Formation and Structure of Stable, Isolable Conjugated Primary Enamines

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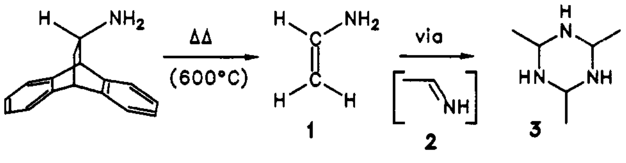
(Butadiene)zirconocene (**4**) was reacted with 2 mol equiv of pivalonitrile to give the nine-membered metallacyclic product **5**. 1,4-Selective coupling of butadiene with the two nitrile functionalities was achieved at the zirconocene template. Subsequent hydrolytic cleavage (H_2O/THF) gave (3*Z*,5*E*,7*Z*)-3,8-diamino-2,2,9,9-tetramethyldeca-3,5,7-triene (**13**). The stable conjugated primary enamine **13** was isolated in 54% yield. It was characterized by an X-ray crystal structure analysis. Compound **13** crystallizes in space group *Pbca* with cell parameters a = 6.343(1), b = 23.471(3), c = 10.025(1) Å, Z = 4, R = 0.052, R_w = 0.059. Analogously, coupling of two 4-methylbenzonitrile molecules with butadiene at the zirconocene template followed by hydrolysis yielded 1,6-diamino-1,6-di-*p*-tolyl-1,3,5-hexatriene (**6b**). Compound **6b** crystallizes in space group $P2_1/a$ with cell parameters a = 12.778(8), b = 4.722(1), c = 14.203(5) Å, β = 110.6(1)°, Z = 2, R = 0.043, R_w = 0.049. Both primary enamines contain planar conjugated polyene frameworks with alternating carbon–carbon double and single bonds. The geometries at the sp^2-CNH_2 groups of the stable conjugated primary enamines **6b** and **13** are very similar as observed in aromatic amines. It was shown by ab initio calculation of suitable model systems on the MP2/6-31+G*//6-31+G* level that the conjugated tail-to-tail connection of two $CH{=}C(NH_2)H$ primary enamine moieties results in an unfavorable repulsive electron interaction which may become effectively compensated when the conjugated system separating the NH_2 substituents is sufficiently extended as is the case in the frameworks found in **6** or **13**. Therefore, some development of the chemistry of stable, isolable primary enamines may be based on suitably substituted 1,6-diamino-1,3,5-hexatriene systems which will be easily available by our novel template synthesis.

Tertiary enamines are very important building blocks in organic synthesis.[1] They can easily be prepared starting from most ketones or aldehydes by using variants of the general carbonyl to enamine conversion procedures that were systematically introduced to the chemical literature by the pioneering work of Mannich et al.[2] Much less detailed structural and chemical knowledge is available about secondary and especially about primary enamines, although the latter had been formulated as reactive intermediates as far back as in the year 1914.[3] It is the rapid tautomerization with their ket- or aldimine isomers that makes primary (as well as secondary) enamines so hard to handle and so difficult to isolate and structurally characterize. Not earlier than 1980 was the simple primary enamine aminoethene (**1**) generated (by flash thermolysis) and characterized spectroscopically at low temperatures.[4] However, **1** has only a fleeting existence: upon increasing the temperature from −80 °C it rapidly and irreversibly cyclotrimerizes (to **3**) via its acetaldehyde imine tautomer **2**.[5]



^{13}C NMR (-80°C): δ 139.1(C^{α}), 84.3(C^{β})

Most of what is known today about primary enamines and the equilibration with their imine tautomers is due

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† Theoretical study.

‡ X-ray crystal structure analyses.

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[1] Stork, G.; Terrell, R.; Szmuszkovic, J. *J. Am. Chem. Soc.* **1954**, *76*, 2029.

[2] Mannich, C.; Davidsen, H. *Chem. Ber.* **1936**, *69*, 2106. Review: Pitacco, G.; Valentin, E. In *The chemistry of amino, nitroso and nitro compounds and their derivatives*. (*The chemistry of functional groups*, suppl. F); Patai, S., Ed.; Wiley: New York, 1982.

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[4] Ripoll, J. L.; Lebrun, H.; Thuillier, A. *Tetrahedron* **1980**, *36*, 2497.

[5] Pickard, P. L.; Vaughan, D. J. *J. Am. Chem. Soc.* **1950**, *72*, 876. Pickard, P. L.; Polly, G. W. *J. Am. Chem. Soc.* **1954**, *76*, 5169. Clark, R. A.; Parker, D. C. *J. Am. Chem. Soc.* **1970**, *92*, 7257. Shin, C.; Masaki, M.; Onta, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1657. Ollinger, P.; Remp, W.; Junek, H. *Monatsh. Chem.* **1974**, *105*, 346. Pfau, M.; Ribiere, C. *Bull Soc. Chim. Fr.* **1971**, 2584. Brocas, J.-M.; de Jeso, B.; Pommier, J.-C. *J. Organomet. Chem.* **1976**, *120*, 217. de Jeso, B.; Pommier, J.-C. *J. Chem. Soc., Chem. Commun.* **1977**, 565. Ohtsuka, Y. *J. Org. Chem.* **1978**, *43*, 3231. Compagnon, P. L.; Gasquez, F.; Kimny, T. *Synthesis* **1986**, 948. Sevin, A.; Masure, D.; Giessner-Prettre, C.; Pfau, M. *Helv. Chim. Acta* **1990**, *73*, 552. Walsh, P. J.; Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 1708. Calculation: Smith, B. J.; Radom, L. *J. Am. Chem. Soc.* **1992**, *114*, 36. Review: Shainyan, B. A.; Mirskova, A. N. *Russ. Chem. Rev.* **1979**, *48*, 107.

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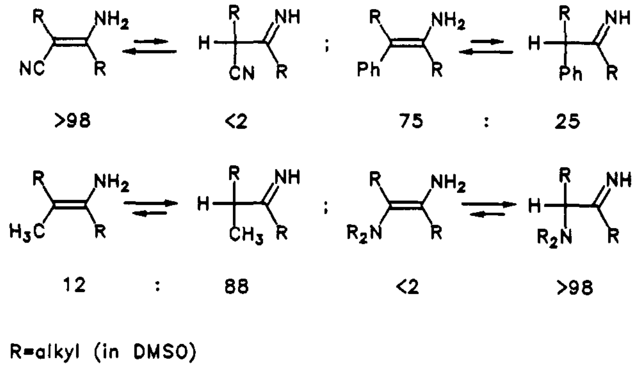
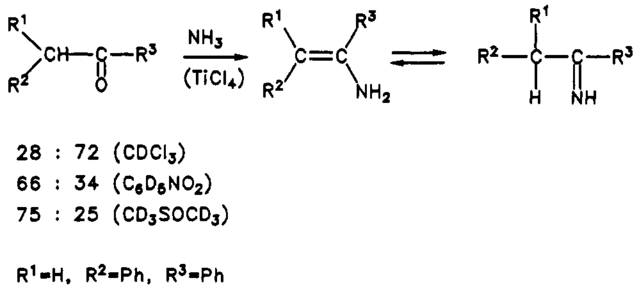
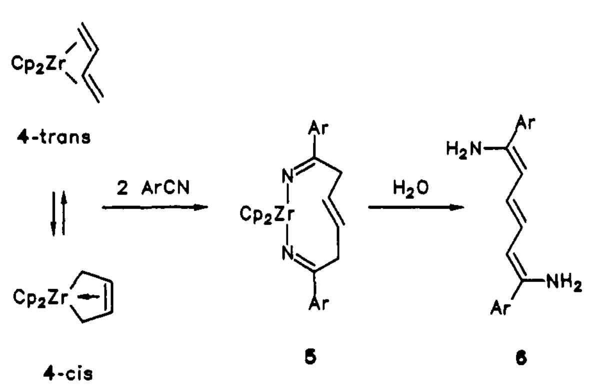
Scheme I



to the work of Ahlbrecht et al.[6] They prepared a variety of primary enamine/ketimine systems by reacting the corresponding carbonyl compounds with ammonia in the presence of the titanium tetrachloride Lewis-acid catalyst and studied the primary enamine–ketimine tautomeric equilibrium especially with regard to its solvent and substituent dependence. It was found that increasing solvent polarity strongly stabilizes the primary enamine component under equilibrium conditions, and that the equilibrium ratio depends very much on the substitution pattern at the primary enamine carbon–carbon double bond. Substituents in the α-position (i.e. at the carbon atom bearing the NH_2 group) have only a rather small influence, whereas the β-substituents are of great importance for the ratio of the enamine–ketimine tautomers observed under thermodynamic control. Electron-withdrawing carbonyl groups and their analogues (e.g. C≡N) strongly favor the primary enamine form (especially in dipolar aprotic solvent); π-conjugating hydrocarbyl β-substituents (phenyl, vinyl) also tend to stabilize the enamine form, but to a lesser extent. Inductively electron-donating alkyl groups tend to disfavor the enamine tautomer, and strong mesomeric electron donors (e.g. NR_2) make the primary enamine isomers energetically even more unfavorable (see Scheme I).[7]



We have recently found a simple organometallic route for the synthesis of a novel type of very stable conjugated primary enamines.[8] Aryl nitriles (2 equiv) were coupled with butadiene in the coordination sphere of bis(η-cyclopentadienyl)zirconium. The resulting organometallic nine-membered metallacycle **5** was then hydrolyzed to directly yield the stable, easily isolated 1,6-diamino-1,6-diarylhexatriene system **6**. Several derivatives and conjugated analogues of this very special primary enamine system were prepared.[9]



These diaminohexatriene systems (**6**) are characterized as having two ordinary primary enamine units coupled tail-to-tail through a connecting conjugated CH=CH unit to have their respective enamine dipoles completely compensated. So far only a single example of this class of compounds had been characterized by X-ray diffraction, namely 1,6-diamino-1,6-diphenyl-1,3,5-hexatriene (**6a**).[8] We considered it important to have detailed structural information available for a number of such unusually stable primary enamine systems. Therefore, a low temperature X-ray crystal structure analysis of a related example (1,6-diamino-1,6-di-*p*-tolyl-1,3,5-hexatriene (**6b**)) was carried out and its results are reported in this account.

The examples studied so far all contain a π-system extending beyond the central 1,6-diaminohexatriene unit. It would be highly desirable to have examples of this novel class of stable organic primary aminoalkenes available for study that have the electronic features of its central $C(NH_2)=CHCH=CHCH=C(NH)_2$ section not interferring with conjugating substituents at the ends of the alternating polyolefin chain. We were able to extend our novel synthesis and prepare 1,6-dialkyl-substituted conjugated primary enamines of this type. We describe here a first example of this interesting class of stable primary alkenamines, namely 3,9-diamino-2,2,10,10-tetramethyl-3,5,7-decatriene, discuss its molecular structure in the crystal, and report the results of a theoretical analysis of the special electronic features leading to such a high thermodynamic stability of the diaminohexatriene systems containing tail-to-tail coupled primary enamine units.

Results and Discussion

Formation of the 1,6-Diamino-1,6-dialkylhexatrienes. The basis of our general metal-mediated conjugated primary enamine synthesis is the sequential coupling of an organic nitrile with the butadiene building block at zirconium.[10,11] We, therefore, reacted pivalonitrile with 1 mol equiv of the (*s-cis*/*s-trans*-η^4-butadiene)zirconocene equilibrium mixture[12] at room temperature in toluene. The reaction was complete after about 1 h and furnished an 80:20 mixture of two isomeric 1:1 addition products. The major component **9** of this product mixture contains a N-metalated ketimine functionality (IR ν 1674

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[6] Ahlbrecht, H.; Fischer, S. *Tetrahedron* **1973**, *29*, 659. Ahlbrecht, H.; Blecher, J.; Hanisch, H.; Papke, G.; Reiner, M. T. *Tetrahedron* **1973**, *29*, 3079. Ahlbrecht, H.; Funk, W.; Reiner, M. T. *Tetrahedron* **1976**, *32*, 479. Ahlbrecht, H.; Papke, G. *Tetrahedron Lett.* **1972**, 4443. *Idem. Tetrahedron* **1974**, 2571.

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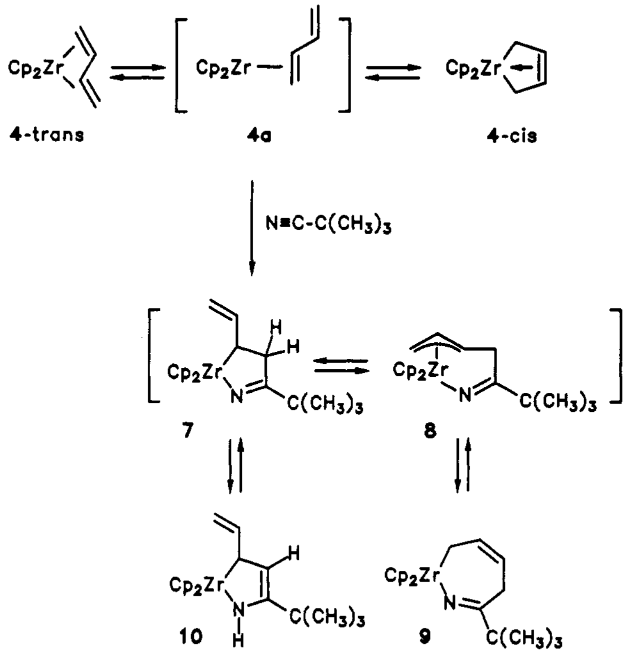
[9] Erker, G.; Pfaff, R. *Organometallics* **1993**, *12*, 1921.

cm^{-1}; ^{13}C NMR δ 180.8 ppm). It exhibits ^{1}H/^{13}C NMR signals of the C_4H_6 section originating from the butadiene building block that are typical for a seven-membered metallacyclic (σ-allyl)metallocene complex[13] [δ 1.50/32.2 (MCH_2), 6.21, 5.56/107.3, 138.5 (CH=CH)] and a Cp resonance at δ 5.56/107.5. The minor congener **10** is a five-membered N-metalated enamido zirconium complex [IR ν(NH) 3375 cm^{-1}; ^{1}H δ 4.23 (N*H*), 4.77 (=CH); ^{13}C NMR δ 131.6 (NC(R)=), 97.4 (=CH)] which contains a zirconium bound σ-allyl unit[14] [^{1}H/^{13}C NMR δ 1.09/66.5 (*C*H), 6.51/143.2 and 5.14, 4.97/94.7 (*C*H=*C*H_2)]. The chiral five-membered metallacyclic (σ-allyl)zirconocene complex exhibits the ^{1}H/^{13}C NMR signals of a pair of diastereotopic η-cyclopentadienyl ligands at δ 5.42, 5.10/106.5, 103.4.

The formation of these two products (**9** and **10**) fits into the general scheme established for the reaction course taken upon addition of carbonyl compounds and analogues thereof to the (butadiene)zirconocene system.[15] It has to be assumed that initially the formation of the five-ring heterocycle **7** takes place formally by a metallacyclic [2 + 2 + 2] cycloaddition reaction. The *N*-metallaketimine **7** then undergoes a ketimine–enamine tautomerization (probably proceeding intermolecularly, although this was not checked experimentally in this study[16]) to produce the stable N-metalated enamine **10**. Alternatively, the metallacyclic (σ-allyl)zirconium complex **7** can equilibrate with its (π-allyl)metallocene isomer **8**, which in turn then rearranges to the observed final major product **9**. The (σ-allyl)zirconium complex **9** retains its metalated ketimine structure and shows no tendency of forming the respective N-metalated enamino tautomer. In contrast to **7**, the seven-membered ring structure of **9** very likely allows for efficient electronic nitrogen to zirconium back-donation which makes the early transition metal center much less electrophilic and the adjacent nitrogen heteroatom much less basic.[13,17] This could explain that only the complexes **9** and **10** have been observed as stable (butadiene) zirconocene plus pivalonitrile 1:1 addition products under thermodynamic control and not their isomers **8** and **7**.[18] However, the latter are very likely to be available by rapid equilibration for subsequent coupling reactions. This we have used for preparing the (butadiene)$ZrCp_2$ coupling products with 2 mol equiv of pivalonitrile as was planned for our conjugated primary enamine synthesis.

Scheme II



The mixture of **9** and **10** is not stable in the presence of additional pivalonitrile. We thus reacted the (*s-cis-/s-trans*-butadiene)zirconocene equilibrium mixture with 2 mol equiv of pivalonitrile for a prolonged period of time at ambient temperature and obtained the nine-membered metallacyclic 2:1 addition products **11** and **12** in a 1:9 ratio. As expected,[10,11] the metal-coordinated butadiene nucleophile had added the pivalonitrile electrophiles selectively at the conjugated diene termini.[19a] The 1,4-addition

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[10] For related examples see: Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120. Yasuda, H.; Nakamura, A. *Angew. Chem.* **1987**, *99*, 745. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 723. Yasuda, H.; Okamoto, T.; Matsuoka, Y.; Nakamura, A.; Kai, J.; Kanehisa, N.; Kasai, N. *Organometallics* **1989**, *8*, 1139. Erker, G.; Sosna, F.; Betz, P.; Werner, S.; Krüger, C. *J. Am. Chem. Soc.* **1991**, *113*, 564. Erker, G.; Sosna, F.; Zwettler, R.; Krüger, C. *Organometallics* **1989**, *8*, 450. Erker, G.; Sosna, F.; Noe, R. *Chem. Ber.* **1990**, *123*, 821. Erker, G.; Sosna, F. *Organometallics* **1990**, *9*, 1949. Erker, G.; Sosna, F.; Pfaff, R.; Noe, R.; Sarter, C.; Kraft, A.; Krüger, C.; Zwettler, R. *J. Organomet. Chem.* **1990**, *394*, 99. Erker, G.; Pfaff, R.; Krüger, C.; Werner, S. *Organometallics* **1991**, *10*, 3559.

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[14] For related five-membered (σ-allyl)Zr complex formation see: Yasuda, H.; Kajihara, Y.; Mashima, K.; Nagasuna, K.; Nakamura, A. *Chem. Lett.* **1981**, 671. Erker, G.; Dorf, U. *Angew. Chem.* **1983**, *95*, 800. *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 777. Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120.

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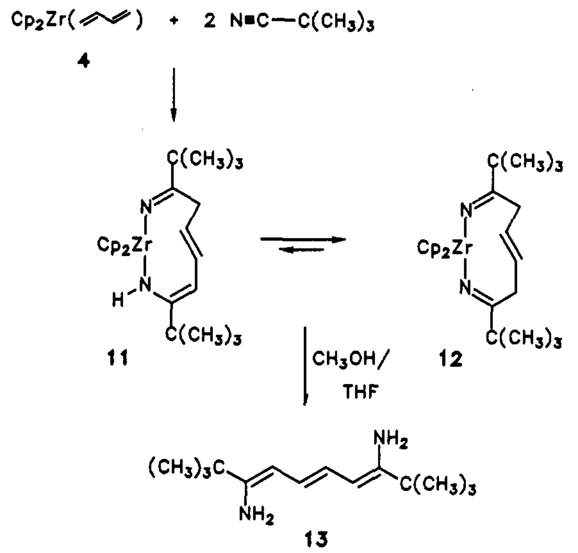
[19] (a) In contrast other butadiene dianion equivalents react predominantly by means of electrophilic 1,2-addition: Fujita, K.; Ohnuma, Y.; Yasuda, H.; Tani, H. *J. Organomet. Chem.* **1976**, *113*, 201. Bahl, J. H.; Bates, R.-B.; Beavers, W. A.; Mills, N. S. *J. Org. Chem.* **1976**, *41*, 1620. Richter, W. J. *Angew. Chem.* **1982**, *94*, 298. *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 292. Dorf, U.; Engel, K.; Erker, G. *Organometallics* **1983**, *2*, 462. (b) The authors have deposited atomic coordinates for **6b** and **13** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge, Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

Scheme III



reaction has led to the formation of chiral metallacyclic frameworks; the products are distinguished from one another as being metalated ketimino/enamino tautomers. Under the reaction conditions applied the major isomer **12** contained a 1-zircona-2,9-diazacyclonona-2,5,8-triene framework having a trans-configured carbon–carbon double bond between the ring-carbon atoms C(5) and C(6). The ^3J(5-H,6-H) coupling constant of 15.2 Hz is typical for this situation. Complex **12** is C_2-symmetric. The minor component **11** is of lower molecular symmetry. It contains a metal–ketimido group and a metalated enamino functionality (^{1}H NMR δ 4.24, N*H*) as part of the nine-membered metallacyclic ring system. Again, the endocyclic C(5)–C(6) double bond is trans-configured [^3J(5-H,6-H) = 15.1 Hz].

The mixture of the **11**/**12** tautomers was dissolved in tetrahydrofuran and the zirconium center cleaved off by reacting it with 3 mol equiv of methanol. Pentane extraction yielded a white crystalline material which had retained both nitrogen atoms according to its elemental analysis. The product is the C_i-symmetric conjugated primary enamine **13**. The α,ω-di-*tert*-butyl-1,6-diaminohexatriene contains two symmetry-equivalent NH_2 groups (IR ν 3446, 3365 cm^{-1}; ^{1}H NMR δ 3.35). The all-*trans*-configurated central sp^2-carbon framework exhibits ^{13}C NMR resonances at δ 148.7, 95.2, and 121.0 of the RC^3(NH$_2$)=C^{4}HC^{5}H= building block. The corresponding ^{1}H NMR signals are observed at δ 6.02 (4-H) and 4.70 (5-H) with coupling constants ^3J(4-H,5-H) = 11.1 Hz and ^3J(5-H,6-H) = 14.5 Hz. In dimethyl sulfoxide-d_6 solution only the ^{1}H and ^{13}C NMR resonances of a single species (**13**) are observed. However, we noticed that the single C(C*H*$_3$) signal of **13** in benzene-d_6 at δ 1.11 was accompanied by two small *tert*-butyl resonances at δ 1.13 and 0.98. The two CMe$_3$ singlets of this second component exhibit an intensity ratio of 1:1. The relative amount of this minor component is ≤2% of the concentration of **13** in benzene solution. We have not positively identified this byproduct exhibiting two different *tert*-butyl resonances. It could represent another stereoisomer of the conjugated primary enamine **13** or just be due to a small amount of a hydrolysis product or some ketimine tautomer of **13** being present in solution. Further work will be aimed at clearing this point.

The 1,6-diamino-1,6-di(p-tolyl)hexatriene system **6b** was prepared analogously. Reaction of the (butadiene)zirconocene reagent **4** with 4-methylbenzonitrile in a 1:2 molar ratio in toluene at room temperature gave the nine-membered metallacyclic coupling product (**5b**, Ar = *p*-tolyl) in >90% isolated yield. Its hydrolysis (H_2O/tetrahydrofuran) furnished the aryl-substituted conjugated primary enamine **6b** (Ar = *p*-tolyl) which was isolated in ca. 30% yield after recrystallization from methylene chloride.

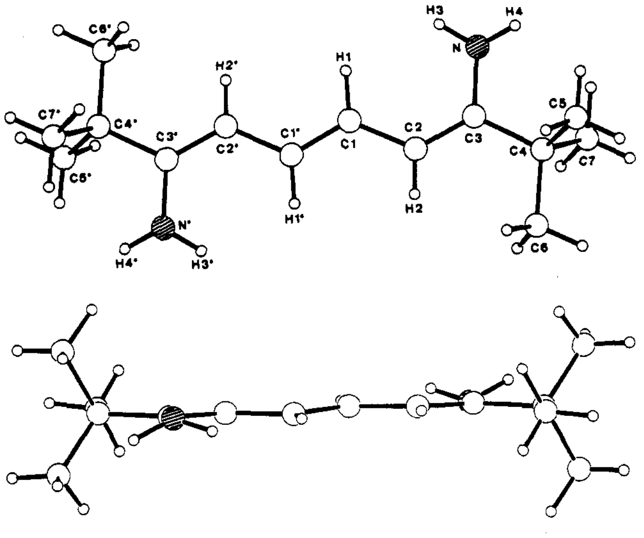


Figure 1. Two views of the molecular structure of the conjugated primary enamine **13** in the crystal (with unsystematic atom numbering scheme).

X-ray Crystal Structure Analyses. To our knowledge only a single X-ray structural analysis of a primary enamine has been reported so far, namely that of 1,6-diamino-1,6-diphenylhexa-1,3,5-triene (**6a**, Ar = phenyl) which was described in our previous study mentioned above. We have now obtained crystals of the α,ω-dialkyl-1,6-diaminohexatriene system **13** from ether, which were suited for an X-ray diffraction analysis.[19b]

In the crystal, compound **13** exhibits a planar central framework consisting of six trigonally planar-coordinated carbon atoms. The hexatriene system contains three carbon–carbon double bonds which are trans-connected with each other. The sp^2-carbon system is fully conjugated and exhibits a markedly alternating short-long-short-long-short carbon–carbon bond lengths sequence. The corresponding independent C–C distances of the C_i-symmetric framework are 1.333(3) Å [C(3)–C(2)], 1.437(3) [C(2)–C(1)], and 1.332(3) [C(1)–C(1*)] (see Figure 1 for the atom numbering used to describe the results of the X-ray crystal structure analysis of **13**). The C–C–C angles along the conjugated carbon chain deviate only slightly from the ideal sp^2 carbon values at 126.5(2)° [C(1*)–C(1)–C(2)], 127.3(2)° [C(1)–C(2)–C(3)], and 125.0(2)° [C(2)–C(3)–C(4)]. The carbon center [C(3)] bearing the amino substituent is trigonally planar with the remaining pertinent bond angles being 113.9(2)° [C(4)–C(3)–N] and 120.0(2)° [C(2)–C(3)–N] (the sum of bonding angles at C(3) is 359.7(2)°).

Crystals of the 1,6-diaryl-substituted conjugated primary enamine **6b** suited for a low temperature X-ray crystal structure analysis were obtained by recrystallization from methylene chloride. Compound **6b** also contains an all-trans-configurated alternating polyolefin carbon chain. The central part of the molecule is arranged almost coplanar [dihedral angles C1–C2–C3–N = 9.92°; C1–C2–C3–C4 = −177.51°].

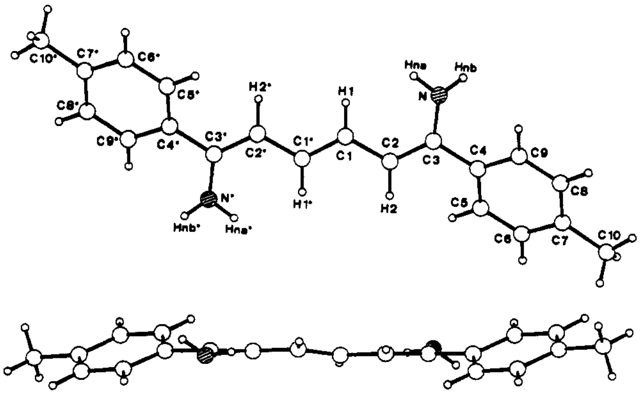


Figure 2. Two projections of the molecular structure of the conjugated primary enamine **6b** (with unsymmetric atom numbering scheme).

Table I. Selected Bond Lengths (Å) and Angles (deg) of 6b and 13

compound 6b		compound 13	
N–C(3)	1.393(2)	N–C(3)	1.397(3)
N–Hna	0.89(2)	N–H(3)	0.89(4)
N–Hnb	0.90(2)	N–H(4)	0.97(4)
C(1)–C(2)	1.437(2)	C(1)–C(2)	1.437(3)
C(1)–H(1)	0.95(2)	C(1)–H(1)	0.98(2)
C(1)–C(1)*	1.353(2)	C(1)–C(1)*	1.332(3)
C(2)–C(3)	1.357(2)	C(2)–C(3)	1.333(3)
C(2)–H(2)	0.99(2)	C(2)–H(2)	0.91(2)
C(3)–C(4)	1.477(2)	C(3)–C(4)	1.516(3)
$(C–C)_{Ph}$	1.393		
Hnb–N–Hna	106(2)	H(4)–N–H(3)	113(3)
Hnb–N–C(3)	117(1)	H(4)–N–C(3)	112(2)
Hna–N–C(3)	118(1)	H(3)–N–C(3)	116(2)
C(1)*–C(1)–H(1)	117(1)	C(1)*–C(1)–H(1)	115(1)
C(1)*–C(1)–C(2)	124.4(1)	C(1)*–C(1)–C(2)	126.5(2)
H(1)–C(1)–C(2)	119(1)	H(1)–C(1)–C(2)	118(1)
H(2)–C(2)–C(3)	116.6(9)	H(2)–C(2)–C(3)	119(1)
H(2)–C(2)–C(1)	117.9(9)	H(2)–C(2)–C(1)	113(1)
C(3)–C(2)–C(1)	125.3(1)	C(3)–C(2)–C(1)	127.3(2)
C(4)–C(3)–C(2)	121.7(1)	C(4)–C(3)–C(2)	125.0(2)
C(4)–C(3)–N	115.6(1)	C(4)–C(3)–N	113.9(2)
C(2)–C(3)–N	122.4(1)	C(2)–C(3)–N	120.8(2)

Table II. Atomic Coordinates of 6b

atom	*x*	*y*	*z*
N	0.7264(1)	0.5666(3)	0.9054(1)
C(1)	0.5372(1)	0.5277(3)	0.9771(1)
C(2)	0.5536(1)	0.3526(3)	0.9007(1)
C(3)	0.6367(1)	0.3838(3)	0.8629(1)
C(4)	0.6445(1)	0.2006(3)	0.7814(1)
C(5)	0.5504(1)	0.0706(3)	0.7125(1)
C(6)	0.5597(1)	−0.1119(3)	0.6397(1)
C(7)	0.6632(1)	−0.1707(3)	0.6311(1)
C(8)	0.7562(1)	−0.0361(3)	0.6975(1)
C(9)	0.7478(1)	0.1481(3)	0.7710(1)
C(10)	0.6718(1)	−0.3754(4)	0.5529(1)
H(1)	0.578(1)	0.700(4)	0.995(1)
H(2)	0.504(1)	0.188(3)	0.877(1)
H(5)	0.476(1)	0.102(3)	0.717(1)
H(6)	0.493(1)	−0.195(4)	0.593(1)
H(8)	0.832(1)	−0.069(4)	0.695(1)
H(9)	0.813(1)	0.235(4)	0.816(1)
H(10a)	0.620(2)	−0.324(5)	0.485(2)
H(10b)	0.650(1)	−0.562(4)	0.566(1)
H(10c)	0.751(2)	−0.384(4)	0.555(1)
Hna	0.721(1)	0.696(4)	0.949(1)
Hnb	0.753(1)	0.658(4)	0.863(1)

Table III. Atomic Coordinates of 13

atom	*x*	*y*	*z*
N	0.0897(5)	0.4279(1)	0.3215(2)
C(1)	0.4184(4)	0.4877(1)	0.4697(3)
C(2)	0.3161(4)	0.4357(1)	0.5090(3)
C(3)	0.1621(4)	0.4085(1)	0.4450(2)
C(4)	0.0652(3)	0.3525(1)	0.4888(2)
C(5)	−0.1728(5)	0.3592(2)	0.5055(5)
C(6)	0.1561(8)	0.3315(2)	0.6203(4)
C(7)	0.1083(7)	0.3068(1)	0.3826(4)
H(1)	0.370(3)	0.5066(9)	0.388(3)
H(2)	0.368(3)	0.4206(9)	0.585(2)
H(3)	0.114(5)	0.464(2)	0.303(3)
H(4)	−0.055(6)	0.417(2)	0.305(3)
H(5a)	−0.246(5)	0.325(2)	0.538(3)
H(5b)	−0.175(5)	0.386(2)	0.575(3)
H(5c)	−0.247(6)	0.374(2)	0.435(4)
H(6a)	0.304(6)	0.325(1)	0.616(3)
H(6b)	0.122(5)	0.363(1)	0.689(3)
H(6c)	0.096(4)	0.294(1)	0.643(3)
H(7a)	0.279(7)	0.302(1)	0.384(3)
H(7b)	0.038(5)	0.322(1)	0.300(3)
H(7c)	0.043(5)	0.273(2)	0.409(3)

Table IV. Details of the X-ray Crystal Structure Analyses of 6b[a] and 13[a]: Data Collection and Structure Solution

	6b	13
formula	$C_{20}H_{22}N_2$	$C_{14}H_{24}N_2$
mol wt	290.4	220.4
crystal color	yellow	yellow
crystal system	monoclinic	orthorhombic
space group [no.]	$P2_1/a$ [14]	*Pbca* [61]
a, Å	12.778(8)	6.343(1)
b, Å	4.722(1)	23.471(3)
c, Å	14.203(5)	10.025(1)
β, deg	110.6(1)	90
V, Å^3	802.5	1492.5
Z	2	4
D_{calcd}, g cm^{-3}	1.20	0.98
μ, cm^{-1}	0.66	0.54
Mo K*α* radiation, λ, Å	0.71069	0.71069
F(000), e	312	488
diffractometer	Enraf-Nonius CAD4	
scan mode	ω–2θ	ω–2θ
$[(\sin\theta)/\lambda]_{max}$, Å^{-1}	0.65	0.59
T, °C	−173	20
abs correction	none	none
no. of measd reflcns	3804 ($\pm h,\pm k,+l$)	2862 ($\pm h,+k,+l$)
no. of indep reflcns	1827	1311
no. of obsd reflcns ($I > 2\sigma(I)$)	1459	858
R_{av}	0.07	0.03
no. of refined params	144	125
R	0.043	0.052
R_w ($w = 1/\sigma^2(F_o)$)	0.049	0.059
resid electron dens, e Å^{-3}	0.36	0.17
structure solution	direct method	direct method

[a] H-atom positions were found and included in the final refinement stage.

The enamine C–N bond length in **13** is 1.397(3) Å and in **6b** it is 1.392(3) Å. As expected this is much shorter than the C–N bond in a saturated primary amine, the accepted averaged X-ray value of the $C(sp^3)–NH_2$ bond length being 1.469 Å.[20] The carbon–nitrogen bond length of methylamine from a microwave analysis is 1.477(5) Å.[21] The C–N bond lengths in **13** and **6b** correspond well to the (sp^2)carbon–nitrogen distances in aromatic amines (averaged X-ray value: 1.394 Å;[20] the reported microwave $C(sp^2)–NH_2$ bond length in aniline itself is 1.402(2) Å[22]).

The structural similarities between the aromatic primary amines and our acyclic conjugated primary enamines (**13**, **6b**) include the geometries at nitrogen. The tricoordinate nitrogen atoms in the aromatic amines are markedly

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(20) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

(21) Nishikawa, T.; Itoh, T.; Shimada, K. *J. Chem. Phys.* **1955**, *23*, 1735. Itoh, T. *J. Phys. Soc. Jpn.* **1956**, *11*, 264. Lide, D. R., Jr. *J. Chem. Phys.* **1957**, *27*, 343. Higginbotham, H. K.; Bartell, L. S. *J. Chem. Phys.* **1965**, *42*, 1131. Ataji, M.; Lipscomb, W. *Acta Crystallogr.* **1953**, *6*, 770.

nonplanar and so are the amino nitrogens in the conjugated primary enamines **13** and **6b**. In **6b** the angle between the NH_2 and $NC_3C_2C_4$ planes amounts to 40°; the primary amino group in aniline is showing a similar deviation from planarity (38°).[22]

We conclude from the low-temperature structural analysis of **6b** (and of **6a**[8] and **13** as well) that primary enamines seem to show a similar structural behavior as is known from the primary aromatic amines. Primary enamines contain a markedly nonplanar enamine-nitrogen atom. Just as in the aromatic amines, the amino nitrogen to C(sp^2) bond is about 0.07–0.08 Å shorter in the primary enamines as compared to the N–C(sp^3) bond. Whether this bond shortening has to be attributed mainly to the difference in carbon (and perhaps nitrogen) hybridization or is to some extent due to additional conjugative effects can not be deduced from this experimental study but may be answered by a theoretical investigation of this general type of a stable conjugated primary enamine system.

Ab initio Computational Studies. In order to rationalize the observed strong dominance of the primary enamine tautomer in the enamine–imine equilibrium of compounds **13** and **6** and to get some theoretical insight into the electronic nature of their extended π-system, quantum mechanical ab initio calculations were performed. The 6-31+G* basis set[23] of the GAUSSIAN 92 program package[24] was used throughout for complete geometry optimizations. All structures obtained correspond to minima on the potential energy surface as indicated by frequency calculations (NIMAG = 0). The differences in zero point energies of the enamines and the corresponding imines were found to be very small; they are therefore not taken into consideration in the calculations of the relative energies. Effects of electron correlations were estimated by use of second-order Møller–Plesset theory.[25] Both, the diffuse functions (+) and the inclusion of electron correlation (MP2) proved to be essential for the adequate description of these systems. These MP2/6-31+G*//6-31+G* single point energies are the basis of the following discussion.

Scheme IV

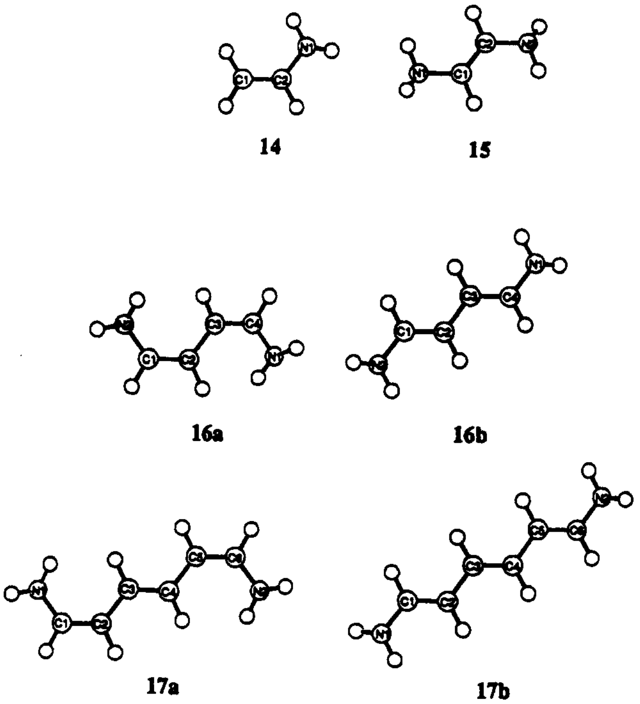

Table V. **Relative Energies [kcal/mol] of the Enamines 14–17, Compared to Their Best Imino Tautomer (E_{rel} = 0.00 kcal/mol)**[a]

enamine	6-31+G*//6-31+G* E_{rel} (kcal/mol)	MP2/6-31+G*//6-31+G* E_{rel} (kcal/mol)
14	6.14	5.77
15	6.72	4.91
16a (*Z-s-trans-Z*)	2.62	1.99
16b (all-*trans*)	2.27	0.61
17a (*Z-s-trans-E-s-trans-Z*)	0.06	−1.67
17b (all-*trans*)	0.99	−0.89

[a] For a drawing of the optimized calculated structures of 14–17 see Scheme IV.

Table VI. **Calculated Bond Lengths of the Enamines 14–17**[a]

enamine	C–N (Å)	C=C (Å)	C–C (Å)
14	1.3916	1.3257	-
15	1.4135	1.3221	-
16a	1.3928	1.3320	1.4694
16b	1.4000	1.3280	1.4650
17a	1.3919	1.3335[b] 1.3349[c]	1.4610
17b	1.3944	1.3303[b] 1.3329[c]	1.4613

[a] For a drawing of the optimized calculated structures of 14–17 see Scheme IV. [b] (C1–C2). [c] (C3–C4).

The bisenamines described above (**6**, **13**) and their model compounds **17** may be looked at as doubly vinylogous 1,2-diaminoethene derivatives. Therefore, 1,2-diaminoethene (**15**) and 1,4-diaminobutadiene (**16**) were also included in this study, together with their monoimine tautomers. For comparison, vinylamine (**14**) and its imine form were considered, too. The relative energies of the enamines, referring to their corresponding imine forms (E_{rel} = 0.00 kcal/mol), are summarized in Table V. Bond lengths of the enamine skeletons are given in Table VI, and the enamine and imine total energies are provided in Table VII. It should be mentioned that the calculations of the imine tautomers bear some degree of uncertainty, since it is not easy to locate the best conformer corresponding to the global minimum on the potential energy surface, especially for the longer systems.[26]

1,2-Diaminoethene (**15**) is a very electron-rich alkene (six π electrons on four centers), which is not known experimentally as a NH_2 compound.[27] It is isoelectronic with the butadiene dianion and its HOMO is likewise predominantly antibonding in character. Its tetraalkyl derivatives are synthetically useful, especially in cycload-

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(22) Lister, D. G.; Tyler, J. K.; Høg, J. H.; Larsen, N. W. *J. Mol. Struct.* **1974**, *23*, 253. Lister, D. G.; Tyler, J. K. *J. Chem. Soc., Chem. Commun.* **1966**, 152. Hatta, A.; Suzuki, M.; Kozima, K. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2321. Evans, J. C. *Spectrochim. Acta* **1960**, *16*, 428. Brand, J. C. D.; Williams, D. R.; Cook, T. J. *J. Mol. Spectrosc.* **1966**, *20*, 359.

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(26) Full calculational details may be obtained from E.-U. Würthwein upon request.

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Table VII. Ab Initio Total Energies (au) for the Enamines 14–17 and for Their Best Imino Tautomers, As Found in This Study

enamine	enamine 6-31+G*// 6-31+G*	imine 6-31+G*// 6-31+G*	enamine MP2/6-31+G*// 6-31+G*	imine MP2/6-31+G*// 6-31+G*
14	−133.06884	−133.07862	−133.48990	−133.49910
15	−188.09054	−188.10125	−188.67802	−188.68584
16a	−264.98775	−264.99193	−265.83075	−265.83392
16b	−264.98658	−264.99020	−265.82800	−265.82898
17a	−341.87822	−341.87831	−342.97400	−342.97134
17b	−341.87924	−341.88081	−342.97426	−342.97285

dition reactions.[28] The influence of two strong donor groups on one simple alkene unit reduces the conjugative interactions in this system as it can be seen from the calculated small rotational barrier of one of the amino groups (1.7 kcal/mol); the corresponding transition state has C_s-symmetry and may be best understood as a push-pull disubstituted alkene with a planar in-plane amino group and second strongly pyramidalized perpendicular amino group. The calculated C–N bonds in **15** are relatively long (1.414 Å). The corresponding barrier of rotation around the C–N bond (1.392 Å) in vinylamine (**14**)[29] is calculated as 4.95 kcal/mol. The superiority of the imine forms over their enamine tautomers is similar in both systems: the calculations favor the imine form of 1,2-diaminoethene (**15**) by 4.9 kcal/mol and that of vinylamine (**14**) by 5.8 kcal/mol.

In 1,4-diaminobutadiene (**16**), having eight π-electrons on six centers, the electronic situation for conjugative stabilization is somewhat better, although the HOMO is still mainly antibonding in character. Here, we have calculated for the *Z-s-trans-Z*-isomer **16a** an energy difference between the enamine and imine tautomers of 2.0 kcal/mol in favor of the imine form. In comparison to 1,2-diaminoethene (**15**) the C–N bond length in 1,4-diaminobutadiene (**16a**) is reduced to 1.393 Å, indicating a better electronic interaction.

Our calculation of (*Z-s-trans-E-s-trans-Z*)-1,6-diaminohexatriene (**17a**) as a model of a 10 π electron/8-center system such as **6** or **13** (only the *tert*-butyl groups and aryl substituents are left off, respectively) has revealed an inversion of preference for the tautomers, compared to the shorter systems. According to the MP2 values, the equilibrium is predicted to lie strongly on the enamine side ($E_{rel} = -1.7$ kcal/mol). It may well be that intermolecular forces or the additional *tert*-butyl substituents in **13** shift the equilibrium even more to the enamine side. The C–N bond lengths of **17a** now are at 1.392 Å, the same value which is obtained for vinylamine (**14**).

For all enamines our 6-31+G* calculations produce strongly pyramidalized amino groups, which is in good agreement with the X-ray results for **6** and **13** and literature data of enamines and anilines.[20-22] The smaller 3-21G basis set, however, favors planar arrangements around nitrogen and is, therefore, not suited for such studies. Table VI clearly shows increasing conjugation in going from **15** through **16** to **17**; the C=C double bonds are getting slightly longer, whereas the C–N and C–C bonds decrease in bond length continuously. Consequently, the surplus of electrons may be better delocalized as the systems are expanded.

Conclusions

We have found a very convenient way of preparing a variety of stable conjugated primary enamines. Our novel synthesis utilizes the ability of the bent metallocene fragment bis(η-cyclopentadienyl)zirconium to act as an organometallic template for assembling and consecutively coupling a conjugated diene (here: 1,3-butadiene) with two organic nitrile functionalities. This extremely high tendency for 1,4-selective coupling of butadiene with two nitriles is probably due to the high thermodynamic stability of the resulting nine-membered metallacyclic ring systems. To a great extent the very special stereoelectronic features of the group 4 bent metallocene unit seem to be responsible for the favored formation of these rigid nine-membered metallacycles (**5**, **12**) as it allows for a strong nitrogen to zirconium back-donation using an acceptor orbital at the metal center that is oriented in the σ-ligand plane.

Most remarkable with our synthesis is the fact that the stoichiometric hydrolysis of these nine-membered metallacycles very selectively produces the stable and easily isolable conjugated primary enamine systems (**6**, **13**). The observed high tendency of the occurrence of the bisenamine tautomer under thermodynamic reaction control is amazing in view of the rare incidents where stable primary aminoalkene examples were found and described so far. At first sight the high kinetic and thermodynamic stability of the systems **6** and **13**, respectively, seems to be even more remarkable as these compounds formally represent electronically destabilized 8-center/10 π-electron systems. However, our ab initio computational analysis has revealed that the destabilizing repulsive electronic interaction is more than compensated for by conjugative effects in such diaminopolyene systems having the NH_2 groups separated by a total of six sp^2-hybridized carbon atoms.

From our theoretical and experimental work we thus conclude that a C_i-symmetric coupled arrangement of $CH{=}C(NH_2)$ functionalities with compensation of the individual dipolar features leads to a novel type of stable, isolable aminoolefins. Such systems should become even more stable with an extending conjugation of the framework to which the NH_2 groups are attached. From our present work it is, therefore, expected that a large variety of similar systems should be easy to synthesize and isolate. We expect that this will rapidly lead to the development of an as yet unknown chemistry of primary enamines on a sound experimental basis.

Experimental Section

Reactions and handling of organometallic reagents and the primary enamines were carried out in an inert atmosphere (argon) using Schlenk-type glassware or in a glove box. Solvents were dried and distilled under argon prior to use. NMR spectra were measured with a Bruker AC 200 P (200 MHz ^{1}H; 50 MHz ^{13}C) or WM 300 (300 MHz ^{1}H; 75.5 MHz ^{13}C) NMR spectrometer. IR spectra were recorded on a Nicolet 5 DXC FT IR spectrometer. Melting points: Büchi SMP 20 (melting points are uncorrected) or Dupont DSC 910 (STA Instruments). Elemental analyses were carried out with a Foss-Heraeus CHNO-RAPID. The (*s-cis-/s-trans*-butadiene)zirconocene mixture **4** was prepared as described in the literature.[12]

(2*E*,5*Z*,8*E*)-1,1-Bis(η-cyclopentadienyl)-3,8-di-*p*-tolyl-1-zircona-2,9-diazacyclonona-2,5,8-triene (5b, R = *p*-tolyl) was prepared analogously as described for **5a** (R = Ph)[8] by adding a solution of 500 mg (4.20 mmol) of 4-methylbenzonitrile in 10 mL of toluene dropwise at room temperature to a solution of 580 mg (2.10 mmol) of (butadiene)zirconocene in 20 mL of toluene. The mixture was stirred for 19 h at ambient temperature and

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[28] Hickmott, P. W. *Tetrahedron* 1984, *40*, 2989.

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then filtered. Solvent was removed from the clear filtrate in vacuo to give 990 mg (93%) of **5b** as a yellow solid: mp 219 °C dec.; ^{1}H NMR (benzene-d_6) δ 7.76, 7.08 (AA′XX′, 8H, arom), 5.81 (s, 10H, Cp), 5.00 (m, 2H, CH=CH), 3.55, 3.05 (br m, 2H each, CH_2), 2.17 (s, 6H, CH_3); IR (KBr) ν 3080, 3040, 2964, 1650, 1623, 1440, 1016, 793 cm^{-1}. Anal. Calcd for $C_{30}H_{30}N_2$ (509.8): C, 70.68; H, 5.93; N, 5.49. Found: C, 69.39; H, 5.95; N, 5.46.

1,6-Diamino-1,6-di-*p*-tolyl-1,3,5-hexatriene (6b). The metallacycle **5b** (990 mg, 1.95 mmol) was dissolved in 20 mL of tetrahydrofuran. Water (6 mL) was added and the mixture stirred for 2.5 h at room temperature. The THF solvent was removed in vacuo and the residue extracted three times with 10 mL of ether. The combined organic phases were dried over magnesium sulfate. Solvent was removed in vacuo and the product recrystallized from 5 mL of boiling methylene chloride to give 150 mg (27%) of **6b** as orange-colored needles. From the mother liquor a few additional crystals of **6b** were obtained at 5 °C over several days that were suited for the X-ray crystal structure analysis: mp 115 °C (DSC); ^{1}H NMR ($CDCl_3$) δ 7.48, 7.02 (AA′XX′, 8H, arom), 6.36, 5.61 (m, 4H, CH=CH), 3.70 (br s, 4H, NH_2), 2.34 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 137.7, 132.0, 129.1, 129.0, 125.2, 123.0 (=CH, C_{ipso}, and arom *C*H), 103.7 ($H_2NC{=}CH$), 21.1 (CH_3); IR (KBr) ν 3346, 2963, 1627, 1580, 1447, 1377, 1262, 961, 865 cm^{-1}. Anal. Calcd for $C_{20}H_{22}N_2$ (290.4): C, 82.72; H, 7.64; N, 9.65. Found: C, 80.08; H, 7.53; N, 9.11.

(2*E*,5*Z*)-1,1-Bis(η-cyclopentadienyl)-3-*tert*-butyl-1-zircona-2-azacyclohepta-2,5-diene (9) and 1,1-Bis(η-cyclopentadienyl)-3-*tert*-butyl-5-vinyl-1-zircona-2-azacyclopenta-3-ene (10). (Butadiene)bis(η-cyclopentadienyl)zirconium (4) (317 mg, 1.15 mmol) was dissolved in 5 mL of toluene at room temperature. Pivalonitrile was added (126 μL, 1.15 mmol) and the mixture was stirred for 1 h at ambient temperature. The solvent was removed in vacuo and the residue was extracted with 20 mL of pentane for 5 h. The obtained red-colored solution was concentrated in vacuo to a volume of 5 mL and the product precipitated at −25 °C (12 h). The solvent was decanted and the residue dried in vacuo to yield 379 mg (92%) of the **9**/**10** mixture as a red oil (**9**/**10** = 8:2). Major component **9**: ^{1}H NMR (C_6D_6) δ 6.21 (dt, 1H, 6-H), 5.56 (s, 10H, Cp), 4.65 (dt, 1H, 5-H), 3.30 (br m, 1H, 4-H′), 1.50 (br m, 3-H, 4-H, 7-H, 7-H′), 1.02 (s, 9H, *tert*-butyl); ^{13}C NMR (C_6D_6) δ 180.8 (C-3), 138.5 (C-5, $^1J_{CH}$ = 145 Hz), 107.5 (Cp, $^1J_{CH}$ = 173 Hz), 107.3 (C-6, $^1J_{CH}$ = 150 Hz), 39.7 (*C*(CH_3)$_3$), 35.4, 32.2 (C-4, C-7, $^1J_{CH}$ = 133 and 134 Hz), 26.8 (C(*C*H_3)$_3$, $^1J_{CH}$ = 122 Hz); IR (KBr) ν 3097, 2961, 2905, 2867, 1674, 1630, 1441, 1013, 801 cm^{-1}. Minor component **10**: ^{1}H NMR (C_6D_6) δ 6.51 (ddd, 1H, 6-H), 5.42 (s, 5H, Cp), 5.14 (d, 1H, 7-H′), 5.10 (s, 5H, Cp), 4.97 (d, 1H, 7-H), 4.77 (dd, 1H, 4-H), 4.23 (s, 1H, NH), 1.09 (dd, 1H, 5-H), 1.13 (s, 9H, *tert*-butyl); coupling constants (Hz) ^3J = 7.8 (4-H, 5-H), 8.2 (5-H, 6-H), 10.5 (6-H, 7-H), 17.1 (6-H, 7-H′); ^4J = 2.6 (4-H, NH); ^{13}C NMR (toluene-d_8, 253 K) δ 143.2 (C-6), 131.6 (C-3), 106.5, 103.4 (Cp), 97.4 (C-4), 94.7 (C-7), 66.5 (C-5), 41.4 (*C*(CH_3)$_3$), 28.6 (C(*C*H_3)$_3$); IR (KBr) ν (NH) 3375 cm^{-1}. Anal. Calcd for $C_{19}H_{25}NZr$ (358.6): C, 63.63; H, 7.03; N, 3.41. Found: C, 63.26; H, 6.95; N, 3.91.

(2*E*,5*Z*,8*E*)-1,1-Bis(η-cyclopentadienyl)-3,8-di-*tert*-butyl-1-zircona-2,9-diazacyclonona-2,5,8-triene (12) and (2*E*,5*E*,7*Z*)-1,1-Bis(η-cyclopentadienyl)-3,8-di-*tert*-butyl-1-zircona-2,9-diazacyclonona-2,5,7-triene (11). Pivalonitrile (356 μL, 3.26 mmol) was added to a solution of 450 mg (1.63 mmol) of (butadiene)zirconocene (4) in 5 mL of toluene. The reaction mixture was stirred for 4 days at ambient temperature. The red mixture was filtered and the solvent removed in vacuo. The resulting residue was extracted with 20 mL of pentane and the product recovered by crystallization at −30 °C to yield 430 mg (60%) of the **11**/**12** (1:9) mixture as a yellow powder: mp 109 °C dec. Anal. Calcd for $C_{24}H_{34}N_2Zr$ (441.8): C, 65.25; H, 7.76. Found: C, 64.20; H, 7.49. Major component (**12**): ^{1}H NMR (toluene-d_8, 238 K) δ 5.60 (s, 10H, Cp), 4.58 (m, 2H, 5-H, 6-H), 3.07 (m, 2H, 4-H′, 7-H′), 2.32 (m, 2H, 4-H, 7-H), 1.03 (s, 9H, C(C*H*$_3$)$_3$). Coupling constants (Hz): ^2J = −15.6 (4-H, 4-H′; 7-H, 7-H′), ^3J = 9.1 (4-H, 5-H; 6-H, 7-H), 5.0 (4-H′, 5-H and 6-H, 7-H′), 15.2 (5-H, 6-H); ^{13}C NMR (toluene-d_8) δ 175.6 (C-3, C-8), 131.4 (C-5, C-6), 108.9 (Cp), 41.3 (*C*(CH_3)$_3$), 37.2 (C-4, C-7), 28.2 (C(*C*H_3)$_3$); IR (KBr) ν 3098, 2963, 1697, 1675, 1473, 1358, 1263, 1216, 1103, 1099, 1051, 1017, 800 cm^{-1}. Minor component (**11**): ^{1}H NMR (C_6D_6) δ 6.02 (dt, 1H, 5-H), 5.82 (s, 10H, Cp), 5.66 (dd, 1H, 6-H), 4.89 (d, 1H, 7-H), 4.24 (s, 1H, N-H), 2.82 (d, 2H, 4-H, 4-H′), 1.13 (s, 9H, C(C*H*$_3$)$_3$, 0.96 (s, 9H, C(C*H*$_3$)$_3$); coupling constants (Hz) ^3J = 7.0 (4-H, 5-H), 15.1 (5-H, 6-H), 3.7 (6-H, 7-H); ^{13}C NMR (toluene-d_8) δ 164.5 (C-3), 130.7 (C-5), 110.0 (Cp), 105.4 (C-7), 41.3 (*C*(CH_3)$_3$), 34.4 (C-4), 29.5, 27.9 (C(*C*H_3)$_3$), C-6 and C-8 not observed.

Synthesis of (3*Z*,5*E*,7*Z*)-3,8-Diamino-2,2,9,9-tetramethyldeca-3,5,7-triene (13). A solution of 3.52 g (7.97 mmol) of the **11**/**12** mixture in 50 mL of tetrahydrofuran was charged with 1 mL (24.0 mmol) of methanol. The reaction mixture was stirred for 22 h at ambient temperature and then the solvent was removed in vacuo. The obtained residue was extracted with three 20-mL portions of pentane. The product **13** was precipitated by cooling to yield 950 mg (54%) of a white crystalline material: mp 104 °C dec; ^{1}H NMR (C_6D_6) δ 6.08 (m, 2H, =CH), 5.05 (m, 2H, =CH), 3.35 (s, 4H, NH_2), 1.11 (s, 18H, *tert*-butyl); coupling constants (Hz) ^3J = 11.1 (CH=C*H*C*H*=C(NH_2), 14.5 (C*H*=C*H*-CH=C-(NH_2); ^{13}C NMR (C_6D_6) δ 148.7 (C-3, C-8), 122.2 (C-5, C-6), 98.7 (C-4, C-7), 34.0 (*C*(CH_3)$_3$), 29.1 (C(*C*H_3)$_3$); ^{1}H NMR [$(CD_3)_2SO$] δ 6.02 (m, 2H, =CH), 4.70 (m, 2H, =CH), 4.31 (s, 4H, NH_2), 1.05 (s, 18H, *tert*-butyl); ^{13}C NMR [$(CD_3)_2SO$] δ 148.7 (C-3, C-8), 121.0 (C-5, C-6), 95.2 (C-4, C-7), 34.6 (*C*(CH_3)$_3$), 28.9 (C(*C*H_3)$_3$); IR (KBr) δ 3446, 3365, 3061, 3002, 2970, 2962, 2957, 1630, 1461, 1455, 1383, 1355, 1307, 1220, 1178, 1038, 947, 801 cm^{-1}. Recrystallization from ether gave crystals of **13** suited for the X-ray crystal structure analysis (for details see Table IV). Anal. Calcd for $C_{14}H_{26}N_2$ (222.6): C, 75.62; H, 11.79; N, 12.60. Found: C, 73.79; H, 11.92; N, 11.98.

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Supplementary Material Available: Full details of ab initio calculations (GAUSSIAN 92 archive entries) (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the Journal, and can be ordered from the ACS; see any current masthead page for ordering information.