$Cp_2Zr(N{=}CPh_2)_2$, an Organometallic Heteroallene-Type Schiff Base Derivative Relevant to Describing sp^2-Hybridized Nitrogen Inversion

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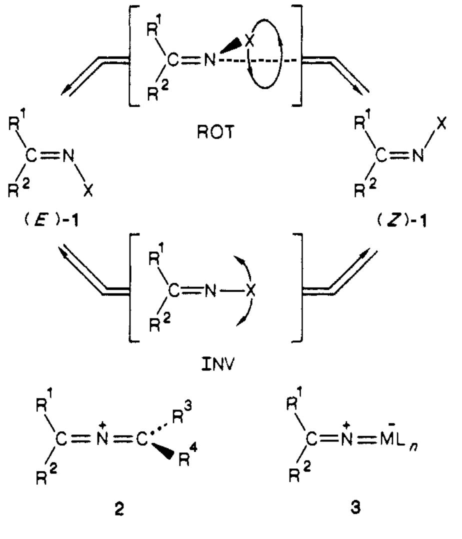
Abstract: (Butadiene)zirconocene reacts with acetone azine by CC coupling to give a seven-membered metallacyclic 1:1 addition product. In contrast, benzophenone azine reacts with the diene metallocene system with liberation of butadiene to form $Cp_2Zr(N{=}CPh_2)_2$ (**9b**). This product is also obtained upon irradiation of $Cp_2Zr(CO)_2$ with $Ph_2C{=}NN{=}CPh_2$ or treatment of Cp_2ZrCl_2 with 2 equiv of $LiN{=}CPh_2$. The molecular structure of the bis(alkylideneamido)metallocene complex **9b** was determined by X-ray diffraction. The zirconocene complex crystallizes in the monoclinic space group $C2/c$ with cell constants $a = 32.878$ (5), $b = 9.697$ (1), $c = 19.653$ (2) Å, $\beta = 111.818$ (8)°, and $Z = 8$. The zirconium bound $—N{=}CPh_2$ ligands (including the ipso carbons of the phenyl substituents) are oriented in the Cp–Zr–Cp bisecting plane. To a first approximation both $Zr\overset{\leftarrow}{-}N{=}CPh_2$ units can be regarded as being of a heteroallene structural type, characterized by bisecting C=N and N=Zr π-bonding planes and near to sp-hybridized nitrogen centers. Accordingly, very short zirconium to nitrogen bond distances are observed: N(1)–Zr, 2.058 (2) Å; N(2)–Zr, 2.063 (2) Å. The Zr–N(2)–C(2) unit (164.1 (2)°) is slightly less linearly arranged than Zr–N(1)–C(1) (173.7 (2)°). The solid-state structure shows a clear distinction of *E*- and *Z*-oriented phenyl substituents at the $Ph_2C{=}N\overset{\leftarrow}{-}Zr$ moieties. This is not observed in solution, however. In the ^{13}C NMR spectrum even at low temperature (198 K) complex **9b** exhibits only one set of phenyl group carbon resonances. This indicates a rapid equilibration of (*E*)- and (*Z*)-phenyl groups. This is an uncommon feature for heteroallene-type (alkylideneamido)metallocene complexes. We propose a linear to bent to linear $(R_2C{=}N)MCp_2(X)$ isomerization reaction sequence to take place rapidly in solution. This unusual dynamic feature attributes to the organometallic compound **9b** an intermediate position between organic Schiff bases (sp^2-hybridized nitrogen, bent structure) and stabilized heteroallene-type (sp-hybridized nitrogen, linear structure) inorganic (alkylideneamido)metal complexes.

Unsymmetrically substituted Schiff bases and related compounds $R^1R^2C{=}NX$ exist in *E*- and *Z*-configurated isomeric forms.[1] Their thermally induced, uncatalyzed interconversion could occur via two principally different intramolecular pathways. The (*E*)-**1** ⇌ (*Z*)-**1** isomerization (Scheme I) could be effected by either a relative rotation of the R^1R^2C and NX groups about the C=N double bond, i.e. migration of X along a circuit oriented *orthogonal* to the C–N vector, or an inversion at nitrogen, i.e. movement of X only *in the* $R^1R^2C{=}N$ plane.[2] Numerous detailed studies in the past have revealed that the latter mechanism seems to apply to most "organic" $R^1R^2C{=}NX$ systems. (*E*)- and (*Z*)-Schiff base isomers are interconverted via an inversion pathway proceeding through a transition state or high-energy intermediate exhibiting an sp-hybridized nitrogen center.[3] Accordingly, the barrier of the (*E*)-**1** ⇌ (*Z*)-**1** interconversion is lowered by substituents X electronically or sterically stabilizing the linear C=NX bonding situation.[4]

There are situations known where this stabilization is strong enough to have the linear $R_2C{=}NX$ arrangement being favored over the ordinary bent form. Two types of examples are shown in Scheme I. Combination of alkyl- or aryl-substituted carbenium ion centers with the $R_2C{=}N$ unit leads to dialkylideneammonium ions **2**.[5] Numerous spectroscopic investigations and several X-ray crystallographic studies[6] have shown that these compounds usually exhibit heteroallene-type structures with linear $[R_2C{=}N{=}CR_2]^+$ frameworks.[7,8] Formal replacement of the (positively charged) carbenium ion center by isolobal transition-metal fragments[9] then leads to neutral (alkylideneamido)metal complexes. Again, linear heteroallene-type structures have been observed for many examples **3**,[10,11] provided there is an acceptor orbital at the metal center suitably oriented for a ligand to metal π-interaction.[12]

Specific use of transition-metal complex fragments in these systems **3** offers a distinct advantage over their organic analogues **2**. Some $R^1R^2C{=}N{=}ML_n$ complexes provide an additional stereochemical probe that may be used for stereochemical analysis of simple achiral systems **3**. Similarly instructive experiments in the dialkylideneammonium salt series would require chiral heteroallene substrates that have to be prepared with either specific prochiral or enantiomerically enriched[5,6] substituents.

Scheme I



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(1) (a) Comprehensive reviews: *The Chemistry of the Carbon–Nitrogen Double Bond*; Patai, S., Ed.; Wiley: New York, 1970. (b) For special examples, see: Guillemin, J.-C.; Denis, J.-M. *Angew. Chem.* **1982**, *94*, 715. Braillon, B.; Lasne, M. C.; Ripoll, J. L.; Denis, J. M. *Nouv. J. Chim.* **1982**, *6*, 122.

(2) Reviews: Kessler, H. *Angew. Chem.* **1970**, *82*, 237. Kalinowski, H.-O., Kessler, H. *Top. Stereochem.* **1973**, *7*, 295. McCarty, C. G. In Reference 1a, p 363.

(3) For selected specific examples, see: Curtin, D. H.; Grubbs, E. J.; McCarty, C. G. *J. Am. Chem. Soc.* **1966**, *88*, 2775. Kessler, H.; Leibfritz, D. *Tetrahedron* **1970**, *26*, 1805. Wettermark, G.; Weinstein, J.; Sousa, J.; Dogliatti, L. *J. Phys. Chem.* **1965**, *69*, 1584. Kanamori, K.; Roberts, J. D. *J. Am. Chem. Soc.* **1983**, *105*, 4698, and references cited therein.

(4) Kerek, F.; Ostrogovich, G.; Simon, Z. *J. Chem. Soc. B* **1971**, 541. Kessler, H.; Leibfritz, D. *Justus Liebigs Ann. Chem.* **1970**, *737*, 53. Rieker, A.; Kessler, H. *Tetrahedron* **1967**, *23*, 3723. Kessler, H. *Angew. Chem.* **1967**, *79*, 997. Kessler, H.; Bley, P. F.; Leibfritz, D. *Tetrahedron* **1971**, *27*, 1687. Asano, T.; Okado, T. *J. Org. Chem.* **1986**, *51*, 4454 loc. cit.

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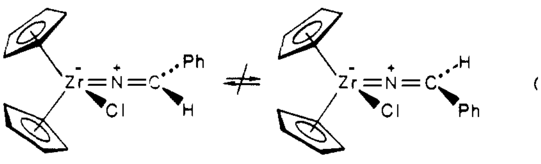
Here is an example. The complex $Cp_2Zr(Cl)N{=}CHPh$ was obtained by hydrozirconation of benzonitrile.[13] A recent X-ray crystallographic study established the expected heteroallene-type structure of the (benzylideneamido)zirconocene complex.[11] A nearly linear Zr–N–C arrangement was found (170.5 (5)°). The zirconium–N(sp) linkage is very short (2.013 (5) Å). The Cp(centroid)–Zr–Cp(centroid) and C(phenyl)–C–H planes are oriented nearly perpendicular to each other. Due to the specific bonding features at the bent metallocene unit,[12] the Zr-bound chlorine ligand is arranged coplanar with the substituents at the $Zr{=}N{=}C$ carbon center. Two isomers can thus be formed, which are characterized by an *E*-, respectively, *Z*-orientation of the substituents of highest priority in this plane.[14]

Complex (*E*)-**4** was stereoselectively synthesized[11] (eq 1). The geometric isomerization (*E*)-**4** ⇌ (*Z*)-**4** could be effected neither thermally nor photochemically. In **4**, the linear heteroallene-type structural unit is of high stereochemical persistence and rigidity.



(*E*)-**4** (*Z*)-**4** (1)

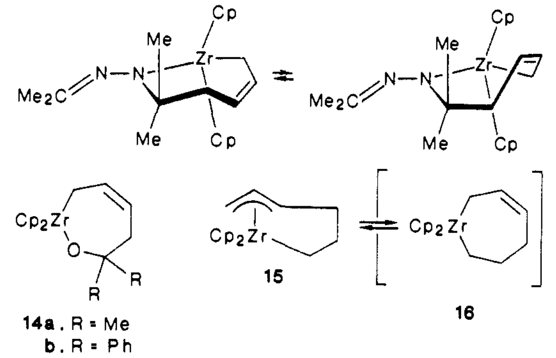
This does not necessarily have to be true for all heteroallene-type (alkylideneamido)metal complexes **3**. It has been shown (see above and Scheme I) that the transition between bent to linear $R^1R^2C{=}NX$ structures (**1**) can strongly be influenced by variations of the substituents X for organic Schiff base derivatives.[2-4] Therefore, it is to be expected that the $(R^1R^2C{=}N)ML_n$ linear to bent transition should similarly be influenced by variations of substituents and structural subunits used in complexes **3**. While such effects seem to be common for organic substrates **1**, to our knowledge complementary findings have not yet been reported for organometallic heteroallene species **3**. We here describe such observations made for $Cp_2Zr(N{=}CPh_2)_2$.

Table I. Comparison of Selected Spectroscopic Data and Topomerization Activation Energies $\Delta G^\ddagger_t$ between Metallacyclic Allylmetallocene Complexes

	^{13}C NMR		^1H NMR		
	$\delta(ZrCH_2)$	^1J(CH), Hz	^3J(CH=CH), Hz	T_c,[a] °C	$\Delta G^\ddagger_t$[b]
14a	39.2	120	10.0	−41	12.6[c]
14b	39.8	131	10.0	−43	12.2[c]
13	34.9	126	10.2	+15	15.1[d]
15	36.0	145, 149		+114	20.9[c]

[a] ^1H NMR coalescence temperature; Cp ligands. [b] Kilocalories per mole at T_c, ±0.3 kcal/mol. [c] From ref 21a. [d] This work.

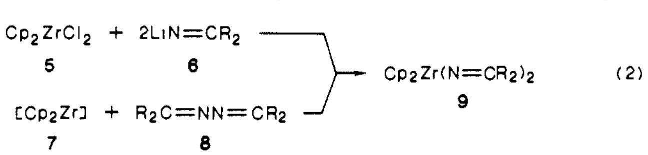
Scheme II



Synthesis and Spectroscopic Characterization

(Alkylideneamido)metal complexes $L_nM(N{=}CR_2)$ can be first by reacting metal halide complexes with $LiN{=}CR_2$.[15] Alternatively, such compounds have become available by treatment of prereduced reactive metal complexes with ketone azines $R_2C{=}NN{=}CR_2$.[16]

We tried the latter varient first and reacted precursors of the elusive bent metallocene Cp_2Zr with acetone azine (**8a**) (eq 2).



$$\left.\begin{array}{l} \underset{\mathbf{5}}{Cp_2ZrCl_2} + \underset{\mathbf{6}}{2LiN{=}CR_2} \\ \underset{\mathbf{7}}{[Cp_2Zr]} + \underset{\mathbf{8}}{R_2C{=}NN{=}CR_2} \end{array}\right\} \longrightarrow \underset{\mathbf{9}}{Cp_2Zr(N{=}CR_2)_2} \qquad (2)$$

Dicyclopentadienylzirconium(II) can be generated as a reactive intermediate from various precursors.[17] With varying efficiencies, **7** has been trapped by added scavengers when generated photochemically from diphenylzirconocene,[18] by heating or by irradiation from zirconocene dicarbonyl,[19] or thermally induced from (butadiene)$ZrCp_2$.[20] Photolysis of $(Me_2C{=}N)_2$ (**8a**) with Cp_2ZrPh_2

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(5) Würthwein, E.-U. *Angew. Chem.* **1981**, *93*, 110. Kleingeld, J. C.; Nibbering, N. M. M.; Halim, H.; Schwarz, H.; Würthwein, E.-U. *Chem. Ber.* **1983**, *116*, 3877. Würthwein, E.-U. *J. Org. Chem.* **1984**, *49*, 2971.

(6) (a) Würthwein, E.-U.; Kupfer, R.; Budzelaar, P. H. M.; Strobol, C.; Beck, H. P. *Angew. Chem.* **1984**, *97*, 327. (b) Al-Talib, M.; Jibril, I.; Würthwein, E.-U.; Jochims, J. C.; Huttner, G. *Chem. Ber.* **1984**, *117*, 3365. (c) Seitz, F.; Fischer, H.; Riede, J. *J. Organomet. Chem.* **1985**, *287*, 87.

(7) Bent heteroallyl-type structures may be favored in cases where extreme cationic stabilization is provided by suited substituents. (a) For a general discussion, see: Würthwein, E.-U.; Kupfer, R.; Allmann, R.; Nagel, M. *Chem. Ber.* **1985**, *118*, 3632. (b) Rahman, M. A.; Zsolnai, L.; Huttner, G.; Jochims, J. C. *Chem. Ber.* **1983**, *116*, 2668. Jochims, J. C.; Abu-El-Halawa, R.; Jibril, I.; Huttner, G. *Chem. Ber.* **1984**, *117*, 1900. Al-Talib, M.; Jibril, I.; Huttner, G.; Jochims, J. C. *Chem. Ber.* **1985**, *118*, 1876.

(8) For the analogous dialkylidenephosphonium salts, see: Schmidpeter, A.; Lochschmidt, S.; Willhalm, A. *Angew. Chem.* **1983**, *95*, 561, and references cited therein.

(9) (a) Hoffmann, R. *Angew. Chem.* **1982**, *94*, 725. (b) Elian, M.; Cheu, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Inorg. Chem.* **1976**, *15*, 1148.

(10) (a) Kilner, M. *Adv. Organomet. Chem.* **1972**, *10*, 162. (b) Selected examples. $CpM(L)_2(N{=}CR_2)$, M = Mo, W: Farmery, K.; Kilner, M.; Midcalf, C. *J. Chem. Soc. A* **1970**, 2279. Kilner, M.; Midcalf, C. *J. Chem. Soc., Chem. Commun.* **1970**, 552; *J. Chem. Soc. A* **1971**, 292. Kilner, M.; Pinkney, J. N. *J. Chem. Soc. A* **1971**, 2887. Green, M.; Mercer, R. J.; Morton, C. E.; Orpen, A. G. *Angew. Chem.* **1985**, *97*, 422. $Cp_2{}^*Sc(N{=}CR_2)$: Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443. $ReCl_2(N{=}CHR)(L)_2$: Chatt, J.; Dosser, R. J.; King, F.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1976**, 2435. $Cp_3U(N{=}CR_2)$: Cramer, R. E.; Panchanatheswaran, K.; Gilje, J. W. *J. Am. Chem. Soc.* **1984**, *106*, 1853. $CpTiCl_2(N{=}CR_2)$: Latham, I. A.; Leigh, G. J.; Huttner, G.; Jibril, I. *J. Chem. Soc., Dalton Trans.* **1986**, 377. $[(ind)_2Ti(N{=}CR_2)(L)]^+$: Bochmann, M.; Wilson, L. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1610. $[(Ar\text{-}H)(PR_3)Os(N{=}CR_2)]^+$: Werner, H.; Knaup, W.; Dziallas, M. *Angew. Chem.* **1987**, *99*, 277. (c) For similarly structured $L_nM(P{=}CR_2)$ complexes, see: Arif, A. M.; Cowley, A. H.; Quashie, S. *J. Chem. Soc., Chem. Commun.* **1986**, 1437. Cowley, A. H.; Norman, N. C.; Quashie, S. *J. Am. Chem. Soc.* **1984**, *106*, 5007. See, however: Gudad, D.; Niecke, E.; Arif, A. M.; Cowley, A. H.; Quashie, S. *Organometallics* **1986**, *5*, 593. Weber, L.; Reizig, K.; Boese, R.; Polk, M. *Organometallics* **1986**, *5*, 1098; *Angew. Chem.* **1985**, *97*, 583.

(11) Erker, G.; Frömberg, W.; Atwood, J. L.; Hunter, W. E. *Angew. Chem.* **1984**, *96*, 72. Frömberg, W.; Erker, G. *J. Organomet. Chem.* **1985**, *280*, 343.

(12) (a) For the specific example of the bent metallocene unit, see: Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729, and references cited therein. (b) Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6416, 6422. Erker, G.; Rosenfeldt, F. *Angew. Chem.* **1978**, *90*, 640; *J. Organomet. Chem.* **1980**, *188*, C1. (c) Hofmann, P.; Stauffert, P.; Schore, N. E. *Chem. Ber.* **1982**, *115*, 2153.

(13) Etievant, P.; Tainturier, G.; Gautheron, G. *C. R. Seances Acad. Sci., Ser. C* **1976**, *283*, 233; *Bull. Soc. Chim. Fr.* **1978**, 292.

(14) Cahn, R. S.; Ingold, C. K.; Prelog, V. *Angew. Chem.* **1966**, *78*, 413. Prelog, V.; Helmchen, G. *Angew. Chem.* **1982**, *94*, 614.

(15) Farmery, K.; Kilner, M. *J. Organomet. Chem.* **1969**, *16*, P51. Keable, H. R.; Kilner, M. *J. Chem. Soc., Chem. Commun.* **1971**, 349. Clegg, W.; Snaith, R.; Shearer, H. M. M.; Wade, K.; Whitehead, G. *J. Chem. Soc., Dalton Trans.* **1983**, 1309.

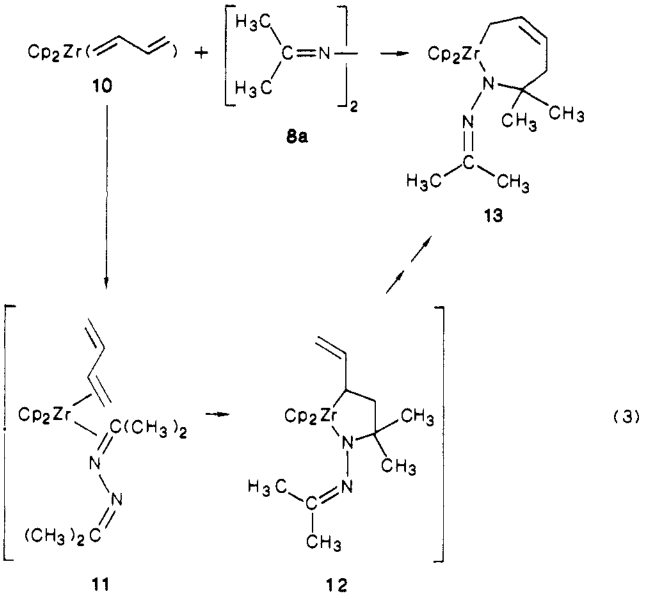
(16) Bright, D.; Mills, O. S. *J. Chem. Soc., Chem. Commun.* **1967**, 245.

(17) Pez, G. P.; Armor, J. N. *Adv. Organomet. Chem.* **1981**, *19*, 1, and references cited therein.

(18) Erker, G.; *J. Organomet. Chem.* **1977**, *134*, 189. 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.; Kropp, K.; Atwood, J. L.; Hunter, W. E. *Organometallics* **1983**, *2*, 1555.

(19) Demerseman, B.; Bouquet, G.; Bigorgne, M. *J. Organomet. Chem.* **1976**, *107*, C19. Sikora, D. J.; Rausch, M. D. *J. Organomet. Chem.* **1984**, *276*, 21.

or $Cp_2Zr(CO)_2$ only led to the formation of mixtures of various unidentified products. In contrast, the thermally induced reaction of $(C_4H_6)ZrCp_2$ (**10**) with acetone azine was much cleaner and produced a readily identified product. At ambient temperature the equilibrium mixture of (*s-cis-* and *s-trans-*η^4-butadiene)zirconocene (**10**) slowly reacts with acetone azine (**8a**) in benzene solution to produce a 1:1 addition product **13**, which was isolated in almost 50% yield (eq 3). The formation of this specific product is atypical for metal complex azine chemistry[16] as the N–N bond has not been cleaved but is clearly retained in the reaction product.



(3)

Complex **13** can be regarded as the addition product of the (butadiene)zirconocene moiety to one of the available $N{=}C(CH_3)_2$ units of the azine reagent. As was shown earlier,[21] such addition is likely to occur stepwise (here through intermediates **11** and **12**) rather than directly. The metallacyclic ring-closure product **12** is a σ-allyl-type metallocene complex, which is expected to undergo a subsequent ring expansion reaction via a $\sigma \rightleftharpoons \pi \rightleftharpoons \sigma$ allyl metallocene rearrangement sequence.[22]

The seven-membered σ-allylzirconocene complex **13** exhibits dynamic NMR spectra, which are very characteristic for this type of metallocene complex (see Table I). At high temperature **13** shows an NMR appearance suggesting C_s molecular symmetry in solution. However, decreasing the temperature results in line broadening and splitting of the Cp resonance as well as the signal of the methyl groups attached to the metallacyclic ring system. At the same time, the protons of each of the endocyclic CH_2 groups become diastereotopic (numerical values are given in the Experimental Section). This dynamic behavior is typical for seven-membered metallacyclic σ-allyl-type zirconocene complexes[21] exhibiting a folded ground-state conformation as depicted for **13** in Scheme II. For **14b** an analogous structure has been found in the solid state by X-ray diffraction.[21] Conformational equilibration for this family of metallacyclic complexes takes place by a simple ring-inversion mechanism. Comparison with closely related examples (see Table I) reveals that the numerical value of the activation barrier for topomerization observed for **13** is typical.

Scheme III

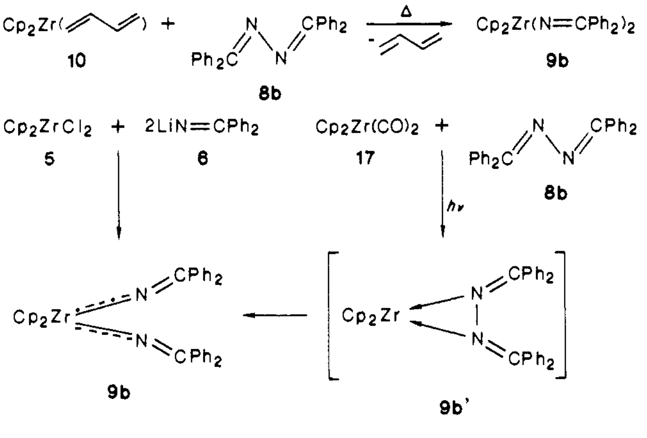


Table II. X-ray Crystal Structure of $Cp_2Zr(N{=}CPh_2)_2$ (**9b**): Selected Bond Distances (Å) and Angles (deg)

Distances			
Zr-N1	2.058 (2)	C1-C11	1.516 (4)
Zr-N2	2.063 (2)	C1-C21	1.506 (4)
N1-C1	1.259 (4)	C2-C31	1.505 (4)
N2-C2	1.266 (4)	C2-C41	1.511 (4)
Angles			
N2-Zr-N1	106.5 (1)	C11-C1-N1	120.5 (3)
C1-N1-Zr	173.7 (2)	C41-C2-C31	116.9 (2)
C2-N2-Zr	164.1 (2)	C41-C2-N2	121.3 (3)
C21-C1-C11	117.6 (2)	C31-C2-N2	121.7 (3)
C21-C1-N1	121.8 (3)		

The thermally induced reaction of the (η-butadiene)zirconocene system **10** with benzophenone azine (**8b**) was found to proceed quite differently. We have not observed the formation of an 1:1 addition product as in the reaction between **10** and acetone azine. Instead, the butadiene ligand is liberated[23] and an 1:1 addition product between the bent metallocene dicyclopentadienylzirconium and benzophenone azine is formed. The same organometallic reaction product $Cp_2Zr(N{=}CPh_2)_2$ (**9b**; Scheme III) was obtained upon irradiation of diphenylzirconocene or $Cp_2Zr(CO)_2$ (**17**) in the presence of **8b**. The route to $Cp_2Zr(N{=}CPh_2)_2$ from $Cp_2Zr(CO)_2$ turned out to be most effective. The complex $Cp_2Zr(N{=}CPh_2)_2$ (**9b**) was prepared accordingly on a preparative scale with a slight excess of zirconocene dicarbonyl and isolated in a yield of 80% (based on **8b**).

Complex **9b** exhibits simple spectra. Its IR spectrum is characterized by $\nu_{C=N}$ = 1630 cm^{-1}. The NMR spectra exhibit single Cp resonances at δ 5.77 (^{1}H NMR, 10 H) and δ 108.9 (^{13}C, ^1J(CH) = 172 Hz). Signals of the four phenyl groups present appear at δ 7.2–7.6. Even in the ^{13}C NMR spectrum at low temperature (198 K), a chemical differentiation of the phenyl groups has not been observed. Only one set of resonances representing four chemically equivalent carbon bound phenyl groups has been found (δ 142.0 (ipso-C), 128.2, 128.5, 128.7) in addition to the N=C signal at δ 170.4. No significant line broadening was monitored in the ^{1}H or ^{13}C experiment on decreasing the temperature from ambient temperature to 198 K.[24]

A complex of the empirical composition $Cp_2Zr(N{=}CPh_2)_2$ was reported by Lappert et al.[25] We repeated the published synthesis and reacted Cp_2ZrCl_2 with 2 mol equiv of $LiN{=}CPh_2$ (obtained by addition of phenyllithium to benzonitrile). The complex ob-

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[20] Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *214*, 1. Erker, G. *Jahrbuch der Akademie der Wissenschaften in Göttingen* **1985**, 19. Erker, G.; Frömberg, W.; Mynott, R.; Gabor, B.; Krüger, C. *Angew. Chem.* **1986**, *98*, 456.

[21] (a) Erker, G.; Engel, K.; Dorf, U.; Atwood, J. L. *Angew. Chem.* **1982**, *94*, 915, 916. Erker, G.; Engel, K.; Atwood, J. L.; Hunter, W. E. *Angew. Chem.* **1983**, *95*, 506. Erker, G.; Dorf, U. *Angew. Chem.* **1983**, *95*, 800. (b) Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120. See also ref 20. (c) Erker, G.; Dorf, U.; Benn, R.; Reinhardt, R.-D.; Petersen, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 7649. Erker, G.; Lecht, R. *J. Organomet. Chem.* **1986**, *311*, 45. For a comparison, see: Erker, G.; Mühlenbernd, T.; Benn, R.; Rufińska, A. *Organometallics* **1986**, *5*, 402.

[22] Hoffmann, E. G.; Kallweit, R.; Schroth, G.; Seevogel, K.; Stempfle, W.; Wilke, G. *J. Organomet. Chem.* **1975**, *97*, 183.

[23] For analogous reactions, see: Skibbe, V.; Erker, G. *J. Organomet. Chem.* **1983**, *241*, 15.

[24] In contrast, the benzophenone azine starting material exhibits two sets of Ph resonances in the ambient-temperature NMR spectra. ^{13}C NMR (benzene-d_6, ^1J(CH), Hz, in parentheses): δ 128.1 (d, 162, *m*-Ph), 128.3 (d, 160, *m*-Ph), 128.7 (d, 160, *p*-Ph), 129.2 (d, 160, *o*-Ph), 129.7 (d, 162, *o*-Ph), 129.8 (d, 160, *p*-Ph), 136.5 (s, ipso-Ph), 138.9 (s, ipso-Ph), 160.0 (s, $N{=}CPh_2$).

[25] Collier, M. R.; Lappert, M. F.; McMeeking, J. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 689.

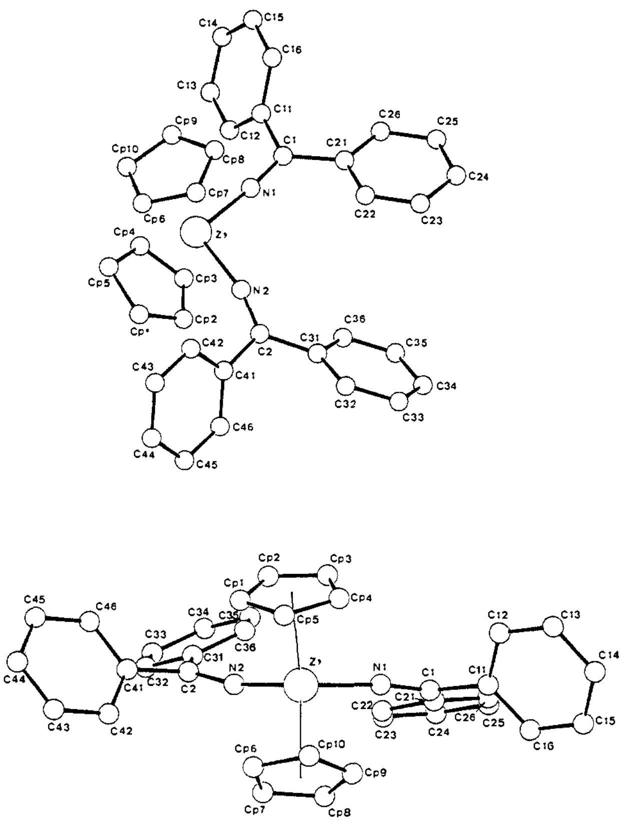

Figure 1. Two views of the molecular geometry of $Cp_2Zr(N{=}CPh_2)_2$ (**9b**) as determined by X-ray diffraction.

tained and isolated in 64% yield turned out to be identical in every respect with **9b** (Figure 1).

In view of these two rather different synthetic entries and the spectroscopic data, the molecular structure of **9b** was not at all clear. It was not obvious if the N–N bond of the starting material **8b** was retained or broken upon complex formation with the bent metallocene unit. Therefore, the molecular structure of $Cp_2Zr(N{=}CPh_2)_2$ (**9b**) in the solid state was determined by X-ray diffraction.

X-ray Crystal Structure of $Cp_2Zr(N{=}CPh_2)_2$ (9b)

Crystals of **9b** (Table II) suitable for an X-ray crystal structure analysis were obtained by recrystallization of $Cp_2Zr(N{=}CPh_2)_2$ from diethyl ether at low temperature. In the crystal **9b** exhibits discrete molecular units, which are composed of a bent metallocene moiety (Cp_2Zr), showing the expected typical structural parameters,[12,26] to which two $N{=}CPh_2$ ligands are coordinated. There is clearly no N–N bond. The observed intramolecular nitrogen-nitrogen separation (N1–N2 = 3.301 (3) Å) is longer than the sum of the nitrogen van der Waals radii (3.10 Å).[27] The N1–Zr–N2 angle is 106.5 (1)°, significantly larger than the σ-ligand angle found in the structurally otherwise closely related (benzylideneamido)zirconium complex $Cp_2Zr(Cl)(N{=}CHPh)$ (*E*)-**4** (Cl–Zr–N = 101.2 (2)°).[11] The overall molecular symmetry in the crystal clearly deviates from the apparent symmetry of **9b** in solution as suggested from the NMR study (see above). In the solid state **9b** is not C_{2v} symmetric but chiral and rather close to internal C_2 symmetry.

However, the two $N{=}CPh_2$ ligands coordinated to zirconium are not strictly symmetry related. The Zr–alkylideneamido linkages are not far from linear. Both nitrogen centers are near to sp hybridized. The observed Zr–N1–C1 angle is 173.7 (2)°. The Zr–N2–C2 moiety is slightly more bent (164.1 (2)°), but still far away from an ordinary bent (120°) Schiff base derivative.

Table III. Atomic Fractional Coordinates and Equivalent Isotropic Thermal Parameters (Å²) with Standard Deviations in Parentheses

atom	*x*	*y*	*z*	U_{eq}[a]
Zr	0.1047 (1)	0.1862 (1)	0.2182 (1)	0.045
N1	0.0623 (1)	0.2089 (2)	0.1113 (1)	0.053
N2	0.1670 (1)	0.1873 (3)	0.2165 (1)	0.056
C1	0.0354 (1)	0.2358 (3)	0.0478 (1)	0.043
C2	0.2062 (1)	0.1576 (3)	0.2256 (2)	0.049
C11	−0.0134 (1)	0.2248 (3)	0.0300 (1)	0.045
C12	−0.0311 (1)	0.1008 (3)	0.0412 (1)	0.049
C13	−0.0759 (1)	0.0874 (3)	0.0235 (2)	0.062
C14	−0.1033 (1)	0.1980 (4)	−0.0043 (2)	0.069
C15	−0.0862 (1)	0.3216 (4)	−0.0147 (2)	0.081
C16	−0.0416 (1)	0.3353 (3)	0.0027 (2)	0.074
C21	0.0503 (1)	0.2744 (3)	−0.0134 (1)	0.045
C22	0.0945 (1)	0.2963 (3)	0.0024 (2)	0.059
C23	0.1102 (1)	0.3229 (4)	−0.0524 (2)	0.076
C24	0.0820 (2)	0.3309 (4)	−0.1236 (2)	0.095
C25	0.0377 (1)	0.3111 (4)	−0.1409 (2)	0.089
C26	0.0216 (1)	0.2824 (3)	−0.0860 (2)	0.064
C31	0.2202 (1)	0.1354 (3)	0.1617 (2)	0.057
C32	0.2629 (1)	0.1626 (3)	0.1668 (2)	0.074
C33	0.2741 (1)	0.1448 (5)	0.1054 (3)	0.107
C34	0.2430 (2)	0.1001 (5)	0.0406 (3)	0.122
C35	0.2009 (2)	0.0733 (4)	0.0354 (2)	0.097
C36	0.1894 (1)	0.0901 (4)	0.0955 (2)	0.069
C41	0.2406 (1)	0.1364 (3)	0.3012 (2)	0.049
C42	0.2440 (1)	0.2279 (3)	0.3577 (2)	0.063
C43	0.2743 (1)	0.2025 (4)	0.4284 (2)	0.073
C44	0.3005 (1)	0.0875 (4)	0.4432 (2)	0.068
C45	0.2973 (1)	−0.0034 (4)	0.3873 (2)	0.071
C46	0.2676 (1)	0.0219 (3)	0.3173 (2)	0.062
Cp1	0.1329 (2)	−0.0288 (5)	0.2935 (3)	0.106
Cp2	0.1254 (2)	−0.0696 (4)	0.2253 (3)	0.101
Cp3	0.0826 (1)	−0.0648 (4)	0.1851 (2)	0.085
Cp4	0.0608 (1)	−0.0210 (4)	0.2271 (3)	0.097
Cp5	0.0917 (3)	0.0042 (5)	0.2979 (3)	0.152
Cp6	0.1227 (2)	0.3528 (5)	0.3231 (2)	0.093
Cp7	0.1310 (1)	0.4243 (4)	0.2696 (3)	0.085
Cp8	0.0913 (1)	0.4453 (4)	0.2117 (2)	0.085
Cp9	0.0585 (1)	0.3870 (4)	0.2303 (2)	0.084
Cp10	0.0774 (2)	0.3312 (5)	0.2993 (2)	0.103
H12	−0.0105	0.0214	0.0626	
H13	−0.0886	−0.0053	0.0300	
H14	−0.1356	0.1887	−0.0174	
H15	−0.1059	0.4045	−0.0318	
H16	−0.0286	0.4262	−0.0058	
H22	0.1152	0.2927	0.0559	
H23	0.1433	0.3372	−0.0406	
H24	0.0927	0.3443	−0.1655	
H25	0.0175	0.3212	−0.1933	
H26	−0.0115	0.2676	−0.0988	
H32	0.2851	0.1921	0.2153	
H33	0.3058	0.1664	0.1096	
H34	0.2510	0.0908	−0.0041	
H35	0.1792	0.0380	−0.0136	
H36	0.1575	0.0701	0.0917	
H42	0.2256	0.3137	0.3473	
H43	0.2765	0.2714	0.4691	
H44	0.3217	0.0706	0.4953	
H45	0.3162	−0.0885	0.3970	
H46	0.2652	−0.0446	0.2755	
Hcp0	0.0615	0.2764	0.3271	
Hcp1	0.1638	−0.0214	0.3338	
Hcp2	0.1485	−0.1023	0.2045	
Hcp3	0.0687	−0.0869	0.1293	
Hcp4	0.0271	−0.0069	0.2103	
Hcp5	0.0894	0.0393	0.3445	
Hcp6	0.1441	0.3177	0.3717	
Hcp7	0.1609	0.4566	0.2743	
Hcp8	0.0878	0.4942	0.1635	
Hcp9	0.0258	0.3853	0.1999	

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$.

The Zr–N bond distances in **9b** (Zr–N1) = 2.058 (2) Å, Zr–N2 = 2.063 (2) Å) are longer than the one found in (*E*)-**4** (Zr–N = 2.013 (5) Å, to our knowledge the shortest zirconium–nitrogen linkage observed). However, in comparison with suitable refer-

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(26) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Wiley: New York, 1986.

(27) Bondi, A. *J. Chem. Phys.* **1964**, *68*, 441. Weast, R. C., Ed. *Handbook of Chemistry and Physics*; CRC: Boca Raton, FL, 1974.

ences ($Cp_2Zr(NC_4H_4)_2$,[28] Zr-N1 = 2.171 (2), Zr-N2 = 2.169 (2) Å; $Cp_2Zr(NCO)_2$,[29] Zr-N1 = 2.110 (5), Zr-N2 = 2.124 (5) Å), the Zr-N bonds in $Cp_2Zr(N{=}CPh_2)_2$ are significantly shorter.

Similar conclusions have to be drawn for the C=N bonds of the $N{=}CPh_2$ ligands. These are equivalent within experimental error (N1-C1 = 1.259 (4), N2-C2 = 1.266 (4) Å).[30] The corresponding C=N bond distance in the related mono(alkylideneamido)zirconocene complex (*E*)-**4** is 1.259 (1) Å. X-ray crystal structure analyses reveal only slightly longer C=N distances as being typical for dialkylideneammonium salts in the solid state ($[Ph_2C{=}N{=}C(C_{13}H_8)]^+$, C=N = 1.27 (1), 1.28 (1) Å;[6a] $[(2\text{-adamantylidene})_2N]^+$, C=N = 1.30 (9), 1.35 (9) Å).[6b]

A further characteristic of the molecular structure of $Cp_2Zr(N{=}CPh_2)_2$ is the almost coplanar arrangement of the core atoms of the alkylideneamido ligands. To a first approximation, alkylideneamido ligand atoms including the *ipso*-carbon centers of the phenyl substituents are oriented in the N1-Zr-N2 plane. If one assumes no significant conjugative interaction of the C=N π-system (oriented orthogonal to the central metal/ligand plane) with the acceptor orbital at the metal center,[12,31] both $[Zr]{=}N{=}CPh_2$ moieties in **9b** can be regarded as being heteroallene-type structural subunits.

In accordance with the general structural characteristics of **9b**, two rather differently oriented phenyl substituents are observed in the solid-state structure. One phenyl group each at C1 and C2 is zusammen (*Z*) positioned with regard to the other $N{=}CPh_2$ ligand; the remaining two aryl substituents are oriented entgegen (*E*).

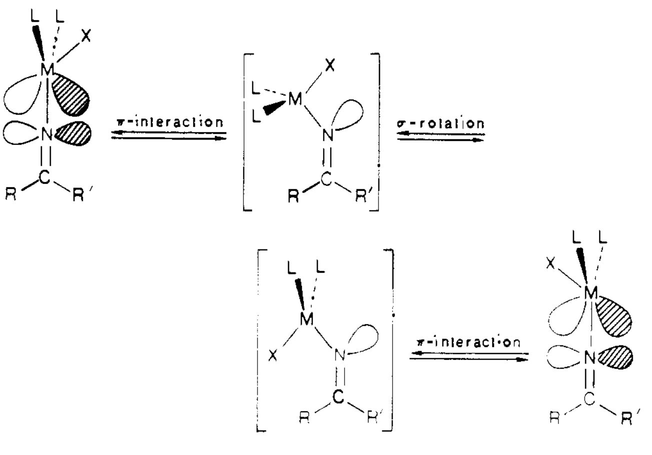
In addition, the planes of the phenyl groups (C21-C26 and C31-C36) that are pointing to the central sector in front of the bent metallocene unit are only slightly deviating from the central N1-Zr-N2 plane while the phenyl substituents (C11-C16, C41-C46) pointing to the lateral sectors are rotated away from that plane. This observed conformational preference may be insignificant for the discussion of the structural properties of **9b** in solution. However, the solid-state structure of $Cp_2Zr(N{=}CPh_2)_2$ appears to exhibit two pairs of distinctively different phenyl substituents at C1 and C2, respectively. This experimental result is contrasted by the observation that the phenyl substituents in **9b** could not be distinguished even at low temperature by NMR techniques in solution. We propose a rather simple explanation for this dichotomy.

Discussion and Conclusions

From the results of the X-ray crystal structure analysis, **9b** appears to be a rather unexceptional heteroallene-type metallocene alkylideneamido complex.[10,11] It is characterized by having both strong C=N and Zr=N bonds, the latter having at least partial multiple-bond character. The nitrogen centers are close to being sp hybridized. Along the [Zr]=N=C vector, [Zr]=N and C=N π-bonds are oriented perpendicular to one another as judged from the spatial arrangement of the ligands at the pseudotetrahedral zirconium and the trigonal-planar carbon centers at the heteroallene termini.

In view of this solid-state structure, one would expect NMR spectra in solution indicating a molecular symmetry giving rise to two sets of phenyl group resonances (if one assumes rapid phenyl group rotation about the C-Ph single bonds). Instead, even at low temperature, we have only observed one type of aromatic substituent. We consider it unlikely that this is indicating a principally different structural type in solution. It is rather likely that we are observing the result of a rapidly proceeding dynamic process that effects an apparent higher overall symmetry in the typical NMR experiment.

Scheme IV



Two "rotational" processes could in principle cause such equilibration of phenyl substituents. A direct thermally induced rotation about the C=N double bond seems to be very unlikely. We were not able to "freeze out" the automerization process at low temperature in the ^{13}C NMR experiment using a high-field NMR spectrometer. Therefore, a very low activation barrier has to be assumed for this rotational process. However, the torsional barriers of C=N bonds in Schiff bases are usually very high. For ordinary substituents, activation energies of about 45 kcal/mol have been estimated.[2] This is supported by the observed rather large isomerization barriers of many protonated Schiff base derivatives $[R^1R^2C{=}NHR]^+$, which cannot react anymore via the otherwise preferred nitrogen-inversion process.[32] In addition, there is no indication that dialkylideneammonium systems $[R^1R^2C{=}N{=}CR^3R^4]^+$ exhibit exceptionally low C=N rotational barriers.[5,6]

The bent metallocene unit may possibly not provide sufficient stabilization of the transition state of [Zr]=N bond rotation while retaining sp hybridization at nitrogen.[12,31] This is probably the reason for the strong resistance of (*E*)-**4** toward *E*/*Z* isomerization.[11]

Therefore, **9b** might possibly automerize via a pathway that is characterized by a change in hybridization at the azomethine nitrogen. We discuss a mechanism, schematically depicted in Scheme IV, that allows for decoupling of the M=N multiple bond between zirconium and one of the $N{=}CPh_2$ ligands (possibly being assisted by simultaneously strengthening the remaining π-interaction with the second alkylideneamido moiety).[30] Rapid rotation about the Zr-N σ-bond in the resulting σ-$N{=}CPh_2$ intermediate followed by reestablishing the metal to nitrogen π-interaction would then complete the reaction cycle.

An evaluation of the general characteristics of the energy profile of the Schiff base nitrogen-inversion isomerization process may serve to illustrate this explanation for the observed phenomenon. In Scheme V the energy profile for nitrogen inversion of simple "organic" Schiff base derivatives A ("bent" ground state with sp^2 nitrogen, "linear" high-energy isomerization intermediate with sp nitrogen[2-4]) is contrasted by an inverse isomerization profile C. The majority of organometallic heteroallene-type Schiff base derivatives $R_2C{=}N{=}ML_n$ belongs to the latter.[10,11] There should be a continuous variation of stabilizing/destabilizing effects of groups X and Z, respectively, on the energy content of linear relative to bent structures of these Schiff base systems. Therefore, in addition to the extremes A and C, there should be a distinct chance to find systems that are characterized by an "intermediate" energy profile B. Coming from A, any stabilizing effect of substituents (X) at nitrogen would tend to lower the isomerization activation barrier E_a. An extreme stabilization of the linear structure (situation C) would also result in a high E_a value.

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[28] Bynum, R. V.; Hunter, W. E.; Rogers, R. D.; Atwood, J. L. *Inorg. Chem.* **1980**, *19*, 2368.

[29] Kossiakoff, A. A.; Wood, R. H.; Burmeister, J. L. unpublished results. Cited in: Petersen, E. J.; Von Dreele, R. B.; Brown, T. M. *Inorg. Chem.* **1976**, *15*, 309. Further examples can be found in ref 26.

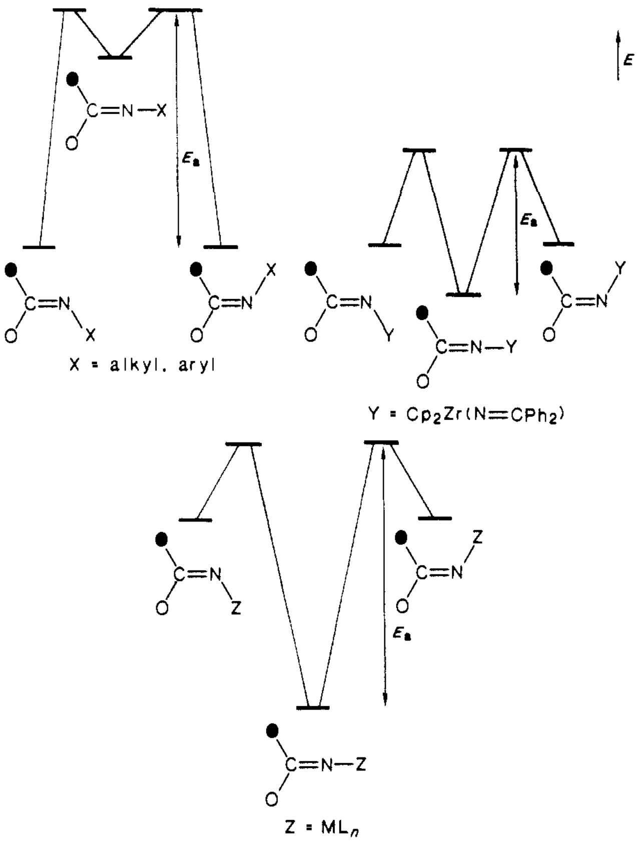
[30] Complexes $Cp_2Hf(PR_2)_2$ already exhibit an "unsymmetrical" ground state, characterized by two rather different metal to phosphorus bond distances: Baker, R. T.; Whitney, J. F.; Wreford, S. S. *Organometallics* **1983**, *2*, 1049.

[31] For a somewhat different view, see: Osborne, J. H.; Rheingold, A. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1985**, *107*, 7945.

[32] Kessler, H.; Leibfritz, D. *Tetrahedron Lett.* **1969**, 427. See also ref 2.

[33] Pattison, I.; Wade, K.; Wyatt, B. K. *J. Chem. Soc. A* **1968**, 837.

Scheme V



Situations close to B where linear and bent $R_2C{=}NY$ structures are not far apart in energy are expected to exhibit the lowest isomerization barriers. We think that **9b** may be an example of this situation. Therefore, this organometallic compound might be representing an important intermediate situation between bent "organic" and linear "inorganic" Schiff base derivatives.[9a]

Experimental Section

All reactions with organometallic compounds were carried out in an argon atmosphere with Schlenk-type glassware. Solvents were dried and freshly distilled from potassium/benzophenone, lithium aluminum hydride, or P_4O_{10} under argon prior to use. Deuteriated solvents benzene-d_6 and toluene-d_8 were treated with sodium/potassium alloy, distilled, and stored under argon. The following spectrometers were used: NMR, Bruker WP 80-FT (^1H, 80 MHz), Bruker WM 300-FT (^{13}C, 75.5 MHz), and Bruker WH 400-FT (^1H, 400 MHz; ^{13}C, 100.6 MHz); IR, Nicolet 7199 FT IR spectrometer; MS, Finnigan 311 A (70 eV), the *m/e* values given correspond to isotopes of highest natural abundance. Elemental analyses were carried out by Dornis and Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr. Melting points are uncorrected. Acetone azine (**8a**), benzophenone azine (**8b**),[34] (butadiene)zirconocene (10),[20] zirconocene dicarbonyl,[19] zirconocene diphenyl,[18] and $LiN{=}CPh_2$[33] were prepared following literature procedures.

Reaction of Acetone Azine (8a) with (Butadiene)zirconocene (10). A solution of 1.4 g (5.1 mmol) of (butadiene)zirconocene (**10**) and 0.7 g of (6.6 mmol) acetone azine (**8a**) in 40 mL of benzene is stirred for 6 h at room temperature. Solvent is evaporated in vacuo. The remaining solid is washed with 20 mL of pentane and filtered to give the pure 1:1 adduct **13** (0.9 g, 46%). Mp: 172 °C. MS: *m/e* 386 (M^+). Anal. Calcd for $C_{20}H_{28}N_2Zr$ (387.68): C, 61.96; H, 7.28; N, 7.23. Found: C, 60.31, H, 7.09, N, 7.38. ^1H NMR (toluene-d_8, 400 MHz, 193 K); δ 5.44 (s, 5 H, Cp), 5.59 (s, 5 H, Cp), 1.03, 1.05 (s, 3 H each, ring CH_3), 1.57, 1.59 (s, 3 H each, $N{=}C(CH_3)_2$), 1.19, 3.02 (m, 1 H each, $ZrCH_2$), 2.11, 2.88 (m, 1 H each, $={CHCH_2}$), 5.19 (m, 1 H, $={CHCH_2}$), 6.95 (m, 1 H, $ZrCH_2CH{=}$). Topomerization barrier determined from the Cp coalescence: $\Delta\nu(273\ K) = 9.8 + 0.1$ Hz, $\Delta G^{\ddagger}(288\ K) = 15.1 + 0.2$ kcal/mol. ^{13}C NMR toluene-d_8, 243 K, $^1J(CH)$ in parentheses): δ 22.5 (q, 127 Hz), 27.1 (q, 124 Hz, ring CH_3), 25.5 (q, 123 Hz), 28.8 (q, 124, $N{=}C(CH_3)_2$), 34.4 (t, 126 Hz, $ZrCH_2$), 43.4 (s, ring $NCMe_2$), 43.6 (t, 126 Hz, $={CHCH_2}$), 107.3 (d, 171 Hz, Cp), 108.3 (d, 171 Hz, Cp), 120.1 (s, $N{=}CMe_2$), 145.2 (d, 146 Hz, $ZrCH_2CH{=}$). The remaining $={CHCH_2CMe_2}$ resonance was hidden under a Cp signal at 243 K; however, it could be located at higher temperature (313 K) at δ 108.7 (d, 155 Hz). IR (KBr): $\nu(C{=}N)$ 1611 cm^{-1}.

Preparation of $Cp_2Zr(N{=}CPh_2)_2$ (9b). (a) From Cp_2ZrCl_2 and $LiN{=}CPh_2$.[33] A solution of 3.1 mL (30.4 mmol) of benzonitrile was added to 30 mL of ethereal phenyllithium solution (29.4 mmol) at −50 °C. The reaction mixture was allowed to warm to room temperature. Then 4.0 g (13.7 mmol) of Cp_2ZrCl_2 was added, and the reaction mixture stirred for 20 h at ambient temperature. The ether was removed in vacuo. The remaining oily residue was extracted with 75 mL of benzene. After filtration a clear red solution was obtained. The benzene solvent was removed in vacuo. To the remaining residue was added 50 mL of pentane. Upon stirring, the product solidified. It was removed from the solution by filtration and dried in vacuo to give 5.1 g (64%) of **9b**.

(b) From $Cp_2Zr(CO)_2$ and Benzophenone Azine. A mixture of 1.3 g (4.7 mmol) of zirconocene dicarbonyl and 1.4 g (3.9 mmol) of benzophenone azine in 350 mL of benzene was irradiated for 2 h with stirring (HPK 125, Pyrex filter). The reaction mixture was removed from the photolysis vessel. Solvent was stripped in vacuo. The remaining residue was well stirred with 100 mL of pentane. The solid reaction product was collected by filtration to give 1.8 g (80%) of red **9b**. Mp: 157 °C. MS: *m/e* 580 (M^+). Anal. Calcd for $C_{36}H_{30}N_2Zr$ (581.87): C, 74.31; H, 5.20; N, 4.81. Found: C, 74.26; H, 5.22; N, 4.83. ^1H NMR (benzene-d_6): δ 5.77 (s, 10 H, Cp), 7.1–7.3 (m, 12 H, Ph), 7.5–7.7 (m, 8 H, Ph). ^{13}C NMR (benzene-d_6, 311 K, $^1J(CH)$ in parentheses): δ 108.9 (d, 172 Hz, Cp), 128.2 (d, 159 Hz, Ph), 128.5 (d, 158 Hz, Ph), 128.7 (d, 160 Hz, Ph), 142.0 (s, Ph), 170.4 (s, $Ph_2C{=}N$). ^{13}C NMR (CD_2Cl_2, 198 K): δ 108.0 (d, 173 Hz, Cp), 127.3 (d, 160 Hz, Ph, *m*-CH), 128.1 (d, 160 Hz, Ph, *o*- and *p*-CH), 139.7 (s, Ph, *ipso*-C), 169.4 (s, $Ph_2C{=}N$). IR (KBr): $\nu(C{=}N)$ 1630 (s), 1650 (sh) cm^{-1}.

Thermally Induced Reaction of Benzophenone Azine with (Butadiene)zirconocene. A mixture of 50 mg (0.2 mmol) of (butadiene)zirconocene and 100 mg (0.3 mmol) of benzophenone azine in 10 mL of toluene was stirred for 5 days at room temperature. NMR analysis of a sample (in benzene-d_6) revealed the formation of **9b** (approximately 30% in addition to a variety of unidentified organometallic compounds). Toluene was removed in vacuo. Extraction of the residue with 10 mL of pentane gave an enriched (ca. 90% pure) sample of $Cp_2Zr(N{=}CPh_2)_2$.

Photolysis of Diphenylzirconocene in the Presence of Benzophenone Azine. A sample of 20 mg (0.05 mmol) of diphenylzirconocene and 20 mg (0.05 mmol) of benzophenone azine was dissolved in 0.5 mL of benzene-d_6, and the resulting mixture irradiated for 6 h at room temperature in a sealed NMR tube (HPK 125, Pyrex filter). NMR analysis revealed the formation of $Cp_2Zr(N{=}CPh_2)_2$ (**9b**) (ca. 70%) in addition to biphenyl.

X-ray Crystal Structure Analysis of 9b. A sample of 0.8 g of $Cp_2Zr(N{=}CPh_2)_2$ (**9b**) was dissolved in 40 mL of diethyl ether. The solution was kept at +5 °C for 16 h. Several red cube-shaped crystals of **9b** had formed during this time. This material was suitable for structure determination by X-ray diffraction. For a detailed description of the methods used for collecting data and solving the structure, see ref 35.

Crystallographic Data for 9b: $C_{36}H_{30}N_2Zr$; M_r 581.9; crystal size 0.25 × 0.68 × 0.54 mm; monoclinic; space group $C2/c$; $a = 32.878$ (5), $b = 9.697$ (1), $c = 19.653$ (2) Å; $\beta = 111.818$ (8)°; $V = 5816.7$ Å^3; $Z = 8$; $d_{calcd} = 1.33$ g cm^{-3}; graphite-monochromated Mo Kα ($\lambda = 0.71069$ Å); $\mu = 3.96$ cm^{-1}; reflections measured, 7163 ($\pm h,+k,+l$); unique reflections, 6587; observed reflections 4753 ($I > 2\sigma(I)$); number of variables, 352; $R = 0.037$; $R_w = 0.044$; Nonius CAD-4; goodness of fit, 2.22; final average shift/error, 0.05; final difference Fourier, 0.44 e Å^{-3}.

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Registry No. 5, 1291-32-3; **6**, 19112-47-1; **8a**, 627-70-3; **8b**, 983-79-9; **9b**, 11106-18-6; **10**, 75374-50-4; **13**, 112713-05-0; **17**, 1291-32-3; Cp_2ZrPh_2, 51177-89-0.

Supplementary Material Available: Tables of data and data collection details, atomic coordinates and thermal parameters, and selected interatomic distances and angles (8 pages); listing of observed and calculated structure factors for **9b** (21 pages). Ordering information is given on any current masthead page.

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(34) Szmant, H. H.; McGinnis, C. *J. Am. Chem. Soc.* **1950**, *72*, 2890.

(35) Krüger, C.; Müller, G.; Erker, G.; Dorf, U.; Engel, K. *Organometallics* **1985**, *4*, 215.