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Formation and Structures of Cationic Pyrazole and Pyrazolyl Zirconocene Complexes

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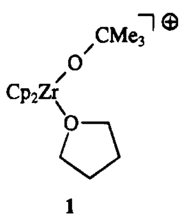
Dimethylzirconocene (**4**) was treated with 1 molar equiv of pyrazole to give methane and (pyrazole-*N*)methylzirconocene (**5**). Treatment of **5** with tributylammonium tetraphenylborate gave the cationic (η^2-pyrazolyl-*N*,*N*′)(tetrahydrofuran)zirconocene complex **6**, isolated as the tetraphenylborate salt in >60% yield. The related (η^2-pyrazolyl-*N*,*N*′)(η^1-pyrazolyl-*N*)zirconocene tetraphenylborate salt was obtained by treating the methylzirconocene cation **7** with pyrazole in dichloromethane. Cationic (η^2-pyrazolyl-*N*,*N*′)(tetrahydrofuran)zirconocene **6** reacts with acetylacetone by proton transfer to give (acetylacetonato)(η^1-pyrazole-*N*)zirconocene tetraphenylborate (**9**). Complexes **6** and **9** were characterized by X-ray diffraction. Complex **6** was employed as a general Lewis-acid catalyst in the Mukaiyama aldol reaction between [(trimethylsilyl)oxy]cyclopentene and benzaldehyde.

Cationic $Cp_2Zr(R)^+$ complexes are of great importance as the essential intermediates in homogeneous Ziegler−Natta catalysis.[1] Their donor ligand-stabilized counterparts $Cp_2Zr(R)L^+$ can readily be prepared and isolated.[2] Jordan, Bochmann, and others have in recent years established the organometallic chemistry of such species.[3] Mostly, examples were used having hydrocarbyl groups R bonded to zirconium. At present there are only a few related complexes $Cp_2Zr(X)L^+$ known containing groups X that are σ-bonded to Zr through an element more electronegative than carbon (O, S, N).[4] Complexes **1** and **2** are typical examples. Having oxygen or nitrogen containing ligands X bonded to zirconium may lead to a partial compensation of the electron deficiency at the metal due to ligand to metal π-back-bonding effects.[5] There is evidence that such internally stabilized metallocene cations can serve as effective Lewis-acid catalysts in many synthetically important carbon-carbon coupling reactions of organic substrates.[4a]



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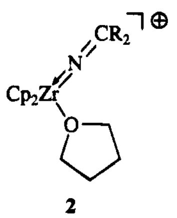

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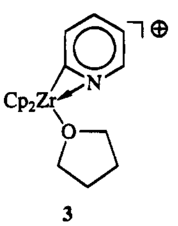

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Stabilization of $Cp_2Zr(R)L^+$ complexes by means of internal heteroatom coordination of nitrogen or oxygen containing σ-hydrocarbyl ligands is more common. Metallocene cations containing η^2-2-pyridyl (**3**), η^2-acyl, or η^2-iminoacyl ligands are typical examples.[6] We have now for the first time prepared cationic zirconocene complexes that have both these structural features combined. Having pyrazolyl ligands attached to the electron deficient metallocene cation leads to stable easily isolated $Cp_2Zr(X)L^+$ complexes that exhibit some remarkable structural and dynamic features. In addi-

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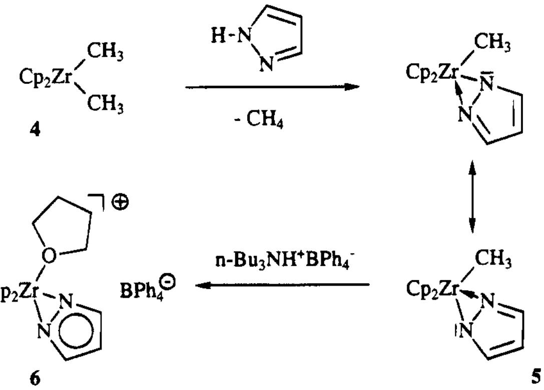
tion, it appears that this novel type of cationic group 4 metallocene complexes will be very useful as an efficient organometallic Lewis-acid catalyst in organic synthesis. The preparation and properties of several typical examples are described in this article.

Results and Discussion

Synthesis and Solid State Structures. Dimethylzirconocene (**4**) was treated with 1 molar equiv of pyrazole at ambient temperature in pentane solution. Rapid methane evolution was observed and the clean formation of (pyrazolyl-*N*)methylzirconocene (**5**) achieved within a short period of time. Complex **5** was isolated in 90% yield.



The pyrazolylzirconium complex **5** was then treated with tri-*n*-butylammonium tetraphenylborate in tetrahydrofuran solution at 50 °C. This resulted in the selective abstraction of the methyl group at zirconium and formation of the cationic (η^2-pyrazolyl-*N*,*N'*)zirconocene complex **6**. The metallocene salt **6** was recrystallized from tetrahydrofuran and characterized by X-ray diffraction.

The crystalline complex **6** exhibits an overall composition of [Cp$_2$Zr(η^2-pyrazolyl)(THF)]$^+$BPh$_4$·0.5THF. The asymmetric unit contains a tetraphenylborate anion that is well separated from the organometallic cation. There are two tetrahydrofuran entities. One of these is just independently present in the crystal with a site occupation of 0.5; there are no noteworthy close contacts to the components of **6**. The other tetrahydrofuran unit is coordinated to zirconium. The C_4H_8O ring shows the typical twisted conformation. The mean plane of this tetrahydrofuran ring is oriented nearly parallel to the major σ-ligand plane of the bent metallocene wedge (i.e. which is bisecting the Cp—Zr—Cp angle). The Zr—O(1) bond length is 2.240(5) Å. This is a typical value for such a situation where a significant oxygen to zirconocene π-interaction is prevented due to a geometric restriction of suitable orbital overlap.[7]

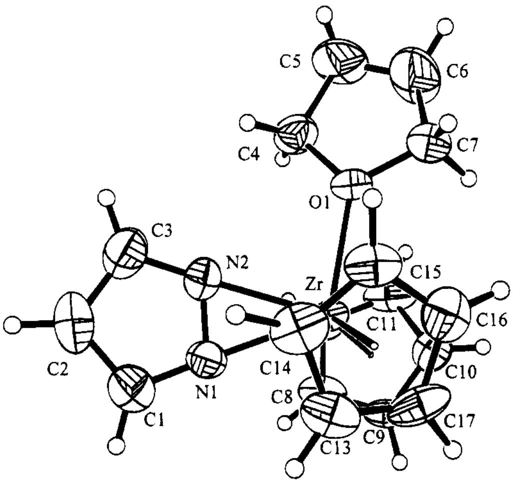


Figure 1. Molecular geometry of **6** (with unsystematic atom numbering scheme). Only the cationic part is depicted.

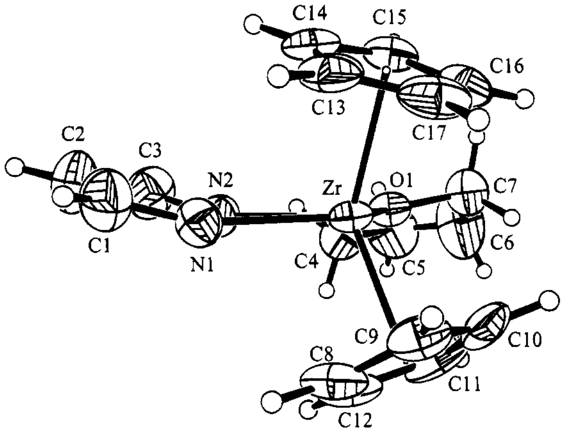


Figure 2. Side view of the molecular structure of **6**.

Complex **6** contains a η^2-pyrazolyl-*N*,*N'* ligand bonded to zirconium. Both nitrogen centers are nearly equidistant from zirconium at Zr—N(1) 2.182(8) and Zr—N(2) 2.207(8) Å. The pyrazolyl ligand is planar and close to a regular pentagon [N(1)—N(2) 1.347(10), N(1)—C(1) 1.306(12), C(1)—C(2) 1.39(2), C(2)—C(3) 1.39(2), C(3)—N(2) 1.324(12) Å; the sum of the bonding angles inside the five-membered heterocycle is 540° ($\overline{\angle}$ = 108(2)°)]. The D(1)—Zr—D(2) angle at the bent metallocene unit is 130.8° [D(1) and D(2) denote the centroids of the η^5-cyclopentadienyl ligands]. The atoms N(1), N(2), and O(1) are oriented coplanarly in the central σ-ligand plane. The N(1)—Zr—O(1) angle is 119.2(3)°. This is within the range often observed for σ-ligand bite angles at pentacoordinated zirconium in edge-capped pseudotetrahedral bent metallocene geometries.[8] The nitrogen atom N(2) is coordinated at the "inside" position in the σ-ligand plane (syn to the tetrahydrofuran oxygen). The N(2)⋯O(1) separation is 2.96 Å.

It is noteworthy that the η^2-pyrazolyl ligand is not oriented exactly in the σ-ligand plane at zirconium but markedly tilted from it (see Figure 2). The angle between the planes Zr,N(1),N(2) and N(1),N(2),C(1),C(2),C(3) is 16.7°.[9]

The cationic methylzirconocene complex **7** reacts similarly with pyrazole. We have treated [Cp$_2$ZrCH$_3$(THF)]$^+$BPh$_4^-$ (**7**) with 2 molar equiv of pyrazole in dichloromethane at room temperature. Rapid methane evolution was observed. From the reaction mixture we have isolated the cationic pyrazolylzirconocene complex **8** in >70% yield. From the physical and spectroscopic

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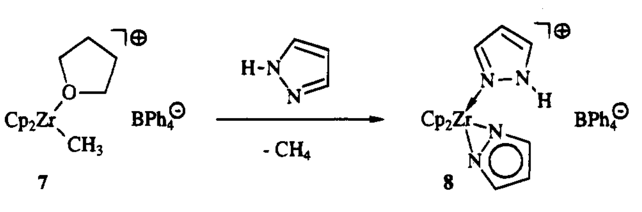
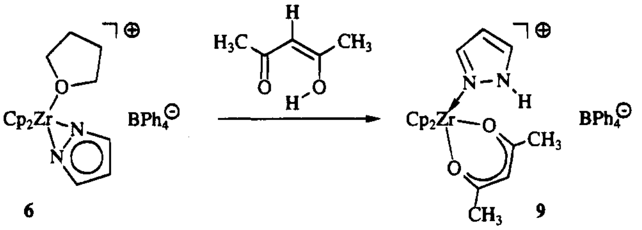


properties (see below) it is evident that 1 equiv of pyrazole is coordinated to the electrophilic early transition metal center in this complex.

The cationic (η^2-pyrazolyl-*N,N'*)zirconocene complex **6** served as a starting material for the preparation of another (η^1-pyrazole)zirconocene complex. In this case the neutral donor ligand was formed in the coordination sphere of the bent metallocene by protonating a nitrogen of the pyrazolyl ligand. The (η^2-pyrazolyl-*N,N'*)zirconocene tetraphenylborate salt **6** was dissolved in dichloromethane and treated with an equimolar quantity of 2,4-pentanedione. Addition of the acacH reagent and proton transfer occurred rapidly and the cationic (acetylacetonate) zirconocene complex **9** was isolated in 65% yield.



The (pyrazole)(acetylacetonate)zirconocene tetraphenylborate salt **9** was recrystallized from dichloromethane/toluene and characterized by X-ray diffraction. Complex **9** contains an acetylacetonate ligand in its characteristic delocalized form [C(5)—C(6) 1.37(2), C(6)—C(7) 1.363(14) Å] bonded to zirconium,[10] although the pairs of zirconium—oxygen linkages and their adjacent carbon oxygen bonds are rather different in length [Zr—O(1) 2.131(6) Å vs 2.183(7) Å for Zr—O(2); O(1)—C(5) 1.304(12) Å vs 1.279(11) Å for O(2)—C(7)].

These differences are probably caused by the crowded situation in the σ-ligand plane of the bent metallocene system. In addition to the planar acetylacetonate moiety, there is an additional N-bonded pyrazole ligand coordinated to zirconium. This pyrazole donor ligand is oriented almost perfectly coplanar with the acac moiety. This means that the pyrazole atoms N(1), N(2), and C(1)—C(3) are coplanar with Zr, O(1), O(2), and C(4)—C(8) with maximum deviations being −0.154 Å [for C(3)] and +0.115 Å [for C(6)]. This naturally leads to substantial angle deformations of the distorted edge-capped bent metallocene tetrahedron in the σ-plane. The N(1)—Zr—O(2) σ-ligand bite angle is large (149.1(3)°); the O(2)—Zr—O(1) angle is 75.6(2)°, and the O(1)—Zr—N(1) angle is 73.6(3)°. The hydrogen atom at N(2) was not observed but placed in the calculated position with N(2)—H(2) 0.86 Å. The corresponding O(1)—H(2) separation is then calculated to be ca. 2.17 Å. Together with the observed O(1)—N(2) distance of 2.67 Å this clearly indicated that in complex **9** the pyrazole and acetylac-

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 6

Zr—N(1)	2.182(8)	Zr—N(2)	2.207(8)
Zr—O(1)	2.240(5)	N(1)—C(1)	1.306(12)
N(1)—N(2)	1.347(10)	N(2)—C(3)	1.324(12)
O(1)—C(4)	1.462(10)	O(1)—C(7)	1.464(11)
C(1)—C(2)	1.39(2)	C(2)—C(3)	1.39(2)
C(4)—C(5)	1.50(2)	C(5)—C(6)	1.34(2)
C(6)—C(7)	1.46(2)		
N(1)—Zr—N(2)	35.7(3)	N(1)—Zr—O(1)	119.2(3)
N(2)—Zr—O(1)	83.5(3)	C(1)—N(1)—N(2)	107.8(9)
C(3)—N(2)—N(1)	109.9(9)	C(4)—O(1)—C(7)	109.4(7)
N(1)—C(1)—C(2)	110.0(11)	C(3)—C(2)—C(1)	104.3(10)
N(2)—C(3)—C(2)	108.0(11)	O(1)—C(4)—C(5)	102.3(9)
C(6)—C(5)—C(4)	109.7(11)	C(5)—C(6)—C(7)	108.8(11)
C(6)—C(7)—O(1)	104.1(9)		

$\bar{d}(\mathrm{Zr{-}C_{Cp}}) = 2.50$
$\bar{d}(\mathrm{C{-}C})_{\mathrm{Cp}} = 1.40(2)$
$\bar{\alpha}(\mathrm{C{-}C{-}C})_{\mathrm{Cp}} = 108(1)$

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for 6

	x	y	z	$U_{eq}{}^{a}$ Å^2
Zr	0.1048(1)	0.5290(1)	0.2154(1)	0.039(1)
N(1)	0.1343(3)	0.4468(3)	0.1690(6)	0.058(2)
N(2)	0.1771(3)	0.4829(3)	0.1562(5)	0.058(2)
O(1)	0.1635(2)	0.6024(2)	0.2093(4)	0.049(1)
O(2)	0.1013(6)	0.2653(6)	0.0954(13)	0.079(4)
B	0.8425(4)	0.4505(4)	0.2780(6)	0.038(2)
C(1)	0.1446(5)	0.4020(5)	0.1189(9)	0.083(3)
C(2)	0.1969(6)	0.4075(5)	0.0730(10)	0.099(4)
C(3)	0.2146(5)	0.4607(5)	0.098(8)	0.084(3)
C(4)	0.2246(4)	0.5968(4)	0.2127(8)	0.071(3)
C(5)	0.2434(5)	0.6566(6)	0.2210(12)	0.109(5)
C(6)	0.2004(6)	0.6885(6)	0.2493(14)	0.133(6)
C(7)	0.1481(4)	0.6613(4)	0.2223(8)	0.069(3)
C(8)	0.0939(5)	0.4694(4)	0.3599(6)	0.065(3)
C(9)	0.0451(4)	0.4998(4)	0.3509(6)	0.057(2)
C(10)	0.0598(5)	0.5571(5)	0.3672(6)	0.067(3)
C(11)	0.1185(5)	0.5596(6)	0.3838(6)	0.079(4)
C(12)	0.1402(5)	0.5040(6)	0.3776(6)	0.074(3)
C(13)	0.0326(4)	0.5021(5)	0.0994(7)	0.064(3)
C(14)	0.0746(4)	0.5280(5)	0.0456(6)	0.061(3)
C(15)	0.0771(4)	0.5840(4)	0.0707(6)	0.059(3)
C(16)	0.0359(4)	0.5934(5)	0.1403(7)	0.070(3)
C(17)	0.0075(4)	0.5422(5)	0.1552(7)	0.071(3)
C(18)	0.9005(3)	0.4145(3)	0.2787(5)	0.036(2)
C(19)	0.9304(3)	0.4017(3)	0.1959(5)	0.044(2)
C(20)	0.9804(4)	0.3713(4)	0.1954(6)	0.050(2)
C(21)	1.0040(4)	0.3544(4)	0.2782(7)	0.056(2)
C(22)	0.9774(4)	0.3675(4)	0.3613(7)	0.056(2)
C(23)	0.9271(3)	0.3969(3)	0.3618(6)	0.043(2)
C(24)	0.8624(3)	0.5170(3)	0.2773(6)	0.042(2)
C(25)	0.8866(4)	0.5398(4)	0.3585(7)	0.059(2)
C(26)	0.9069(5)	0.5945(5)	0.3594(10)	0.087(4)
C(27)	0.9027(5)	0.6281(5)	0.2820(13)	0.101(5)
C(28)	0.8796(5)	0.6072(4)	0.2005(10)	0.081(3)
C(29)	0.8595(4)	0.5523(4)	0.2000(7)	0.059(2)
C(30)	0.8012(3)	0.4363(3)	0.1892(5)	0.038(2)
C(31)	0.8028(3)	0.3868(4)	0.1378(5)	0.047(2)
C(32)	0.7642(4)	0.3730(4)	0.0686(7)	0.064(3)
C(33)	0.7207(4)	0.4092(5)	0.0469(6)	0.061(3)
C(34)	0.7166(4)	0.4578(4)	0.0971(6)	0.060(3)
C(35)	0.7555(4)	0.4710(4)	0.1665(6)	0.049(2)
C(36)	0.8030(3)	0.4365(4)	0.3706(5)	0.042(2)
C(37)	0.7975(4)	0.3826(4)	0.4048(6)	0.051(2)
C(38)	0.7617(4)	0.3693(5)	0.4789(7)	0.071(3)
C(39)	0.7291(4)	0.4111(6)	0.5194(7)	0.076(4)
C(40)	0.7324(4)	0.4656(5)	0.4874(6)	0.067(3)
C(41)	0.7694(4)	0.4770(4)	0.4137(6)	0.055(2)
C(42)	0.1256(11)	0.2430(9)	0.1629(18)	0.076(7)
C(43)	0.1678(11)	0.2048(13)	0.1381(19)	0.108(10)
C(44)	0.1667(12)	0.2022(12)	0.0358(22)	0.115(10)
C(45)	0.1280(10)	0.2485(11)	0.0158(16)	0.084(7)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

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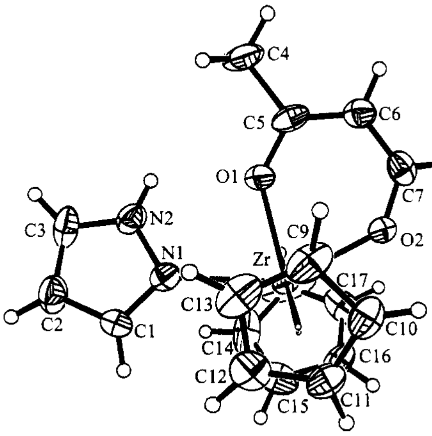

Figure 3. View of the molecular geometry of **9** (with unsystematic atom numbering scheme). Only the cationic part is shown.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 9

Zr—O(1)	2.131(6)	Zr—O(2)	2.183(7)
Zr—N(1)	2.369(9)	N(1)—C(1)	1.324(13)
N(1)—N(2)	1.345(10)	N(2)—C(3)	1.321(13)
O(1)—C(5)	1.304(12)	O(2)—C(7)	1.279(11)
C(1)—C(2)	1.38(2)	C(2)—C(3)	1.36(2)
C(4)—C(5)	1.499(14)	C(5)—C(6)	1.37(2)
C(6)—C(7)	1.363(14)	C(7)—C(8)	1.509(14)
O(1)—Zr—O(2)	75.6(2)	O(1)—Zr—N(1)	73.6(3)
O(2)—Zr—N(1)	149.1(3)	C(1)—N(1)—N(2)	102.9(8)
C(3)—N(2)—N(1)	113.3(10)	N(1)—C(1)—C(2)	112.4(10)
C(3)—C(2)—C(1)	104.4(11)	N(2)—C(3)—C(2)	106.9(11)
O(1)—C(5)—C(6)	121.7(9)	O(1)—C(5)—C(4)	114.4(12)
C(6)—C(5)—C(4)	123.9(10)	C(7)—C(6)—C(5)	124.2(10)
O(2)—C(7)—C(6)	123.7(10)	O(2)—C(7)—C(8)	115.1(10)
C(6)—C(7)—C(8)	121.0(10)		

$\bar{d}(\mathrm{Zr{-}C_{Cp}}) = 2.52(2)$
$\bar{d}(\mathrm{C{-}C})_{\mathrm{Cp}} = 1.38(2)$
$\bar{\alpha}(\mathrm{C{-}C{-}C})_{\mathrm{Cp}} = 108(2)$

Table 4. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for 9

	x	y	z	U_{eq},[a] Å^2
Zr	0.4211(1)	0.0344(1)	0.6054(1)	0.034(1)
N(1)	0.3957(5)	0.0739(7)	0.7302(5)	0.041(2)
N(2)	0.4179(5)	0.1747(7)	0.7638(4)	0.048(2)
O(1)	0.4751(4)	0.2000(5)	0.6295(3)	0.046(2)
O(2)	0.4701(4)	0.0917(6)	0.5013(4)	0.049(2)
B	0.6096(7)	0.4473(10)	0.8957(6)	0.035(3)
C(1)	0.3585(6)	0.0160(9)	0.7823(6)	0.050(3)
C(2)	0.3602(7)	0.0759(11)	0.8483(6)	0.061(3)
C(3)	0.3976(7)	0.1791(12)	0.8333(6)	0.060(3)
C(4)	0.5523(6)	0.3703(10)	0.6466(7)	0.070(4)
C(5)	0.5235(5)	0.2726(7)	0.5981(8)	0.048(2)
C(6)	0.5430(6)	0.2612(9)	0.5259(6)	0.054(3)
C(7)	0.5127(6)	0.1778(9)	0.4801(6)	0.049(3)
C(8)	0.5240(7)	0.1864(11)	0.3985(6)	0.072(4)
C(9)	0.5520(6)	−0.0603(10)	0.6162(10)	0.062(4)
C(10)	0.5127(7)	−0.1232(10)	0.5578(7)	0.056(3)
C(11)	0.4531(6)	−0.1834(10)	0.5907(7)	0.053(3)
C(12)	0.4529(7)	−0.1599(10)	0.6644(8)	0.060(3)
C(13)	0.5160(7)	−0.0821(11)	0.6794(9)	0.065(4)
C(14)	0.2777(6)	0.0608(16)	0.6238(6)	0.077(5)
C(15)	0.2882(5)	−0.0499(11)	0.5972(11)	0.068(4)
C(16)	0.3142(6)	−0.0392(12)	0.5281(7)	0.062(3)
C(17)	0.3172(7)	0.0774(15)	0.5105(8)	0.072(4)
C(18)	0.2977(8)	0.1440(11)	0.5683(12)	0.098(6)
C(19)	0.5133(5)	0.4601(8)	0.9004(5)	0.034(2)
C(20)	0.4700(5)	0.4227(8)	0.9602(6)	0.041(2)
C(21)	0.3894(7)	0.4247(10)	0.9619(7)	0.051(3)
C(22)	0.3496(6)	0.4637(12)	0.9036(8)	0.061(4)
C(23)	0.3875(7)	0.5021(11)	0.8431(8)	0.058(3)
C(24)	0.4705(6)	0.5005(9)	0.8416(6)	0.045(3)
C(25)	0.6493(6)	0.5582(8)	0.8535(6)	0.034(2)
C(26)	0.6385(6)	0.5845(10)	0.7792(6)	0.042(3)
C(27)	0.6713(6)	0.6800(10)	0.7444(6)	0.058(3)
C(28)	0.7213(7)	0.7557(9)	0.7827(8)	0.069(4)
C(29)	0.7343(7)	0.7355(8)	0.8546(7)	0.057(3)
C(30)	0.7005(6)	0.6397(8)	0.8888(6)	0.049(3)
C(31)	0.6271(5)	0.3199(8)	0.8527(5)	0.034(2)
C(32)	0.6824(6)	0.3023(8)	0.8006(6)	0.047(3)
C(33)	0.6973(6)	0.1932(9)	0.7701(6)	0.058(3)
C(34)	0.6580(6)	0.0941(9)	0.7915(6)	0.054(3)
C(35)	0.6025(6)	0.1059(9)	0.8446(6)	0.051(3)
C(36)	0.5887(6)	0.2165(8)	0.8738(6)	0.044(2)
C(37)	0.6458(5)	0.4387(7)	0.9777(5)	0.034(2)
C(38)	0.7116(5)	0.3666(8)	0.9934(5)	0.038(2)
C(39)	0.7490(7)	0.3713(9)	1.0605(7)	0.060(3)
C(40)	0.7245(7)	0.4479(9)	1.1117(9)	0.064(3)
C(41)	0.6625(6)	0.5195(9)	1.1009(9)	0.055(3)
C(42)	0.6248(6)	0.5144(9)	1.0344(6)	0.042(2)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

etonate ligands are not linked together by hydrogen bridging. The D(1)—Zr—D(2) angle in **9** is 128.6°.

Behavior of the Complexes in Solution. When crystals of $[Cp_2Zr(\eta^2\text{-pyrazolyl-}N,N')(THF)]^+BPh_4^-\cdot 0.5\text{-}THF$(**6**) were dissolved in [D$_2$]dichloromethane, two sets of tetrahydrofuran signals were observed by ^{1}H NMR spectroscopy at ambient temperature. Under these conditions the exchange between free and coordinated tetrahydrofuran was apparently slow on the NMR time scale. The signal of the pyrazolyl β-H was observed at δ 6.61. As expected in view of the molecular structure of **6** (see above), we observed two signals for the inequivalent pyrazolyl α-protons at δ 7.75 and 7.50. However, these signals have already become broad and lost their fine structure, indicating the beginning of a dynamic process of **6** taking place in solution whereby the $H_\alpha/H_{\alpha'}$ inequivalency is lost. The rate of this process is only marginally affected by changing the solvent to [D$_8$]tetrahydrofuran. In this solvent the coordinated THF ligand is rapidly liberated due to exchange with perdeuterated THF at ambient temperature. When the temperature is lowered to 243 K, a clearly resolved spectrum of **6** is obtained, showing inequivalent pyrazolyl H_α ^{1}H NMR resonances at δ 7.77 and 7.56 [^{13}C NMR in [D$_8$]tetrahydrofuran (pyrazolyl α-CH): δ 138.6 and 134.9 (both signals show $^1J_{CH}$ = 188 Hz)].

The neutral pyrazolylzirconocene complex **5** shows an analogous dynamic behavior. At 300 K in [D$_6$]benzene there is only a single set of pyrazolyl methine ^{1}H/^{13}C NMR signals in a 2:1 ratio [7.37, 6.35/134.8, 112.59]. With decreasing temperature in CD_2Cl_2 solution the pyrazolyl α-CH signals rapidly broaden and eventually split into two ^{1}H/^{13}C sets of resonances at 7.55, 7.32/134.9, and 132.9 at 198 K [^{1}H NMR coalescence at T_c = 205 K; $\Delta G^\ddagger$ (automerization) = 9.4 ± 0.3 kcal mol^{-1} at 230 K[11,12]]. Formally, this process could be described by a rotation of a η^2-pyrazolyl-N,N' ligand around the Zr—C$_\beta$ vector. However, we regard this process as unlikely in view of the special frontier orbital features of the group 4 bent metallocene fragment.[7,13] We assume that it is more likely that η^2-pyrazolyl-N,N' dynamic equilibration at the zirconocene framework is taking place by means of a reaction sequence involving

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Table 5. X-ray Crystal Structure Analyses of 6 and 9: Details of the Data Collection and Structure Solutions

	6	9
formula	$C_{43}H_{45}BN_2O_{1.5}Zr$	$C_{42}H_{41}BN_2O_2Zr$
fw	715.84	707.80
syst	tetragonal	orthorhombic
space group	$P4_{2/n}$	$Pna2_1$
a, Å	23.821(5)	17.355(3)
b, Å	23.831(5)	11.241(2)
c, Å	14.201(1)	18.309(4)
V, Å^3	8058(3)	3572(1)
Z	8	4
T, K	223	223
d_{calc}, g cm^{-3}	1.180	1.316
cryst size, mm	0.4 × 0.4 × 0.3	0.3 × 0.15 × 0.1
μ, mm^{-1}	0.31	0.35
abs corr	none	none
index ranges	$-29 \leq h \leq 0$ $0 \leq k \leq 29$ $0 \leq l \leq 17$	$-21 \leq h \leq 0$ $-14 \leq k \leq 0$ $-22 \leq l \leq 0$
θ range, deg	2.39–26.30	2.22–26.33
radiation; λ, Å	Mo Kα; 0.710 73	Mo Kα, 0.710 73
no. of reflns collcd	8576	3749
no. of ind reflns	8176	3749
R_{int}[a]	0.091	0
no. of obs reflns [$I > 2\sigma(I)$]	3621	2191
GOF	1.055	1.060
R[b]	0.068	0.050
R_w^2[c]	0.195	0.114
a	0.1264	0.0742
b	18.437	

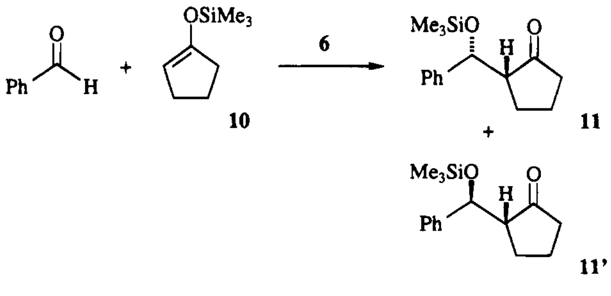
[a] $R_{int} = \sum|F_o^2 - F_o^2(\text{mean})|/\sum[F_o^2]$. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [d] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (\max(F_o^2 \text{ or } 0) = 2\ F_c^2)/3$.

reversible η^2- $\rightleftharpoons$ η^1-ligand equilibration coupled with Zr—N σ-bond rotation.[13,14]

In the (η^2-pyrazolyl-*N,N'*)(η^1-pyrazole)zirconocene cation (**8**) this positional automerization reaction of the η^2-pyrazolyl ligand is coupled with proton transfer between the two adjacent heterocyclic ring systems. In the ^{1}H NMR spectrum of **8** in [D$_2$]dichloromethane at 300 K the NH signal is observed at δ 9.58 and there is only a single set of pyrazole/pyrazolyl methine hydrogen resonances at δ 7.61 (broad doublet, four hydrogens, H_α) and 6.57 (triplet, two hydrogens, H_β). When the temperature is decreased, the C*H* resonances rapidly broaden and split into two sets of H_α/H_β resonances. In the low temperature limiting ^{1}H NMR spectrum the inequivalency of the two heterocyclic ring systems is clearly visible and the $H_\alpha/H_{\alpha'}$ degeneracy is also resolved. Consistent with the proposed structure of **8** one observes the pyrazole/pyrazolyl $H_\alpha/H_{\alpha'}$ resonances at δ 7.80 (1H), 7.56 (2H), and 7.01 (1H) at 233 K in [D$_2$]dichloromethane; the corresponding H_β resonances appear at δ 6.59 (1H) and 6.42 (1H).

For the (pyrazole)(acetylacetonate)zirconocene cation (**9**) a similar dynamic process (i.e. "left/right" equilibration of the nitrogen heterocycle at zirconium) would probably require intermediate cleavage of an acetylacetonate oxygen to zirconium linkage to allow the η^1- $\rightleftharpoons$ η^2- $\rightleftharpoons$ η^1-pyrazole/pyrazolyl rearrangement to occur. Consequently, the automerization process of the N-heterocycle might be observed being associated with dynamic intramolecular symmetrization of the adjacent acac ligand. That is actually what is observed experimentally. At high temperatures (i.e. 300 K in [D$_2$]dichloromethane) complex **9** exhibits a broad N*H* resonance centered at δ 11.2, an ^{1}H NMR pyrazole β-C*H* signal at δ 6.61 (pseudotriplet), and only *one* α-C*H* doublet (broad) at δ 7.58 representing two hydrogen atoms. Likewise, the acetylacetonate ligand shows only a single ^{1}H NMR methyl resonance at δ 2.14 (six hydrogens). Lowering the temperature rapidly results in freezing the dynamic exchange and symmetrization process on the NMR time scale. In the low temperature limiting spectra in [D$_2$]dichloromethane (for details see Experimental Section) one observes the separation of signals as was expected from the result of the X-ray crystal structure analysis of **9** [e.g. ^{1}H NMR (360 MHz, 223 K): pyrazole H_α signals at 7.53 and 7.50; acetylacetonate methyl resonances at δ 2.15 and 2.11].

The pyrazolylzirconocene cation **6** cleanly catalyzes the aldol type reaction of the trimethylsilyl enol ether **10** with benzaldehyde. Under such conditions of a general Lewis-acid catalysis employing 10 mol % of the [(η^2-pyrazolyl-*N,N'*)(THF)ZrCp$_2$]$^+$BPh$_4$ salt a 1:1 mixture of the syn- and anti-aldol diastereomers **11** and **11′** was obtained.[15] Details of the specific action of internally stabilized group 4 bent metallocene derived cations as Lewis-acid catalyst systems in aldol condensations and related reactions are presently investigated and will be discussed in a forthcoming publication.



Experimental Section

All reactions were performed in an argon atmosphere using Schlenk type glassware or in a MBrown glovebox. Solvents were purified by distillation from appropriate drying agents and stored under argon prior to use. The NMR spectra were obtained on a Bruker ARX 300, AC 200 P, or AM 360 NMR spectrometer. IR spectra were recorded on a Nicolet 5 DXC FT-IR spectrometer. Melting points were determined by DSC (DuPont 2910 DSC, STA Instruments). The starting materials **4**, **7**, and **10** were prepared according to methods described in the literature.[3,17,18]

Preparation of (Pyrazolyl-*N*)methylzirconocene (5). A solution of dimethylzirconocene **4** (2.40 g, 9.54 mmol) and

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pyrazole (650 mg, 9.55 mmol) in pentane (10 mL) was stirred at ambient temperature until the methane evolution had ceased. Cooling the solution to −30 °C gave a white precipitate which was collected by filtration and dried in vacuo to yield 2.60 g (90%) of **5**, mp 67 °C dec. Anal. Calcd for $C_{14}H_{16}N_2Zr$: C, 55.40; H, 5.31; N, 9.23. Found: C, 55.20; H, 5.39; N, 9.21. ^1H NMR (300 K, C_6D_6): δ 7.37 (d, 2H, H_α, ^3J = 1.6 Hz), 6.35 (d, 1H, H_β, ^3J = 1.6 Hz), 5.56 (s, 10H, Cp), 0.59 (s, 3H, Me). ^{13}C NMR (300 K, C_6D_6): δ 134.8 (C_α), 112.5 (C_β), 109.7 (Cp), 20.0 (Me). ^1H NMR (198 K, CD_2Cl_2): δ 7.55 (m, 1H, H_α), 7.32 (m, 1H, $H_{\alpha'}$), 6.40 (m, 1H, H_β), 5.78 (s, 10H, Cp), 0.09 (s, 3H, Me). ^{13}C NMR (198 K, CD_2Cl_2): δ 134.9 (C_α), 132.9 (C_α), 111.6 (C_β), 108.8 (Cp), 18.2 (Me). IR (KBr): $\tilde{\nu}$ 3107, 2922, 2807, 1475, 1439, 1407, 1239, 1014, 1005, 800, 774, 619 cm^{-1}.

Preparation of the Cationic (η^2-Pyrazolyl-*N,N'*)(THF)-zirconocene Complex 6. Tributylammonium tetraphenylborate (500 mg, 0.99 mmol) and 300 mg (0.99 mmol) of compound **5** were dissolved in THF (5 mL) and stirred at 50 °C for 3 h. After cooling to room temperature, pentane was added dropwise. The white precipitate formed was isolated and dried in vacuo to yield 460 mg (62%) of **6**. Crystals of **6** for the X-ray diffraction analysis were obtained by recrystallization from THF, mp 76 °C dec. Anal. Calcd for $C_{41}H_{41}N_2OBZr\cdot 0.5C_4H_8O$: C, 72.15; H, 6.34; N, 3.91. Found: C, 71.02; H, 6.61; N, 4.27. ^1H NMR (300 K, CD_2Cl_2): δ 7.75, 7.50 (each: br s, 1H, H_α), 6.61 (pt, 1H, H_β), 6.13 (s, 10H, Cp), 3.97−3.90 (m, 4H, THF_{coord}), 3.72−3.66 (m, 4H, THF_{free}), 2.04−1.98 (m, 4H, THF_{coord}), 1.86−1.79 (m, 4H, THF_{free}); (BPh_4^-) δ 7.41−7.32 (m, 8H, Ph), 7.10−7.00 (m, 8H, Ph), 6.95−6.85 (m, 4H, Ph). ^{13}C NMR (300 K, CD_2Cl_2): δ 138.4 (C_α), 135.7 (C_α), 115.8 (C_β), 114.7 ($^1J_{CH}$ = 176 Hz, Cp), 77.7 (THF), 68.1 (THF), 25.9 (THF); (BPh_4^-) δ 164.4 ($^1J_{BC}$ = 50 Hz, ipso-C), 136.3, 126.0, 122.2. ^1H NMR (243 K, THF-d_8): δ 7.77 (d, 1H, H_α), 7.56 (d, 1H, $H_{\alpha'}$), 6.55 (pt, 1H, H_β), 6.19 (s, 10H, Cp), 3.64−3.60 (m, 4H, THF_{coord}), 1.80−1.76 (m, 4H, THF_{coord}); (BPh_4^-) δ 7.36−7.28 (m, 8H, Ph), 6.95−6.90 (m, 8H, Ph), 6.81−6.76 (m, 4H, Ph). ^{13}C NMR (243 K, THF-d_8): δ 138.6 ($^1J_{CH}$ = 188 Hz, C_α), 134.9 ($^1J_{CH}$ = 188 Hz, $C_{\alpha'}$), 115.6 ($^1J_{CH}$ = 176 Hz, C_β), 115.3 ($^1J_{CH}$ = 176 Hz, Cp); (BPh_4^-) δ 164.9 ($^1J_{BC}$ = 50 Hz, ipso-C), 138.6, 125.8, 122.0. IR (KBr): $\tilde{\nu}$ 3102, 3052, 2998, 2982, 1580, 1427, 1300, 1150, 1014, 994, 821, 738, 707, 607 cm^{-1}.

Preparation of (η^2-Pyrazolyl-*N*)(η^1-pyrazole-*N*)zirconocene Tetraphenylborate (8). Methylzirconocene **7** (300 mg, 0.48 mmol) and pyrazole (68.0 mg, 1.00 mmol) were dissolved in dichloromethane (10 mL). After 30 min methane evolution had ceased and pentane was added to the reaction mixture. The resulting white precipitate was collected by filtration. Recrystallization from dichloromethane/toluene gave **8** (230 mg, 71%), mp 148 °C dec. Anal. Calcd for $C_{40}H_{37}N_4BZr$: C, 71.09; H, 5.52; N, 8.29. Found: C, 70.44; H, 5.49; N, 8.23. ^1H NMR (300 K, CD_2Cl_2): δ 9.58 (s, 1H, NH), 7.61 (d, 4H, H_α, ^3J = 2 Hz), 6.57 (t, 2H, H_β, ^3J = 2 Hz), 5.99 (s, 10H, Cp); (BPh_4^-) δ 7.45−7.35 (m, 8H, Ph), 7.10−7.00 (m, 8H, Ph), 7.00−6.85 (m, 4H, Ph). ^{13}C NMR (300 K, CD_2Cl_2): δ 138.8 (C_α), 114.1 (Cp), 112.2 (C_β); (BPh_4^-) δ 164.4 ($^1J_{BC}$ = 50 Hz, ipso-C), 136.4, 126.2, 122.4. ^1H NMR (198 K, CD_2Cl_2): δ 9.22 (s, 1H, NH), 7.79 (m, 1H, H_α), 7.55 (m, 2H, 2 × H_α), 6.96 (m, 1H, H_α), 6.58 (m, 1H, H_β), 6.40 (m, 1H, H_β), 5.89 (s, 10H, Cp); (BPh_4^-) δ 7.45−7.35 (m, 8H, Ph), 7.10−7.00 (m, 8H, Ph), 7.00−6.85 (m, 4H, Ph). ^{13}C NMR (198 K, CD_2Cl_2): δ 143.7 (C_α), 138.2 (C_α), 135.0 (C_α), 134.7 (C_α), 115.0 (C_β) 113.2 (Cp), 108.1 (C_β); (BPh_4^-) δ 163.1 ($^1J_{BC}$ = 49 Hz, ipso-C), 135.2, 125.8, 121.6. IR (KBr): $\tilde{\nu}$ 3371, 3102, 3055, 3016, 2998, 2967, 1580, 1480, 1303, 1042, 817, 744 cm^{-1}.

Preparation of (Acetylacetonato)(η^1-pyrazole-*N*)zirconocene Tetraphenylborate (9). To a solution of **6** (700 mg, 0.93 mmol) in dichloromethane (50 mL) was added 2,4-pentanedione (95 mg, 0.95 mmol). After addition of toluene (50 mL) the solution volume was reduced in vacuum to one-third, effecting the separation of a yellow oil which was isolated and evaporated to dryness. Washing with toluene gave pure white **9** (430 mg, 65%). Single crystals suitable for X-ray analysis were obtained by recrystallization from dichloromethane/toluene solution, mp 164 °C dec. Anal. Calcd for $C_{42}H_{41}BN_2O_2Zr$: C, 71.27; H, 5.84; N, 3.96. Found: C, 69.82; H, 5.98; N, 4.15. ^1H NMR (300 K, CD_2Cl_2): δ 11.4−10.9 (broad, 1H, NH), 7.58 (d, 2H, H_α, ^3J = 2 Hz), 6.61 (t, 1H, H_β, ^3J = 2 Hz), 6.09 (s, 10H, Cp), 5.80 (s, 1H, =C−H), 2.14 (s, 6H, Me); (BPh_4^-) δ 7.40−7.30 (m, 8H, Ph), 7.10−7.00 (m, 8H, Ph), 7.00−6.90 (m, 4H, Ph). ^1H NMR (223 K, CD_2Cl_2): δ 11.3 (s, 1H, NH), 7.53 (pt, 1H, H_α), 7.50 (pt, 1H, $H_{\alpha'}$), 6.63 (pq, 1H, H_β), 6.07 (s, 10H, Cp), 5.77 (s, 1H, =C−H), 2.15 (s, 3H, Me), 2.11 (s, 3H, Me); (BPh_4^-) δ 7.40−7.30 (m, 8H, Ph), 7.10−7.00 (m, 8H, Ph), 7.00−6.90 (m, 4H, Ph). ^{13}C NMR (223 K, CD_2Cl_2): δ 194.4 (s, CO), 189.1 (s, CO), 141.6 ($^1J_{CH}$ = 187 Hz, C_α), 130.9 ($^1J_{CH}$ = 193 Hz, C_α), 115.2 ($^1J_{CH}$ = 175 Hz, Cp), 109.9 ($^1J_{CH}$ = 182 Hz, C_β), 103.9 ($^1J_{CH}$ = 166 Hz, CH), 27.7 ($^1J_{CH}$ = 128 Hz, CH_3), 26.4 ($^1J_{CH}$ = 127 Hz, CH_3); (BPh_4^-) δ 163.6 ($^1J_{BC}$ = 50 Hz, ipso-C), 135.5, 125.7, 121.8. IR (KBr): $\tilde{\nu}$ 3370, 3122, 3053, 2999, 2983, 1581, 1524, 1479, 1428, 1360, 1341, 1282, 1122, 1054, 1024, 939, 819, 735, 705, 611, 539 cm^{-1}.

Formation of 2-[((Trimethylsilyl)oxy)phenylmethyl]-cyclopentanone (11). A solution of benzaldehyde in dichloromethane (20 mL) (820 mg, 7.73 mmol) was added dropwise to a mixture of 1-[(trimethylsilyl)oxy]cyclopentene (**10**) (1.20 g, 7.68 mmol) and 9.5 mol % of **6** (520 mg, 0.69 mmol) in dichloromethane (70 mL) at −78 °C. The reaction mixture was stirred for 1 h and then allowed to warm to room temperature. After hydrolysis the organic layer was extracted with ether, and the extract was washed twice with water and dried over $MgSO_4$. The solvent was evaporated under reduced pressure, and the residue was purified by column chromatography (silica gel; pentane/ether 1:1) to give a 1:1 mixture of the syn and anti isomers of **11** (1.05 g, 52%). HRMS (*m/z*) calcd for $C_{14}H_{19}O_2Si$ ($M^+ - CH_3$): 247.1154. Found: 247.1149. ^1H NMR (300 K, $CDCl_3$): δ 7.30−7.20 (m, 10H, Ph), 5.30 (d, 1H, *erythro*-CHO, $^3J_{CH}$ = 2.4 Hz), 5.17 (d, 1H, *threo*-CHO, $^3J_{CH}$ = 4.5 Hz), 2.40−1.50 (m, 14H, $-CH_2-$), 0.04 (s, 9H, $SiMe_3$), −0.01 (s, 9H, $SiMe_3$).

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Supplementary Material Available: Details of the X-ray crystal structure analyses of complexes **6** and **9**, including complete listings of bond lengths and angles, thermal parameters, and atomic positional parameters and ORTEP diagrams (11 pages). Ordering information is given on any current masthead page.

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