-diazadodeca-1,11-dien-6-yne ligand, have been determined by single-crystal X-ray crystallography (Table S1; see the Supporting Information). Both compounds crystallize in the orthorhombic crystal system.

The molecules of complex **3** (space group *Pbcn*, No. 60) lie on a crystallographic C_2 axis which passes through the Ni atom and the midpoint of the C≡C bond (Figure 2). Thus, whereas a mixture of the C_2 and the C_s isomers appears in solution, the crystal contains only the C_2 isomer. Individual molecules in the crystal are chiral, but the crystal as a whole is a racemate. In the solid the Ni atom has trigonal-planar coordination, with the metal, the two terminal C═C bonds, including both C atoms, and the midpoint of the C≡C bond lying in the coordination plane. The in-plane location of the C═C bonds is a notable feature of the structure. The Ni atom, the central C≡C bond, and its two CH_2 substituents also lie in an approximate plane (C4−C5−C5*−C4* torsional angle 1.8(1)°), within which the CH_2 substituents are bent away from Ni, giving a C≡C−CH_2 angle of 158.9(1)°. The $CH_2C{\equiv}CCH_2$ entity is twisted out of the coordination plane by 22°, as a result of the geometrical constraint of the chain.

The lengths of the coordinated C═C bonds C1−C2 at 1.390(12) Å and the Ni1−C bonds to the terminal (2.0296(8) Å) and internal alkene C atoms (2.0379(8) Å) are as expected, which is also the case for the lengths of the C≡C bond C5−C5* (1.2499(15) Å) and the Ni1−C5/5* bonds (1.9755(8) Å).

The Ni atom and the chain sections from the substituted C atom of one C═C bond to the corresponding inner C atom of the C≡C bond give rise to two identical pseudo-azanickelacyclohexanic rings. The conformation of these rings can best be described as twist-boat, with Ni and N at the tips of the boat. The dihedral angles within the six-membered rings range from a low 21.9(1)° to a normal 60.5(1)°. The geometry at N is a flattened pyramid (the sum of the three angles is 350.4(2)°), and the SO_2-tolyl substituents occupy formal axial positions in the

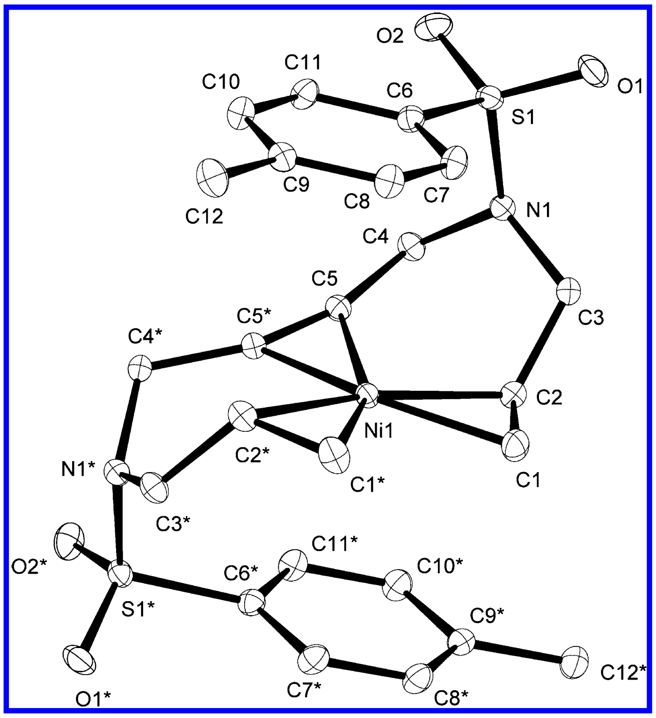


Figure 2. Molecular structure of **3** (at the 50% probability level). Selected bond distances (Å) and bond angles (deg): C1−C2 = 1.3901(12), C5−C5* = 1.2499(15), Ni(1)−C(1) = 2.0296(8), Ni(1)−C(2) = 2.0379(8), Ni(1)−C(5) = 1.9755(8); C5*−C5−C4 = 158.9(4), (midpoint C1−C2)−Ni1−(midpoint C1*−C2*) = 124.3(5), (midpoint C1−C2)−Ni1−(midpoint C5−C5*) = 117.9(4).

pseudo-azanickelacyclohexanic rings. The orientation of the tolyl groups is antiperiplanar to the N lone pairs; thus, the two groups bend over the Ni atom and sandwich it (closest Ni−arene contacts are Ni1−C7 at 3.608 Å and Ni1−C6 at 3.617 Å). As a result, the molecules take up a relatively compact S-shaped conformation.

In the crystal molecules of **3** pack in parallel columns which run parallel to the *a* axis. Each column is made up of identical C_2-symmetrical molecules having the same chirality and orientation. In each column the molecules are stacked such that the phenyl groups of adjacent molecules lie almost parallel to one another (the interplanar angle is 8°), with the midpoints of the phenyl rings separated by 3.75(1) Å, suggestive of a weak π-electron interaction (the distance of the layers in graphite is 3.354 Å). Each column is surrounded by six nearest neighbors. Along the *b* axis the molecules are related by a glide plane and along the *c* axis by inversion centers.

Molecules of dinuclear **4** (space group $P2_12_12_1$, No. 19) can be thought of as being derived from **3** by coordination of a Ni(cod) moiety to the C≡C bond. The C_2 symmetry of **3** in the crystal is thereby changed to approximate C_s in the crystal of **4** (Figure 3). Whereas in **3** it is the two C=C bonds that lie in the metal coordination plane and the C≡C bond that is twisted out of the plane, in **4** it is the C≡C bond that lies in the Ni1 coordination plane, defined by the metal center and the midpoints of the C≡C bond and the C=C bonds, and the two C=C bonds that are twisted out of the plane (by 15 and 9°). Both azanickelacyclohexanic rings in **4** (assuming an sp^3-type hybridization of the 2-fold metal-coordinated alkyne carbon atoms) adopt chair conformations. Dihedral angles within the six-membered rings range from 45.6 to 70.0°, and the two rings are approximate mirror images of one another. As in **3**, the geometry at N1 and N2 is that of a flattened pyramid (sums of angles at N are respectively 346.3(5) and 346.5(5)°), but in contrast to **3**, the tosyl substituents take up equatorial positions in the chair conformations of the azanickelacyclohexanic rings and are directed away from Ni1. As in **3**, the tolyl groups adopt conformations about the S−N bonds antiperiplanar to the N lone pairs. As a result both groups take up positions on the opposite side of the coordination plane of Ni1 from the Ni(cod) entity. In **4** the C=C bonds (1.388(8) Å, mean) are slightly shorter and the Ni1−C bonds to the terminal (2.035 Å, mean) and internal (2.064 Å, mean) alkene C atoms longer than in the mononuclear **3**. For the 2-fold Ni coordinated alkyne ligand both the C≡C bond C5−C6 at 1.329(3) Å and the Ni1−C5/6 distances at 2.005 Å (mean) are longer than in **3**.

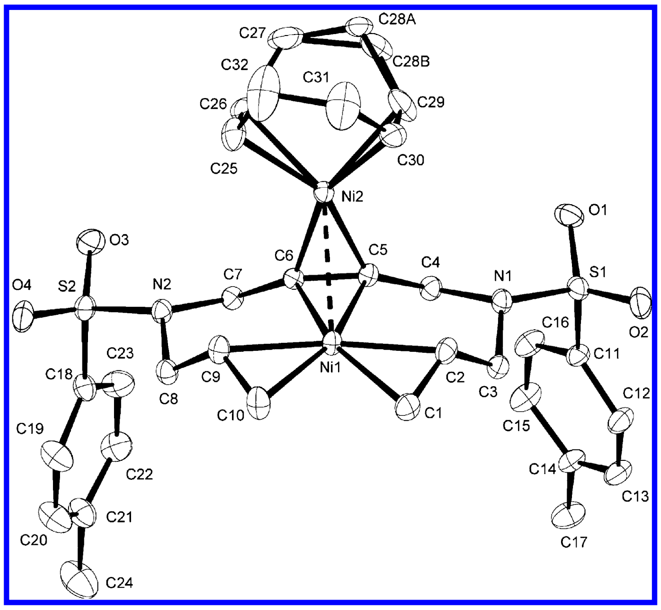


Figure 3. Molecular structure of **4** (at the 50% probability level). Selected bond distances (Å) and bond angles (deg): C1−C2 = 1.382(4), C5−C6 = 1.329(3), C9−C10 = 1.393(4), C25−C26 = 1.370(4), C29−C30 = 1.360(5), Ni1−C1 = 2.033(2), Ni1−C2 = 2.073(3), Ni1−C5 = 2.001(2), Ni1−C6 = 2.009(2), Ni1−C9 = 2.054(2), Ni1−C10 = 2.037(3), Ni2−C5 = 1.913(2), Ni2−C6 = 1.897(2), Ni2−C25 = 2.131(3), Ni2−C26 = 2.080(3), Ni2−C29 = 2.090(3), Ni2−C30 = 2.101(3), Ni1···Ni2 = 2.7352(5); C4−C5−C6 = 136.0(2), C5−C6−C7 = 139.9(2), (midpoint C1−C2)−Ni1−(midpoint C9−C10) = 120.7(3), (midpoint C1−C2)−Ni1−(midpoint C5−C6) = 119.4(2), (midpoint C9−C10)−Ni1−(midpoint C5−C6) = 119.8(2).

The second Ni atom (Ni2) in **4** makes an angle of 96° to the Ni1 coordination plane at midpoint of the C≡C bond (for the related **IX** the corresponding value is 92°). The Ni2−C5/6 bonds to the alkyne (1.905(11) Å, mean) are markedly shorter than the Ni1−C5/6 bonds, reflecting stronger back-bonding of Ni2 to the alkyne than for Ni1. For Ni1 the two C=C bonds are only slightly twisted out of the metal coordination plane, thus effectively withdrawing electron density from Ni1. For Ni2 the C=C bonds are perpendicular to the plane, rendering Ni2 more basic.

The Ni1···Ni2 distance at 2.7352(5) Å is somewhat longer than the corresponding distance in the likewise dinuclear **IX** (2.684(2) Å), and for both compounds some d^{10}−d^{10} interaction between the metal centers cannot be ruled out. Indeed, the midpoint of the C≡C bond and the midpoint of the four C atoms of the cod make an angle of 171(1)° at Ni2, whereas a similar distortion is not found for the coordination plane of Ni1. Attachment of Ni2 to **3** causes the CH_2−C≡C angles to decrease from 158.9(4)° in **3** to 138(3)° (mean) in **4**, which is comparable to that in **IX** (140°). The CH_2−C≡C−CH_2 entity remains approximately planar (C4−C5−C6−C7 torsional angle at 1.7°), but both Ni atoms lie out of this plane on either side so that the plane appears to bisect the Ni1···Ni2 bond. These geometrical features induce the pronounced chair conformation of the azanickelacyclohexanic rings.

The Ni(cod) moiety is unspectacular (mean C=C bond lengths 1.365(7) Å, mean Ni2−C bond lengths 2.10(2) Å). Complex **4** represents a hitherto rare example of a structurally characterized $(L_2Ni)_2(\mu\text{-}RC{\equiv}CR')$-type complex (L = alkene) in which two C=C bonds lie in one C≡C−Ni plane and two others perpendicular to the second plane.[10]

The principal features of the structure of acyclic dinuclear **4** correspond to those of the cyclic dinuclear **IX** and, neglecting the Ni2(cod) moiety, also to those of the cyclic mononuclear **VIII**. Without the Ni2(cod) group, **4** can also be viewed as a rough model for structure of the acyclic mononuclear C_s-**3** which seems to be present in solution (eq 1). A similar conformation of the carbon skeleton would also be expected for a so far uninvestigated M(0)−4,9-diazadodeca-1,(*Z*)-6,11-triene complex.

Synthesis of the Nickel(0) Complexes 5 and 6. Similar to the synthesis of **3** and **4**, a THF solution of 1 or 2 equiv of $Ni(cod)_2$ reacts with the acyclic 4,9-diazatrideca-1,(*E*)-6-dien-11-yne **2**, with its unsymmetrical distribution of the two C=C and one C≡C multiple bonds. Using 1 equiv of $Ni(cod)_2$, the displacement of the cod ligands by **2** can be followed by the color change from yellow via amber to light yellow at ambient temperature over the course of 12 h, and after 1−3 days yellow cubes of mononuclear **5** are formed (Scheme 3). Isolated **5** is only poorly soluble. When 2 equiv of Ni(cod)$_2$ is used, partial further cod displacement by the triple bond in **2** affords an amber solution from which fine yellow felted needles of dinuclear **6** precipitate in about 50% yield after a few days. Interestingly, **6** is more soluble in THF than the mononuclear **5**, whereas the likewise dinuclear crystalline (cyclic) **IX** and (acyclic) **4** are practically insoluble. By slowly cooling a solution of **6** from ambient temperature to −20 °C the complex can be recrystallized to form orange well-formed spherulites (Figure 4). Since intermediate **5** is less soluble than **6**, it is essential that all **5** be converted into **6** before the crystallization starts.

Scheme 3. Synthesis of Complexes 5 and 6

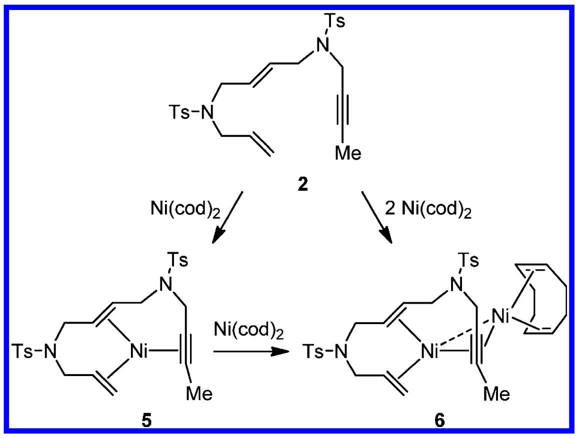


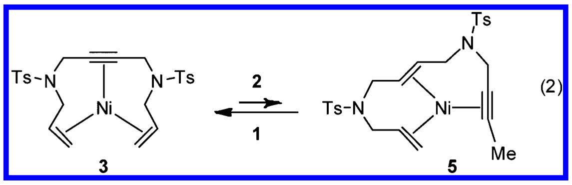
Figure 4. Photo of the spherulites of **6**.

NMR Spectra of 5 and 6. In the ^{1}H and ^{13}C NMR spectra of **5** and **6** all 13 protons (in addition to the methyl group) and all 11 carbon atoms of the 4,9-diazatrideca-1,(*E*)-6-dien-11-yne skeleton give rise to separate signals, on account of the asymmetric structures. Diastereotopy of the geminal NCH$_2$ protons proves that the structures are rigid. In addition, both *N*-tosyl substituents are inequivalent. A conformational analysis of the structures is based on the assignment of the signals of the four NCH*e*H*a* methylene groups by 2D NMR techniques.

As expected (see introductory remarks in NMR Spectra of 3), for the mononuclear **5** (Table 2) all signals of H3*e*, H4*e*, H7*e*, and H8*e* are in the δ(H) 4.42−4.61 range. The protons H3*a* and H4*a* at δ(H) 1.31 and 1.20 resonate at substantially higher field, indicative of a chair conformation of the azanickelacyclohexanic structure involving the two C=C bonds. Such a structural entity is most stable and dictates the further conformation of the ligand. For the pseudo-azanickelacyclohexanic chelate involving the central C=C bond and the C≡C bond, the expected "half-chair" conformation is evident from the lower high-field shift of H7*a* at δ(H) 2.38 in the section between N and C=C and the inconspicuous signal of H8*a* at δ(H) 4.28 in the flat section between N and C≡C. While the upfield (negative) coordination chemical shift of all alkene C atoms at $\Delta\delta$(C) = −57 to −59 ppm is uniform and relatively high, indicating good orbital overlap, the alkyne C atom downfield shift at $\Delta\delta$(C) = 14.0 and 17.3 ppm is lower than in **3** and **VIII** (≥20 ppm).

It is fortunate that dinuclear **6** is quite soluble, so that recording of the NMR spectra is possible, in contrast to the situation for the insoluble **IX** and **4**. Most ^{1}H and ^{13}C data of **6** (Table 2) vary only little from those of the mononuclear **5**. However, as a consequence of the altered hybridization of C9/C10 as compared to **2** and **5**, the alkyne C9/C10 signals of **6** are reshifted to higher field by 3.4−3.6 ppm and the signals of C8 and the methyl C11 are shifted further to lower field. A particularly strong high-field shift is found for the signal of H8a at δ(H) 2.77 as compared to **5** (δ(H) 4.28), due to the chairlike conformation of this part of the ligand as well. For the cod ligand, 12 ^{1}H and 8 ^{13}C signals are observed, which proves the asymmetric structure of the ligand and rules out rapid rotation about the (cod)Ni−alkyne bond axis.

Ligand Exchange Reactions. Trial ligand exchange reactions have shown that the cyclic ligand in **VIII** is not displaced by either acyclic **1** or **2**, and the unreacted **VIII** has been recovered from such solutions. When the mononuclear complexes **3** and **5** are treated with the corresponding 1,6,11-triazacyclopentadeca-3,8-dien-13-yne in THF, both acyclic ligands are displaced and **VIII** is formed. However, displacement reactions between complex **3** and ligand **2** on the one hand and complex **5** and ligand **1** on the other revealed the presence of an equilibrium (eq 2) which is in favor of the left side (about a 2:1 mixture), as shown by NMR. It follows from these studies that (i) complexes **3** and **5** having the acyclic ligands are more reactive than the cyclic **VIII** and that (ii) the nickel atom is able to migrate from one acyclic ligand to the other. This could be relevant for catalytic activity.



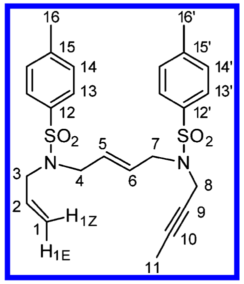
Molecular Structures of 5 and 6. The mono- and dinuclear complexes **5** and **6**, each containing the asymmetric 4,9-bis(4-tolylsulfonyl)-4,9-diazatrideca-1,6-dien-11-yne ligand, both crystallize in the monoclinic crystal system in the space group $P2_1/c$ (No. 14) (Table S1; see the Supporting Information). Both crystal structures include THF solute, but in differing molar ratios. The central trans-substituted C=C

Table 2. ^{1}H and ^{13}C NMR Data of the 4,9-Diazatrideca-1,6-dien-11-yne 2 and the Nickel(0) Complexes 5 and 6[a]

	^{1}H NMR																
	H1Z	H1E	H2	H3*e*	H3*a*	H4*e*	H4*a*	H5	H6	H7*e*	H7*a*	H8*e*	H8*a*	H11	H13/H13′	H14/H14′	H16/H16′
2	5.12 (17.0)	5.08 (10.1)	5.62	3.74		3.73		5.52 (15.4)	5.47 (15.4)	3.68		3.90 (q, 2.4)		1.52 (t, 2.4)	7.70/7.69	7.35/7.33	2.41/2.41
5	2.94 (14.0)	2.78 (8.8)	3.66	4.61 (13.0)	1.31 (13.0)	4.58 (13.2)	1.20 (13.2)	3.48 (13.0)	2.94 (13.0)	4.46 (13.1)	2.38 (13.1)	4.42 (15.0)	4.28 (15.0)	2.40 (t, 1.6)	7.59/7.59	7.28/7.26	2.35/2.34
6[b]	2.84 (13.4)	2.30 (8.8)	3.69	4.51	1.26	4.58	1.32	3.33	3.10	4.39	1.62	4.62	2.77	2.18 (s)	7.62/7.60	7.32/7.30	2.36/2.34

	^{13}C NMR														
	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12/C12′	C13/C13′	C14/C14′	C15/C15′	C16/C16′
2	118.7	134.4	50.4	48.9	130.7	129.5	48.5	37.0	72.6	82.0	2.9	139.0/137.8	128.8/128.1	130.4/130.0	143.9/143.9	21.4/21.4
5	61.5	77.0	50.5	50.0	71.3	71.8	47.5	37.2	89.9	96.0	9.8	136.0/135.3	128.5/128.4	130.3/130.1	144.0/143.9	21.3/21.3
6[b]	62.6	75.9	51.0	51.2	69.2	75.0	48.7	42.6	86.3	92.6	13.3	135.8/134.0	128.7/128.4	130.2/130.1	144.0/143.8	21.3deg

[a] Solvent THF-d_8. Prominent J(H,H) couplings (in hertz) are given in parentheses. Assignment:



[b] cod ligand: δ(H) 5.34, 4.78, 4.36, 4.10, 2.25, 2.12, 2.00, 1.86, 1.76, 1.70, 1.23, 1.10; δ(C) 97.5, 97.2, 96.5, 94.6, 31.4, 30.9, 30.1, 29.6.

bond of the ligand appears to play as crucial a role in determining the mode of attachment of the ligand to the metal in **5** and **6** as the alkyne function does in **3** and **4**. Whereas the terminal functions of the chain in **3** and **4** are the same *N*-allyl, in **5** and **6** they are *N*-allyl and *N*-but-2-yne groups.

As for **3**, the geometry of mononuclear **5** is trigonal planar if one defines the coordination plane by the metal center and the midpoints of the $C{=}C$ and $C{\equiv}C$ bonds (Figure 5). Whereas the three $C{=}C$ bonds in complexes of type **III**, bearing an *acyclic* 4,9-diazadodeca-1,6,11-triene ligand, are coplanar, the three unsaturated moieties in **5** are twisted out of the coordination plane by 8−12°. These distortions appear to be induced by the terminal *N*-but-2-yne function, which restrains C8 to a position close to the coordination plane of the metal. The azanickelacyclohexanic ring in **5**, involving N1 and two α-C atoms of the metal-bound $C{=}C$ bonds, adopts a pronounced chair conformation (dihedral angles within the ring range from 58 to 73°), whereas the conformation of the pseudo-azanickelacyclohexanic ring, involving N2 and one α-C atom of a $C{=}C$ bond and the other of a $C{\equiv}C$ bond, appears to prefer that of a "flattened half-chair" (dihedral angles range from 20 to 78°).

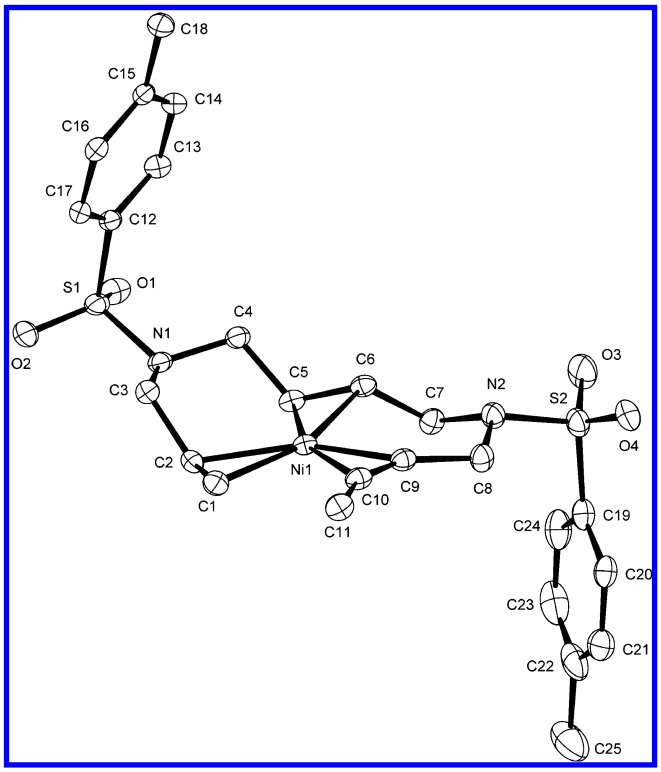


Figure 5. Molecular structure of **5** (at the 50% probability level), without THF solute. Selected bond distances (Å) and bond angles (deg): C1−C2 = 1.387(3), C5−C6 = 1.397(3), C9−C10 = 1.241(4), Ni1−C1 = 2.032(2), Ni1−C2 = 2.060(2), Ni1−C5 = 2.031(2), Ni1−C6 = 2.027(2), Ni1−C9 = 1.931(2), Ni1−C10 = 1.978(2); C8−C9−C10 = 147.0(2), C9−C10−C11 = 153.0(3), (midpoint C1−C2)−Ni1−(midpoint C5−C6) = 120.5(1), (midpoint C5−C6)−Ni1−(midpoint C9−C10) = 119.6(1), (midpoint C1−C2)−Ni1−(midpoint C9−C10) = 119.9(1).

The geometry at N is somewhat more pyramidal in **5** (sum of angles is 343.3(3)° at N1 and 344.6(3)° at N2) than in both **3** and **4**. The two tosyl SO_2 substituents occupy equatorial positions at N, similar to the case for dinuclear **4**. As a result of the trans substitution of the central $C{=}C$ bond, together with the requirement of an antiperiplanar arrangement of the tolyl groups relative to the lone pairs of the N atoms, the tolyl groups are forced to point away from the complex core in opposite directions, thus giving rise to an additional structural motif.

There are four equivalent complex molecules of **5** in the unit cell ($Z = 4$), together with one THF solute molecule. Two molecules each form a centrosymmetric pair in which the metal coordination planes are perforce parallel (distance of planes 3.68(1) Å; Ni1⋯Ni1* distance 4.314(1) Å). The tolyl groups at S2 and S2* align the partner molecules edgewise and point in about the same directions as the tolyl groups at S1* and S1, allowing for mating of the structures. The tolyl group at S2 appears also to undergo a π-electron interaction to one Ni1** center of an adjacent pair (the shortest intermolecular distance here is Ni1**⋯C19 at 3.974(1) Å). Voids around the tolyl group at S1 are filled with THF.

The structure of the dinuclear **6** is derived from that of **5** by the attachment of a Ni(cod) moiety to the $C{\equiv}C$ bond (Figure 6). The major geometrical changes are in the region of

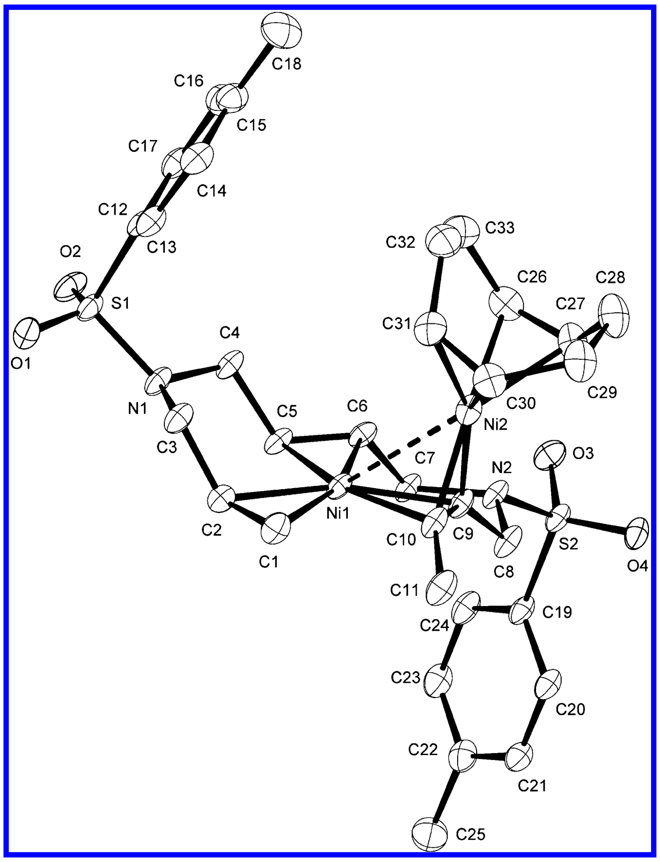


Figure 6. Molecular structure of **6** (at the 50% probability level), without THF solute. Selected bond distances (Å) and bond angles (deg): C1−C2 = 1.388(4), C5−C6 = 1.392(5), C9−C10 = 1.316(5), C26−C27 = 1.371(6), C30−C31 = 1.374(5), Ni1−C1 = 2.022(3), Ni1−C2 = 2.039(3), Ni1−C5 = 2.038(3), Ni1−C6 = 2.038(3), Ni1−C9 = 2.009(3), Ni1−C10 = 2.029(3), Ni2−C9 = 1.903(3), Ni2−C10 = 1.917(4), Ni2−C26 = 2.113(4), Ni2−C27 = 2.080(4), Ni2−C30 = 2.061(3), Ni2−C31 = 2.094(3), Ni1⋯Ni1* = 2.6834(7); C8−C9−C10 = 139.4(3), C9−C10−C11 = 140.9(3), (midpoint C1−C2)−Ni1−(midpoint C5−C6) = 119.8(1), (midpoint C5−C6)−Ni1−(midpoint C9−C10) = 120.5(1), (midpoint C1−C2)−Ni1−(midpoint C9−C10) = 119.7(1).

this bond. Thus, the angle C8−C9−C10 is reduced to 139.4(3)° (**5**, 147.0(2)°) and C9−C10−C11 to 140.9(3)° (**5**, 153.0(3)°) and the bond lengths of C9−C10 at 1.316(5) Å (**5**, 1.241(4) Å) and Ni1−C9/10 at 2.020 Å (mean) (**5**, 1.954 Å, mean) increase. As a consequence of the increase in the C8−C9−C10 angle, the previously partially flat pseudo-azanickelacyclohexanic ring involving N2 is able to adopt a fuller chair conformation, with the dihedral angles within the ring ranging from 50.7 to 74.1°. The pyramidal geometry at N2 also becomes more pronounced (sum of angles is 342.6(7)°). The azanickelacyclohexanic ring involving N1 remains essentially unchanged, with dihedral angles ranging from 58.3 to 73.2° and sum of angles at N1 at 344.6(6)°. As in **5**, both tosyl substituents occupy equatorial positions at N in the azanickelacyclohexanic rings, and the tosyl groups adopt again conformations in which the tolyl groups are antiperiplanar to the lone pairs of the N atoms to which they are attached.

One of the consequences of the geometrical changes at the C≡C bond is that the C atoms of both C=C bonds are now able to take up positions in the coordination plane of Ni1 and the C≡C bond is twisted out of it by only 5(1)°. The Ni2(cod) moiety is bound to the C≡C entity via two short bonds Ni2−C9/10 at 1.91(1) Å (mean), with an associated Ni1,C9,C10/Ni2,C9,C10 interplanar angle of 93(1)°. This leads to a Ni1···Ni2 distance of 2.6834(7) Å, which is just slightly shorter than the Ni···Ni distance in **4**. The CH_2−C≡C−CH_3 entity lies largely in a plane (C8−C9−C10−C11 torsional angle is 8.5°) which bisects the Ni1···Ni2 bond. This mirrors the relationship of the alkyne to the two Ni atoms in **4**. The geometry of the Ni2(cod) moiety is as expected. Interestingly, since the geometrical features of a doubly coordinated C≡C bond are similar to those of a single coordinated C=C bond, the conformation of the ligand around Ni1 in **6** resembles that in **III**.

The packing of centrosymmetric pairs of complexes in the crystal of **6** ($Z = 4$) is quite similar to that of **5**, with the distinction that into each pair of complex molecules two Ni2(cod) moieties have been inserted. The complexes appear to slide away from one another, so that the Ni1···Ni1* distance is almost doubled (8.616(1) Å), while maintaining parallel coordination planes at Ni1 (interplanar distance 6.46(1) Å). In **6**, the coordination planes of Ni1 are flanked by disordered THF solute molecules. Each metal complex crystallizes with one THF solute molecule, resulting in four THF molecules in the unit cell.

The similarities and differences in conformations of the acyclic aza-dien-yne ligands in these complexes and their comparison with those of their cyclic analogues thus yield important information about the conformational properties of the ligands and the zerovalent metal complexes that are formed from them. Particularly important are the conformations of the azanickelacyclohexanic rings and the ability of the unsaturated moieties to adopt a favorable coplanar arrangement around the metals. An ideal chair conformation of the azanickelacyclohexanic rings appears to be best suited for coordination to Ni(0).

■ CONCLUSIONS

The syntheses of mono- and dinuclear nickel(0) complexes containing the open-chain ligands 4,9-bis(4-tolylsulfonyl)-4,9-diazadodeca-1,11-dien-6-yne (**1**) and 4,9-bis(4-tolylsulfonyl)-4,9-diazatrideca-1,(*E*)-6-dien-11-yne (**2**) are reported. These ligands differ in their 1,6,11-sequences of the two ene and one yne functions and may be viewed as distinct, acyclic sections of cyclic 1,6,11-triazacyclopentadeca-(*E*,*E*)-3,8-dien-13-yne, which has previously been used as a ligand in the mono- and dinuclear Ni(0) complexes **VIII** and **IX**.[10] Whereas in M(0)−1,6,11-triaza*cyclo*pentadeca-(*E*,*E*,*E*)-3,8,13-triene complexes such as **IV** (M = e.g., Pd)[8a,c,9e] and **VII** (M = Ni)[10] the three C=C bonds are twisted out of the coordination plane by structural constraint of the cycle, in the related *acyclic* Ni(0)−dodeca-1,6,11-triene-type complexes[6h,15] such as **III**[6h] all C=C bonds lie in the coordination plane. The new mononuclear complexes **3** and **5** and their dinuclear derivatives **4** and **6** were synthesized and their structure and solution properties studied.

(i) In the crystalline Ni(0)−4,9-diazadodeca-1,11-dien-6-yne complex **3** the *acyclic* ligand adopts C_2 point group symmetry, thus giving **C_2-3**, with the two terminal C=C bonds lying in the coordination plane of the Ni(0), which in turn causes an out-of-plane twist of the central C≡C bond. In solution the complex isomerizes, and the mirror-symmetric form **C_s-3** is also present, with which the C_2 structure is in equilibrium. C_s symmetry is observed in M(0)−1,6,11-triazacyclopentadeca-(*E*,*E*)-3,8-dien-13-yne complexes, such as **VIII** (M = Ni),[10] containing the cyclic ligand, but in this case, it is the C≡C bond that lies in the coordination plane of the metal and the C=C bonds that are twisted out of the coordination plane.

(ii) In the structure of the *acyclic* and *unsymmetrical* Ni(0)−4,9-diazadodeca-1,(*E*)-6-dien-11-yne **5**, as a counterpart to **3**, both C=C bonds and the C≡C bond are slightly twisted out of the coordination plane. The structure is governed by the *E* configuration of the diene and the associated chair conformation of the 1,(*E*)-6-diene nickelacycle.

(iii) Mononuclear **VIII**,[10] **3**, and **5** can coordinate a further Ni(0) atom in the form of Ni(cod) at the C≡C bond, to form alkyne-bridged dinuclear complexes **IX**,[10] **4**, and **6**. This goes along with a change in hybridization of the alkyne C atoms toward sp^3 and formation of chairlike azanickelacyclohexanic substructures. Hence, a similar bonding situation arises for the *cyclic* dinuclear **IX**[10] and the *acyclic* and symmetric dinuclear **4**. Since all carbons of the C≡C and C=C bonds lie practically in the coordination plane, the structures appear to favor de facto (**IX**) or approximate (**4**) C_s symmetry. A similar geometry can also be expected for M(0)−1,6,11-triazacyclopentadeca-(*E*,*E*,*Z*)-3,8,13-triene[16] and (so far unsought) acyclic M(0)−4,9-diazadodeca-1,(*Z*)-6,11-triene complexes, where the (C≡C)Ni(cod) is replaced by (*Z*)-C=C.

(iv) In **6** the conformation of the ligand around Ni1 resembles that in **III**, considering that the geometrical features of a doubly coordinated C≡C bond are similar to those of a singly coordinated C=C bond.

(v) While dinuclear **IX** and **4** are insoluble, precluding an NMR characterization, for soluble **6** rotation of the Ni2(cod) entity about the Ni2−alkyne bond has been ruled out by NMR.

The acyclic polyunsaturated aza ligands described here can be used to stabilize Ni(0). These compounds appear more reactive than those with the parent cyclic ligands due to the absence of a macrocyclic effect. Thus, acyclic polyfunctional ligands are particularly suited to confer on metal complexes both thermal stability and reactivity.

■ EXPERIMENTAL SECTION

THF was dried by distillation from $NaAlEt_4$. $Ni(cod)_2$[1c] and ligand **1**[11] ($C_{24}H_{28}N_2O_4S_2$, FW = 472.6) were prepared as reported. For the synthesis of **2** ($C_{25}H_{30}N_2O_4S_2$, FW = 486.6), see the Supporting Information. Microanalyses were performed by Mikroanalytisches Labor Kolbe, Mülheim, Germany. EI mass spectra were recorded at 70 eV. ^1H NMR spectra were measured at 300 and 400 MHz and ^{13}C

NMR spectra at 75 and 100 MHz with Bruker instruments. ^1H and ^{13}C chemical shifts (δ) were referenced to internal solvent resonances and are reported relative to $SiMe_4$. DSC experiments were performed using Mettler Toledo DSC820e and DSC822e instruments under inert conditions (continuous flow of 40 mL/min of high-purity N_2). Aluminum crucibles (40 μL) were used; sample masses were between 4.5 and 7 mg. All handlings of nickel(0) complexes were done with Schlenk-type glassware under an argon atmosphere.

(4,9-Bis(4-tolylsulfonyl)-4,9-diazadodeca-1,11-dien-6-yne)-nickel(0) (($C_{24}H_{28}N_2O_4S_2$)Ni, 3). A solution of $Ni(cod)_2$ (181 mg, 0.66 mmol) in anhydrous THF (20 mL) was combined with a solution of the 4,9-diazadodeca-1,11-dien-6-yne **1** (312 mg, 0.66 mmol) in THF (20 mL) at room temperature. After initial mixing, the solution was left undisturbed. Over the course of 1−3 days yellow crystals of **3** were obtained. These were isolated by filtration, washed with diethyl ether, and dried under vacuum: yield 292 mg (84%). Mp 161−163 °C dec. For NMR data, see Table 1. Anal. Calcd for $C_{24}H_{28}N_2NiO_4S_2$ (531.3): C, 54.25; H, 5.31; N, 5.27; Ni, 11.05. Found: C, 54.22; H, 5.51; N, 5.06; Ni, 11.34.

(4,9-Bis(4-tolylsulfonyl)-4,9-diazadodeca-1,11-dien-6-yne)-dinickel(0) 1,5-Cyclooctadiene (($C_{24}H_{28}N_2O_4S_2$)Ni_2(cod), 4). A solution of $Ni(cod)_2$ (394 mg, 1.43 mmol) in THF (30 mL) was combined with a solution of **1** (338 mg, 0.71 mmol) in anhydrous THF (20 mL) at room temperature. After initial mixing, the solution was left undisturbed, and over the course of 3 days, red crystals of **4** were obtained. These were isolated by filtration, washed with diethyl ether, and dried under vacuum: yield 283 mg (57%). Anal. Calcd for $C_{32}H_{40}N_2Ni_2O_4S_2$ (698.2): C, 55.05; H, 5.77; N, 4.01; Ni, 16.81. Found: C, 53.90; H, 5.54; N, 3.92; Ni, 16.81. Recording of the ^1H and ^{13}C NMR was prevented by the insolubility of the compound.

(4,9-Bis(4-tolylsulfonyl)-4,9-diazatrideca-1,(*E*)-6-dien-11-yne)nickel(0) (($C_{25}H_{30}N_2O_4S_2$)Ni·$^1/_4$THF, 5). The 4,9-diaza-trideca-1,*trans*-6-dien-11-yne **2** (253 mg, 0.52 mmol) was dissolved in 10 mL of THF by gentle heating. After it was recooled to ambient temperature, the solution was briefly stirred with $Ni(cod)_2$ (138 mg, 0.50 mmol) to obtain (via red) a clear amber solution. When the solution was left untouched for several days, the color faded over several hours and eventually yellow cubes slowly crystallized. (Crystallization appears to occur spontaneously and may be accelerated by seeding in a subsequent preparation.) Crystallization was completed by cooling in a refrigerator (−7 °C). After removal of the mother liquor the product was washed with cold THF and dried under vacuum at 0 °C: yield 280 mg (50%). For NMR data, see Table 2. Anal. Calcd for $C_{25}H_{30}N_2NiO_4S_2\cdot{}^1/_4C_4H_8O$ (563.4): C, 55.43; H, 5.73; N, 4.97; Ni, 10.42; O, 12.07; S, 11.38. Found: C, 54.60; H, 5.74; N, 4.79; Ni, 10.11; S, 11.12.

(4,9-Bis(4-tolylsulfonyl)-4,9-diazatrideca-1,(*E*)-6-dien-11-yne)dinickel(0) 1,5-Cyclooctadiene (($C_{25}H_{30}N_2O_4S_2$)-Ni_2(cod)·THF, 6). The reaction was carried out as for **5** by stirring a solution of **2** (243 mg, 0.50 mmol) in 15 mL of THF with $Ni(cod)_2$ (280 mg, 1.02 mmol) in slight excess at ambient temperature until all $Ni(cod)_2$ was dissolved (1 min). Henceforth the orange-red solution was left untouched for $^1/_2$ day, avoiding precipitation of the intermediately formed **5**. After this time the solution was cooled to −20 °C, where usually a yellow precipitate of **6** was formed. The precipitate was redissolved by brief warming to 30−40 °C and addition of just as much THF to allow for a saturated solution (the total volume was about 25 mL). The solution was then recooled to −20 °C for some days and eventually to −40 °C. This way **6** crystallized either in the form of snowball-type clusters of felted fine yellow needles or large orange spherulites; the typical yield was 200 mg (51%). The spherulites were used for the X-ray structure analysis. For NMR data, see Table 2. Anal. Calcd for $C_{33}H_{42}N_2Ni_2O_4S_2\cdot C_4H_8O$ (784.3): C, 56.66; H, 6.43; N, 3.57; Ni, 14.97; O, 10.20; S, 8.18. Found: C, 56.37; H, 6.46; N, 3.68; Ni, 15.21; S, 8.27.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files for complexes **3**−**6**, synthesis protocol for **2**, NMR spectra of complexes **1**, **2**, **3**, **5**, and **6**, and a table of X-ray crystallographic data for **3**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org. Supplementary crystallographic data (**3**−**6**: CCDC 896849−896852) can also be obtained free of charge via http://www.ccdc.cam.ac.uk/deposit.

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Notes

The authors declare no competing financial interest.

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