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4,9-Diazadodeca-1,*trans*-6,11-trienes as Ligands for Nickel(0), Palladium(0), and Platinum(0)

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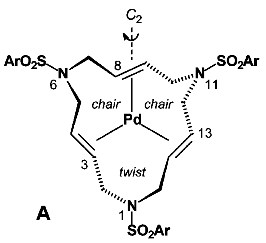
A series of tris-ene trigonal-planar nickel(0), palladium(0), and platinum(0) complexes M(η^2,η^2,η^2-$C_{10}H_{16}N_2Me_2$) (M = Ni−Pt (**2a**−**4a**)) and M(η^2,η^2,η^2-$C_{10}H_{16}N_2(C_3H_5)_2$) (M = Ni−Pt (**2b**−**4b**)) have been prepared using the open-chain aminoalkenes *N*,*N′*-dimethyl-4,9-diazadodeca-1,*trans*-6,11-triene (1,4-bis(allylmethylamino)-*trans*-2-butene, **1a**) and *N*,*N′*-diallyl-4,9-diazadodeca-1,*trans*-6,11-triene (1,4-bis(diallylamino)-*trans*-2-butene, **1b**). The ligands comprise a central diamino-*trans*-2-butene moiety with terminal *N*-allyl groups, so that the C═C groups are positioned in a repetitive 1,6-sequence. This confers useful properties on the metal complexes. The molecular structure of **2b** has been determined by X-ray crystallography.

Introduction

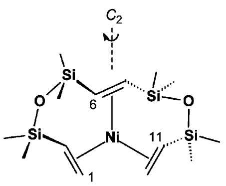
In 1960 Wilke reported the synthesis of trigonal-planar Ni(t,t,t-cdt) (t,t,t-cdt = *trans*,*trans*,*trans*-1,5,9-cyclododecatriene) and tetrahedral Ni(cod)$_2$ (cod = *cis*,*cis*-1,5-cyclooctadiene) as the first homoleptic transition metal(0)−alkene complexes.[1] These thermally quite stable complexes were termed "naked nickel"[1b] because of the ready displacement of the alkene ligands during the course of stoichiometric and catalytic reactions. A series of trigonal-planar derivatives such as the isomeric Ni(c,c,c-cdt) (c,c,c-cdt = *cis*,*cis*,*cis*-1,5,9-cyclododecatriene),[2] tris(*trans*-cyclooctene)nickel(0),[2a] tris(bicyclo[2.2.1]heptene)nickel(0),[3a] and the parent tris(ethene)nickel(0)[3b] also soon became available. In addition, the palladium(0) and platinum(0) homologues M(cod)$_2$, M(C_2H_4)$_3$, and M(C_7H_{10})$_3$ (M = Pd, Pt) have been reported by other groups.[4] While the platinum complexes have a similar stability to the nickel compounds and Pt(cod)$_2$ represents a useful source for platium(0), the palladium derivatives are less stable and not suited for preparative purposes. The Pd and Pt complexes M(t,t,t-cdt) and M(c,c,c-cdt) are not known to date. A common aspect of cod and t,t,t/c,c,c-cdt is that the C═C bonds are in 1,5-sequence.

In 1978 it was observed that the cycloolefins in Ni(t,t,t-cdt) and Ni(cod)$_2$ are displaced by acyclic 4,9-diazadodeca-1,*trans*-6,11-trienes,[5a] containing three C═C bonds in a repetitive 1,6-sequence. This finding was left unconsidered until we launched a systematic exploration of the coordination properties of simple acyclic 1,6-dienes, such as the parent 1,6-heptadiene, diallyl ether (dae), diallylamines, and others at Ni(0), Pd(0), and Pt(0), affording dinuclear trigonal-planar complexes M(0)$_2$(1,6-diene)$_3$ (M = Ni, Pd, Pt) with both metal atoms coordinated by a chelating and a bridging 1,6-diene ligand.[5b,c] The palladium compounds are of substantial interest, since they currently represent the best sources of "naked palladium". A major insight arising from these studies was that a chelating M(0)−1,6-diene coordination is much more stable than a chelating M(0)−1,5-diene coordination and that di- or polyenes with a (repetitive) 1,6-diene sequence strongly favor the formation of trigonal-planar M(0) complexes (M = Ni, Pd, Pt) for conformational reasons.[6]

Recently, (the late) Moreno-Mañas, Roglans, and co-workers have shown that *N*-SO$_2$Ar-substituted 1,6,11-triazacyclopentadeca-all-*trans*-3,8,13-trienes, comprising a 3-fold 1,6-diene sequence in the cycle, form extraordinarily stable Pd(0) complexes **A**, which decompose only above 250 °C.[7] This result, which is in sharp contrast to the so far inaccessible (t,t,t/c,c,c-cdt)Pd with a 1,5-diene sequence, can be rationalized in terms of the macrocyclic effect.[8] Although the three C═C bonds in **A** assume a propeller-like arrangement, the spectroscopic symmetry of the complexes is C_2 because of the conformations of the six-membered chelate rings.



A



B

We now report on volatile and not so stable complexes of the closely related open-chain *N*-Me and *N*-allyl-substituted 4,9-diazadodeca-1,*trans*-6,11-trienes **1a**,**b** with Ni(0), Pd(0), and Pt(0).[5a,d]

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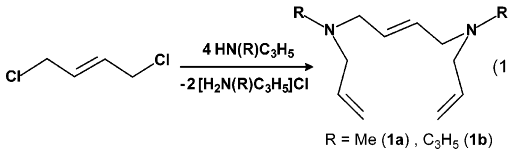
Results and Discussion

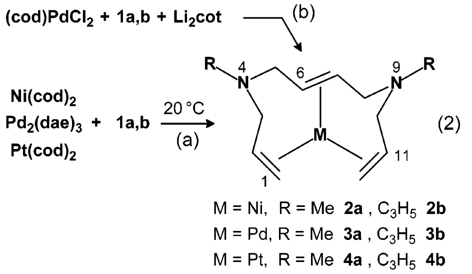
N,*N*′-Dimethyl-4,9-diazadodeca-1,*trans*-6,11-triene (1,4-bis(allylmethylamino)-*trans*-2-butene; new, **1a**) and *N*,*N*′-diallyl-4,9-diazadodeca-1,*trans*-6,11-triene (1,4-bis(diallylamino)-*trans*-2-butene; known, **1b**) were prepared in a procedure reported first by Morey.[9] Heating 1,4-dichloro-*trans*-2-butene with an excess of allylmethylamine or diallylamine in benzene results in nucleophilic substitution of chloride and generation of the tertiary ammonium salt, which becomes deprotonated by the excess secondary amine. After removal of the ammonium salt simple vacuum distillation affords the tertiary aminoalkenes **1a**,**b** in yields of ≥50% in pure form (≥98%). The two ligands comprise a central *trans*-substituted C═C bond and two (**1a**) or four (**1b**) terminal *N*-allyl groups, with all contiguous C═C bonds in a 1,6-sequence (eq 1). Thus, the essential skeleton of the cyclic **A** is retained, with the distinction that **1a**,**b** are acyclic and that they contain inconspicuous substituents at nitrogen.



(1)

In the IR spectra of **1a**,**b** ν(C═C) of the *trans*-disubstituted C═C bonds is silent, but in the Raman spectra it represents a prominent band at 1675 cm^{-1}. The bending vibration δ(HC═) at 978 cm^{-1} (IR) also appears characteristic for the *trans*-disubstituted C═C bond in **1a**,**b**. The terminal C═C bonds give rise to strong IR and RA bands ν(C═C) at 1643 cm^{-1}. The NMR data of **1a**,**b** are quoted in Table 1.

When suspensions of yellow Ni(cod)$_2$, pale yellow Pd$_2$(dae)$_3$·dae,[6c] and colorless Pt(cod)$_2$[4c] in diethyl ether are treated with 1 equiv of **1a**,**b** at ambient temperature, the starting complexes dissolve, and upon cooling the colorless crystalline **2**−**4** separate. The *N*-Me complexes **2a**−**4a** form fibrous dendrimeric solids, so far unsuited for single-crystal structure determinations,[10] whereas the needles of the *N*-bis(allyl) derivatives **2b**−**4b** are more compact. The reactions according to eq 2a occur quantitatively, and the yields given in the Experimental Part refer to the carefully crystallized products.



(2)

Complexes **3a**,**b** are most easily obtained by reaction of (cod)PdCl$_2$ with Li$_2$cot (cot = cyclooctatetraene) in the presence of **1a**,**b** (eq 2b). Besides **A** with a cyclic ligand, complexes **2**−**4** are also related to Ni(0)[*trans*-C$_2$H$_2${Si(Me)$_2$OSi(Me)$_2$(C$_2$H$_3$)}$_2$] (**B**), having an acyclic vinylsiloxane-based 1,*trans*-6,11-triene ligand and formed in only 5% yield by metal-vapor synthesis.[11]

The Ni and Pd complexes dissolve readily in the usual solvents, including diethyl ether, pentane, and benzene, with the Pt complexes being less soluble. Consistent with the nobler character of Pd and Pt, the Ni complexes **2** are exceedingly air sensitive, whereas the Pd and Pt homologues **3** and **4** are stable in air for at least a couple of days both as a solid and in solution. When the solid Ni complexes are heated in the DSC (differential scanning calorimetry), they show broad melting ranges between 50 and 90 °C (**2a**) and 30 and 60 °C (**2b**), attributed to unspecified phase transitions prior to melting. In contrast, **3a** (mp 100 °C), **3b** (mp 73 °C), **4a** (mp 112 °C), and **4b** (mp 77 °C) display sharp melting points without additional noteworthy features (DSC). Thus, for all three metals the melting points of the *N*-Me complexes **2a**−**4a** are about 30 °C higher than those of the *N*-C$_3$H$_5$ derivatives **2b**−**4b**, and the former appear thermally somewhat more stable (**2a**, dec >160 °C; **3a**, >140 °C, **4a**, >200 °C) than the latter (**2b**, dec >160 °C; **3b**, >130 °C; **4b**, >150 °C). At the same time the *N*-Me complexes **2a**−**4a** sublime under vacuum at a lower temperature (≥50 °C) than the *N*-C$_3$H$_5$ derivatives **2b**−**4b** (≥75 °C).

In the EI mass spectra of **2** and **4a** the molecular ion represents the base ion, and the molecular ion is also prominent for the other complexes (39−65%). In the RA and IR spectra the bands of the free ligand at 1675 and 1643 cm^{-1} have vanished for **2a** and **4a** and various new RA bands appear in the range 1520−1465 cm^{-1} (**2a**), which are attributed to the coordinated C═C bonds. The Pd complexes **3** display a strong IR band at 1517 cm^{-1} for the coordinated terminal C═C bonds. Furthermore, complexes **2** show a sharp and strong RA absorption at 385 cm^{-1} (no Raman spectra have been recorded for **3** and **4**).

The ^{1}H and ^{13}C NMR spectra of **2**−**4** (Table 1; the ^{13}C NMR spectrum of **2b** is depicted in ref 2d, Figure 4) are in agreement with C_2 symmetry of the complexes, with the C_2 axis passing through the metal atom and the midpoint of the *trans*-disubstituted C═C bond. The disubstituted C═C bond and one terminal allyl group at each N atom, standing in a 1,6-sequence to each other, chelate the M(0), so that the two chelate rings each assume a chair-like conformation. Because of their axial or equatorial orientations, the geminal NCH$_a$H$_b$ protons at positions 3 and 5 are inequivalent, and we assume that it is the

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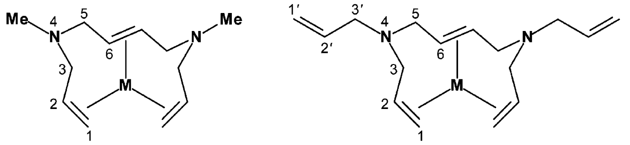
Table 1. ^{1}H and ^{13}C NMR Data of M(η^2,η^2,η^2-$C_{10}H_{16}N_2Me_2$) (M = Ni−Pt (2a−4a)), M(η^2,η^2,η^2-$C_{10}H_{16}N_2(C_3H_5)_2$) (M = Ni−Pt (2b−4b)), and the Free Ligands 1a,b[a] [15]



M = Ni **2a** , Pd **3a** , Pt **4a**

M = Ni **2b** , Pd **3b** , Pt **4b**

	δ(H)						δ(C)								
	1	2	3	5	6	Me	1	Δδ(C1)	2	Δδ(C2)	3	5	6	Δδ(C6)	Me
1a	5.14, 5.09	5.83	2.95	2.95	5.60	2.14	117.1		136.4		60.7	59.6	131.1		42.1
1b	5.09, 5.03	5.83	3.01	3.01	5.58		116.8		135.4		56.0	54.7	130.1		
2a[b]	3.07, 2.79	3.67	3.60, 0.90	3.58, 0.93	3.49	2.23	53.9	−63.2	75.5	−60.9	61.1	60.1	72.0	−59.1	44.6
2b[c]	3.09, 2.78	3.68	3.70, 1.03	3.70, 1.03	3.45		53.7	−63.1	74.5	−60.9	58.3	57.4	70.9	−59.2	
3a	3.44, 3.04	4.14	3.53, 1.22	3.54, 1.25	3.98	2.32	54.7	−62.4	82.5	−53.9	60.0	59.3	78.8	−52.3	45.3
3b[d]	3.42, 3.02	4.12	3.63, 1.31	3.62, 1.35	3.95		54.6	−62.2	82.2	−53.2	57.7	57.0	78.5	−51.6	
4a	3.18, 2.57	3.60	3.51, 0.92	3.58, 1.01	3.52	2.31	40.1	−77.0	66.6	−69.8	59.3	58.7	67.7	−63.4	45.5
4b[e]	3.17, 2.55	3.56	3.61, 1.02	3.63, 1.10	3.50		39.5	−77.3	65.7	−69.7	56.7	56.0	66.9	−63.2	

[a] Temperature 25 °C. Solvent CD_2Cl_2. [b] Solvent THF-d_8. [c] δ(H) 5.15, 5.10 (1′), 5.95 (2′), 3.04 (3′); δ(C) 117.0 (1′), 136.6 (2′), 60.4 (3′). [d] δ(H) 5.17, 5.11 (1′), 5.93 (2′), 3.11 (3′); δ(C) 117.1 (1′), 136.6 (2′), 60.9 (3′). [e] δ(H) 5.17, 5.11 (1′), 5.95 (2′), 3.11 (3′); δ(C) 117.2 (1′), 136.5 (2′), 60.8 (3′).

axial protons that are shifted to higher field by about 2 ppm and the equatorial protons that are shifted to lower field by up to 0.75 ppm. The magnitude of the underlying anisotropic effect of the metal center appears to be independent of the respective metal Ni, Pd, or Pt. The conformational aspects are similar to those discussed for M(0)−1,6-diene complexes.[6c] Possible exchange of the coordinated and uncoordinated allyl groups in **2b** and **3b** is slow on the NMR time scale.

Of particular interest is a comparison of the ^{13}C NMR coordination chemical shifts Δδ(C)[2d] of the three different types of olefinic carbon atoms with Δδ(C) of the ethene ligands in the homoleptic $Ni(C_2H_4)_3$ (−65.5), $Pd(C_2H_4)_3$ (−59.7), and $Pt(C_2H_4)_3$ (−74.8),[2d] which may be considered as benchmarks for optimal orbital overlap. For all complexes **2**−**4** Δδ(C) is smallest (referring to the absolute numbers) for C6 of the central C═C bond, and it increases on going to the outer olefinic carbon atoms C2 and C1 in this series (Table 1). There is generally a good agreement between the **a** and **b** complexes for a given metal. For the Ni complexes **2** Δδ(C6) falls only a little short of its benchmark (e.g., for **2a**, −59.1 vs −65.5, corresponding to −10%), and it comes even closer to it for C2 and C1, so that the coordination of the various C═C bonds appears quite uniform and close to what may be thought of as the optimal situation in $Ni(C_2H_4)_3$. For the Pd complexes **3** and the Pt complexes **4** the Δδ(C) shortfall for C6 from the benchmarks is more pronounced (**3**, −13%, and **4**, −15%). At the same time there is a stronger increase of Δδ(C) for the vinyl carbon atoms C2 and C1, so that for both **3** and **4** Δδ(C1) even exceeds the benchmark values. In agreement herewith, for the Pt complexes **4** the coupling J(PtC1) = 154 Hz is stronger than J(PtC2) ≈ 120 Hz, while J(PtC6) is poorly developed. We conclude from these data that the 4,9-diazadodeca-1,6,11-trienes are the best fitting ligands for *TP*-3 Ni(0) and less so for the larger Pd(0) and Pt(0) and that for the latter metals the orbital overlap is least for the central C6 and best for the terminal vinyl carbon atoms C1.

Table 2. Crystal Data for 2b

empirical formula	$C_{16}H_{26}N_2Ni$
color	colorless
fw (g mol^{-1})	305.10
temp (K)	100
wavelength (Å)	0.710 73
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
unit cell dimens	
a (Å)	13.2497(3)
b (Å)	4.75470(1)
c (Å)	25.7761(5)
α (deg)	90.0
β (deg)	104.6360(1)
γ (deg)	90.0
V (Å^3)	1571.16(6)
Z	4
V/*Z* (Å^3)	392.8
calcd density (Mg·m^{-3})	1.290
abs coeff (mm^{-1})	1.224
F(000)	656
cryst size (mm^3)	0.18 × 0.08 × 0.02
θ range for data collecn (deg)	3.18−33.17
index ranges	$-20 \le h \le 20$ $-7 \le k \le 7$ $-39 \le l \le 39$
no. of rflns collected	38 040
no. of indep rflns	6000 (R_{int} = 0.0462)
no. of rflns with $I > 2\sigma(I)$	5027
completeness (%)	99.8 (θ = 33.17°)
abs corr	Gaussian
max./min. transmn	0.98/0.83
full-matrix least-squares	F^2
no. of data/restraints/params	6000/0/172
goodness of fit on F^2	1.037
final *R* indices ($I > 2\sigma(I)$)	
R1	0.0290
wR2	0.0708
R indices (all data)	
R1	0.0388
wR2	0.0755
largest diff peak/hole (e Å^{-3})	0.398/−0.502

Single crystals of **2b** were obtained from diethyl ether, and the molecular structure has been determined by X-ray crystallography (Table 2) and is shown in Figure 1. A schematic diagram of the structure is depicted in Figure 2. The compound crystallizes in the monoclinic space group $P2_1/n$ in parallel stacks of molecules.[12] Within the stacks the coordination planes of the Ni atoms are tilted toward the direction of the stacks by 32°, with a distance between the coordination planes of 4.02 Å and a Ni···Ni separation of 4.755 Å. The Ni atoms are coordinated by three C═C bonds of a 4,9-diazadodeca-1,6,11-triene skeleton, leaving the other two *N*-allyl groups uncoordinated. The conformation of the ligand is such that the two Ni−1,6-diene chelate rings each assume chair-like geometry, and due to the *trans*-disubstitution of the central C═C bond shared by the two chelates, the two halves of the complex are related by C_2 symmetry. Within the two chelates the midpoint D2 of the central C═C bond and the midpoints of the terminal C═C groups, D1 or D3, subtend angles of 118.4° and 118.9° at the

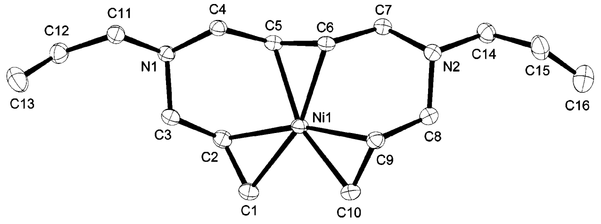


Figure 1. Molecular structure of Ni(η^2,η^2,η^2-$C_{10}H_{16}N_2(C_3H_5)_2$) (**2b**) (atomic displacement ellipsoids shown at the 50% probability level). Selected bond distances (Å): C1−C2 = 1.393(2), C5−C6 = 1.395(2), C9−C10 = 1.389(2), C12−C13 = 1.318(2), C15−C16 = 1.318(2), Ni1−C1 = 2.015(1), Ni1−C2 = 2.044(1), Ni1−C5 = 2.036(1), Ni1−C6 = 2.036(1), Ni1−C9 = 2.050(1), Ni1−C10 = 2.017(1).

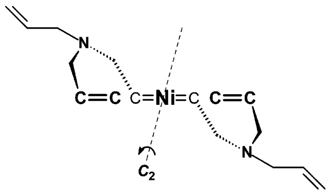


Figure 2. Schematic diagram of **2b**, viewed along the C_2 axis of the molecule (perpendicular to the plane of the paper), showing the relationship of the two six-membered heterocyclic rings to one another.

Ni atom, while an only slightly larger D1−Ni−D3 angle of 122.7° is observed in the "open" part of the molecule. The three C═C bonds lie exactly in the *TP*-3 Ni(0) coordination plane (deviation of C atoms from the mean plane ± 0.02 Å), consistent with optimum back-bonding from the Ni atom. The chair-like geometry of the Ni−1,6-diene chelate[13] ensures little conformational strain, so the chelate effect has maximum efficacy. The three coordinated C═C bonds are of about the same length (1.393 Å, mean) and, expectedly, longer than the two uncoordinated C═C bonds (1.318 Å). For the central C═C bond (C5, C6) the Ni−C bond lengths are at 2.036 Å (mean), while for the coordinated terminal C═C bonds the Ni−C bond lengths to the inner C atoms (C2, C9) at 2.047 Å are slightly longer and those to the outer C atoms (C1, C10) at 2.016 Å are shortest of all, indicating bonding preference of the Ni atom to the terminal C atoms.

Thus, it has emerged from this and other studies that acyclic and cyclic diene and triene ligands with (repetitive) 1,6-diene sequences are more suitable for coordination at *TP*-3 M(0) (M = Ni, Pd, Pt) than similar ligands with a 1,5-diene sequence. It must be conceded that the Wilke reagents Ni(cod)$_2$ and Ni(t,t,t-cdt) are the Ni(0) complexes of first choice for stoichiometric and catalytic reactions because of their ready accessibility, thermal stability, and at the same time high reactivity ("naked nickel"), and similarly Pt(cod)$_2$ for Pt(0). For Ni(0) and Pt(0) the acyclic 1,6,11-triene ligands impart exceedingly high stability and consequently low reactivity to the complexes (**2** and **4**), and this can be expected to be even more so for cyclic 1,6,11-triene ligands, making them unsuitable for such purposes.

In contrast, currently the best sources for "naked palladium" Pd_2(1,6-diene)$_3$ (1,6-diene = 1,6-heptadiene and diallyl ether) are both thermally only modestly stable, whereas **A** with the 1,6,11-cyclotriene is extraordinarily stable, so that there still appears to be a need for a Pd(0)−alkene complex[14] of easy accessibility, sufficient thermal stability, and still high reactivity as a correspondent to the Wilke complexes. We suggest that this gap can be filled by the acyclic 1,6,11-triene derivatives **3**. In view of the high thermal stability and simultaneously high volatility, complexes **2**−**4** appear as viable compounds for metal transport, purification, and vapor deposition techniques.

Experimental Part

All manipulations were carried out under argon with Schlenk-type glassware. Solvents were dried prior to use by distillation from $NaAlEt_4$. Ni(cod)$_2$,[1c] (cod)$PdCl_2$,[16] $Pd_2(C_6H_{10}O)_3 \cdot C_6H_{10}O$,[6c] and Pt(cod)$_2$[4c] were prepared as published. Microanalyses were performed by the local Mikroanalytisches Labor Kolbe. EI mass spectra were recorded at 70 eV and refer to ^{58}Ni, ^{106}Pd, and ^{195}Pt. ^{1}H NMR spectra were measured at 300 MHz and ^{13}C NMR spectra at 75.5 MHz (both relative to TMS) on Bruker AMX-300 and DPX-300 instruments. The NMR data of all products are listed in Table 1.

N**,*****N*****′-Dimethyl-4,9-diazadodeca-1,*****trans*****-6,11-triene (1a).** A solution of 1,4-dichloro-*trans*-2-butene (12.5 g, 100 mmol) and an excess of allylmethylamine (40 g, 562 mmol) in 100 mL of benzene turned orange when refluxed for 17 h. Upon cooling, the corresponding ammonium chloride deposited and was removed by filtration. Vacuum distillation of the organic phase gave a colorless liquid: yield 9.71 g (50%); bp 44−46 °C at 0.001 mmHg; *d* = 0.8332 g mL^{-1}. $C_{12}H_{22}N_2$ (194.3). The aminoalkene was finally dried by distillation from $LiAlH_4$.

N**,*****N*****′-Diallyl-4,9-diazadodeca-1,*****trans*****-6,11-triene (1b).**[9] Synthesis was analogous to that of **1a** by refluxing a benzene solution of 1,4-dichloro-*trans*-2-butene (12.5 g, 100 mmol) and diallylamine (55 g, 566 mmol): yield 17.2 g (70%); bp 80 °C at 0.001 mmHg. $C_{16}H_{26}N_2$ (246.4).

Ni(η^2,η^2,η^2-$C_{10}H_{16}N_2Me_2$) (2a). A suspension of Ni(cod)$_2$ (550 mg, 2.00 mmol) in 20 mL of diethyl ether was stirred with **1a** (388 mg, 2.00 mmol) at ambient temperature. The resulting light yellow solution was filtered to remove some insoluble impurities. Cooling the solution to −25 °C afforded colorless microneedles, which were freed from the mother liquor, washed with cold ether, and dried under vacuum: yield 360 mg (71%). EI-MS (70 °C): *m*/*e* (%) 252 ([M]$^+$, 100). $C_{12}H_{22}N_2Ni$ (253.0).

Ni(η^2,η^2,η^2-$C_{10}H_{16}N_2(C_3H_5)_2$) (2b). A suspension of Ni(cod)$_2$ (2.75 g, 10.0 mmol) in 30 mL of diethyl ether was stirred with **1b** (2.46 g, 10.0 mmol) at ambient temperature. The resulting light yellow solution was filtered to remove some insoluble impurities. Cooling the solution to −78 °C afforded colorless crystals, which

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[12] In 1976 the structure of a second crystal modification of compound **2b** was determined in these laboratories (*P*2$_1$/*a* (No. 14), *a* = 14.6784(3) Å, *b* = 9.1641(3) Å, *c* = 11.9046(6) Å, *β* = 82.230(4)°, *V* = 1586.64(1) Å^3, R1 = 0.061, wR2 = 0.083). The molecules pack differently (no longer parallel stacks, Ni···Ni 5.235 Å) and adopt a slightly different conformation of the terminal allyl groups. This polymorph was obtained under apparently similar conditions, but could not be reproduced now. For disappearing polymorphs, see: Dunitz, J. D.; Bernstein, J. *Acc. Chem. Res.* **1995**, *28*, 193.

[13] For structures of L−Ni(1,6-diene) complexes, see: (a) Proft, B.; Pörschke, K.-R.; Lutz, F.; Krüger, C. *Chem. Ber.* **1991**, *124*, 2667. (b) Rosenthal, U.; Pulst, S.; Kempe, R.; Pörschke, K.-R.; Goddard, R.; Proft, B. *Tetrahedron* **1998**, *54*, 1277.

[14] In Pd_2(dba)$_3$ (dba = dibenzylideneacetone),[14a−c] which is frequently used as a source for Pd(0), complete displacement of all three dba ligands occurs only reluctantly.[14c] (a) Takahashi, Y.; Ito, T.; Sakai, S.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1970**, 1065. (b) Mazza, M. C.; Pierpont, C. G. *Inorg. Chem.* **1973**, *12*, 2955. (c) Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253.

[15] The assignment of the resonances is exemplified for **3a**: The low-field 16-line multiplet at δ(H) 4.14 is attributed to H2 of the terminal *N*-allyl groups; in the 2D COSY NMR spectrum this signal shows cross-peaks with H1a,b (δ(H) 3.44 and 3.04, each representing a doublet (d) that is further split by a 1.1 Hz geminal coupling) and H3a,b (δ(H) 3.53 (br d, *J*(HH) = 13.4 Hz) and 1.22 (dd, *J*(HH) = 13.4 and 10.6 Hz)). A further low-field higher-order multiplet at δ(H) 3.98 is attributed to H6 of the internal CH═CH group; this signal shows cross-peaks with H5a,b (δ(H) 3.54 (d, *J*(HH) = 13.4 Hz) and 1.25 (multiplet)). Allocation of the ^{13}C resonances is supported by ^{13}C,^{1}H-correlated spectroscopy.

[16] Chatt, J.; Vallarino, L. M.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 3413.

were washed with cold pentane and dried under vacuum: yield 2.47 g (81%). EI-MS (60 °C): *m*/*e* (%) 304 ($[M]^+$, 100). Anal. Calcd for $C_{16}H_{26}N_2Ni$ (305.1): C, 62.99; H, 8.59; N, 9.18; Ni, 19.24. Found: C, 62.78; H, 9.16; Ni, 19.12.

Pd(η^2,η^2,η^2-$C_{10}H_{16}N_2Me_2$) (3a). Route a. To a suspension of $Pd_2(C_6H_{10}O)_3 \cdot C_6H_{10}O$ (303 mg, 0.50 mmol) in 10 mL of diethyl ether was added **1a** (97 mg, 0.50 mmol) at −30 °C. When the mixture was warmed to ambient temperature a light yellow solution was obtained, from which colorless dendrimeric needles separated below −25 °C: yield 117 mg (78%).

Route b. A suspension of (cod)$PdCl_2$ (286 mg, 1.00 mmol) in 5 mL of diethyl ether was combined with **1a** (194 mg, 1.00 mmol) and 3.8 mL of a 0.27 M diethyl ether solution of Li_2cot (1.00 mmol) at −78 °C. The stirred mixture was warmed to ambient temperature, and the precipitated LiCl was removed by filtration. Cooling the solution to −25 °C afforded colorless dendrimeric needles, which were washed with cold ether and dried under vacuum: yield 237 mg (79%). EI-MS (65 °C): *m*/*e* (%) 300 ($[M]^+$, 65). Anal. Calcd for $C_{12}H_{22}N_2Pd$ (300.7): C, 47.93; H, 7.37; N, 9.31; Pd, 35.39. Found: C, 48.06; H, 7.35; Pd, 35.22.

Pd(η^2,η^2,η^2-$C_{10}H_{16}N_2(C_3H_5)_2$) (3b). Synthesis was as for **3a**, route b, but reacting (cod)$PdCl_2$ (857 mg, 3.00 mmol) and **1b** (739 mg, 3.00 mmol) in 10 mL of diethyl ether with 11.4 mL of a 0.28 M diethyl ether solution of Li_2cot (3.00 mmol); colorless needles: yield 980 mg (89%). EI-MS (75 °C): *m*/*e* (%) 352 ($[M]^+$, 57). Anal. Calcd for $C_{16}H_{26}N_2Pd$ (352.8): C, 54.47; H, 7.43; N, 7.94; Pd, 30.16. Found: C, 54.95; H, 7.65; Pd, 28.85.

Pt(η^2,η^2,η^2-$C_{10}H_{16}N_2Me_2$) (4a). To a suspension of $Pt(cod)_2$ (411 mg, 1.00 mmol) in 20 mL of pentane was added **1a** (194 mg, 1.00 mmol) at ambient temperature. The mixture was stirred for about 1 h, whereupon all $Pt(cod)_2$ dissolved and some product already precipitated. The latter was dissolved again by addition of about 2 mL of diethyl ether. Cooling the solution to −25 °C afforded colorless dendrimeric crystals, which were separated from the mother liquor, washed with cold pentane, and dried under vacuum: yield 195 mg (50%). EI-MS (60 °C): *m*/*e* (%) 389 ($[M]^+$, 100). Anal. Calcd for $C_{12}H_{22}N_2Pt$ (389.4): C, 37.01; H, 5.69; N, 7.19; Pt, 50.10. Found: C, 37.14; H, 5.43; Pt, 50.14.

Pt(η^2,η^2,η^2-$C_{10}H_{16}N_2(C_3H_5)_2$) (4b). Synthesis was as for **4a** by reacting a solution of $Pt(cod)_2$ (411 mg, 1.00 mmol) in 5 mL of THF with **1b** (246 mg, 1.00 mmol) at 20 °C to afford colorless needles: yield 210 mg (48%). EI-MS (105 °C): *m*/*e* (%) 441 ($[M]^+$, 39). Anal. Calcd for $C_{16}H_{26}N_2Pt$ (441.5): C, 43.53; H, 5.94; N, 6.35; Pt, 44.19. Found: C, 43.83; H, 6.03; Pt, 44.19.

Acknowledgment. We thank Dr. Richard Mynott for the NMR spectra of **2** and Dr. Klaus Seevogel for the Raman spectra.

Supporting Information Available: CIF containing X-ray crystallographic data for **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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