Formation of a Dynamic $\eta^2(O,N)$-Hydroxylaminato Zirconocene Complex by Nitrosoarene Insertion into a Zr−C σ-Bond

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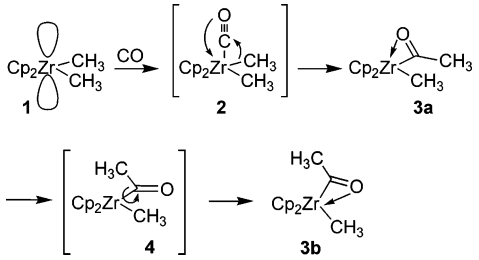
Received November 3, 2005

The reaction of dimethylzirconocene with nitrosobenzene gave the hydroxylaminatozirconium complex **6**. Its structure in the solid state was characterized as the N-inside isomer [$\eta^2(O,N)$-ON(CH_3)Ph](CH_3)-$ZrCp_2$ (**6a**) by X-ray diffraction. Dynamic ^{1}H NMR spectroscopy indicated a rapid enantiomerization process of the chiral system **6a** in solution, probably taking place via a rapid equilibration with a reactive $\eta^1(O)$ isomer.

Introduction

Hydroxylaminato complexes of the transition metals are usually prepared by reaction routes involving the intact hydroxylamine reagents. Most of the resulting complexes, especially those of the early d metals, feature η^2 coordination (i.e. an O,N-bonded situation).[1,2] However, a variety of examples are known that are characterized by an $\eta^1(O)$-ONR^{1}R^2 ligand that is bonded to the metal only through the oxygen atom.[3] Though most of the known ($\eta^2(O,N)$-ONR^{1}R^2)[M] complexes do not exhibit dynamic behavior, a few complexes show evidence for reversible cleavage of the [M]−N linkage, usually with a high energy barrier.[4] We have now prepared a novel η^2-ONR^{1}R^2 zirconocene complex by a rarely encountered nitrosoarene insertion route.[5] The resulting coordinatively saturated 18-electron zirconocene complex showed an unusually low activation barrier of the η^2-ONR^{1}R^2 automerization process. Details of this rather exceptional hydroxylaminato zirconocene system are described in this article.

Scheme 1



Results and Discussion

Dimethylzirconocene (**1**) is a 16-electron complex. After some early discussion it is now clear that its LUMO is laterally extending in the major σ-ligand plane.[6] Consequently, a donor ligand or reagent is expected to enter the molecule from the side (and not the central position between the σ-ligands) under kinetic control. This has been demonstrated experimentally for a number of cases.[7] As a typical example, carbonylation was found to kinetically yield the O-outside (η^2-acetyl)zirconocene complex (**3a**), which subsequently was shown to isomerize to the thermodynamically favored O-inside (η^2-acetyl)zirconocene complex (**3b**).[8] Computational chemistry has revealed a pathway that involved formation of an energetically high lying (η^1-acetyl)[Zr] intermediate (**4**) and rotation[9] (Scheme 1). Isonitrile insertion follows a similar pathway, though an equilibrium mixture of N-inside and N-outside (η^2-iminoacyl)zirconocene isomers may be observed in some cases.[10]

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§ X-ray crystal structure analysis.

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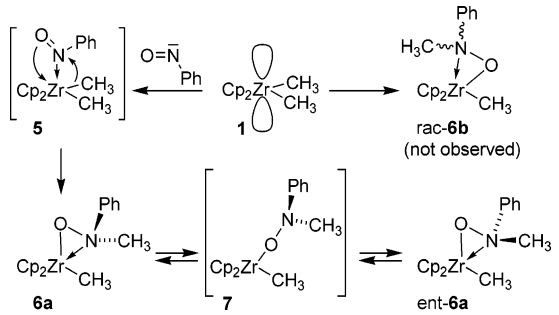
Publication on Web 01/10/2006

Scheme 2



The reaction of dimethylzirconocene with nitrosobenzene can be envisioned to proceed through a similar reaction course. Addition of the nucleophilic ON−Ph reagent to a lateral coordination site could lead to a reactive N-adduct (**5**)[11] that subsequently undergoes rapid methyl migration and metal−oxygen bond formation to yield an O-outside (η^2-hydroxylaminato)zirconocene complex (**6a**). The O-outside complex **6a** could then equilibrate with the $\eta^1(O)$ isomer (**7**) to lead to the $\eta^2(O,N)$ O-inside isomer (**6b**) (Scheme 2).

Consequently, we have treated dimethylzirconocene (**1**) with 1 molar equiv of nitrosobenzene. The reaction was carried out at 0 °C in dichloromethane and the 1:1 insertion product (**6**) isolated in ca. 50% yield as an off-white solid after ca. 1 h reaction time. The ambient-temperature ^{1}H NMR spectrum shows a single remaining [Zr]−CH_3 group (δ 0.37, s, 3H) and a new N-coordinated CH_3 resonance (δ 2.63, s, 3H) in addition to the signals of a C_6H_5 substituent and a sharp Cp singlet at δ 5.55 (10H, ^{13}C NMR signal at δ 110.0).

However, the simple overall appearance of the ambient-temperature ^{1}H/^{13}C NMR spectra of complex **6** is due to a rapid dynamic exchange process. This became apparent by monitoring the ^{1}H NMR spectrum of the ON−Ph insertion product at variable temperature. To eventually reach a sufficiently low temperature to securely observe the static 600 MHz ^{1}H NMR situation, a $CDFCl_2$ solvent was used.[12] In this solvent, complex **6** at 253 K exhibits three ^{1}H NMR singlets at δ 0.17 (3H, [Zr]−CH_3), 2.96 (3H, [N]CH_3), and 5.73 (10H, $ZrCp_2$) in addition to three multiplets derived from the C_6H_5 group at δ 7.17 (*p*), 7.31 (*o*), and 7.36 (*m*). When the monitoring temperature is lowered, the Cp signal rapidly gets broad and below a temperature of ca. 198 K splits into a 1:1 intensity pair of ^{1}H NMR Cp singlets. In addition, the *o*-C_6H_5 resonance also gets broad with decreasing temperature, followed by the *m*-C_6H_5 signal. Each of them eventually splits into a 1:1 pair of multiplets, whereas the *p*-C_6H_5 resonance as well as the [Zr]−CH_3 and [N]−CH_3 ^{1}H NMR signals remain sharp over the investigated temperature range. Eventually at 163 K the ^{1}H NMR spectrum of complex **6a** in the $CDFCl_2$ solvent features pairs of *m*-C_6H_5 multiplets at δ 7.36 and 7.41 (1H each), pairs of *o*-C_6H_5 multiplets at δ 7.11 and 7.44 (1H each), and a *p*-C_6H_5 signal at 7.20. It shows a 1:1 intensity pair of Cp singlets (representing 5H each) at δ 5.47 and 6.00 and practically unchanged [N]−CH_3 (δ 2.94) and [Zr]−CH_3 (δ 0.13) signals (see Figure 1).

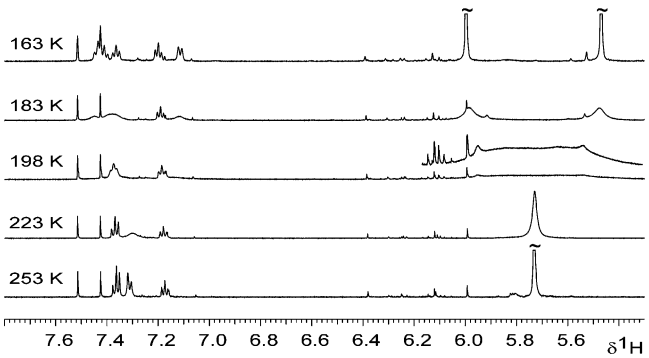


Figure 1. Temperature-dependent 600 MHz ^{1}H NMR spectra of complex **6** in $CDFCl_2$.

Apparently, we have observed the "freezing out" of two different dynamic processes in complex **6** on the NMR time scale with decreasing monitoring temperature. The nonequivalency of the pairs of *m*- and *o*-C_6H_5 signals obviously results from a hindered rotation of the *N*-phenyl substituent around the N−C(aryl) bond at low temperature. From the coalescence of the respective pairs of *o*-aryl as well as *m*-aryl ^{1}H NMR signals we have estimated a Gibbs activation energy[13] of $\Delta G_{aryl-rot}^{\ddagger} = 9.4 \pm 0.3$.kcal/mol for this rotational process.

The Cp coalescence is probably caused by an unrelated dynamic process. Consequently, this exchange is characterized by a different magnitude of its activation barrier. From the coalescence of the pair of ^{1}H NMR Cp singlets, $\Delta G_{exchange}^{\ddagger}(198\ K) = 8.8 \pm 0.3$ kcal/mol was obtained. The observation of a 1:1 pair of Cp singlets in the low-temperature NMR suggests an ($\eta^2(O,N)$-hydroxylaminato)zirconocene global minimum structure of compound **6** in solution. It is likely that the observed enantiomerization process that leads to intramolecular Cp exchange is initiated by Zr−N bond cleavage and equilibration with an ($\eta^1(O)$-hydroxylaminato)[Zr] isomer (**7**) of higher energy, in which the nonequivalency of the Cp ligands is lost. Re-forming the Zr−N bond then leads back to the more stable η^2-coordination stage of this system. The observed pair of diastereotopic Cp ligands at Zr in complex **6** is a strong indication that the η^2-hydroxylaminato coordination mode is favored for the product of ON−Ph insertion into the Zr−CH_3 bond of dimethylzirconocene in solution, but it was not apparent from the NMR experiment whether the single observed $\eta(O,N)$ compound was the N-inside (**6a**) or the N-outside isomer (**6b**) (see Scheme 2). Which of the two isomers was favored in the solid state could be shown by an X-ray crystal structure analysis.

Single crystals of complex **6a** were obtained by allowing the neat orange oil, as it was obtained from the insertion reaction, to crystallize at room temperature over a period of 2 days. Colorless crystals were obtained that were used for the X-ray structure determination. In the crystal there are two independent molecules of **6a** that are chemically equivalent (the corresponding parameters of the second molecule will be given in brackets). The structure of **6a** features a typical bent-metallocene framework with a pair of uniformly η^5-coordinated Cp ligands with Zr−C(Cp) bond lengths in a close range between 2.509(2) and 2.557(2) Å [2.499(2)−2.551(2) Å]. There is a single CH_3 group σ-bonded to zirconium (Zr−C1 = 2.296(2) Å [2.305(2) Å]). The second methyl group is found attached to nitrogen (N1−

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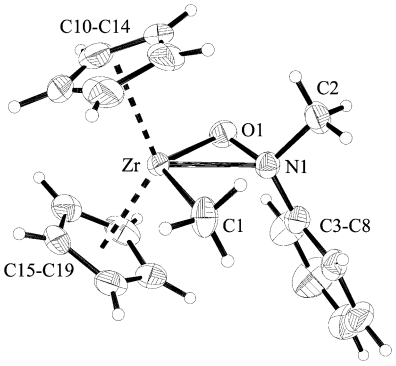

Figure 2. Molecular structure of **6a**.

C2 = 1.474(3) Å [1.475(2) Å]). The nitrogen center also bears a phenyl group originating from the nitrosobenzene reagent. The N−C(aryl) bond length amounts to 1.442(3) Å [1.445(2) Å]. As expected, this N−C(sp^2) linkage is slightly shorter than the adjacent N−C(sp^3) bond. An essential feature of the structure of complex **6a** is that the hydroxylaminato ligand is strongly bonded to zirconium through both the oxygen and nitrogen atoms (Zr−O1 = 2.101(2) Å [2.091(1) Å], Zr−N1 = 2.284(2) Å [2.286(2) Å]) and the nitrogen atom is located in the central position in the σ-ligand plane bisecting the O1−Zr−C1 angle (O1−Zr−C1 = 117.80(7)° [118.60(7)°], O1−Zr−N1 = 37.46(6)° [37.36(5)°]). The O1−N1 bond is in the typical single-bond range at 1.419(2) Å [1.414(2) Å], and the Zr−O1−N1 angle amounts to 78.28(9)° [78.85(9)°]. The adjacent O1−N1−Zr angle (64.25(9)° [63.79(8)°]) is slightly smaller. The nitrogen center is distorted tetrahedral, with the remaining five bond angles being 110.71(16)° [109.80(15)°] (O1−N1−C2), 112.33(15)° [112.63(14)°] (O1−N1−C3), 111.84(17)° [110.71 (16)°] (C3−N1−C2), 123.45(12)° [126.27(12)°] (C3−N1−Zr), and 122.04(13)° [120.88(13)°] (C2−N1−Zr). The phenyl substituent at N1 is found in a conformational orientation that is characterized by dihedral angles θ_1 (O1−N1−C3−C4) being −10.5(3)° [−10.9(2)°] and θ_2 (Zr1−N1−C3−C4) being −83.6(2)° [−84.2(2)°].

We conclude that the N-inside (η^2-hydroxylaminato)zirconocene isomer **6a** was identified by X-ray diffraction in the crystal state. We consider it likely that the N-inside (η^2-hydroxylaminato)zirconocene isomer **6a** identified in the crystal form is also favored in solution. Since complex **6a** is the only isomer oberved under equilibrium conditions, it appears that the expected kinetic product is identical with the thermodynamically favored product, probably because the η^2(*O,N*) N-outside isomer is sterically less favored. However, the observed η^2(*O,N*) N-inside isomer (**6a**) seems to be separated by less than 8.8 ± 0.3 kcal/mol from the alternative [η^1(*O*)-hydroxylaminato]-zirconocene isomer (**7**), as judged from the dynamic NMR features of **6a** (see above). This indicates that coordinative equilibration could constitute a more important feature of hydroxylaminato early-metal chemistry than previously anticipated.[4]

Experimental Section

General Considerations. Reactions with organometallic compounds were carried out under argon using Schlenk-type glassware or in a glovebox. Solvents (including deuterated solvents for the NMR measurements) were dried and distilled under argon prior to use. Some predried solvents were further purified using an aluminum oxide column. Pentane and toluene were similarly cleaned and deoxygenated by this technique using a copper catalyst.[14] $CDFCl_2$ was prepared according to a literature procedure (δ(^{1}H) 7.47 d, J_{HF} = 50 Hz).[12] Dimethylzirconocene was synthesized as described in the literature.[15] ^{1}H NMR spectra were recorded using a Bruker AC 200 P spectrometer (^{1}H, 200.1 MHz; ^{13}C, 50.3 MHz) or a Varian Unity Plus 600 NMR spectrometer (^{1}H, 599.1 MHz; ^{13}C, 150.7 MHz; variable temperature and 2D measurements). IR spectra were obtained on a Nicolet 5 DXC FT IR spectrometer.

X-ray Crystal Structure Analysis. The data set was collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator. Programs used: data collection, COLLECT;[16] data reduction, Denzo-SMN;[17] absorption correction, SORTAV;[18] structure solution, SHELXS-97;[19] structure refinement SHELXL-97;[20] graphics, XP.[21]

Reaction of Dimethylzirconocene with Nitrosobenzene. Preparation of Complex 6a, $Cp_2Zr(Me)[\eta^2(N,O)$-N(Me)(Ph)O]. A colorless solution of Cp_2ZrMe_2 in dichloromethane (20 mL) was cooled to 0 °C. To this was added a teal blue solution of nitrosobenzene in dichloromethane (10 mL). The resulting solution immediately turned yellow upon addition of the nitrosobenzene. The reaction mixture was stirred at 0 °C for 30 min before being warmed to room temperature and stirred for 1 h. The solvent was removed to yield an orange oil, which crystallized as a colorless solid over the course of 2 days at room temperature. Crystals suitable for X-ray diffraction were also obtained in this manner. Alternately, a pale yellow/off-white precipitate can be obtained with THF/pentane and toluene/pentane solutions. Yield: 0.34 g, 49%. ^{1}H NMR (600 MHz, C_6D_6, 298 K): δ 7.34 (m, 2H, *o*-Ph), 7.04 (m, 2H, *m*-Ph), 6.86 (m, 1H, *p*-Ph), 5.55 (s, 10H, Cp), 2.63 (s, 3H, NMe), 0.37 (s, 3H, ZrMe). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 298 K): δ 155.9 (*i*-Ph), 128.7 (*m*-Ph), 125.1 (*p*-Ph), 119.7 (*o*-Ph), 110.0 (Cp), 54.7 (NMe), 17.8 (ZrMe). IR (KBr): 2950, 1252, 1083, 1013, 797 cm^{-1}. Anal. Calcd ($C_{18}H_{21}NOZr$): C, 60.29; H, 5.90; N, 3.91. Found: C, 59.83; H, 5.99; N, 3.88.

Low-Temperature VT-NMR Experiments. These experiments were performed in $CDFCl_2$, which was prepared according to previous methods[12] and was vacuum-transferred prior to use. Coalescence of the Cp peaks ($\Delta\nu$(163 K) = 317 Hz) was observed at 198 K ($\Delta G_{exchange}^{\ddagger}$(198 K) = 8.8 kcal mol^{-1}). Coalescence of phenyl ortho signals ($\Delta\nu$(163 K) = 196 Hz; $\Delta G_{aryl-rot}^{\ddagger}$(208 K) = 9.5 ± 0.3 kcal mol^{-1}) was observed at 208 K and of phenyl meta signals ($\Delta\nu$(163 K) = 28 Hz; $\Delta G_{aryl-rot}^{\ddagger}$(188 K) = 9.3 ± 0.3 kcal mol^{-1}) at 188 K.

X-ray Crystal Structure Analysis of 6a. Crystal data: formula $C_{18}H_{21}NOZr$, M_r = 358.58, colorless crystal, 0.35 × 0.30 × 0.10 mm, a = 17.558(1) Å, b = 7.936(1) Å, c = 23.267(1) Å, β = 97.76(1)°, V = 3212.3(5) Å^3, ρ_{calcd} = 1.483 g cm^{-3}, μ = 0.683 mm^{-1}, empirical absorption correction (0.796 ≤ T ≤ 0.935), Z = 8, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.710 73 Å, T = 198 K, ω and φ scans, 20 783 reflections collected (±*h*, ±*k*, ±*l*), (sin θ)/λ = 0.66 Å^{-1}, 7642 independent (R_{int} = 0.049) and 6251 observed reflections ($I \geq 2\sigma(I)$), 384 refined parameters, R1 = 0.032, wR2 = 0.075, maximum (minimum) residual electron density 0.36 (−0.87) e Å^{-3}, two almost identical independent molecules in the asymmetric unit, hydrogen atoms calculated and refined as riding atoms.

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Acknowledgment. Financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowleged. R.R. thanks the International NRW Graduate School of Chemistry at Münster and S.A.C. thanks the SFB 424 for supporting their stays at the Organisch-Chemisches Institut der Universität Münster.

Supporting Information Available: A CIF file giving details of the X-ray crystal structure determination of complex **6a**, text giving details of the calculations, and figures giving additional DNMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050946N