Nitrile Addition to (η^4-Butadiene)zirconocene: The Formation of Organometallic and Metal-Free Hexatrienediamine Derivatives

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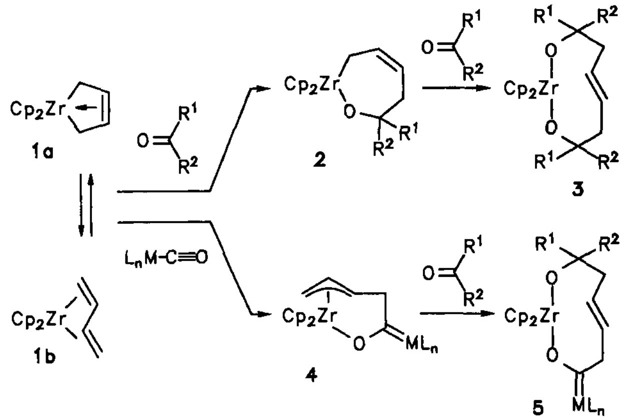
(η^4-Butadiene)zirconocene adds one equivalent of benzonitrile to form the five-membered azazirconacyclopentene derivative **7**, which contains an NH group in the ring and a vinyl substituent at the α-carbon center. The reaction of **7** with an additional equivalent of benzonitrile furnishes the chiral nine-membered metallacycle [$\overline{Cp_2ZrN(H)C(Ph)=CHCH=CHCH_2C(Ph)=N}$] (**12**) which may be isomerized to the thermodynamically favored tautomer [$\overline{Cp_2ZrN=C(Ph)CH_2CH=CHCH_2C(Ph)=N}$] (**13**). The Gibbs activation energy of the enantiomerization of the *trans*-cycloalkene-like **13** is $\Delta G^{+}(323\ K) = 15.5 \pm 0.3$ kcal mol^{-1}. The analogous conformational equilibration of **12** has a lower activation barrier of ΔG^{+} (236 K) = 12.1 ± 0.3 kcal mol^{-1}; complex **13** is characterized by X-ray diffraction. Hydrolysis of **13** yields the conjugated 1,6-diamino-1,6-diphenylhexatriene **16** which is characterized by X-ray diffraction.



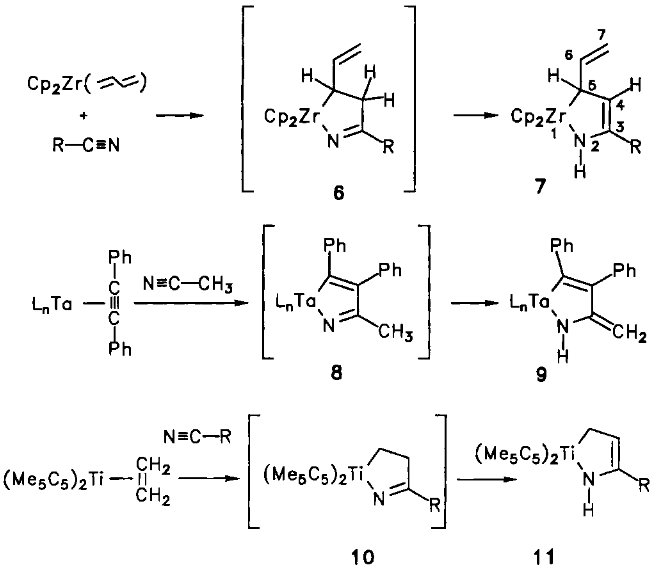
Ordinary butadiene dianion equivalents such as "butadiene-magnesium" add electrophiles at their 1- and 2-positions[1]. This selectivity pattern of the two-step reaction sequence is governed by the structure and chemical properties of the substituted allyl anion-type intermediate formed. Transmetalation of the butadiene dianion reagent from e.g. magnesium to bis(η^5-cyclopentadienyl)zirconium results in a fundamental reactivity/selectivity change of the butadiene double carbon nucleophile: only 1,4-addition of electrophilic reagents is observed in cases where the second reaction step is sufficiently rapid. Yasuda et al. have described many such examples where (η^4-butadiene)zirconocene takes up two equivalents of an organic carbonyl reagent to form nine-membered metallacycles[2]. The corresponding seven-membered metallacyclic intermediates have been observed or even isolated in a few cases[3]. We have used a similar reaction sequence to couple the (η^4-butadiene)metallocene with a (carbonyl)metal and an organic carbonyl compound consecutively to produce the nine-membered metallacyclic (oxycarbene)metal complexes **5**[4]. Metallacyclic (oxycarbene)metal complexes **4** can in many cases be isolated in the course of the reaction[5]. The overall addition of the two electrophiles in the great number of examples looked at has always been 1,4-selective. There has been no evidence of a 1,2-addition of carbonyl electrophiles (organic or organometallic).

We have now investigated the reaction course of the 1,4-selective addition of two nitrile electrophiles to the conjugated diene ligand bound to bis(η^5-cyclopentadienyl)zirconium. The RCN/(η^4-butadiene)ZrCp$_2$ 1:1-addition product has been isolated and characterized. Subsequent addition of a second RCN equivalent followed by hydrolysis has opened a simple synthetic route to a stable conjugated bis(enamine) product. Some details of this investigation are described for a selected example, namely the reaction of (η^4-butadiene)zirconocene with benzonitrile.

Results and Discussion

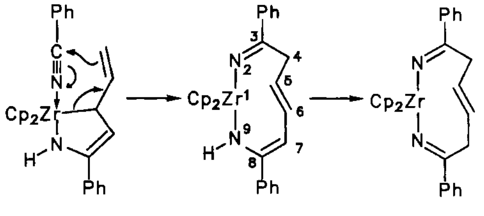
The (s-*cis*-/s-*trans*-η^4-butadiene)zirconocene equilibrium mixture of isomers[6] (**1a**:**1b** ≈ 1:1) reacts readily with one molar equivalent of benzonitrile at room temperature in toluene solution. Carbon–carbon bond formation between a conjugated diene terminus and the nitrile carbon atom is observed. At the same time a thermodynamically strong zirconium-to-nitrogen linkage is formed. According to the spectroscopic data we have obtained the five-membered metallacyclic zirconium-substituted enamine derivative **7**. Complex **7** exhibits an N–H IR band at $\tilde{\nu} = 3376$ cm^{-1}.

The ^{1}H-NMR spectrum shows the typical resonance signals of a vinyl group at δ = 6.64, 4.92, and 4.74 (^3J = 10.5 and 17.1 Hz). Hydrolysis of **7** furnishes a mixture of (*cis-/trans-*) 1-phenyl-3-penten-1-one and 1-phenyl-4-penten-1-one (ca. 2:3 ratio).



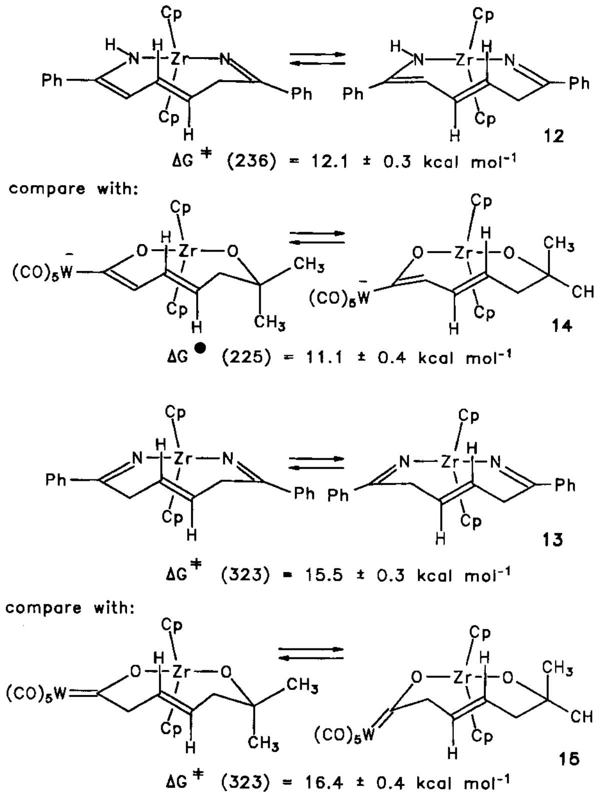
It is likely that benzonitrile adds to (η^4-butadiene)zirconocene to give the metallacycle **6** as the primary product[7] which is then rearranged to the –NH–-containing metal complex. Such (imido-to-amido)metallocene transformations have precedence in the chemistry of the respective Cp_2M complexes[8]. Labeling experiments have shown that the related **8** → **9** rearrangement proceeds intermolecularly[9] whereas the corresponding H-shift of the **10** → **11** reaction takes place intramolecularly[10]. The latter probably represents an exceptional case due to the steric bulk of the permethylated bent metallocene unit. Although we have not checked this experimentally, it is likely that the formal 1,3-hydrogen shift during the **6** → **7** rearrangement also takes place intermolecularly. The imido nitrogen atom in the five-membered ring of **6** is certainly strongly basic and therefore suited to abstract an allylic ring hydrogen atom from an adjacent molecule to initiate the base-catalyzed **6** → **7** tautomerization. The stable organometallic product **7** has been isolated from the reaction mixture in >90% yield.

The five-membered metallacyclic benzonitrile/(η^4-butadiene)zirconocene 1:1 addition product **7** is then treated with one additional molar equivalent of benzonitrile in benzene solution at room temperature. After two hours, the addition reaction is complete and has resulted in an almost quantitative formation of the nine-membered metallacycle **12**. The Zr–NH-containing complex is the kinetically controlled product. In a very slow isomerization reaction (1 week at 60 °C) it is completely converted into the (imido)zirconium tautomer **13**. The latter complex can be obtained directly as the major reaction product when the (η^4-butadiene)zirconocene starting material (**1a**/**1b**) is treated at room temperature in toluene solution (16 h) with two molar equivalents of benzonitrile. Subsequent workup then yields a nonthermodynamic mixture of the tautomers **12** and **13** enriched in the more stable isomer (**13**:**12** $\approx$ 2:1). Probably, the rather basic precursor **7** here serves as a catalyst for the kinetically accelerated formation of the nine-membered bis(imido)zirconium complex **13** from its kinetically preferentially formed nine-membered (amido,imido)zirconocene precursor **12**.



The structural assignment of the tautomeric complexes **12** and **13** is based on their very characteristic spectroscopic data (see Experimental). In addition, both products exhibit a very diagnostic dynamic behavior which is followed and characterized by temperature-dependent dynamic ^{1}H-NMR spectroscopy. Complex **12** has a chiral structure which, however, is obscured by a rapid dynamic conformational equilibration leading to spectra at room temperature of apparent C_s molecular symmetry. Consequently, the single ^{1}H-NMR Cp resonance signal of **12** at room temperature is rapidly broadened on lowering the monitoring temperature. Below the coalescence temperature of T_c = 236 K (at 4.7 Tesla) it separates into two lines of equal intensity (separated by ca. 48 Hz at the low-temperature limiting situation). Apparently, complex **12** contains a *trans*-configurated C=C bond in the metallacyclic ring system.

The Gibbs activation energy of the conformational equilibration of this organometallacyclic *trans,cis*-cyclononadiene analogue is $\Delta G^{+}(263\ \mathrm{K}) = 12.1 \pm 0.3$ kcal mol^{-1} as estimated from the dynamic NMR experiment described above. A very similar ΔG^{+} value has recently been observed for the related topomerization of the "ester-enolate-like" (zirconiooxy)carbene anion system **14**, which has been obtained by α-deprotonation of the nine-membered metallacyclic (zirconiooxy)carbene complex **15**[4a]. The neutral (carbene)tungsten complex **15** also contains a *trans*-configurated C=C bond and is therefore chiral[4]. Its ring-inversion barrier has been determined as $\Delta G^{+}(323\ \mathrm{K}) = 16.6 \pm 0.4$ kcal mol^{-1}. The nine-membered bis(imido)zirconocene complex **13** is structurally related to the metallacyclic system **15**. It also contains a *trans*-C=C bond within the medium-sized ring system. It exhibits dynamic NMR spectra. From the coalescence behavior of the allylic CH_2 hydrogen resonance signals we have estimated a Gibbs activation energy of $\Delta G^{+}(323\ \mathrm{K}) = 15.5 \pm 0.3$ kcal mol^{-1} for the conformational equilibration of **13**. As for the many examples of *trans*-configurated nine-membered (zirconiooxy)carbene complexes of the general structural type of **15** [complex **15** containing the =W(CO)$_5$ moiety is only a specific example[4]] this tautomerization reaction of the bis(imido)zirconocene complex **13** probably takes place by a concerted rotational process around two ring C–C σ-bonds. In each case one of the hydrogen atoms at the *trans*-C=C bond must move through the inside of the medium-sized ring system. In complexes **13** and **15** this process is closely related and therefore is expected to exhibit similar activation energies, as is experimentally observed. The introduction of an additional C=C bond into the ring system (i.e. by formally going from **15** to **14** or analogously from **13** to **12**) probably slightly increases the ring strain of the ground states of these systems and, at the same time, may lead to a stabilization of the transition state of the topomerization reaction by means of conjugation. Consequently, the activation barrier of the conformational equilibration process of these systems, as observed by dynamic NMR spectroscopy, is decreased.



Complex **13** is characterized by X-ray diffraction. It contains a nine-membered metallacyclic ring system and in addition benzene as a solvent molecule at a center of inversion. Unfortunately, the structure is highly disordered with regard to the carbon atoms C9 and C10 of the *trans*-C=C bond within the medium-sized metallacyclic ring system and also for one Cp ring. Similar disorder effects have rather frequently been encountered previously in similarly structured metallacyclic (zirconiooxy)carbene complexes such as $Cp_2\overline{ZrOC[=W(CO)_5]CH_2CH=CHCH_2C(Ph)N}$[4b]. The gross molecular structure is depicted in Figure 1[11]. The bad disorder precludes a detailed discussion of the structure.

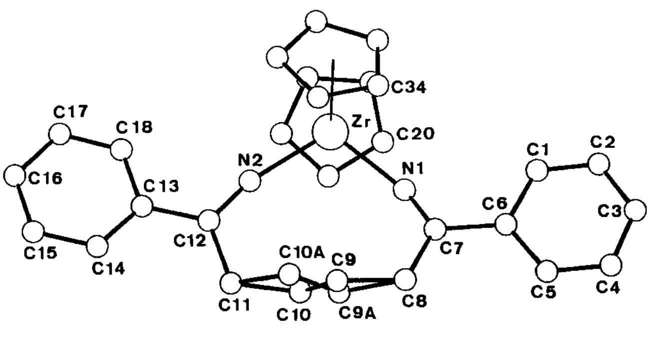
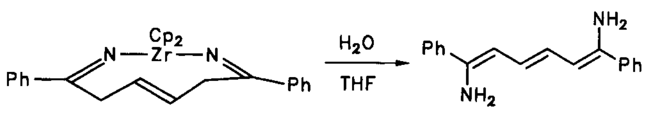


Figure 1. A projection of the molecular structure of complex **13** in the crystal with nonsystematical numbering scheme; the carbon centers C9 and C10 are disordered

A mixture of organometallic 2:1 benzonitrile/(η^4-butadiene)zirconocene addition products **12** and **13** (ca. 1:2 ratio) is dissolved in tetrahydrofuran and then hydrolyzed by the addition of excess of water at ambient temperature. After workup, a single orange-colored organic product is obtained in >90% yield. According to the spectroscopic analysis a single isomer of 1,6-diphenyl-1,3,5-hexatriene-1,6-diamine (**16**) is obtained[12].



13 (+ its isomer **12**) **16**

The hexatrienediamine **16** is also characterized by X-ray diffraction (Figure 2). It contains a nearly-planar conjugated sp^2-carbon framework. The symmetry-equivalent trisubstituted double bonds (C7–C8) are (*Z*)-configurated. The central C9–C9* double bond is *trans*-disubstituted. The fully alternating chain of C(sp^2)–C(sp^2) single and double bonds has thus adopted the expected most stable arrangement exhibiting all conjugated diene subunits in *s-trans* conformations which gives the overall conjugated system its greatest possible extension.

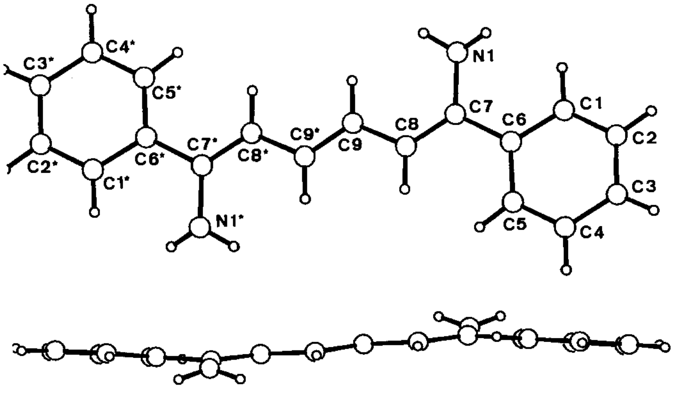


Figure 2. Two views of the molecular geometry of **16**; selected bond distances [Å] and angles [°]: N(1)–C(7) 1.385(2), C(1)–C(2) 1.381(3), C(1)–C(6) 1.390(2), C(2)–C(3) 1.374(3), C(3)–C(4) 1.375(3), C(4)–C(5) 1.375(3), C(5)–C(6) 1.399(2), C(6)–C(7) 1.480(2), C(7)–C(8) 1.356(2), C(8)–C(9) 1.437(2), C(9)–C(9)* 1.349(2); C(8)–C(7)–C(6) 122.8(1), C(8)–C(7)–N(1) 121.1(1), C(6)–C(7)–N(1) 115.9(1), C(9)–C(8)–C(7) 125.7(2), C(9)*–C(9)–C(8) 124.4(2)

This selected example emphasizes the potential of the (conjugated diene) group-4 bent metallocene complexes as useful synthetic equivalents of 1,4-selective butadiene dianion dinucleophiles. The organometallic starting material used here (as well as many substituted analogues) is readily available even on a large scale[6]. It reacts with many organic electrophiles under mild reaction conditions and appears to be completely 1,4-selective. We are currently examining the synthetic potential of the reaction type described above for preparing specifically substituted analogues of extended conjugated systems related to **16**.

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Experimental

Reactions with organometallic reagents and workup were carried out under Ar by using Schlenk-type glassware or in a drybox. All solvents used for the preparations were dried and distilled under Ar prior to use. For a description of further general conditions including a list of spectrometers used for the characterization of products see ref.[4c]. The NMR signal assignments are in accordance with the atomic numbering in the formula schemes but not with the IUPAC nomenclature rules.

Aza-zircona-cyclopentene 7: (η^4-Butadiene)zirconocene (882 mg, 3.2 mmol) was dissolved in 20 ml of toluene. To this solution was added dropwise at 0°C a solution of 310 µl (3.0 mmol) of benzonitrile in 20 ml of toluene during 1.5 h. The mixture was then stirred for 3 h at room temperature. A precipitate was removed by filtration and the clear filtrate concentrated in vacuo to a volume of 10 ml. Product 7 was precipitated by the addition of 10 ml of pentane. Complex 7 was recovered by filtration and dried in vacuo; yield 1.05 g (92%), m.p. 125°C (dec.). – ^{1}H-NMR (C_6D_6, 200 MHz): δ = 7.40–7.00 (m, 5H, Ph), 6.64 [ddd, 1H, 6-H ($CH{=}CH_2$)], 6.10 (s, 1H, NH), 5.53 (s, 5H, Cp), 5.33 (dd, 1H, 4-H), 5.08 (s, 5H, Cp), 4.92 (d, 1H, 7-H), 4.74 (d, 1H, 7-H′), 1.54 (dd, 1H, 5-H); coupling constants [Hz]: ^3J = 8.3 (4,5), 8.2 (5,6), 17.1 (6,7′); ^4J = 2.0 (4, NH). – ^{13}C-NMR (C_6D_6, 50 MHz, DEPT): δ = 142.4 (C-6), 139.1 (arom. C-*i*), 133.1 (C-3), 129.3, 128.7, 126.0 (arom. C), 107.1, 103.7 (Cp), 102.2 (C-4), 99.3 (C-7), 68.5 C-5). – IR (KBr): $\tilde{\nu}$ = 3376 cm^{-1}, 3103, 3066, 3052, 2990, 2919, 1679, 1651, 1595, 1577, 1488, 1444, 1015, 955, 800.

$C_{21}H_{21}NZr$ (378.6) Calcd. C 66.62 H 5.59 N 3.70
Found C 67.40 H 5.79 N 3.67

Hydrolysis of 7 gave a mixture of *cis*- and *trans*-1-phenyl-3-penten-1-one and 1-phenyl-4-penten-1-one in a 2:3 ratio (characterized NMR-spectroscopically). A sample of 7 (310 mg, 0.82 mmol) was dissolved in 5 ml of THF. Water (1 ml) and 5 drops of 2 N HCl were added, and the mixture was stirred for 3 h at ambient temperature. Solid decomposition products were removed by decanting the supernatent clear solution. The THF was then removed in vacuo and the residue extracted with three 3-ml portions of ether. The combined ethereal extracts were dried with Na_2SO_4, and then the solvent was evaporated in vacuo to give 106 mg (82%) of a mixture of hydrolysis products as a red oil which was not further separated. – ^{1}H NMR of the mixture of isomers ($CDCl_3$, 200 MHz): δ = 8.05–7.90, 7.60–7.30 (m, Ph), 6.00–5.60 (m, $CH{=}CH$), 5.03, 4.98 (m, $={CH_2}$), 3.80–3.77, 3.68–3.65 (m, CH_2), 3.06 (m, CH_2CO), 2.48 (m, CH_2CH_2CO), 1.70 (CH_3). – ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 199.3, 198.5, 197.9 (CO), 137.2 ($CH{=}CH_2$), 137.2, 136.9, 136.5 (C-*i*), 133.1, 132.9, 128.7, 128.0, 126.7 (Ph, alkene C), 115.2 ($CH{=}CH_2$), 42.4, 42.3, 37.6, 28.1 (CH_2). – IR (film): $\tilde{\nu}$ = 3085 cm^{-1}, 3073, 3063, 3028, 2964, 2917, 1675, 1597, 1580, 1448, 1364, 1261, 1209, 1181, 1091, 1070, 1015, 955, 800.

Diaza-zircona-cyclononatrienes **12** *and* **13**: To a solution of 2.45 g (8.9 mmol) of (η^4-butadiene)zirconocene in 40 ml of toluene was added dropwise a solution of 1.83 µl (17.8 mmol) of benzonitrile in 10 ml of toluene. The reaction mixture was then stirred for 16 h at room temperature. The dark-red mixture was filtered and the solvent removed in vacuo to give 3.59 g (84%) of a mixture of isomers **13** and **12** in a ratio of 2:1, m.p. 162°C (dec.).

$C_{28}H_{26}N_2Zr$ (481.8)
Calcd. C 69.81 H 5.44 N 5.81
12/13: Found C 69.67 H 5.64 N 6.20

The thermodynamically more stable product was **13**. A sample of the material prepared as described above was dissolved in C_6D_6 and heated for one weak at 60°C to give pure **13**, m.p. 164°C (dec.). – **13**: ^{1}H NMR (C_6D_6, 200 MHz): δ = 7.80–7.20 (m, 10H, Ph), 5.76 (s, 10H, Cp), 4.97 (m, 2H, 5-H, 6-H), 3.60 (br., 2H, 7-H′, 4-H′), 3.00 (br., 2H, 7-H, 4-H); ^{1}H NMR ([D$_8$]toluene, 200 MHz, 273 K): δ = 7.80–7.10 (m, 5H, Ph), 5.68 (s, 10H, Cp), 4.91 (ddd, 2H, 5-H, 6-H), 3.05 (dd, 2H, 7-H′, 4-H′), 2.30 (ddd, 2H, 7-H, 4-H); coupling constants (Hz): ^2J = 15.6 (4,4′; 7,7′); ^3J = 6.2 (4′,5; 6,7′), 4.1 (4,5; 6,7); ^4J = 2.1 (4,6; 5,7); dynamic ^{1}H-NMR spectroscopy ([D$_8$]toluene, 200 MHz, variable temperature): $\Delta\nu$ of the CH_2 resonance signals at the low-temperature limit: 149.3 Hz; coalescence temperature T_c = 323 K; Gibbs activation energy of the topomerization process at T_c: $\Delta G^{\neq}$(323 K) = 15.5 ± 0.3 kcal mol^{-1}. – ^{13}C NMR (C_6D_6, 50 MHz): δ = 165.1 (C-3, C-8), 139.6 (arom. C-*i*), 131.3, 129.0, 128.8 (Ph), 126.8 (C-5, C-6), 108.9 (Cp), 39.4 (C-4, C-7). – IR (KBr): $\tilde{\nu}$ = 3095 cm^{-1}, 3051, 2919, 1680, 1651, 1443, 1262, 1079, 1016, 798. – X-ray crystal structure: Suitable crystals were grown from [D$_6$]benzene. **13** crystallized with half an equivalent of benzene per molecule. Crystal size: 0.40 × 0.36 × 0.50 mm; Enraf-Nonius CAD4 diffractometer; Cu-K_α radiation (λ = 1.54178 Å); orthorhombic; space group *Pbca* (No. 61); a = 8.226(1), b = 21.472(2), c = 29.109(4) Å; V = 5141.6 Å^3; Z = 8, $d_{\text{calcd.}}$ = 1.35 g cm^{-3}; $F(000)$ = 2152 e; μ = 36.84 cm^{-1} (empirical absorption correction; min. 0.744, max. 0.998); 7394 reflections collected $(+h, +k, +l)$; 5365 independent and 3560 observed reflections; 265 refined parameters; R = 0.104, R_w = 0.076; final residual electron density 0.96 e Å^{-3}. Heavy-atom method, carbon atoms C9 and C10 disordered (60:40), no satisfactory resolution of the disordered Cp ring C30–34[13].

Kinetically controlled formation of **12**: A sample of 46 mg (0.12 mmol) of 7 was dissolved in 600 µl of [D$_6$]benzene. Benzonitrile (12 µl, 0.12 mmol) was added, and the progress of the reaction was followed periodically by ^{1}H-NMR spectroscopy. The product formed under kinetic control was **12**. The reaction had gone to completion after ca. 2 h to give the complexes **12** and **13** in a 80:20 ratio. – **12**: ^{1}H NMR (C_6D_6, 200 MHz): δ = 7.80–7.20 (m, 10H, Ph), 6.42 (ddd, 1H, 5-H), 5.94 (dd, 1H, 6-H), 5.81 (s, 10H, Cp), 5.36 (dd, 1H, 7-H), 4.37 (s, 1H, NH), 3.34 (d, 2H, 4-H, 4-H′); coupling constants (Hz): ^3J = 7.2 (4,5), 15.9 (5,6), 4.8 (6,7); ^4J = 1.1 (5,7); ^{1}H NMR ([D$_8$]toluene, 200 MHz, 233 K): δ = 7.30–6.70 (m, 10H, Ph), 6.42 (ddd, 1H, 5-H), 5.83 (dd, 1H, 6-H), 5.78 and 5.57 (each s, 5H, Cp), 5.33 (dd, 1H, 7-H), 4.35 (s, 1H, NH), 3.51 (br., 1H, 4-H′), 3.00 (br., 1H, 4-H); dynamic ^{1}H-NMR spectroscopy ([D$_8$]toluene, 200 MHz, variable temperature): $\Delta\nu$ of the Cp resonance signals at the low-temperature limit: 48 Hz; coalescence temperature T_c = 236 K; Gibbs activation energy of the topomerization process at T_c: $\Delta G^{\neq}$(236 K) = 12.1 ± 0.3 kcal mol^{-1}. – ^{13}C NMR (C_6D_6, 50 MHz): δ = 168.8 (C-3), 157.2 (C-8), 146.5 (arom. C-*i* at C-8), 138.6 (arom. C-*i* at C-3), 132.0, 130.7, 129.7, 128.9, 128.3, 126.5, 126.3, 126.0 (C-5, C-6, Ph), 110.1 (Cp), 103.5 (C-7), 37.5 (C-4). – IR (KBr): $\tilde{\nu}$ = 3350 cm^{-1}, 3345, 1679, 1594, 1576, 1486, 1444.

Hydrolysis of the **12/13** *Mixture; Formation of the Diamine* **16**: A mixture of the isomers **12** and **13** (ratio 1:2) (710 mg, 1.47 mmol) was dissolved in 20 ml of THF. Water (5 ml) was added and the reaction mixture stirred for 2 h at room temperature. The THF was then removed in vacuo. The residue was extracted with three 20-ml portions of ether. The combined ethereal solutions were dried with $MgSO_4$ and then the solvent was evaporated in vacuo to give 350 mg (91%) of **16** as an orange-colored powder, m.p. 140 °C (decomp. with NH_3 formation). – ^1H NMR (C_6D_6, 200 MHz): δ = 7.50–7.45 and 7.15–7.04 (m, 10H, Ph), 6.28 (dd, 2H, =CH), 5.76 (dd, 2H, =CH), 3.13 (br. s, 4H, NH_2); coupling constants (Hz): ^3J = 7.7 (2,3); ^4J = 3.0 (2,4). – ^{13}C NMR ($CDCl_3$, 200 MHz): δ = 140.4 (=CNH_2), 139.2 (arom. C-*i*), 128.5, 127.8, 125.3, 123.3 (Ph and =CH), 104.3 [*H*C=C(NH_2)]. – IR (KBr): $\tilde{\nu}$ = 3450 cm^{-1}, 3371, 3055, 3032, 2964, 1621, 1602, 1571, 1560, 1495, 1447, 1379, 1330, 968, 802, 816. – UV (CH_2Cl_2): λ_{max} (ε) = 403 nm (27000).

$C_{18}H_{18}N_2$ (262.4) Calcd. C 82.41 H 6.92 N 10.68
Found C 80.79 H 6.98 N 9.48

X-ray crystal structure analysis of **16**: suitable crystals were obtained by crystallization of **16** from dichloromethane. Crystal size 0.05 × 0.32 × 0.42 mm; Enraf-Nonius CAD4 diffractometer; Cu-K_α radiation (λ = 1.54178 Å); monoclinic; space group *C2/c* (No. 15); a = 31.374(2), b = 5.473(1), c = 8.275(1) Å; β = 97.06(1)°; V = 1410.2 $Å^3$; Z = 4; $d_{calcd.}$ = 1.24 g cm^{-3}; $F(000)$ = 560 e; μ = 5.27 cm^{-1}; 2997 reflections measured ($\pm h$, $\pm k$, $+l$); 1450 independent and 1149 observed reflections; 127 refined parameters; R = 0.047, R_w = 0.055; final residual electron density 0.06 $Å^{-3}$. Direct methods, H-atom positions were calculated and included in the final least-squares refinement. Atomic parameters are listed in Table 1.

Table 1. Atomic coordinates and thermal parameter [$Å^2$] of **16**; $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \bar{a}_i \cdot \bar{a}_j$

Atom	x	y	z	U_{eq}
N(1)	0.0524(1)	0.4852(3)	–0.1897(2)	0.063(1)
C(1)	0.1375(1)	0.4292(3)	–0.2583(2)	0.059(1)
C(2)	0.1801(1)	0.4186(4)	–0.2839(3)	0.068(1)
C(3)	0.2070(1)	0.2445(4)	–0.2073(2)	0.064(1)
C(4)	0.1906(1)	0.0788(4)	–0.1064(3)	0.067(1)
C(5)	0.1481(1)	0.0891(3)	–0.0806(2)	0.061(1)
C(6)	0.1202(1)	0.2660(3)	–0.1554(2)	0.044(1)
C(7)	0.0746(1)	0.2805(3)	–0.1275(2)	0.045(1)
C(8)	0.0546(1)	0.1005(3)	–0.0532(2)	0.049(1)
C(9)	0.0096(1)	0.0921(3)	–0.0358(2)	0.050(1)

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[12] For related rather rare examples of stable NH_3-derived enanime systems see e.g.: F. Kröhnke, I. Vogt, *Justus Liebigs Ann. Chem.* **1954**, *589*, 26; H. Ahlbrecht, F. Kröhnke, *ibid.* **1967**, *701*, 126; H. Ahlbrecht, G. Rauchschwalbe, *Tetrahedron Lett.* **1971**, *51*, 4897; C. Shin, M. Masaki, M. Ohta, *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1657 and references cited in these articles; reviews: R. W. Layer, *Chem. Rev.* **1963**, *63*, 489; B. A. Shainyan, A. N. Mirskova, *Russ. Chem. Rev.* **1979**, *48*, 107.

[13] Because of the poor quality of the crystal structure determination of **13** no further details are given in this paper. – Further details of the crystal structure investigations of compound **13** and **16** are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2 (Germany), on quoting the depository number CSD-56255, the names of the authors, and the journal citation.

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1a: 83780-95-4 / **1b**: 83780-93-2 / **7**: 139705-57-0 / **12**: 139705-58-1 / **13**: 139705-59-2 / **13**·0.5 C_6H_6: 139705-60-5 / **16**: 139705-56-9 / PhCN: 100-47-0 / *cis*-1-phenyl-3-penten-1-one: 61752-45-2 / *trans*-1-phenyl-3-penten-1-one: 74157-93-0 / 1-phenyl-4-penten-1-one: 3240-29-7