Zirconocene and *rac*-[1,2-Ethylene-1,1′-bis(η^5-tetrahydroindenyl)]zirconium Complexes of 2-Vinylpyridine: Syntheses, X-ray Crystal Structures, and Reactions with $H_2C{=}CH_2$, H_2O, HBF_4, and CO_2

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Reactions of $Cp_2Zr(thf)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**1**) and *rac*-(ebthi)$Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**2**; ebthi = 1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)) with 2-vinylpyridine lead, under elimination of the alkyne, to the five-membered azazirconacycles, which are best described as 1-zircona-2-azacyclopent-3-enes (1-azadiene complexes). One of these complexes couples with ethylene to yield a stable α-2-pyridyl-substituted zirconacyclopentane and reacts in a 2:1 ratio with water to yield a β-2-pyridyl-substituted dimeric σ-ethylzirconoxane. In the reaction of the **2**-derived complex with HBF_4, *rac*-[1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)]zirconium difluoride was obtained. Both 1-zircona-2-azacyclopent-3-enes insert carbon dioxide to give structurally different binuclear carbonate-bridged complexes.

Introduction

Five-membered zirconacycles often are intermediates in coupling reactions of unsaturated hydrocarbons with a zirconocene complex fragment,[1] but only a few of these metallacycles have been isolated and structurally characterized.[2] One special case is the 1-zircona-2-azacyclopent-3-enes, prepared by coupling of ethylene and nitriles in the coordination sphere of permethyltitanocene, which give metallacycloimine complexes and isomerize by a subsequent 1,3-hydrogen shift to metallacycloenamine tautomers.[3] Another method for the preparation of these complexes is the oxidative addition of 1-aza-1,3-dienes $RN{=}CH{-}CH{=}CHR$ to zirconocene and, alternatively, the reaction of allylic amides $LiN(R)CH_2CH{=}CH_2$ with $Cp_2Zr(Me)Cl$ to give, by elimination of LiCl and methane, η^2-imine complexes as intermediates, which rearrange.[4] Later, the reduction of Cp_2ZrCl_2 in THF by Mg in the presence of 1-aza-1,3-dienes was used to prepare these complexes.[5] Also, saturated 1-zircona-2-azacyclopentanes derived from cationic $[Cp_2Zr(\eta^2\text{-pyrid-2-yl})]^+$ complexes,[6] which insert olefins were synthesized, providing the basis for extensive stoichiometric and catalytic chemistry.[7]

After having investigated the reactions of the zirconocene sources $Cp_2Zr(thf)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**1**)[8] and *rac*-(ebthi)$Zr(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**2**)[9] (ebthi = 1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)) with ethylene and styrene,[10] we report here the interactions of these complexes with substituted olefins such as 2-vinylpyridine ($2\text{-}PyCH{=}CH_2$), which give the 1-zircona-2-azacyclopent-3-enes (1-azadiene complexes) **3** and **4** via elimination of the alkyne. The reactivity of these complexes toward $H_2C{=}CH_2$, H_2O, HBF_4, and CO_2 was investigated.

Experimental Section

All operations were carried out under an inert atmosphere (argon) using standard Schlenk techniques. Prior to use, solvents were freshly distilled from sodium tetraethylaluminate under argon. Deuterated solvents were treated with sodium or sodium tetraethylaluminate, distilled, and stored under argon. NMR: Bruker ARX 400 at 9.4 T (chemical shifts given in ppm relative to TMS). Melting points were measured in sealed capillaries on a Büchi 535 apparatus. Elemental analyses: Leco CHNS-932 elemental analyzer.

Preparation of Cp_2Zr(2-vinylpyridine) (3). A 342 mg (738 μmol) amount of $Cp_2Zr(thf)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**1**) was dissolved in 15 mL of THF/hexane (1:3), and 79.5 μL (738 μmol) of 2-vinylpyridine was added via syringe. After 1 min, the color of the solution changed from orange to deep red. The

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solution was cooled to −30 °C to produce brown-red crystals, 108 mg (45%), which were isolated by filtration. Evaporation of the mother liquor and recrystallization from pentane yielded a further 54 mg (22%) of pure material. Total yield: 162 mg (67%). Mp: 103 °C. Anal. Calcd for $C_{17}H_{17}NZr$ (326.54): C, 70.39; H, 6.78; N, 3.04. Found: C, 69.93; H, 6.78; N, 3.48. ^1H NMR (235 K, toluene-d_8): δ −0.79 ("t", $^2J \approx {}^3J \approx 9.5$ Hz, 1H, C1−H′), 3.23 ("t", $^2J \approx {}^3J \approx 9.7$ Hz, 1H, C1−H″), 4.19 ("t", $^3J = 9.7$ Hz, C2−H), 4.90 (s, 5H, Cp), 5.43 (s, 5H, Cp), 5.38 ("dt", $^3J = 6.2$ Hz, $^4J = 1.2$ Hz, 1H, C6−H), 6.29 (ddd, $^3J = 9.0$ Hz, $^3J = 6.0$ Hz, $^4J = 1.5$ Hz, 1H, C5−H), 6.29 ("dt", $^3J = 9.1$ Hz, $^4J = 1.2$ Hz, 1H, C4−H), 7.21 ("d", $^3J = 6.3$ Hz, 1H, C7−H). ^{13}C NMR (235 K, toluene-d_8): δ 49.5 ($^1J_{CH} = 140$ Hz, C1), 88.4 ($^1J_{CH} = 156$ Hz, C2), 101.0 (Cp), 103.4 ($^1J_{CH} = 164$ Hz, aromatic C6), 105.5 (Cp), 122.3 ($^1J_{CH} = 163$ Hz, aromatic C4), 138.4 (aromatic C3), 146.4 ($^1J_{CH} = 175$ Hz, aromatic C7). C5 hidden by solvent (about 128 ppm).

Preparation of *rac*-(ebthi)Zr(2-vinylpyridine) (4). To a solution of 213 mg (441 μmol) of *rac*-(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$) (**1**) in 10 mL of hexane/toluene (1/1) was added 47.4 μL (441 μmol) of 2-vinylpyridine. The reaction mixture was stirred for 10 min while the color changed from green to deep red. After standing at −30 °C for several hours, red crystals separated from solution. The crystals were isolated by filtration and washed with hexane. Yield: 172 mg (85%). Mp: 190 °C. Anal. Calcd for $C_{27}H_{31}NZr$ (460.75): C, 70.57; H, 6.80; N, 3.05. Found: C, 70.10; H, 6.66; N, 3.00. ^1H NMR (298 K, toluene-d_8): δ −1.43 ("t", $^2J \approx {}^3J \approx 8.5$ Hz, 1H, C1−H′), 3.09 ("t", $^2J \approx {}^3J \approx 9.5$ Hz, 1H, C1−H″), 4.37 (dd, $^3J = 8.2$ and 9.8 Hz, 1H, C2−H), 4.81 (d, $^3J = 3.0$ Hz, 1H, CH ebthi), 4.91 (d, $^3J = 3.2$ Hz, 1H, CH ebthi), 5.00 (d, $^3J = 3.2$ Hz, 1H, CH ebthi), 5.51 (d, $^3J = 3.0$ Hz, 1H, CH ebthi), 5.43 ("dt", $^3J = 6.2$ Hz, $^4J = 1.1$ Hz, 1H, aromatic C6−H), 6.14 (ddd, $^3J = 9.1$ Hz, 1H, $^3J = 6.0$ Hz, $^4J = 1.5$ Hz, 1H, aromatic C5−H), 6.49 ("dt", $^3J = 9.1$ Hz, $J = 2.2$ Hz, 1H, aromatic C4−H), 7.28 ("d", $^3J = 6.3$ Hz, 1H, aromatic C7−H). ^{13}C NMR (298 K, toluene-d_8): δ 54.6 (dd, $^1J_{CH} = 130$ Hz, $^1J_{CH} = 151$ Hz, C1), 86.6 (d, $^1J_{CH} = 156$ Hz, C2), 100.3 (CH ebthi), 100.5 (CH ebthi), 102.4 (CH ebthi), 104.3 (aromatic C6), 108.5 (CH ebthi), 115.2 (C ebthi), 116.0 (C ebthi), 118.3 (C ebthi), 119.5 (C ebthi), 123.6 (C ebthi), 124.8 (aromatic C4), 125.2 (C ebthi), 126.9 (aromatic C5), 140.0 (aromatic C3), 146.1 (aromatic C7).

Preparation of $Cp_2Zr{-}CH(2\text{-}Py){-}CH_2{-}CH_2{-}CH_2$ (5). A solution of 247 mg (756 μmol) of Cp_2Zr(2-vinylpyridine) (**3**) in 20 mL of toluene was exposed to an ethylene atmosphere. After 10 min, the color of the solution changed from red to yellow. The reaction solution was filtered and concentrated to leave a yellow oil, which was analyzed by NMR spectroscopy. ^1H NMR (THF-d_8): δ 0.81 (m, $^2J = 11.3$ Hz, 1H, α-H), 1.39 (m, $^2J = 11.3$ Hz, 1H, α-H), 2.11 (m, 1H, β-H), 2.27 (m, 1H, β-H), 2.43 (m, 1H, β-H′), 2.59 (m, 1H, β-H′), 2.79 (m, 1H, α-H′), 5.09 (s, 5H, Cp), 5.84 (s, 5H, Cp), 6.18 (m, 1H, pyridyl), 6.53 ("dt", $^3J = 8.8$ Hz, 1H, pyridyl), 7.10 (m, $^3J = 8.8$ Hz, 1H, pyridyl), 7.65 (m, 1H, pyridyl). ^{13}C NMR (THF-d_8): δ 28.7 (β-C), 37.4 (α-CH_2), 43.2 (β-C), 66.5 (α-CH), 110.3, 110.9 (Cp), 110.3, 112.9, 135.4, 149.9, 151.3 (pyridyl).

Preparation of $[Cp_2Zr{-}CH_2\text{-}CH_2{-}(2\text{-}Py)]_2(\mu\text{-}O)$ (6). A 310 mg (951 μmol) amount of Cp_2Zr(2-vinylpyridine) (**3**) was dissolved in 15 mL of toluene (which was not dried but stored under argon) and kept at room temperature until the color of the solution changed from red to colorless. After standing for 1 week at 4 °C, 175 mg (55%) of colorless crystals separated out of solution. Mp: 173−176 °C. Anal. Calcd for $C_{34}H_{36}N_2OZr_2$ (671.11): C, 60.85; H, 5.41; N, 4.19. Found: C, 60.81; H, 5.45; N, 4.12. ^1H NMR (THF-d_8): δ 1.14 (AA′XX′, 4H, α-CH_2), 3.05 (AA′XX′, 4H, β-CH_2,), 6.09 (s, 20H, Cp), 6.95, 7.14, 7.50, 8.41 (8H, pyridyl). ^{13}C NMR (THF-d_8): δ 43.3 (CH_2), 44.1 (CH_2), 113.0 (Cp), 121.7, 123.4, 137.6, 150.9, 170.7 (pyridyl).

Preparation of *rac*-(ebthi)ZrF_2 (7). To a solution of 130 mg (282 μmol) of *rac*-(ebthi)Zr(2-vinylpyridine) (**4**) in 10 mL of THF was added 38.8 μL (282 μmol) of HBF_4 etherate in diethyl ether. The reaction mixture immediately turned colorless, and a white precipitate was formed. Evaporation of the solvent and recrystallization from hot THF yielded white needles. Yield: 81 mg (73%). Mp: 170 °C. Anal. Calcd for $C_{20}H_{24}F_2Zr$ (393.63): C, 61.03; H, 6.15. Found: C, 60.35; H, 5.97. ^1H NMR (THF-d_8): δ 1.45−1.56 (2H, CH_2 ebthi), 1.58−1.68 (2H, CH_2 ebthi), 1.76−1.91 (4H, CH_2 ebthi), 2.37−2.45 (2H, CH_2 ebthi), 2.50−2.60 (4H, CH_2 ebthi), 2.60−2.70 (2H, CH_2 ebthi), 3.05−3.13 (2H, CH_2 ebthi), 3.18−3.27 (2H, CH_2 ebthi), 5.71 (d, $^3J = 3.1$ Hz, 2H, CH ebthi), 5.88 (d, $^3J = 3.1$ Hz, 2H, CH ebthi). ^{13}C NMR (THF-d_8): δ 24.5 (CH_2 ebthi), 24.7 (CH_2 ebthi), 25.4 (CH_2 ebthi), 25.5 (CH_2 ebthi), 25.9 (CH_2 ebthi), 108.5 (CH ebthi), 118.0 (CH ebthi), 123.6 (C ebthi), 133.1 (2C ebthi).

Preparation of $[Cp_2Zr{-}CH_2{-}CH(2\text{-}Py){-}C(O){-}O]_2$ (8). A solution of 210 mg (643 μmol) of Cp_2Zr(2-vinylpyridine) (**3**) in 25 mL of toluene was exposed to a CO_2 atmosphere. The color of the solution changed from red to pale yellow after standing for 24 h. The volume of the solution was reduced to ca. 10 mL, and the concentrate was stored for 1 week at room temperature to yield colorless crystals of **8**·toluene. Yield: 119 mg (49%). Mp: 172−175 °C (dec). Anal. Calcd for $C_{43}H_{42}Zr_2N_2O_4$ (833.26): C, 61.98; H, 5.08; N, 3.36. Found: C, 62.30; H, 4.93; N, 3.43. ^1H NMR (THF-d_8): δ 0.81 (dd, $^3J = 5.4$ Hz, $^2J = 12.3$ Hz, 2H, CH_2), 1.93 ("t", $^2J \approx {}^3J \approx 12.8$ Hz, 2H, CH_2), 4.02 (dd, $^3J = 5.4$ Hz, $^3J = 13.2$, 2H, CH), 6.10 (s, 10H, Cp), 6.11 (s, 10H, Cp), 7.03 (m, $J = 7.3$ and 4.7 Hz, 2H, pyridyl), 7.18 (m, $J = 7.7$ Hz, 2H, pyridyl), 7.58 (m, $J = 7.5$ and 1.3 Hz, 2H, pyridyl), 8.45 (m, $J = 4.5$ Hz, 2H, pyridyl). ^{13}C NMR (THF-d_8): δ 50.0 (CH_2), 59.5 (CH), 112.9, 114.0 (Cp), 122.4, 124.5, 137.7, 151.3, 169.6 (pyridyl), 183.8 (CO_2).

Preparation of [*rac*-(ebthi)$Zr{-}CH_2{-}CH(2\text{-}Py){-}C(O){-}O]_2$ (9). A solution of 216 mg of *rac*-(ebthi)Zr(2-vinylpyridine) (**4**) (467 μmol) in 10 mL of toluene was exposed to a CO_2 atmosphere. After 12 h, the red solution became colorless. The volume of the solution was reduced to about 5 mL and stored in the refrigerator at 4 °C. After 3 days colorless crystals of **9**·toluene were obtained. Yield: 129 mg (55%). Mp: 193 °C. Anal. Calcd for $C_{63}H_{70}N_2O_4Zr_2$ (1101.7): C, 68.68; H, 6.40; N, 2.54. Found: C, 69.18; H, 6.47; N, 2.61.

X-ray Crystallographic Study of Complexes 3, 4, 6, 7, 8, and 9. Data were collected with a STOE-IPDS diffractometer using graphite-monochromated Mo Kα radiation. The structures were solved by direct methods (SHELXS-86)[11] and refined by full-matrix least-squares techniques against F^2 (SHELXL-93).[12] The hydrogen atoms were included at calculated positions. All other non-hydrogen atoms were refined anisotropically. Cell constants and other experimental details were collected and recorded in Table 2. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Results and Discussions

Complex Syntheses. An orange solution of the zirconocene−alkyne complex $Cp_2Zr(thf)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**1**)[8] in THF/hexane (1:3) reacts with 2-vinylpyridine at room temperature via elimination of the alkyne to yield red crystals of the azazirconacycle **3** (67% yield) (eq 1).

A similar product was observed in the reaction of the green solution of *rac*-(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$) (**2**)[9] with 2-vinylpyridine in toluene/*n*-hexane (1:3) at room

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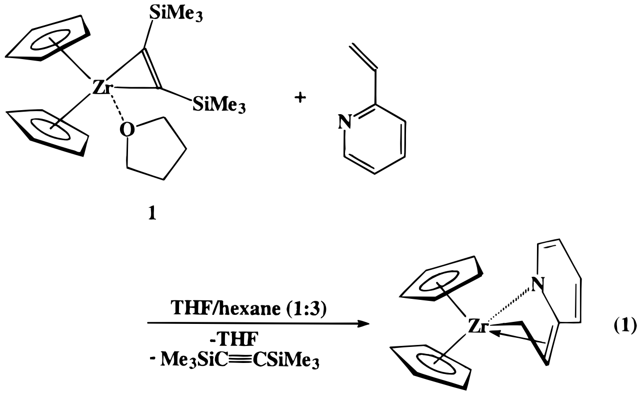
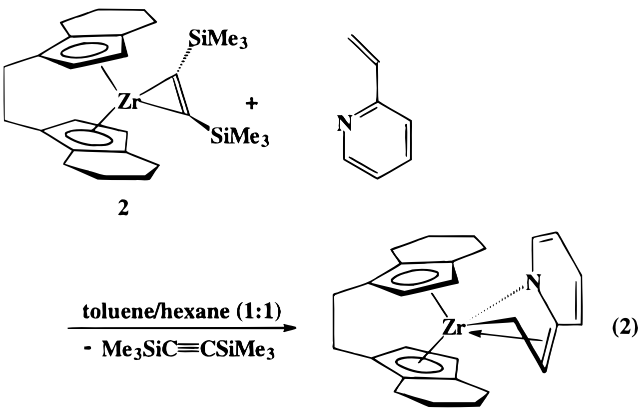
[12] Sheldrick, G. M. *SHELXL-93*; University of Göttingen: Göttingen, Germany, 1993.



1

3

temperature, which changed immediately to red, giving, after workup under argon, red crystals of **4** in 85% yield (eq 2).

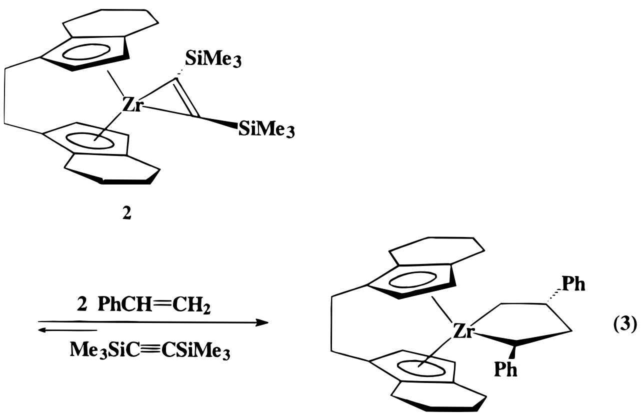


2

4

In solution, complex **4** has C_1 symmetry and we could only observe one of the two possible diastereomers by NMR spectroscopic investigations. Even at higher temperatures an inversion of the five-membered ring could not be observed, while inversion for complex **3** proceeds readily at room temperature. (cf. NMR Characteristics).

Both 2-vinylpyridine-derived products **3** and **4** stand in contrast to the products of the reaction of **2** with styrene, which gave the unsymmetrically substituted zirconacyclopentane *rac*-(ebthi)Zr–CHPh–CH$_2$–CHPh–CH$_2$ under analogous conditions (eq 3).[10]



2

This can be explained by the chelating interaction of the 2-vinylpyridine (see below) involving N-coordination, which prevents the coordination of a second 2-vinylpyridine molecule. It is reasonable to assume that the first intermediate in the reaction is an alkyne–olefin complex *rac*-(ebthi)Zr(η^2-Me$_3$SiC$_2$SiMe$_3$)(η^2-2-vinylpyridine) or a zirconacyclopentene *rac*-(ebthi)Zr–C(SiMe$_3$)=C-(SiMe$_3$)–CH$_2$–CH(2-Py), which eliminates bis(trimethylsilyl)acetylene to give the azazirconacycle.

Structural Investigations. Complexes **3** and **4** were investigated by X-ray crystal structure analysis. The molecular structures are shown in Figures 1 and 2.

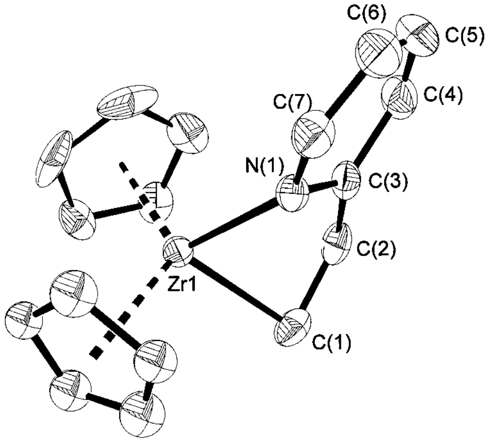


Figure 1. ORTEP plot of the molecular structure of complex **3** (30% probability). Selected bond distances (Å) and angles (deg): C(1)–Zr 2.272(5); C(2)–Zr 2.567(5); C(3)–Zr 2.652(5); N–Zr 2.163(4); C(1)–C(2) 1.439(7); C(2)–C(3) 1.386(7); C(3)–C(4) 1.437(7); C(4)–C(5) 1.344(9); C(5)–C(6) 1.391(10); C(6)–C(7) 1.349(9); C7–N 1.360(6); C(2)–C(1)–Zr 84.3(3); C(1)–C(2)–C(3) 126.9(5); C(2)–C(3)–N 117.6(5); C(3)–N–Zr 93.6(3); C(7)–N–C(3) 118.5(5); C(7)–N–Zr 141.1(4).

The bond lengths in the five-membered zirconacycle and the fused pyridine ring of both complexes are listed in Table 1 and compared with one example of a 1-zircona-2-azacyclopent-3-ene (1-monoazadiene complex (**mad**)).

The Zr–C1 distance is typical for Cp$_2$Zr–C σ-bonds, and the Zr–N bond length is in the typical range of zirconium amides and not of pyridine N-coordination.[13] The large distances from zirconium to the internal C atoms indicate a weak Zr–π(C=C) interaction. The σ^2,π-interaction adopts the typical "envelope" structure with angles at the C1–N axis Zr–C1–N/C1–C2–C3–N (**3** 58.2(2)°; **4** 52.3(2)°], as found also in **mad** (57.6°). Also, the alternating C–C– and C–N bond lengths in the five-membered ring are analogous to the well-known zirconocene(s-cis-diene) complexes. The bond distances in the 2-vinylpyridine part of complex **3** (the alternating bond distances in the pyridine as well as the long C1–C2 and the short C2–C3 bond) show some similiarities with 2-dihydropyridin-2-ylidene manganese complexes.[14]

NMR Characteristics. This description (**A**, see below) of complexes **3** and **4** is further supported by their

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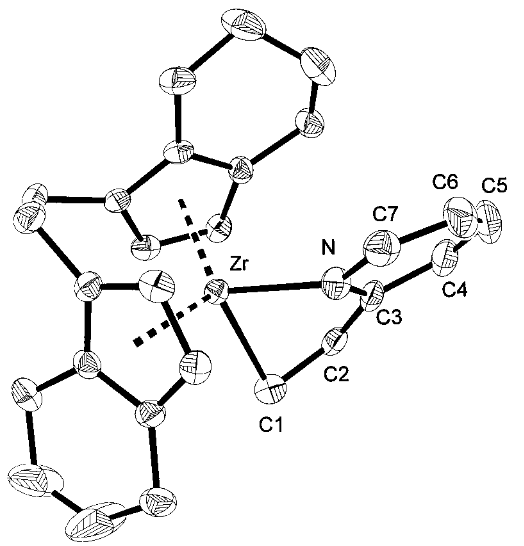


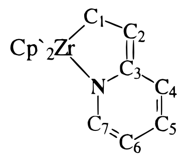
Figure 2. ORTEP plot of the molecular structure of complex **4** (30% probability). Selected bond distances (Å) and angles (deg): C(1)−Zr 2.263(5); C(2)−Zr 2.629(5); C(3)−Zr 2.715(5); N−Zr 2.165(4); C(1)−C(2) 1.437(7); C(2)−C(3) 1.382(7); C(3)−C(4) 1.438(7); C(4)−C(5) 1.332(8); C(5)−C(6) 1.416(8); C(6)−C(7) 1.367(8); C7−N 1.360(6); C(2)−C(1)−Zr 87.6(3); C(1)−C(2)−C(3) 126.5(5); C(2)−C(3)−N 117.7(4); C(3)−N−Zr 96.8(3); C(7)−N−C(3) 118.4(4); C(7)−N−Zr 140.8(3).

NMR properties. The "localization" of the double bonds within the pyridine ring is reflected by the vicinal coupling constants between 4-H, 5-H, and 6-H. They are almost equal in the free ligand, but upon complexation, ${}^3J$(4-H,5-H) is raised by 1.5 Hz and ${}^3J$(5-H,6-H) is diminished by the same value, and these changes in J clearly resemble the changes in the carbon−carbon π bond order. The coordination-induced chemical shifts, especially in the ^{13}C NMR spectra, also indicate that the electronic structure is modified. For complexes of pyridine or 2,2′-bipyridine with N-coordination, these shifts rarely exceed 6 ppm, either high-field or low-field.[15−18] For **3** and **4**, rather unusual high-field shifts of about 18 ppm (at C3 and C6) are observed.

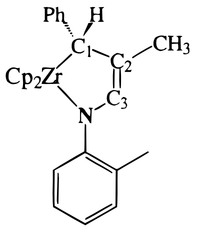
The spectroscopic features of the vinyl group also support formula **A**. The vicinal coupling constants between 1-H (*cis,trans*) and 2-H are no longer different, as expected for double-bond systems, both have the same value of about 9 Hz. The coupling constants at the terminal position (**3** ${}^2J$(H,H) = 9.5 Hz, ${}^1J$(C,H) = 140 Hz) show that C1 is better described as a sp^3 than sp^2 carbon. One of these protons exhibits an unusual high-field shift, which might be a consequence of the folding of the metallacycle: the proton is pointing toward the center of one cyclopentadienyl ligand.

The complexes of 2-vinylpyridine are similar to group 4 metallocene complexes of 1,3-dienes, 1-aza-1,3-dienes, or 1,4-diaza-1,3-dienes, and they show an analogous behavior. All of these five-membered rings are fluxional metallacyclopentenes which undergo a "ring flipping" around the axis along which the ring is folded. For complex **3**, this process exchanges the cyclopentadienyl groups and the protons at C1 and they are observed separately in the NMR spectra at 240 K. The Cp singlets coalesce at 303 K, and from their separation at low temperature (215 Hz), a free activation enthalpy of 58.6 kJ mol^{-1} is estimated (this is very similar to values reported for other monoaza-[4] or diazadiene[5] complexes). The fluxionality of complex **4** is not clearly detectable (only slight changes in the line widths occur) for a ring flip is no longer a degenerate process but leads to a chemically inequivalent species, which is probably present only in very low concentration and was, therefore, not found.

Table 1. Selected Bond Lengths (Å) of 3, 4, and mad



3,4

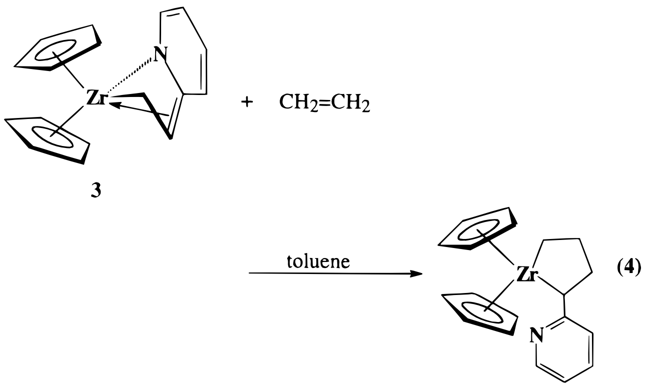


mad

	3	4	mad[5]
Zr−N	2.163(4)	2.165(4)	2.094(2)
N−C3	1.406(6)	1.401(6)	1.385(2)
C3−C2	1.386(7)	1.382(7)	1.375(3)
C2−C1	1.439(7)	1.437(7)	1.455(3)
C1−Zr	2.272(5)	2.263(5)	2.328(2)
C2−Zr	2.567(5)	2.629(5)	2.665(2)
C3−Zr	2.652(5)	2.715(4)	2.604(2)
C3−C4	1.437(7)	1.438(7)	
C4−C5	1.344(9)	1.332(8)	
C5−C6	1.391(10)	1.416(8)	
C6−C7	1.349(9)	1.367(8)	
C7−N	1.360(6)	1.360(6)	

Bonding Description. The bonding situation in complexes **3** and **4** is best described as a 1-zircona-2-azacyclopent-3-ene complex (**A**) rather than the formulation as an η^4-1-azadiene complex (**B**) or an olefin complex stabilized by pyridine N-atom coordination (**C**) (Chart 1).

Reactions. The zirconocene complex **3** couples with ethylene to yield the stable α-2-pyridyl-substituted zirconacyclopentane **5** (eq 4). For 1-η^4-azadiene and 1,4-η^4-diazadienezirconium complexes, coupling reactions with olefins have not been described in the literature. The reaction pattern of complex **3** indicates the forma-



3 **5**

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(15) Rosenthal, U.; Ohff, A.; Baumann, W.; Tillack, A.; Görls, H.; Burlakov, V. V.; Shur, V. B. *Z. Anorg. Allg. Chem.* **1995**, *621*, 77.

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(17) Rosenthal, U.; Pulst, S.; Arndt, P.; Baumann, W.; Tillack, A.; Kempe, R. *Z. Naturforsch.* **1995**, *50b*, 368.

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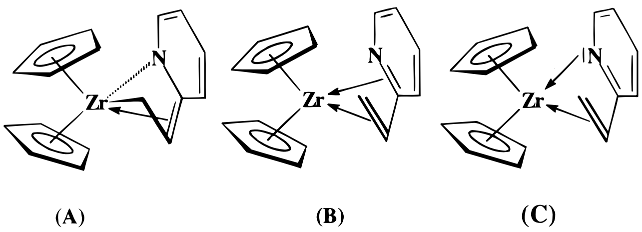
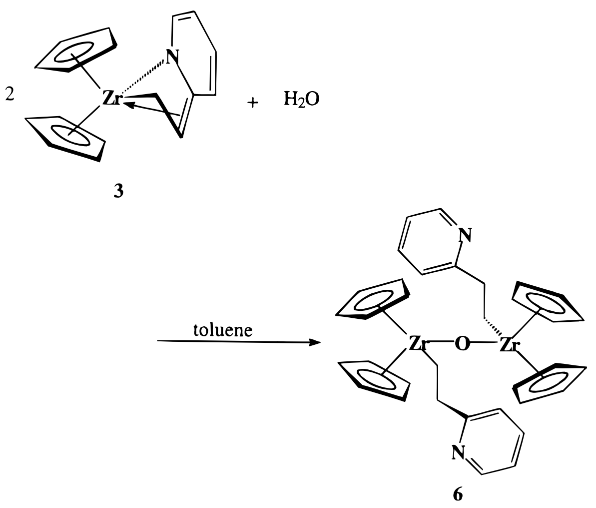
Table 2. Crystallographic Data of 3, 4, 6, 7, 8, and 9

	3	4	6	7	8	9
cryst color, habit	brown, prism	brown, prism	colorless, prism	colorless, prism	yellow, prism	yellow, prism
cryst syst	orthorhombic	triclinic	monoclinic	orthorhombic	monoclinic	monoclinic
space group	*Pbca*	$P\bar{1}$	$P2_1/a$	*Pbcn*	$P2_1/c$	*C*2/*c*
lattice constants						
a (Å)	8.155(2)	8.8020(11)	10.719(2)	11.562(2)	9.2920(12)	28.213(6)
b (Å)	15.702(3)	9.6200(12)	18.934(3)	8.242(2)	16.881(2)	12.385(2)
c (Å)	22.086(4)	12.728(2)	15.036(3)	17.683(4)	11.843(2)	21.899(4)
α (deg)		91.170(12)				
β (deg)		96.740(12)	102.150(13)		101.580(11)	129.26(3)
γ (deg)		100.380(12)				
Z	8	2	4	4	4	4
cell volume	2828.1(19)	1051.8(2)	2983.3(9)	1685.1(6)	1819.9(4)	5924.7(0)
density (g/cm^{-3})	1.534	1.455	1.494	1.552	1.513	1.280
temp (K)	200(2)	200(2)	293(2)	293(2)	293(2)	293(2)
μ(Mo Kα) (mm^{-1})	0.763	0.536	0.727	0.669	0.618	0.399
θ range (deg)	1.84−24.35	2.15−21.02	2.22−24.33	2.30−24.29	2.13−24.35	1.89−24.26
no. of rflns (measd)	7869	2140	8803	4661	5376	8579
no. of rflns (indep)	2201	2140	4585	1321	2898	4695
no. of rflns (obsd)	1496	1907	3605	1064	2263	3761
no. of params	180	274	352	106	219	352
R1 ($I > 2\sigma(I)$)	0.040	0.030	0.046	0.028	0.066	0.048
wR2 (all data)	0.105	0.084	0.139	0.078	0.180	0.166

Chart 1



tion of a reactive N-donor-stabilized η^2-alkene complex (**C**) as an intermediate, which yields, after oxidative coupling of ethylene, the metallacycle **5**. In complex **5**, there is no evidence for any interaction of the pyridine N-atom with the zirconium atom. NMR investigations showed that a single isomer is obtained with the pyridine residue in the α-position of the metallacycle. No cycloreversion of the metallacycle could be observed, as found for the styrene product (eq 3).[10]



(5)

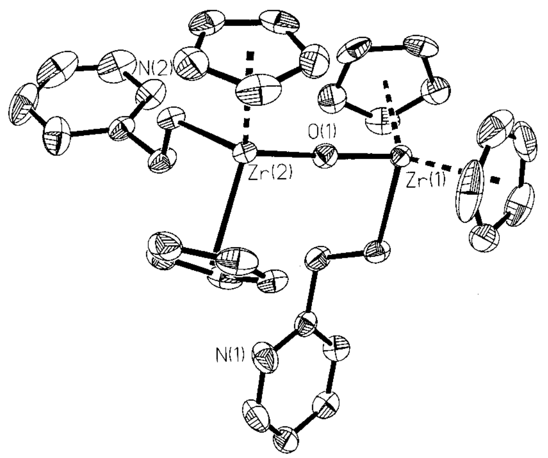


Figure 3. ORTEP plot of the molecular structure of complex **6** (30% probability). Selected bond distances (Å) and angles (deg): O−Zr(1) 1.949(4); O−Zr(2) 1.955(4); Zr(1)−C(11) 2.308(7); C(11)−C(12) 1.506(10); Zr(2)−C(23) 2.285(6); C(23)−C(24) 1.537(9); Zr(1)−O−Zr(2) 178.3(3); O−Zr(2)−C(23) 97.1(3); O−Zr(1)−(C11) 97.8(2).

Two equivalents of the zirconocene complex **3** react with 1 equiv of water via ring opening of the 1-zircona-2-azacyclopent-3-ene to yield the β-2-pyridyl-substituted, dimeric σ-ethylzirconoxane **6** (eq 5). A similar product was obtained in the reaction of the ethylene complex $Cp_2Zr(PMe_3)(C_2H_4)$ with water.[19a] Also, in this case, we assume that the N-donor-stabilized olefin complex (**C**) reacts under substitution to give the olefin complex stabilized by water $[Cp_2Zr(OH_2)(CH_2{=}CH{-}(2\text{-}Py))]$ in the first step, which can rearrange to an unstable and not isolated hydroxy alkenyl complex $[Cp_2Zr(OH)(CH_2CH_2\text{-}(2\text{-}Py))]$. In a second step, this assumed intermediate reacts with a second molecule of complex **3** to yield complex **6**.

The molecular structure of complex **6** is shown in Figure 3. In the reaction of complex **4** with HBF_4 etherate, the expected *rac*-[1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)]zirconium difluoride (**7**)[20] was obtained (eq 6). In the first step of the assumed reaction path protonation of the complexed 2-vinylpyridine yields the highly reactive d^0 species *rac*-[(ebthi)Zr−(CH$_2$−CH$_2$−

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(19) (a) Alt, H. G.; Denner, C. E. *J. Organomet. Chem.* **1990**, *391*, 53. (b) Alt, H. G.; Denner, C. E. *J. Organomet. Chem.* **1990**, *390*, 53.

(20) Complex **7** is unknown to the best of our knowledge. The analogous (*S*,*S*)-[1,2-ethylene-1,1′-bis(η^5-tetrahydroindenyl)]titanium difluoride was reported by Verdaguer, X.; Lange, U. E. W.; Reding, T. W.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 6784.

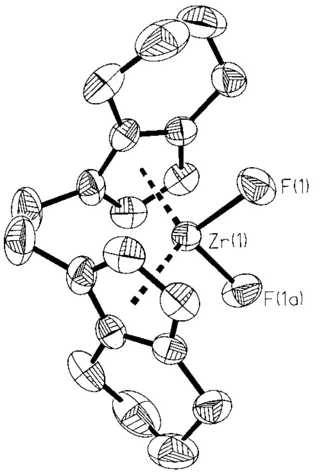
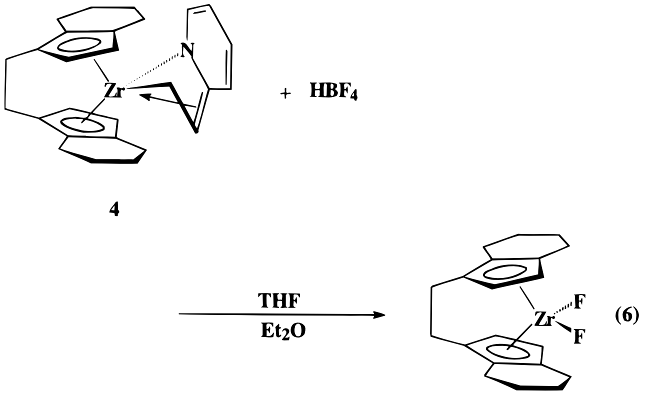


Figure 4. ORTEP plot of the molecular structure of complex **7**, (30% probability). Selected bond distances (Å) and angles (deg): Zr−F(1) 1.959(2); Zr−F(1a) 1.959(2); F(1)−Zr−F(1a) 98.32(12).



4

7

$(2\text{-Py}))]^+$, which is able to abstract F^- from the BF_4^- counterion to give [*rac*-(ebthi)ZrF(CH_2−CH_2−(2-Py))].[21] By an alkyl/F exchange between BF_3 and [*rac*-(ebthi)-ZrF(CH_2−CH_2−(2-Py))], *rac*-(ebthi)ZrF_2 is presumbly formed.[22]

The molecular structure of complex **7** is shown in Figure 4. Complexes **3** and **4** both insert carbon dioxide to give the dimeric complexes **8** and **9**, which have a different type of a binuclear structure (eq 7 and 8). The molecular structure of complexes **8** and **9** are shown in Figures 5 and 6. Both reactions are similar to that described for the ethylene complex $Cp_2Zr(PMe_3)(C_2H_4)$ with carbon dioxide.[19b]

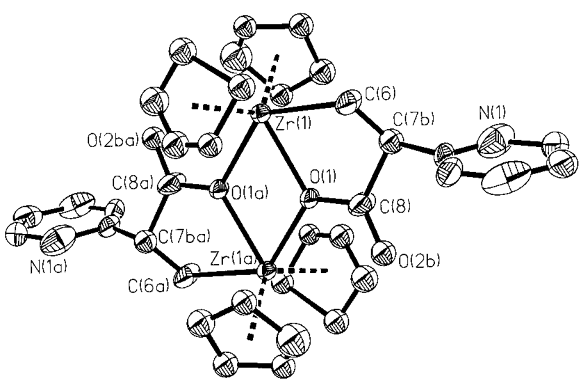
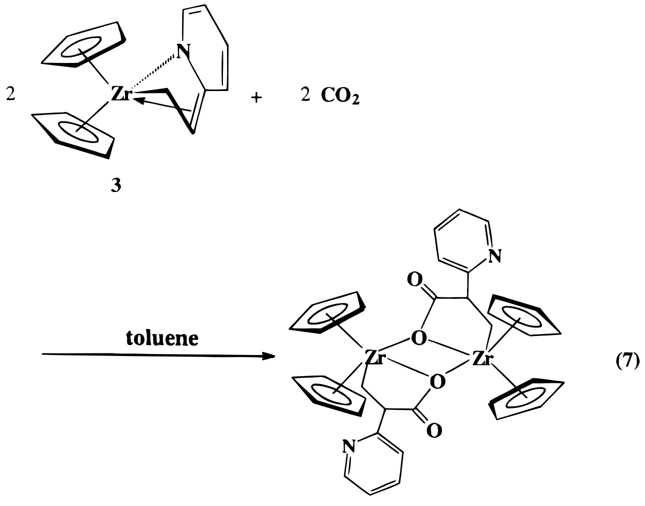
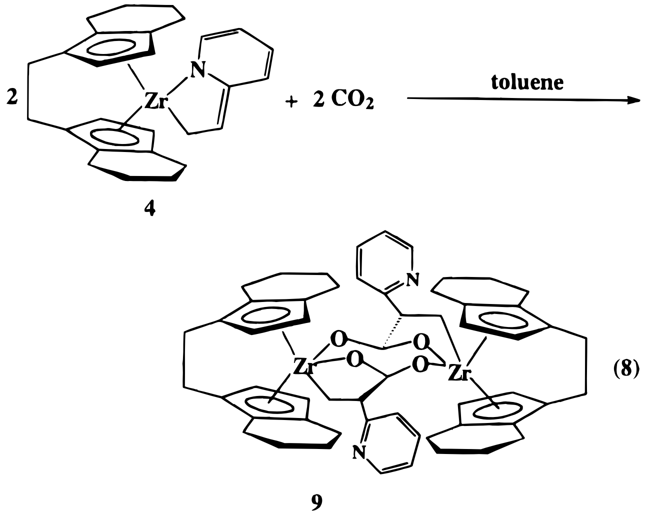


Figure 5. ORTEP plot of the molecular structure of complex **8** (30% probability). Selected bond distances (Å) and angles (deg): Zr(1)−O(1) 2.267(5); Zr(1)−O(1a) 2.338-(5); Zr(1)−C(6) 2.337(8); C(6)−C(7b) 1.381(2); C(7b)−C(8) 1.572(2); C(8)−O(1) 1.339(10); O(1)−Zr(1)−O(1) 64.2(2); Zr-(1)−O(1)−Zr(1a) 115.8(2); O(1)−Zr(1)−C(6) 69.5(2); Zr(1)−C(6)−C(7b) 113.4(9); C(6)−C(7b)−C(8) 107.6(12); C(7b)−C(8)−O(1) 109.9(9); C(8)−O(1)−Zr(1) 123.0(5).



3

8



4

9

The class of bis(cyclopentadienyl)carboxylates of zirconium is not well characterized.[23] Four-membered ring systems [−Zr−O−]$_2$, as found in **8**, are known for many other zirconocene compounds.[8] The structure of **9** with eight-membered rings [−Zr−O−C−O−]$_2$ is also verified in some dinuclear mono(cyclopentadienyl)titanium(III) biscarboxylates.[24] The assumed route to the insertion products **8** and **9** is, in principle, similar to the above-discussed steps, leading to complexes **5** and **6**: substitu-

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(21) Jordan, R. F.; Dasher, W. E.; Echols, S. F. *J. Am. Chem. Soc.* **1986**, *108*, 1718.

(22) (a) Jordan, R. F. *J. Organomet. Chem.* **1985**, *294*, 321. (b) Bruce, P. M.; Kingston, P. M.; Lappert, M. F.; Spalding, T. R.; Srivasta, R. C. *J. Chem. Soc. A* **1969**, 2106.

(23) Cardin, D. J.; Lappert, M. F.; Raston, C. L.; Riley, P. I. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 3, p 559.

(24) Dang, Y. *Coord. Chem. Rev.* **1994**, *136*, 93 and references therein.

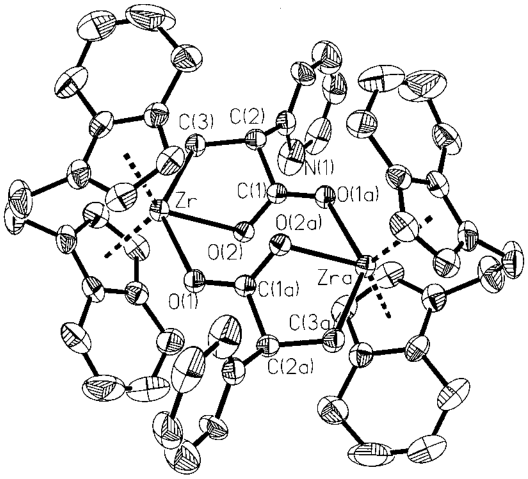

Figure 6. ORTEP plot of the molecular structure of complex **9** (30% probability). Selected bond distances (Å) and angles (deg): Zr−O(1) 2.261(3); Zr−O(2) 2.248(2); Zr−C(3) 2.361(4); C(3)−C(2) 1.539(5); C(2)−C(1) 1.526(5); C(1)−O(2) 1.256(4); C(1)−O(1) 1.257(4); O(1)−Zr−O(2) 70.11(9); Zr−O(1)−C(1)127.3(2); O(1)−C(1)−O(2) 124.2(3); C(1)−O(2)−Zr 127.3(2).

tion of N-donation by substrate complexation [$Cp_2Zr(CO_2)(CH_2{=}CH{-}(2\text{-}Py))$] and, in a second step, oxidative coupling of carbon dioxide with the olefin to give the metallacycle with the pyridine ring in an α-position. In both cases, the reaction product obtained showed a centrosymmetric structure which indicates that the reaction is proceeding in a regio- and stereoselective manner. The oxidative coupling always occurs in the α-position to the pyridine ring, and the newly formed stereocenters are of opposite stereochemistry. The NMR data obtained for compound **8** are in agreement with the results of the X-ray analysis and show that only one isomer is formed. Due to its insolubility in common solvents, NMR analysis of **9** has not been possible so far. The different types of carboxylate-bridged structures are due to steric restrictions due to the ebthi ligand. The obtained products are in all cases different from those obtained with typical monazadiene complexes.[5]

Conclusions

On the basis of NMR investigations and X-ray structural data, the interaction of 2-vinylpyridine with the zirconocene unit in complexes **3** and **4** is best described as a 1-zircona-2-azacyclopent-3-ene complex rather than the formulation as a η^4-1-azadiene complex or an olefin complex stabilized by pyridine N-atom coordination.

Nevertheless, the reactions of these complexes show behavior typical of olefin complexes, which seem to be the reactive intermediates in the reactions. In general, this differs from the behavior of the products of reactions of typical monazadiene complexes with heteroolefins $R_2C{=}E$ (E = O, NR), which give (by insertion into the Zr−C bond) seven-membered ring systems in which the Zr−N interaction remains.[5]

The explanation for this different reactivity could be the aromaticity of the pyridine ring. Dearomatization is observed in the starting materials **3** and **4** and may be considered as a 2-dihydropyridin-2-ylidene in conjugation with the unsaturated zirconacycle. Considering the reaction pattern of **3** and **4** with HBF_4, H_2O, and CO_2, a π,η^2-coordination mode of the diene is obvious, because the attack of the electrophilic species (H^+, CO_2) always occurs at the C atom (C2) in the α-position to the pyridine ring and not at C1, as found in typical diene and azadiene complexes. The driving force for the formation of the N-donor-stabilized alkene complex as the intermediate is the rearomatization of the pyridine ring under cleavage of the Zr−N bond. The products of the reactions with $H_2C{=}CH_2$, H_2O, and CO_2 (**5**, **6**, **8**, and **9**) all have intact pyridine moieties.

Acknowledgment. This research was supported by the Max-Planck-Gesellschaft and the Fonds der Chemischen Industrie.

Supporting Information Available: Tables of crystal structure parameters and details of data collection, bond angles and distances, and atomic positional and thermal parameters and ORTEP diagrams of **3**, **4**, and **6**−**9** (57 pages). Ordering information is given on any current masthead page.

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