Reaction of "Floriani's Metallaoxirane" $[(Cp_2ZrCl)_2(\mu{:}\eta^1(O),\eta^2(C,O)\text{-}CH_2O)]$ with Isonitriles

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*Summary: The (μ-formaldehyde)($Cp_2ZrCl)_2$ complex **1** reacts with alkyl isocyanides RNC (R = $-CH_2SiMe_3$, $-CMe_3$) with insertion into the Zr—C bond and opening of the metallaoxirane unit by cleavage of the adjacent Zr—O bond to give the "N-inside" (η^2-iminoacyl)zirconocene complexes **2(a,b)** $[(Cp_2ZrCl)C(CH_2OZrCp_2Cl){=}NR]$. This insertion behavior of **1** is unusual as compared to the (η^2-formaldehyde)zirconocene dimer **4** that reacts with Me_3SiCH_2NC without Zr—O bond cleavage to give a four-membered metallacyclic (η^1-iminoacyl)zirconocene complex. The isonitrile insertion product **2a** was characterized by X-ray diffraction. It crystallizes in the space group $P\bar{1}$ with cell parameters a = 10.884(2) Å, b = 12.326(1) Å, c = 13.611(4) Å, α = 70.33(1)°, β = 72.57(2)°, γ = 86.43(1)°, Z = 2, R = 0.045, R_w^2 = 0.125. The C=N bond length in **2a** is 1.257(2) Å. The adjacent Zr—C(iminoacyl) bond is 2.198(4) Å.*

Zirconium complexes containing metallaoxirane units [Zr]—O—CH_2 sometimes undergo reactions that resemble the chemistry of methylene groups on a metal oxide surface.[1] A typical example is the cyclodimeric (η^2-formaldehyde)zirconocene complex **4** which is readily available from the carbon monoxide hydrozirconation product **1** ("Floriani's metallaoxirane") by treatment with 2 molar equiv of methyllithium (see Scheme 1).[2] Complex **4** can be looked at as a molecular metal oxide (Zr_2O_2) containing edge-bridging methylene units. The (η^2-formaldehyde)zirconocene dimer **4** shows molecular Fischer−Tropsch behavior: when exposed to a catalytic quantity of R_3B, repetitive transfer and coupling of CH_2 occurs with formation of a Poisson-distributed mixture of linear saturated hydrocarbon chains (**7**).[3] With a variety of stoichiometric reagents (X—Y or Y=Z) insertion into the metalloxirane Zr—C bond takes place. Typically, the central four-membered Zr_2O_2 core is retained in most of these reactions; the obtained products usually exhibit dimetallabicyclic structures (e.g. **5**, **6**, **8**).[4] The starting material of the $[(\eta^2\text{-}CH_2O)ZrCp_2]_2$ (**4**) synthesis, the dinuclear CO-hydrozirconation product **1**, also contains a ($\mu{:}\eta^1(O),\eta^2(C,O)$-formaldehyde) subunit. Comparison of typical structural data has revealed a pronounced metallaoxirane character of the $Cp_2Zr—CH_2—O$-unit in **1** similar to **4** [**1** (**4**)]: Zr—C 2.19(1) Å (2.243(3) Å); Zr—O 2.13(1) Å (2.103(2) Å); C—O 1.43(2) Å (1.395(4) Å)]. This posed the question whether insertion reactions of Floriani's metallaoxirane (**1**)[5] take a course similar to that observed for **4**, i.e. lead to cyclic coupling products with retaining the strong Zr—O—Zr linkage of the starting material. It is conceivable that **1** might undergo insertion reactions (similar to **4**) expected for a chemistry of methylene on the intact [Zr]—O—[Zr] metal oxide surface-like backbone. Alternatively, it may be possible that such a reaction type is only observed at the rigid cyclic $(ZrO)_n$ (n = 2, 3) frameworks. We have tried to find out by a suitable experiment whether CC coupling of the Zr—O bound CH_2 group is generally taking place with keeping the strong metal—oxygen template intact or if Zr—O cleavage can prevail if a suitable energetic compensation is provided. As depicted in Scheme 1 the controlled insertion of isonitriles[6] may be suited to answer this question. We have therefore reacted the metallaoxirane complex **1** with the isonitriles CN−R [R = $-CH_2(Si(CH_3)_3)$ and $-C(CH_3)_3$] and determined the preferred structure of the 1,1-insertion products.

Results and Discussion

The (μ-formaldehyde)($ZrCp_2Cl)_2$ complex (**1**) was treated with 1 molar equiv of (trimethylsilyl)methyl isocyanide. Periodic ^{1}H NMR measurements indicated that this insertion reaction is complete within ca. 1 day at room temperature and affords a single product. From a reaction on a preparative scale this was isolated in ca. 80% yield. The product (**2a**, R = CH_2SiMe_3) exhibits cyclopentadienyl resonances in the ^{1}H/^{13}C NMR spectra at δ 6.40, 5.04/113.8, and 109.3. The ^{1}H NMR resonance of the Zr−O−CH_2 group appears at δ 5.04 (s). The ^{13}C NMR signal of the corresponding methylene carbon atom is at δ 79.2 ($^1J_{CH}$ = 140 Hz). The presence of an iminoacyl functionality in **2a** is indicated by the ^{13}C NMR resonance at δ 234.8 and an infrared band at 1639 cm^{-1}. The reaction of **1** with *tert*-butyl isocyanide proceeds similarly to give **2b**.

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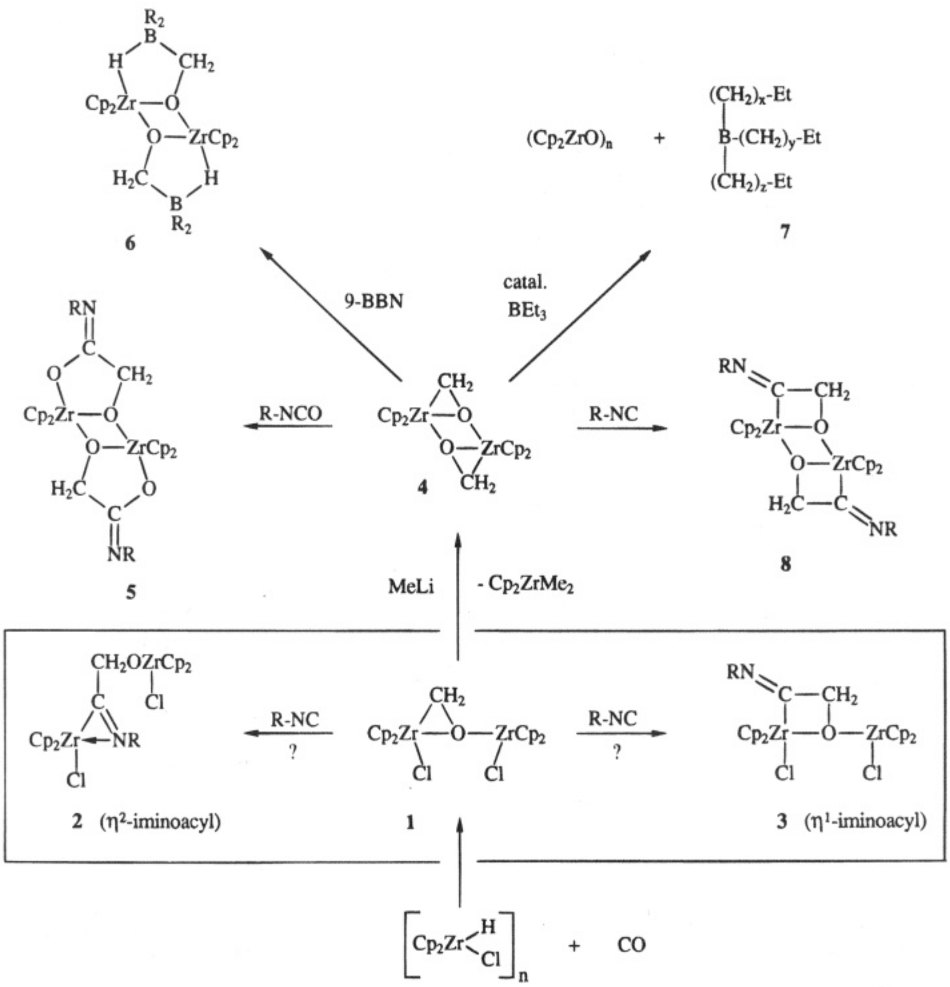
Scheme 1



The spectroscopic data for the isonitrile insertion products of **1** are very similar to those of the four-membered metallacyclic η^1-iminoacyl complex **8**[4a] (see Scheme 1) [$-CH_2C{=}N-$(**8**): ^{13}C NMR δ 65.7 ($^1J_{CH}$ = 143 Hz), 233.0; ^1H NMR δ 4.88 ($^5J_{HH}$ = 1.6 Hz)]. Because these spectroscopic data cannot readily differentiate between an η^1- or η^2-coordinated iminoacyl moiety,[7] an X-ray crystal structure analysis of **2a** was performed to establish its mode of coordination. Suitable crystals were obtained from benzene. The X-ray diffraction study has revealed that one of the Zr–O linkages of **1** was broken during the reaction with $(Me_3Si)CH_2-NC$ and a (η^2-iminoacyl)zirconocene complex was formed. In **2a** the iminoacyl C(2)–N bond length is 1.257(5) Å, consistent with a C=N double bond.[8] The bond angles around the iminoacyl carbon atom are 126.1(4)° [N–C(2)–C(1)], 159.9(3)° [Zr(2)–C(2)–C(1)], and 73.8(2)° [Zr(2)–C(2)–N]. These values are very typical of (η^2-iminoacyl)metal complexes. Related (η^2-iminoacyl)zirconocene complexes show very similar bonding parameters.[7] It should be noted, however, that the pertinent bonding features of the η^1-iminoacyl group in **8** are not enormously different [d(C=N) 1.274(2) Å; angles at the iminoacyl carbon atom 118.6(1)° ($N-C-CH_2$), 147.8(1)° (N–C–Zr), 93.6(1)° ($Zr-C-CH_2$)].

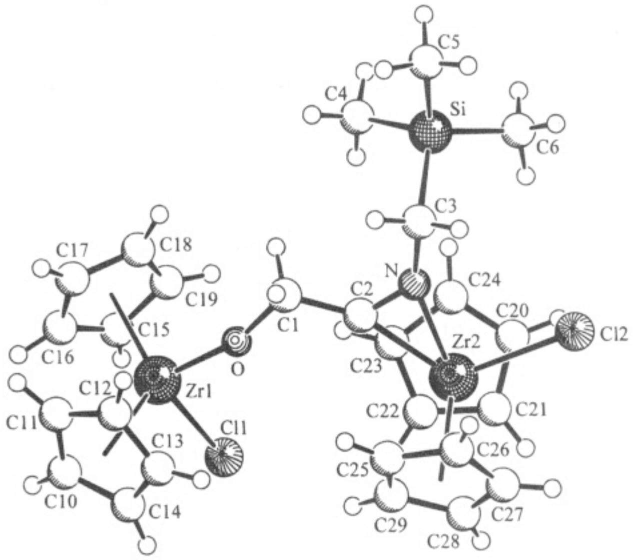


Figure 1. View of the molecular geometry of the (η^2-iminoacyl)zirconocene complex **2a** in the crystal (with atom numbering scheme).

In **2a** the C(2)–C(1) distance is 1.481(6) Å. The C(1)–O–Zr(1) linkage is almost linear [162.6(3)°; C(1)–O 1.369(5) Å, O–Zr(1) 1.917(3) Å; angle C(2)–C(1)–O 113.3(3)°]. The O–Zr(1)–Cl(1) angle is 97.6(1)°. The

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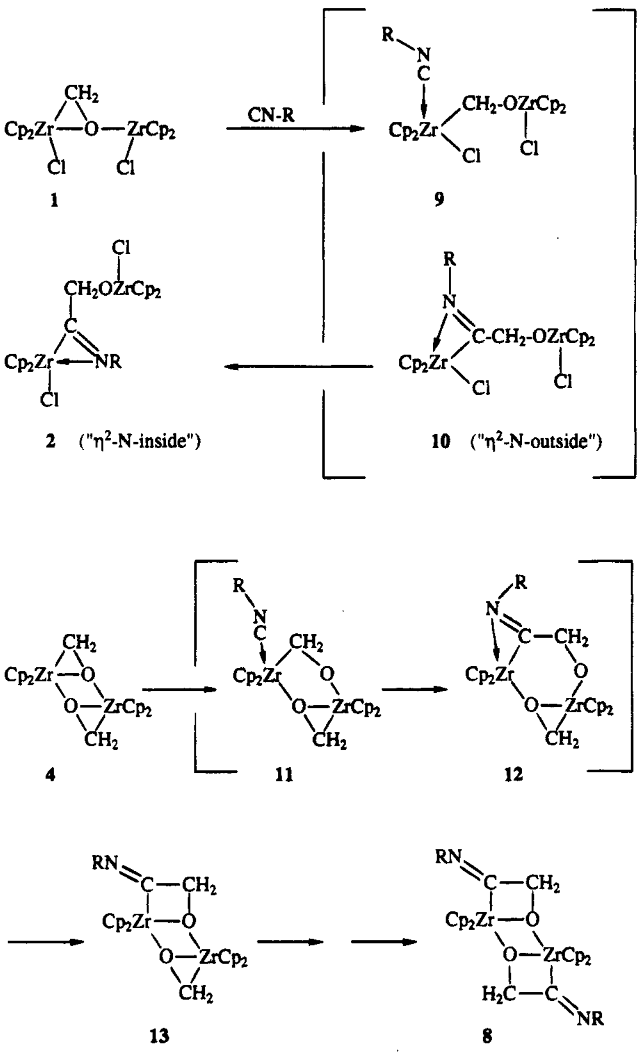
C(2)–Zr(2)–Cl(2) angle at the five-coordinate zirconium center is much larger at 115.7(1)° [Zr(2)–Cl(2) 2.551(1) Å]. The η^2-iminoacyl coordination at Zr(2) results in very small C(2)–Zr(2)–N [33.2(1)°] and C(2)–N–Zr(2) [73.1(2)°] angles. The Zr(2)–C(2) bond is very short at 2.198(4) Å. The Zr(2)–N distance is 2.206(3) Å [C(3)–N 1.464(5) Å; angles C(2)–N–C(3) 129.8(4)°, Zr(2)–N–C(3) 156.7(3)°]. The central (iminoacyl)zirconium unit is coplanar with Cp–metal–Cp bisecting the major plane at Zr(2) [including C(1), C(2), N, C(3), Zr(2), and Cl(2); maximum deviation from planarity −0.043 Å (N)]. The nitrogen center of the (η^2-iminoacyl)zirconocene moiety is located at the central coordination site in the σ-ligand plane of the bent metallocene unit.[9] Of the two possible positional isomers,[10,13] complex **2a** attains the "N-inside" η^2-iminoacyl orientation, which is probably thermodynamically preferred over the "N-outside" η^2-iminoacyl alternative.

Contrary to what is observed with **4** the alkyl isocyanide insertion of the metallaoxirane complex **1** proceeds with overall cleavage of the Zr–O–Zr backbone. We assume that the addition of an isonitrile molecule to the five-coordinate zirconium center requires opening of the adjacent Zr–O linkage.[11] After insertion and CC coupling is complete, there are two alternatives for stabilization: either the Zr–O bond is re-formed or the iminoacyl nitrogen center is coordinated to zirconium. It appears that the latter predominates in the reaction starting with Floriani's metallaoxirane (**1**), whereas the former alternative[12] is favored during the insertion reactions starting from the (η^2-formaldehyde)zirconocene dimer **4**. The structural outcome of these insertion reactions seems to be thermodynamically controlled. It appears that there is a high tendency of the central $(ZrO)_n$ frameworks to be retained, which is potentially due to an oxametallacyclic chelate effect, when reactions are taking place with groups attached at their edges, whereas linear Zr–O–Zr backbones are more likely to be cleaved and ultimately lost in related reaction sequences.

Experimental Section

All reactions were carried out in an inert atmosphere (argon) using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. For a description of additional general experimental conditions including a listing of spectrometers used for characterization see ref 13. Complex **1** was prepared by a modified literature procedure.[5,14]

Scheme 2



Reaction of 1 with (Trimethylsilyl)methyl Isocyanide. $(Me_3Si)CH_2NC$ (62 mg, 0.55 mmol) was added to a suspension of 300 mg (0.55 mmol) of **1** in 10 mL of toluene. The mixture was stirred for 1 day at ambient temperature and then concentrated in vacuo to a volume of ca. 2 mL. The mixture was kept for 2 days at −18 °C. The precipitated product was collected by filtration and dried in vacuo to give 283 mg (78%) of **2a**. Mp: 191 °C (DSC). Anal. Calcd for $C_{26}H_{33}NCl_2OSiZr_2$ (626.89): C, 47.53; H, 5.06; N, 2.13. Found: C, 47.45; H, 4.93; N, 2.01. IR (KBr): $\tilde{\nu}$ = 3085, 2966, 1636 (C=N), 1439, 1413, 1331, 1260, 1133, 1123, 1084, 1013, 857, 840, 802, 775, 738 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 6.40 (s, 10H, Cp), 5.87 (s, 10H, Cp), 5.04 (s, 2H, [ZrOC*H*$_2$]), 3.20 (s, 2H, SiC*H*$_2$N), 0.11 (s, 9H, SiMe$_3$). ^{13}C NMR (benzene-d_6): δ 234.8 (s, C=N), 113.8 (^1J = 173 Hz) and 109.3 (^1J = 173 Hz, Cp), 79.2 (^1J = 140 Hz, [ZrOCH$_2$]), 42.4 (^1J = 129 Hz, SiCH$_2$), −1.5 (^1J = 120 Hz, SiMe$_3$).

X-ray Crystal Structure Analysis of 2a. Crystals from benzene: $C_{26}H_{33}Cl_2NOSiZr_2 \cdot C_6H_6$, MW = 735.07, space group $P\bar{1}$, a = 10.884(2) Å, b = 12.326(1) Å, c = 13.611(4) Å, α = 70.33(1)°, β = 72.57(2)°, γ = 86.43(1)°, V = 1639.0(6) Å^3, d_{calc} = 1.489 g cm^{-3}, μ = 8.6 cm^{-1}, Z = 2, λ = 0.710 69 Å, measured reflections 6304 ($+h,\pm k,\pm l$), $(\sin\theta)/\lambda_{max}$ = 0.62 Å^{-1}, 5085 observed reflections, 356 refined parameters, R = 0.045, $R_w{}^2$ = 0.125, $\Delta\varrho$ = 0.88 (−1.24) e Å^{-3} (near Zr). The structure was

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[12] For a related example see: Askham, F. R.; Carroll, K. M.; Alexander, S. J.; Rheingold, A. L.; Haggerty, B. S. *Organometallics* **1993**, *12*, 4810.

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[14] Erker, G.; Kropp, K. *Chem. Ber.* **1982**, *115*, 2437.

solved by the heavy-atom method, and hydrogen atom positions were calculated and kept fixed in the final refinement.

Reaction of 1 with *tert*-Butyl Isocyanide. To a suspension of 1 (300 mg, 0.55 mmol) in 5 mL toluene was given 46 mg (0.55 mmol) of *tert*-butyl isocyanide. The mixture was stirred for 3 days at room temperature. The precipitated product was collected by filtration and dried in vacuo to give 311 mg (90%) of **2b**. Mp: 229 °C (DSC). A preliminary X-ray crystal structure analysis (crystals from toluene, $R = 11\%$) has confirmed the N-inside (η^2-iminoacyl)zirconocene type structure of **2b**, analogous to **2a**. Anal. Calcd for $C_{26}H_{31}NCl_2OZr_2$ (626.89): C, 49.82; H, 4.98; N, 2.23. Found: C, 49.18; H, 5.04; N, 2.14. IR (KBr): $\tilde{\nu} = 3098, 2960, 2869, 2854, 1653$ (C=N), 1437, 1362, 1262, 1200, 1115, 1014, 779, 738 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.42 (s, 10H, Cp), 5.87 (s, 10H, Cp), 5.25 (s, 2H, [ZrOC*H*$_2$]), 1.31 (s, 9H, CMe$_3$). ^{13}C NMR ($CDCl_3$): δ 236.3 (s, C=N), 113.9 ($^1J = 173$ Hz, Cp), 108.9 ($^1J = 173$ Hz, Cp), 78.2 ($^1J = 141$ Hz, [ZrOCH$_2$]), 62.3 (s, *C*Me$_3$), 29.3 ($^1J = 123$ Hz, C*Me*$_3$).

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Supplementary Material Available: For **2a**, tables of detailed information of the X-ray crystal structure determination, final atomic positional parameters, final thermal parameters, and interatomic distances and angles (7 pages). Ordering information is given on any current masthead page.

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