Developing an Organometallic (Butadiene)bis(cyclopentadienyl)zirconium-Based Template Synthesis for the Preparation of Stable Conjugated Primary Enamines

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Reaction of (butadiene)bis(cyclopentadienyl)zirconium with 2 molar equiv of *trans*-cinnamonitrile gives a mixture of N-metalated enamine and imine tautomers of the 3,8-(–CH=CH—CN)-disubstituted 1-zircona-2,9-cyclononatriene framework. Subsequent hydrolysis furnishes a single isomer of the 3,8-diamino-1,10-diphenyl-1,3,5,7,9-decapentaene system. This compound (**7**) is an example of a stable isolable conjugated primary enamine. In similar ways one can couple difunctional nitriles, such as fumaronitrile or terephthalonitrile, with butadiene at the bis(cyclopentadienyl)zirconium template to give analogously structured nine-membered diazazirconacycles containing free nitrile functionalities. Subsequent hydrolysis yields cyano-functionalized conjugated primary enamines. When the stoichiometry of the starting components and the reaction conditions are varied, an organometallic building-block system is developed which allows for the preparation of di- and polynuclear nitrile/(butadiene)bis(cyclopentadienyl)-zirconium coupling products exhibiting various combinations of reactive functionalities. Coupling of fumaronitrile or terephthalonitrile with (butadiene)bis(cyclopentadienyl)zirconium in a strict 1:1 stoichiometry gave good yields of organometallic polymers which were hydrolyzed to yield conjugated organic (polyacetylene-like) polymers containing $-NH_2$ substituents attached systematically in conjugated positions.

Enamines are carbon nucleophiles which are of great importance as carbanion equivalents in organic synthesis. Easy to prepare and handle are the tertiary enamines; lacking a remaining hydrogen bonded to nitrogen prevents them from equilibrating with their imine tautomers.[1] In contrast, there are only relatively few examples of stable secondary and primary enamines known so far. This is mainly due to the rapid tautomerization to their reactive azomethine and imine isomers. Primary enamines especially have a high tendency to be rapidly decomposed in condensed media by means of bimolecular condensation reactions with their reactive imine tautomeric forms.[2,3]

We have recently found and described an example of a potentially useful organometallic template reaction which eventually allowed for the high-yield synthesis of a special example of a stable primary enamine. (Butadiene)bis(cyclopentadienyl)zirconium (**1**) was reacted subsequently with 2 molar equiv of benzonitrile.[4,5] Selective 1,4-addition of the nitrile functionalities to the formal butadiene dianion equivalent[6] took place via the isolated intermediate **2** (see Scheme I). The 2:1 addition product **3**, exhibiting a pair of endocyclic N-metalated imine and enamine functionalities, was isolated. It was slowly converted to the thermodynamically favored bis(imido) isomer **4** on gentle heating.[7] Complex **4** was then subjected to controlled hydrolysis, which surprisingly produced the stable primary enamine **5** in high yield.

Compound **5** is a thermodynamically stable conjugated primary enamine. To our knowledge it represents the first example of a primary enamine ever to be characterized by X-ray diffraction.[4] In benzene-d_6 solution we could not detect any indication for the presence of its imine tautomers within the limits of the ^1H NMR analysis.

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(1) For leading references on the historical background of synthetic tertiary enamine chemistry, see: Wittig, G.; Blumenthal, H. *Chem. Ber.* **1927**, *60*, 1088. Mannich, C.; Davidsen, H. *Chem. Ber.* **1936**, *69*, 2106. Stork, G.; Terrell, R.; Szmuszkovicz, J. *J. Am. Chem. Soc.* **1954**, *76*, 2029. Review: Pitacco, G.; Valentin, E. In The Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives. *The Chemistry of Functional Groups*; Patai, S., Ed.; Wiley: New York, 1982; Suppl. F.

(2) For representative examples see: von Auwers, K.; Susemihl, W. *Chem. Ber.* **1930**, *63*, 1072. von Auwers, K.; Wunderling, H. *Chem. Ber.* **1931**, *64*, 2748, 2758. Wegler, R.; Ruzicka, A. *Chem. Ber.* **1935**, *68*, 1059. 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. Ahlbrecht, H.; Fischer, S. *Tetrahedron* **1970**, *26*, 2837.

(3) Representative references: Moureau, C.; Mignonac, G. *C. R. Hebd. Seances Acad. Sci.* **1914**, *158*, 1395. Weissberger, A.; Glass, D. B. *J. Am. Chem. Soc.* **1942**, *64*, 1724. Kröhnke, F.; Vogt, I. *Justus Liebigs Ann. Chem.* **1954**, *589*, 26. Review: Layer, R. W. *Chem. Rev.* **1963**, *63*, 489. Ahlbrecht, H.; Kröhnke, F. *Justus Liebigs Ann. Chem.* **1967**, *701*, 51. Ahlbrecht, H. *Tetrahedron Lett.* **1968**, *42*, 4421. Ahlbrecht, H.; Rauchschwalbe, G. *Tetrahedron Lett.* **1971**, *51*, 4897. Shin, C.; Masaki, M.; Ohta, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1657. Ahlbrecht, H.; Blecher, J.; Hanisch, H.; Papke, G.; Reiner, M. T. *Tetrahedron* **1973**, *29*, 3097. Ahlbrecht, H.; Funk, W.; Reiner, M. T. *Tetrahedron* **1976**, *32*, 479. Shainyan, B. A.; Mirskova, A. N. *Russ. Chem. Rev.* (*Engl. Transl.*) **1979**, *48*, 107. Ripoll, J. L.; Lebrun, H.; Thuiller, A. *Tetrahedron* **1980**, *36*, 2497. See also references cited in these articles.

(4) Erker, G.; Pfaff, R.; Krüger, C.; Nolte, M.; Goddard, R. *Chem. Ber.* **1992**, *125*, 1669.

(5) For topologically 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. *Angew. Chem.* **1989**, *101*, 411; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 397.

(6) In contrast, other butadiene dianion equivalents, such as (butadiene)magnesium, react predominantly by means of 1,2-addition of electrophilic reagents: 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.

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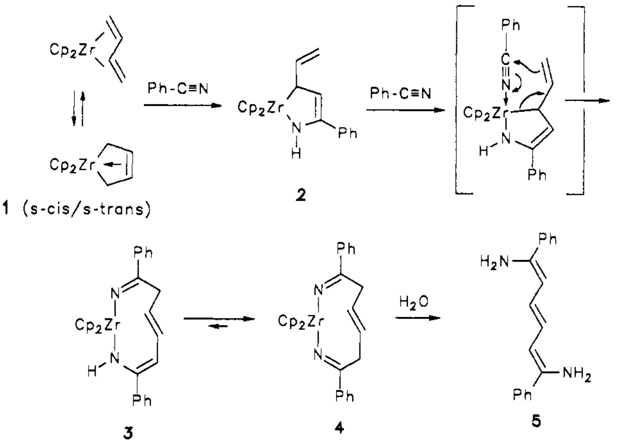
Scheme I

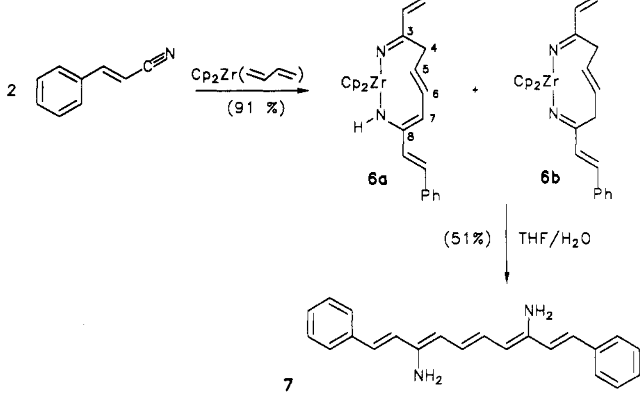


Conjugative effects are probably responsible for the high thermodynamic preference of the enamine tautomer. The specific substitution pattern at the conjugated polyene framework may in addition account for the rather high kinetic stability of this system. The counteracting enamine dipoles in **5** cancel each other. The C_i-symmetric enamine **5** has no remaining net dipole moment; it is best characterized as a stable 1,6-diaminohexatriene derivative.

We thought it would be interesting to use analogues of the simple template reaction sequence as depicted in Scheme I for the synthesis of a variety of related examples of amino-substituted conjugated polyene systems. We especially wondered whether extended polyene frameworks could be prepared by this route and if other functionalities (especially electron-withdrawing groups) would be compatible with the chemical characteristics of the reactions involved and with the presence of the primary enamine functions in the final product. In a series of experiments, which are described below, we have found that this synthetic scheme can be employed for the preparation of a variety of expanded and substituted conjugated primary enamines. The stepwise synthetic sequence can in fact be used in a way similar to a building-block system. In a variety of experiments we have shown that our new synthesis may eventually even open simple new ways for the production of interesting novel polymeric materials. Some representative examples of this development are described in this paper.

Results and Discussion

Preparation of a Diaminodecapentaene System. Expanding the conjugated π-system of a product prepared by a template synthesis analogous to the one outlined in Scheme I requires the use of a conjugated nitrile starting material. Therefore, we have reacted the (butadiene)-$ZrCp_2$ equilibrium mixture of isomers[8] with 2 molar equiv of *trans*-cinnamonitrile. A moderately fast reaction takes place at ambient temperature in toluene solution. The mixture becomes deeply colored within a couple of hours. The reaction goes to completion within a time period of 1 day, and an intensely violet organometallic product is then isolated in >90% yield. According to the elemental analysis a 2:1 nitrile/(butadiene)$ZrCp_2$ adduct is formed. The spectroscopic characterization reveals that exclusively 1,4-addition of the nitrile functionalities to the butadiene ligand system has occurred. The product exhibits a nine-membered metalla heterocyclic framework containing two –CH=CH—Ph side chains attached at the 3- and 6-positions of the central ring system. Under the specific reaction conditions applied, a mixture of the metalated imine/enamine and the bis(imine) tautomeric forms is obtained. The **6a**/**6b** ratio observed is approximately 70:30. It was not checked whether this already represents the equilibrium ratio of these isomers at room temperature. The ^1H NMR spectrum reveals that the –CH=CH—Ph substituents originating from the *trans*-cinnamonitrile reagent have retained their trans-configurated double bond ($^3J \approx$ 16–17 Hz). The central C=C bond in the "unsymmetrical" metallacyclic imine/enamine type tautomer **6a** is trans-configured (^3J[C(5), C(6)] = 16.2 Hz). We assume that the other tautomer (**6b**) also contains a central trans-C=C double bond in the nine-membered ring system.[9]



The **6a**/**6b** mixture was hydrolyzed (tetrahydrofuran/water). A single organic product (**7**) was isolated in ca. 50% yield. The elemental analysis revealed that both nitrogen atoms were retained in the product. Thus, we conclude that the hydrolytic cleavage of the zirconocene template from the nine-membered metallacyclic ring system has again produced a conjugated primary enamine system, namely 3,8-diamino-1,10-diphenyldecapentaene (**7**). A single isomer of this diaminopolyene system was produced. In view of its NMR spectral data (see Experimental Section) we have tentatively assigned it the depicted structure containing an all-trans-configurated polyolefinic carbon framework (i.e. product **7** has a 1-*E*,3-*Z*,5-*E*,7-*Z*,9-*E*

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(7) Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443. Doxsee, K. M.; Farahi, J. B. *J. Am. Chem. Soc.* **1988**, *110*, 7239; *J. Chem. Soc., Chem. Commun.* **1990**, 1452. Doxsee, K. M.; Mouser, J. K. M. *Organometallics* **1990**, *9*, 3012. See also: Buchwald, S. L.; Watson, B. T.; Lum, R. T.; Nugent, W. A. *J. Am. Chem. Soc.* **1987**, *109*, 7137. Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047 and references cited therein. Buchwald, S. L.; Watson, B. T.; Wannamaker, M. W.; Dewan, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 4486. Hessen, B.; Blenkers, J.; Teuben, J. H.; Helgesson, G.; Jagner, S. *Organometallics* **1989**, *8*, 830. Walsh, P. J.; Carney, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 6343. Doxsee, K. M.; Farahi, J. B.; Hope, H. *J. Am. Chem. Soc.* **1991**, *113*, 8889. Stricker, J. R.; Wigley, D. E. *Organometallics* **1990**, *9*, 1665. Cohen, S. A.; Bercaw, J. E. *Organometallics* **1985**, *4*, 1006.

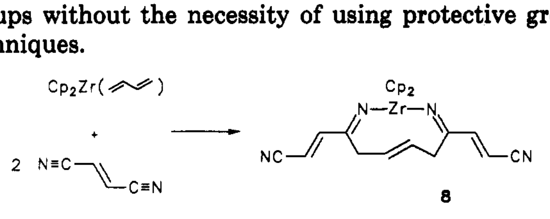
(8) (a) Erker, G.; Wicher, J.; Engel, K.; Rosenfeldt, F.; Dietrich, W.; Krüger, C. *J. Am. Chem. Soc.* **1980**, *102*, 6344. Erker, G.; Wicher, J.; Engel, K.; Krüger, C. *Chem. Ber.* **1982**, *115*, 3300. Erker, G.; Engel, K.; Krüger, C.; Chiang, A.-P. *Chem. Ber.* **1982**, *115*, 3311. Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1. (b) Yasuda, H.; Kajihara, Y.; Mashima, K.; Nagasuna, K.; Lee, K.; Nakamura, A. *Organometallics* **1982**, *1*, 388. Erker, G.; Engel, K.; Sarter, C. In *Organometallic Synthesis*; King, R. B., Eisch, J. J., Eds.; Elsevier: Amsterdam, 1986; Vol. 3, p 32.

(9) For a variety of structurally related examples, see: 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. *Z. Anorg. Allg. Chem.* **1990**, *581*, 16. 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.

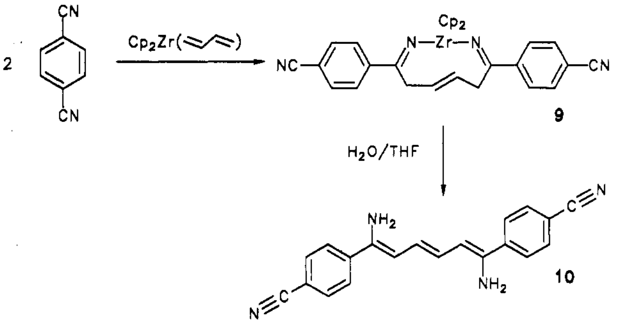
configuration). The diaminodecapentaene system **7** possesses an intensely red color; its characteristic UV/vis absorption is at λ_{max} = 462 nm (ϵ = 97 000, dichloromethane). Relative to the related 1,6-diamino-1,6-diphenylhexatriene (**5**: λ_{max} = 403 nm, ϵ = 27 000)[4] this lowest energy vis transition is bathochromically shifted by 59 nm and has considerably increased in intensity. The parent α,ω-diphenylhexatriene and -decapentaene systems behave similarly, showing UV/vis absorptions at λ_{max} = 377 (benzene) and λ_{max} = 424 nm (benzene), respectively.[10,11] We notice that attaching the $-NH_2$ substituents to the conjugated polyene chain has resulted in a 26–38-nm bathochromic shift in the systems **5** and **7** relative to their unfunctionalized hydrocarbon analogues.

The primary enamine **7** exhibits IR bands of the $-NH_2$ group at ν = 3388 and 3366 cm^{-1} (KBr). There is no IR indication of the presence of the imine tautomer of the $-CH{=}C(NH_2)-$functionality. The ^{1}H and ^{13}C NMR spectra of **7** (DMSO-d_6) were carefully checked for the presence of the tautomeric $-C{=}NH$ unit. Within the limits of the NMR detection we have not obtained any evidence for the population of an imine tautomeric form of **7** under equilibrium conditions at ambient temperature. Compound **7** thus has to be regarded as another example of an extraordinarily stable conjugated primary enamine.

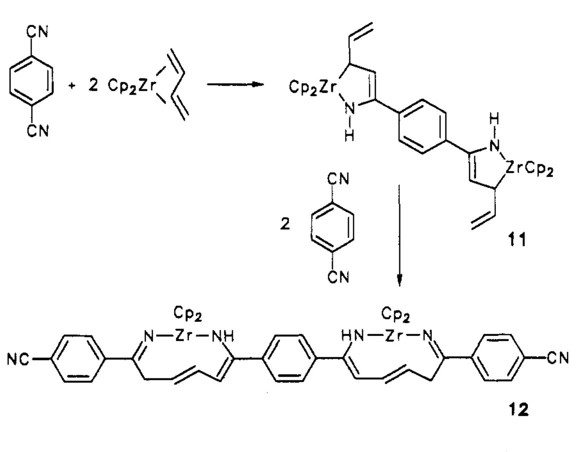
Developing a Template Building-Block System by Introducing Free Nitrile Substituents. In order to develop a flexible template building-block system for the synthesis of specifically structured organometallics containing the nine-membered zirconadiazacyclononatriene moieties, we intended to couple the butadiene reagent with multifunctional unsaturated organic reagents. A logical starting point for this part of our investigation was the use of unsaturated conjugated α,ω-dinitrile substrates. In a first orientating experiment we slowly added 1 molar equiv of (*s-cis-/s-trans-*η^4-butadiene)bis(cyclopentadienyl)zirconium to a solution of fumaronitrile in toluene at room temperature. The major product (ca. 70–80%) was a red precipitate (see below), which was filtered off in this experiment and was not further characterized. From the remaining clear solution we obtained the 2:1 fumaronitrile/(butadiene)$ZrCp_2$ addition product **8**. Complex **8** (ca. 20% yield isolated) is a single isomer containing N-metalated imine functionalities inside the nine-membered-ring system (^{13}C NMR δ 162.8 (C3, C8)). *trans*-$CH{=}CH{-}C{\equiv}N$ moieties are attached at the ring in positions 3 and 8 (^{1}H NMR δ 6.14, 5.11, ^3J = 16.4 Hz; IR ν = 2216 cm^{-1} ($C{\equiv}N$)). Thus, it seems that our template coupling reaction can be used to make functionalized metallacycles even from reagents bearing a pair of identical reactive functional groups without the necessity of using protective group techniques.



(Butadiene)bis(cyclopentadienyl)zirconium reacted analogously when added dropwise to an excess of terephthalonitrile in toluene solution to give the bis(imido)Zr-containing nine-membered metallacycle **9**, exhibiting two free symmetry-equivalent nitrile substituents (IR (KBr): ν = 2231 cm^{-1}). Hydrolysis of **9** with H_2O in tetrahydrofuran gave the metal-free organic product **10**, which was isolated in >60% yield. The 1,6-diaryl-1,3,5-hexatriene system contains $-NH_2$ groups at the polyene termini in addition to cyano substituents at the aromatic para positions. Our simple two-step synthetic scheme (consisting of the coupling of the organic nitrile and butadiene starting components at the organometallic bent metallocene template followed by controlled hydrolysis) has thus been used to prepare a stable conjugated primary enamine which contains additional electron-withdrawing nitrile substituents at conjugated positions. Compared to the parent (i.e. unsubstituted) 1,6-diamino-1,6-diphenyl-1,3,5-hexatriene system **5**, the push–pull substituted chromophore of **10** has caused a marked bathochromic shift in the UV/vis spectrum (λ_{max} = 460 nm, ϵ = 75 300). Again, the enamino tautomer seems to be very much dominating, as judged from the NMR and IR spectra (ν = 3440, 3356 cm^{-1} (NH_2), 2220 cm^{-1} (CN)) of **10**. We have not detected the imino tautomers spectroscopically.



The structure and composition of the organometallic addition products of terephthalonitrile and (butadiene)bis(cyclopentadienyl)zirconium depend strongly on the stoichiometry used and the reaction conditions applied. Both nitrile functionalities of the organic component are used when terephthalonitrile (1 molar equiv) is slowly added to (butadiene)$ZrCp_2$ (2 equiv) in toluene solution. A dimetallic addition product (**11**) was isolated in which the central *p*-phenylene unit connects two five-membered (σ-allyl)zirconium enamido units (IR: ν = 3365 cm^{-1} (NH)). Each of the azametallacyclopentenes contains a stereogenic center. Therefore, the occurrence of two diastereomeric *p*-phenylene-bridged dinuclear systems is expected. These are formed in a ca. 90:10 ratio.[12]



The dimetallic 2:1 (butadiene)$ZrCp_2$/$NC{-}C_6H_4{-}CN$ addition product **11** contains two reactive (σ-allyl)zirconium units which can be used for coupling with further nitrile-containing reagents.[4,5] This was demonstrated by treating the isolated complex **11** with terephthalonitrile. Spectroscopically the formation of the linear organome-

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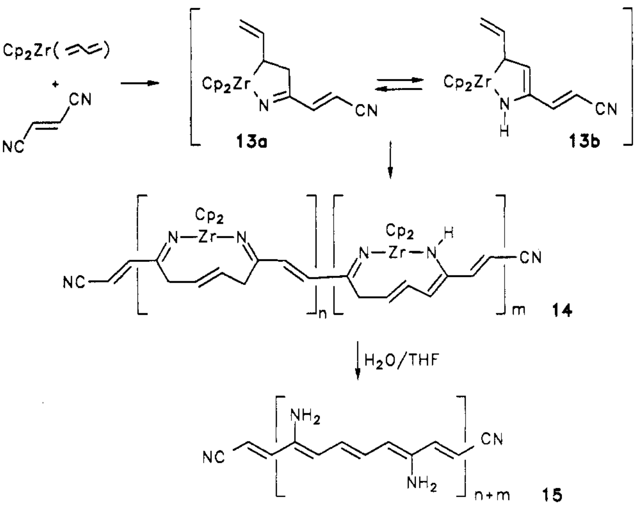
(10) Kuhn, R.; Winterstein, A. *Helv. Chim. Acta* **1928**, *11*, 87.

(11) Kuhn, R. *J. Chem. Soc.* **1938**, 605. Hausser, K. W.; Kuhn, R.; Smakula, A. Z. *Phys. Chem.* **1935**, *B29*, 384.

tallic coupling product between three terephthalonitrile moieties and two (butadiene)bis(cyclopentadienyl)zirconium species was observed. The product **12** contains nitrile groups (^{13}C NMR: δ 118.9 (*C*N)) at both ends of the organometallic chain and NH functionalities (^{1}H NMR: δ 4.59) within the nine-membered metallacyclic substructures. Probably a mixture of tautomeric isomers is formed.

Template-Directed Polymer Formation. From the experiments described above, it is expected that (butadiene)bis(cyclopentadienyl)zirconium will react with an equimolar quantity of e.g. fumaronitrile with formation of an unstable 1:1 addition product (**13**)—unstable in the sense that it contains two complementary reactive groups, namely the zirconium-bound η^1-allyl moiety, which is partly a component of the metallacyclic ring structure, and a free cyano group. It is expected that the special spatial arrangement of these two functional groups at the core of the initially formed intermediate **13** will preclude the isolation of the monomeric 1:1 addition product because of very favorable subsequent polymer formation. This is in fact observed experimentally.

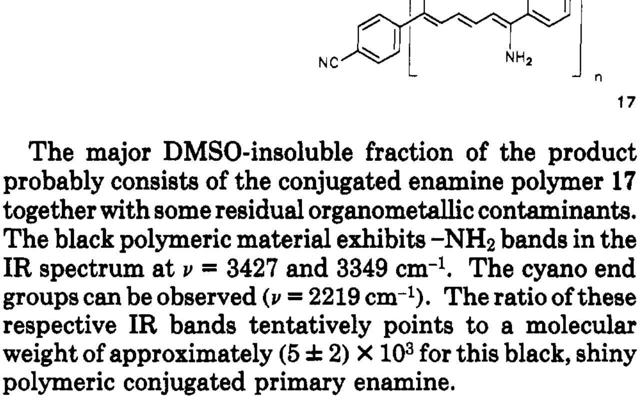


When fumaronitrile was added to 1 molar equiv of (butadiene)bis(cyclopentadienyl)zirconium in toluene at −50 °C and the mixture was then slowly warmed to room temperature, a black suspension resulted from which a dark brown insoluble organometallic product was isolated (>80%). The product seems to be an organometallic polymer of as-yet undisclosed molecular weight. It gives an adequate analysis for a multiple of the ($C_{18}H_{18}N_2Zr$) monomeric unit. The typical IR bands of the bent metallocene unit are found at ν = 3099, 1441, 1015, and 802 cm^{-1}. In addition there seems to be an occasional NH group in the product (ν = 3377 cm^{-1}), as is expected from the general behavior characteristic for accumulating a number of nine-membered 1-zircona-2,9-diazacyclononatriene frameworks in a product (see above).

The organometallic polymer **14** was hydrolyzed. Treatment with H_2O in tetrahydrofuran resulted in an almost metal-free insoluble organic polymer of dark brown color and of as-yet undisclosed molecular weight. It exhibits amino NH bands in the IR spectrum at ν = 3325 and 3184 cm^{-1} (KBr). Extraction with dimethyl sulfoxide gave a black solution from which a black shiny polymeric material was isolated in ca. 20% yield (mp 194 °C, DSC), which probably consists of the polymeric conjugated primary enamine **15**. The elemental analysis of this material falls somewhat short of the expected C,H,N values of the alleged monomeric $C_8H_{10}N_2$ unit (Anal. Calcd: C, 71.61; H, 7.51; N, 20.88. Found: C, 65.11; H, 6.70; N, 16.42). This may indicate that some of the primary amino groups have become hydrated during the aqueous workup procedure. Cleavage of the organometallic polymer **14** with anhydrous ethereal HCl produced a similar organic polymer, now probably containing occasional ammonium substituents. From the residue ca. 98% of the organometallic template was recovered as a mixture of Cp_2ZrCl_2 and $(Cp_2ZrCl)_2O$.

The reaction between (butadiene)bis(cyclopentadienyl)zirconium and terephthalonitrile in a 1:1 stoichiometry proceeded similarly. A red insoluble precipitate formed rapidly after mixing the two components at ambient temperature in toluene solution. The insoluble red organometallic polymer was isolated in >90% yield. It gave the correct analysis (C,H,N) as expected for a multiple of the $C_{22}H_{20}N_2Zr$ periodical. The –CN end groups can be spotted by IR (ν = 2225 cm^{-1}).

Hydrolysis of the organometallic polymer **16** with H_2O in tetrahydrofuran gave a black metallically shining organic polymer, ca. 10% of which could be extracted into DMSO. The resulting DMSO solution is dark violet (λ_{max} = 507 nm, $\epsilon \approx$ 75 000). In the ^{1}H NMR spectrum (DMSO-d_6) it shows broad resonances in the region typical for aromatic (δ 7.67, 7.50), olefinic (δ 6.60, 5.50), and enamine –NH_2 hydrogens (δ 5.10) in a 1:1:1 ratio.



The major DMSO-insoluble fraction of the product probably consists of the conjugated enamine polymer **17** together with some residual organometallic contaminants. The black polymeric material exhibits –NH_2 bands in the IR spectrum at ν = 3427 and 3349 cm^{-1}. The cyano end groups can be observed (ν = 2219 cm^{-1}). The ratio of these respective IR bands tentatively points to a molecular weight of approximately (5 ± 2) × 10^3 for this black, shiny polymeric conjugated primary enamine.

Conclusions

From the results of this study it can be expected that the template-directed coupling of two nitrile functionalities with butadiene will be developed into a rather widely applicable synthetic method for the preparation of stable conjugated primary enamines and related systems. This sequential ternary coupling of organic building blocks at the zirconocene template is a simple, easily performed practical method for constructing the basic framework of

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(12) 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.; Engel, K.; Atwood, J. L.; Hunter, W. E. *Angew. Chem.* **1983**, *95*, 506; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 494. 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. Yasuda, H.; Nakamura, A. *Angew. Chem.* **1987**, *99*, 745; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 723.

this interesting new class of organic target molecules. Subsequently eliminating the bent metallocene fragment after it has served its purpose has turned out to be very facile. We have seen that a simple hydrolytic workup is often sufficient to set the organic primary enamine free.

At first sight it appears amazing that the resulting primary enamines have turned out to be such remarkably stable compounds. They seem to possess a high kinetic stability with regard to further hydrolysis, and more remarkably, they are very stable thermodynamically with respect to forming their imine tautomers under equilibrium conditions as well. Both effects may be appropriately explained when specific composition and structural properties of the conjugated primary enamines synthesized by our method are considered.

From the pioneering studies of Ahlbrecht et al.[3] it is well-known that conjugating substituents stabilize primary enamines relative to their imine tautomers most efficiently when they become attached at the β-position of the $-C^{\beta}H{=}C^{\alpha}(NH_2)-$ unit. Thus, the 1,3,5-hexatriene conjugation is expected to strongly stabilize the enamine forms in the compounds described in this paper. Additional thermodynamic enamine preference has originated from attaching conjugating groups (here phenyl or styryl) at the α-carbon atoms. The 1,6-positioning of amino groups at the hexatriene framework seems to provide an additional favorable feature. These C_i-symmetric diaminohexatrienes have no residual dipole moment. Their two $-CH{=}CRNH_2$ structural subunits are connected tail to tail by the connecting *trans*-$CH{=}CH-$ moiety to make their individual enamine properties cancel out. This probably serves to explain the surprisingly high kinetic stability of these unusual compounds. At the same time the repulsive $-NH_2$/$-NH_2$ interaction, which strongly reduces the thermodynamic stability of e.g. the primary enamine 1,2-diaminoethylene,[3] is overcompensated by the favorable conjugative interaction allowed for by placing the two amino functionalities remote from one another in conjugatively active positions at the ends of the 1,3,5-hexatriene framework.[13]

It seems that our preparative method will make interesting new types of polymeric materials synthetically available. Similar to the related monomeric systems, it is expected that the same stabilizing factors will favor the conjugated primary enamine structures in these polymeric materials obtained. They are probably characterized by having long conjugated (polyacetylene-like[14]) frameworks to which the $-NH_2$ functionalities are attached at the respective conjugated positions. We have begun to investigate their properties as advanced materials, especially their function as electrical conductors after doping, and their respective magnetic properties.

Experimental Section

Reactions with organometallic reagents and workup and handling of the conjugated primary enamine products were carried out under an argon atmosphere using Schlenk-type glassware or in a drybox. All solvents used for the preparations and the spectroscopic characterization were dried and distilled under argon prior to use. For a description of further general conditions, including a list of spectrometers used for the product characterization, see ref 9. (Butadiene)bis(cyclopentadienyl)zirconium was prepared as described in the literature.[8b]

(2*E*,5*E*,8*E*)-1,1-Bis(η-cyclopentadienyl)-3,8-bis((*E*)-2′-phenylethenyl)-1-zircona-2,9-diazacyclonona-2,5,8-triene (6b) and (2*E*,5*E*,7*Z*)-1,1-Bis(η-cyclopentadienyl)-3,8-bis((*E*)-2′-phenylethenyl)-1-zircona-2,9-diazacyclonona-2,5,7-triene (6a). (Butadiene)bis(cyclopentadienyl)zirconium (1.87 g, 6.78 mmol) was dissolved in 100 mL of toluene at room temperature. *trans*-Cinnamonitrile (1.03 mL, 13.6 mmol) was added and the mixture stirred for 23 h at ambient temperature. The dark violet suspension was filtered. The filtrate was concentrated in vacuo. The resulting solid product was washed with pentane and dried in vacuo to give 3.29 g (91%) of a 70:30 mixture of **6a** and **6b**, mp 190 °C dec. Anal. Calcd for $C_{32}H_{30}N_2Zr$ (533.8): C, 72.00; H, 5.66; N. 5.25. Found: C, 70.66; H. 5.97; N, 5.34. ^1H NMR (benzene-d_6): **6a**, δ 7.50–7.00 (m, 10H, Ph), 4.99 (2 m, 2H each, $-CH{=}CH$Ph), 6.36 (dt, 1H, 5-H), 6.09 (dd, 1H, 6-H), 5.85 (s, 10H, Cp), 5.35 (d, 1H, 7-H), 4.20 (s, 1H, NH), 3.18 (d, 2H, 4-H), coupling constants (Hz) $^3J = 7.4$ (4-H, 5-H), 16.2 (5-H, 6-H), 5.8 (6-H, 7-H), 16.7 ($-CH{=}CH$Ph); **6b**, δ 5.84 (s, 10H, Cp), 4.96 (m, 2H, 5-H, 6-H), 3.50–2.50 (br m, 4H, CH_2), remaining signals under those of the major component. ^{13}C NMR (benzene-d_6, DEPT): δ 170 (**6a**), 166.2 (**6b**), 153.0 (**6a**, *C*N), 138.3, 137.7, 137.1 (ipso C, phenyl), 133.8, 133.6, 132.3, 130.9, 130.6, 130.0, 129.3, 129.1, 129.0, 128.7, 128.3, 127.6, 127.3, 127.1, 126.9, 126.8, 124.5 (Ph and olefinic C), 110.0 (**6a**, Cp), 108.8 (**6b**, Cp), 96.9 (**6a**, C4), 40.9 (**6b**, CH_2), 39.4 (**6a**, CH_2). IR (KBr): ν 3101, 2908, 1628, 1615, 1595, 1494, 1446, 1378, 1073, 1014, 969, 798 cm^{-1}. UV (CH_2Cl_2): $\lambda_{max} = 464$ nm, $\epsilon = 50\,000$.

3,8-Diamino-1,10-diphenyldeca-(1*E*,3*Z*,5*E*,7*Z*,9*E*)-pentaene (7). A solution of 1.80 g (3.37 mmol) of the 70:30 **6a**/**6b** mixture in 40 mL of tetrahydrofuran was charged with 10 mL of water and then stirred for 24 h at ambient temperature. Solvent was then removed in vacuo and the red residue extracted with 40 mL of methylene chloride (16-h stirring). The red solution was concentrated in vacuo to a volume of 10 mL and the precipitated product collected by filtration to yield 510 mg (51%) of **7**, mp 182 °C dec (DSC). Anal. Calcd for $C_{22}H_{22}N_2$ (314.4): C, 84.04; H, 7.05; N, 8.91. Found: C, 82.89; H, 7.05; N, 8.55. ^1H NMR (DMSO-d_6): δ 6.63–6.31 (m, 10H, Ph), 5.89, 5.72 (each d, 4H, Ph—$CH{=}CH-$), 5.66, 4.43 (each dd, 4H, 4-H, 7-H and 5-H, 6-H), 4.14 (s, 4H, NH_2), coupling constants (Hz) $^3J = 16.2$ (1-H, 2-H), 8.2 (4-H, 5-H), $^4J = 2.9$ (4-H, 6-H). ^{13}C NMR (DMSO-d_6): δ 139.7 (ipso C, Ph), 137.5 (C3, C8), 128.6, 126.0 (Ph), 127.3, 126.8, 124.4, 124.0 (Ph, p-C, C1 and C10, C2 and C9, C5 and C6), 110.3 (C4 and C7). IR (KBr): ν 3388, 3366, 3054, 3053, 2998, 2962, 1616, 1593, 1584, 1571, 1448, 1404, 1349, 1261, 1074, 970, 955, 946, 931, 913, 819, 806, 751, 691 cm^{-1}. UV (CH_2Cl_2): $\lambda_{max} = 462$ nm, $\epsilon = 97\,000$.

(2*E*,5*E*,8*E*)-1,1-Bis(η-cyclopentadienyl)-3,8-bis((*E*)-2′-cyanoethenyl)-1-zircona-2,9-diazacyclonona-2,5,8-triene (8). To a solution containing 831 mg (10.6 mmol) of fumaronitrile in 40 mL of toluene was added dropwise a solution of 1.46 g (5.32 mmol) of (butadiene)bis(cyclopentadienyl)zirconium in 10 mL of toluene. The resulting brown suspension was filtered and the filtrate stripped in vacuo to give an oily residue, which was solidified by treatment with 10 mL of pentane. Complex **8** was recovered as a red amorphous solid (440 mg, 21%), mp 76 °C dec. Anal. Calcd for $C_{22}H_{20}N_4Zr$ (431.7): C, 61.22; H, 4.67. Found: C, 61.27; H, 4.67. ^1H NMR (benzene-d_6): δ 6.14, 5.11 (AX, 4H, $-CH{=}CH$—CN), 5.40 (s, 10H, Cp), 4.48 (m, 2 H, 5-H, 6-H), 2.40 (br m, 4H, 4′-H, 7-H, 7′-H), coupling constant (Hz) $^3J = 16.4$ ($-CH{=}CH$—CN). ^{13}C NMR (benzene-d_6): δ 162.8 (C3, C8), 146.6 ($=CH-$), 129.9 (C5, C6), 118.2 (CN), 109.0 (Cp), 100.8 ($=CH-$), 40.8 (C4, C7). IR (KBr): ν 2216 ($C{\equiv}N$), 1660 ($C{=}N$), 1645 ($C{=}C$), 1591, 1586 cm^{-1}.

(2*E*,5*E*,8*E*)-1,1-Bis(η-cyclopentadienyl)-3,8-bis(4′-cyanophenyl)-1-zircona-2,9-diazacyclonona-2,5,8-triene (9b) and (2*E*,5*E*,7*Z*)-1,1-Bis(η-cyclopentadienyl)-3,8-bis(4′-cyanophenyl)-1-zircona-2,9-diazacyclonona-2,5,7-triene (9a). Terephthalonitrile (1.94 g, 15.1 mmol) was dissolved in 300 mL of toluene. To this solution was added dropwise a solution containing 2.09 g (7.59 mmol) of (butadiene)bis(cyclopentadienyl)zirconium in 300 mL of toluene over 6.5 h. The mixture was then stirred for 8 h. A precipitate was removed by filtration and

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(13) Würthwein, E.-U. Unpublished results.

(14) Naarmann, H. *Synth. Met.* **1987**, *17*, 223. Basecu, N.; Liu, Z.-X.; Moses, D.; Heeger, A. J.; Naarmann, H. *Nature* **1987**, *327*, 403. Ito, T.; Shirakawa, S.; Ikedea, H. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 11. Shirakawa, S.; Ikedea, H. *Synth. Met.* **1980**, *1*, 175.

the clear filtrate concentrated in vacuo to a volume of 30 mL. The product was precipitated by cooling to −25 °C for 12 h and recrystallized to yield 810 mg (40%), still contaminated by small amounts (ca. 5%) of terephthalonitrile. Compound **9** exists in two isomeric forms (**9b**:**9a** = 92:8), mp 104 °C dec. Anal. Calcd for $C_{30}H_{24}N_4Zr$ (531.8): C, 67.76; H, 4.55. Found: C, 67.08; H, 4.65. ^{1}H NMR (benzene-d_6): **9b**, δ 7.37, 7.24 (AA′XX′, 8H, Ph), 5.62 (s, 10H, Cp), 4.82 (m, 2H, 5-H, 6-H), 3.40–2.70 (s, 4H, 3-H, 7-H); **9a**, δ 5.67 (s, Cp), remaining signals under **9b**. ^{13}C NMR (benzene-d_6): **9b**, δ 163.8 (C3, C8), 141.4 (ipso C, Ph), 132.2, 130.9, 126.8 (C5, C6, C(Ph)), 119.0 (CN), 111.6 (ipso C, Ph), 109.0 (Cp), 39.2 (C4, C7). IR (KBr): ν 2231 (C≡N), 1662 (C=N), 1653 (C=C) cm^{-1}.

1,6-Diamino-1,6-bis(4′-cyanophenyl)hexa-1,3,5-triene (10). To a solution of 0.51 g (0.94 mmol) of **9** in 20 mL of tetrahydrofuran was added 10 mL of water. The mixture was stirred for 16 h, and then all volatiles were removed in vacuo. The resulting solid residue was washed with three 50-mL portions of toluene and 50 mL of dichloromethane. The residue was extracted with 20 mL of dichloromethane for 14 h. The product was recovered by filtration to yield 110 mg (64%) of a red powder, mp 184 °C dec. Compound **10** was only characterized spectroscopically. ^{1}H NMR (DMSO-d_6): δ 7.75, 7.68 (AA′BB′, 4H, Ph), 6.65 (m, 2H, 3-H, 4-H), 5.58 (m, 2H, 2-H, 5-H), 5.26 (s, 4H, NH, NH_2). ^{13}C NMR (DMSO-d_6): δ 143.2 (C1, C6), 139.5 (ipso C, Ph), 132.1, 125.6 (each C(Ph), double intensity), 124.8 (C3, C4), 119.1 (CN), 109.0 (ipso C, Ph), 104.5 (C2, C5). IR (KBr): ν 3440, 3356 (NH), 2220 (C≡N), 1630 (C=N), 1601, 1565, 1542 cm^{-1}. UV (DMSO): λ_{max} = 460 nm, ε = 75 300.

Reaction of Terephthalonitrile with 2 Equiv of (Butadiene)bis(cyclopentadienyl)zirconium: Formation of 11. To a solution of 1.51 g (5.46 mmol) of (butadiene)bis(cyclopentadienyl)zirconium in 20 mL of toluene was added dropwise a solution containing 350 mg (2.73 mmol) of terephthalonitrile in 40 mL of toluene at 0 °C. The mixture was then stirred for 2 h at room temperature to allow the reaction to go to completion. A small amount of a precipitate was filtered off, and the filtrate was reduced in vacuo to a volume of 20 mL. The solution was cooled to −25 °C and kept at this temperature for 12 h. Complex **11** was recovered by filtration and dried in vacuo: yield 1.14 g (62%) of the mixture of two diastereoisomers **11a** and **11b** (90:10), mp 183 °C dec. Anal. Calcd for $C_{36}H_{36}N_2Zr$ (679.1): C, 63.67; H, 5.34; N, 4.12. Found: C, 62.21; H, 5.72; N, 4.46. ^{1}H NMR (benzene-d_6): **11a**, δ 7.36 (s, 4H, Ph), 6.65 (ddd, 2H, 6-H), 6.17 (s, 2H, N-H), 5.57 (s, 10H, Cp), 5.51 (dd, 2H, 4-H), 5.14 (s, 10H, Cp), 4.91 (d, 1H, 7′-H), 4.73 (d, 1H, 7-H), 1.63 (dd, 1H, 5-H), coupling constants (Hz) ^3J = 8.2 (4-H, 5-H), 8.2 (5-H, 6-H), 10.2 (6-H, 7-H), 16.5 (6-H, 7′-H), ^4J = 2.0 (4-H, N-H); **11b**, δ 5.19, 5.59 (s, Cp), remaining signals under **11a**. ^{13}C NMR (benzene-d_6): δ 142.4 (C6), 138.7 (ipso C, Ph), 129.6 (C3), 128.8 (Ph), 107.3, 103.8 (Cp), 102.8 (C4), 99.4 (C7), 68.8 (C5). IR (KBr): ν 3365 (NH), 1643, 1621, 1600 cm^{-1}.

Reaction of 11 with Terephthalonitrile: Formation of 12. Complex of **11** (17 mg, 0.03 mmol) was dissolved in 0.5 mL of benzene-d_6 in an NMR tube. Terephthalonitrile (8 mg, 0.06 mmol) was added, and the reaction mixture was investigated spectroscopically. ^{1}H NMR (benzene-d_6): δ 7.69 (s, 4H, Ph), 7.16 (s, 8H, Ph), 6.33 (dt, 2H, 5-H, 5′-H), 6.00 (dd, 2H, 6-H, 6′-H), 5.80 (s, 20H, Cp), 5.55 (d, 2H, 7-H, 7′-H), 4.59 (s, 2H, N-H, N′-H), 3.13 (d, 4H, 4-H, 4′-H), coupling constants (Hz) ^3J = 7.1 (4-H, 5-H), 16.1 (5-H, 6-H), 4.7 (6-H, 7-H). ^{13}C NMR (benzene-d_6): δ 166.4 (C3), 156.9 (C8), 145.0 (ipso C, Ph), 140.8 (ipso C, Ph), 132.3, 132.0, 131.2, 126.3, 126.0 (C5, C6, and C(Ph)), 118.9 (CN), 113.3 (ipso C, Ph), 110.2 (Cp), 104.1 (C7), 37.8 (C4).

Reaction of (Butadiene)bis(cyclopentadienyl)zirconium with Fumaronitrile: Formation of 14. A solution of 3.71 g (13.5 mmol) of (butadiene)bis(cyclopentadienyl)zirconium in 50 mL of toluene was added to a solution containing 1.05 g (13.5 mmol) of fumaronitrile in 100 mL of toluene at −50 °C. The suspension was warmed to room temperature and stirred for 3 days at this temperature. The mixture was filtered and dried in vacuo to yield 3.90 g (82%) of a brown powder (**14**), mp 182 °C dec. Anal. Calcd for $C_{18}H_{18}N_2Zr$ (353.6) (monomeric unit): C, 61.15; H, 5.13; N, 7.92. Found: C, 61.53; H, 5.26; N, 8.28. IR (KBr): ν 3377 (NH), 3099, 2915 (CH), 1635 (C=N), 1441, 1015, 802 cm^{-1}.

Formation of 15. Method A (Reaction with H_2O). Complex **14** (2.58 g, 7.30 mmol) was suspended in 50 mL of tetrahydrofuran and treated with 10 mL of water. The reaction mixture was stirred at room temperature for 22 h and the solvent removed in vacuo to yield 930 mg (94%) of a brown powder, mp 305 °C dec. The product was extracted with 100 mL of DMSO. The resulting black solution was evaporated in vacuo to yield 250 mg (26%) of a black, shiny solid (mp 194 °C (DSC)), the UV/vis spectrum of which showed a maximum absorption at λ = 252 nm with a featureless tailing up to λ ≈ 700 nm. Anal. Calcd for $C_8H_{10}N_2$ (134.2): C, 71.61; H, 7.51; N, 20.88. Found: C, 65.11; H, 6.70; N, 16.42. IR (KBr): ν 3325 (NH), 3184, 2966 (CH), 2279 (C≡N), 1645 (C=N), 1420, 1265, 1096, 1019, 801 cm^{-1}.

Method B (Reaction with HCl). Compound **14** (0.93 g, 2.64 mmol) was suspended in tetrahydrofuran. Then 1.10 mL of a 4.8 M etheral HCl solution was added. The reaction mixture was stirred for 16 h. The precipitated product (**15**) was filtered and dried in vacuo to yield 365 mg of a brown powder, mp 150 °C dec. IR (KBr): ν 3311, 3140, 3085, 2964, 2242, 2193, 1684, 1641 cm^{-1}. Solvent was removed from the filtrate in vacuo to recover 98% of the zirconium employed as 690 mg of a mixture of bis(η-cyclopentadienyl)dichlorozirconium and (μ-oxo)bis[bis(η-cyclopentadienyl)chlorozirconium] in a 3:1 ratio.

Reaction of Terephthalonitrile with (Butadiene)bis(cyclopentadienyl)zirconium: Formation of 16. To a solution of 2.55 g (19.9 mmol) of terephthalonitrile in 200 mL of toluene was added a solution containing 5.48 g (19.9 mmol) of (butadiene)bis(cyclopentadienyl)zirconium in 100 mL of toluene. The deep red solution was stirred at room temperature for 3 days. The resulting suspension was filtered. The recovered solid was washed with 20 mL of toluene and dried in vacuo for several hours to give 7.33 g (91%) of **16** as an insoluble red powder, mp 216 °C dec. Anal. Calcd for $C_{22}H_{20}N_2Zr$ (403.6) (monomeric unit): C, 65.47; H, 4.99; N, 6.85. Found: C, 65.39; H, 5.19; N, 6.92. IR (KBr): ν 3101, 3024, 2885 (CH), 2225 (C≡N), 1681 (C=N), 1645 (C=C) cm^{-1}.

Formation of 17. Method A (Reaction with H_2O). Complex **16** (1.90 g, 4.71 mmol) was suspended in 60 mL of tetrahydrofuran and the mixture treated with 10 mL of water. The mixture was stirred for 22 h at room temperature and then the solvent removed in vacuo. The solid residue was washed with dichloromethane to yield 1.09 g of a black powder, mp 198 °C dec. IR (KBr): ν 3427, 3349, 3209, 3029, 2964, 2926, 2219, 1617, 1601 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 7.67, 7.50 (each br s, 2H, Ph), 6.60, 5.50 (each s, 1H, olefinic), 5.10 (s, 4H, NH_2). UV (DMSO): λ_{max} = 507 nm, ε = 75 000.

Method B (Reaction with HCl). To a suspension of 2.80 g (7.00 mmol) of **16** in 100 mL of tetrahydrofuran was added 2.95 mL of a 4.8 M ethereal HCl solution. The mixture was stirred for 20 h at room temperature and filtered. The solid was washed with two 10-mL portions of toluene and dried in vacuo: yield 1.28 g (99%) of a black powder, mp 176 °C dec. Anal. Calcd for $C_{12}H_{12}N_2{\cdot}HCl$ (220.7): C, 65.31; H, 5.94; N, 12.69. Found: C, 66.79; H, 6.08; N, 11.33. IR (KBr): ν 3444, 3324 (NH), 3128, 3037, 2959 (CH), 2221 (C≡N), 1621 (C=N), 1601 (C=C) cm^{-1}. The filtrate was concentrated in vacuo to yield 92% of the employed zirconium as a mixture of bis(η-cyclopentadienyl)dichlorozirconium and (μ-oxo)bis[bis(η-cyclopentadienyl)chlorozirconium] in a 4:1 ratio (1.72 g).

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