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Reaction of (η^4-butadiene)-zirconocene and -hafnocene with 2-methyl-2-nitrosopropane

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Abstract

(η^4-Butadiene)-zirconocene and -hafnocene each react with two molar equivalents of 2-methyl-2-nitrosopropane to give nine-membered metallacycles $\mathrm{Cp_2\overline{MON(R)CH_2CH{=}CHCH_2N(R)O}}$ (**8a**: R = t-Bu; M = Zr; **8b**: R = t-Bu, M = Hf), which have a *trans*-carbon–carbon double bond in the ring. In solution two different dynamic processes can be observed by variable temperature NMR spectroscopy. Enantiomerization of the chiral ring system ($\Delta G^{\ddagger}_{\text{ent}}$ (390 K) ≈ 19 kcal/mol) is observed at high temperature, whereas at low temperature an equilibration process involving hindered N–$\mathrm{CMe_3}$ rotation becomes slow on the NMR time scale ($\Delta G^{\ddagger}_{\text{rot}}$ (190 K) ≈ 8 kcal/mol).

Introduction

(Conjugated diene)-zirconocene and -hafnocene complexes (**1**-*cis*, **1**-*trans*) often undergo carbon–carbon coupling with carbonyl compounds to give metallacyclic products. With aldehydes or ketones, reaction of 1/1 stoichiometry is sometimes observed, yielding seven-membered metallacyclic σ-allyl complexes (oxametallacycloheptenes **2**). In some cases a second molar equivalent of an organic carbonyl compound is consumed, yielding a nine-membered metallacycle (**3**) [1].

Similarly, the butadiene Group 4 metallocene complexes react cleanly with many metal carbonyls to give metallacyclic heteroatom-stabilized Fischer-type carbene complexes **4** in high yield [2]. These metallacyclic (π-allyl)metallocenes commonly insert a ketone or aldehyde to give chiral medium-sized metallacycles **5**. Complexes **5** exhibit dynamic behavior in solution. The chiral metallacyclic nine-membered ring systems containing a *trans*-configurated C=C bond show energy barriers to enantiomerization similar to that of their parent hydrocarbon *trans*-cyclononene [3].

The N=O functionality in nitrosoalkanes has bonding features similar to those found in organic and inorganic carbonyl groups, and so it was tempting to speculate that (butadiene)-zirconocene and -hafnocene complexes might show similar reac-

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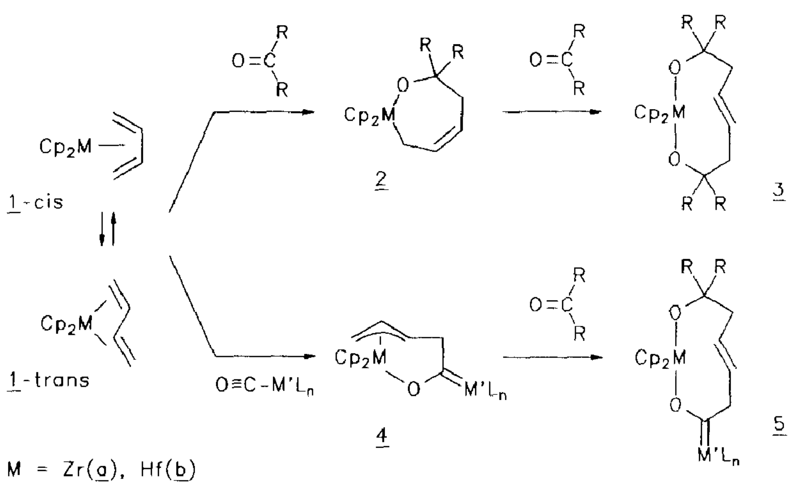


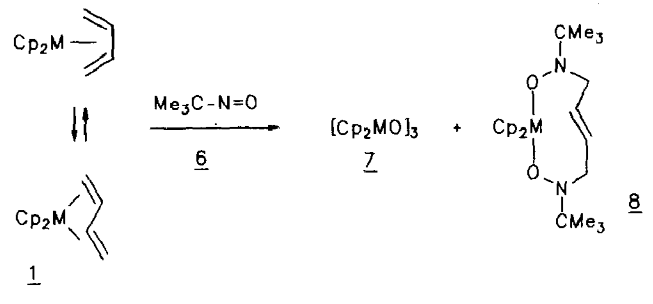
tions when treated with an R–N=O reagent. Moreover, reactions of organometallic compounds with organic nitroso compounds seem to have been studied in only a few cases [4]. To our knowledge, 1,2-insertion of RNO into early transition metal to carbon bonds with carbon to nitrogen bond formation had not been observed previously [5]. We here describe the reactions of (butadiene)-zirconocene and -hafnocene with 2-methyl-2-nitrosopropane, which, respectively, produce oxygen- and nitrogen-containing nine-membered metallacycles which show several remarkable dynamic features in solution.

Results and discussion

The (*s-cis*/*s-trans*-η^4-butadiene)zirconocene equilibrium mixture (**1**-*cis*/**1**-*trans*: ca. 1/1) reacts rapidly with Me_3CNO (**6**) in toluene at room temperature. About two molar equivalents of the nitrosyl reagent **6** are needed to achieve complete reaction. Monitoring by ^1H NMR spectroscopy revealed that a thermally induced reaction between **1** and **6** begins at about +10 °C. Only the final reaction products were detected. Two organometallic products were recovered; under typical reaction conditions at room temperature they were obtained in about equal amounts, and because of their different solubilities they were readily separated.

Extraction of the product mixture with pentane left a white solid (ca. 50% of the products by weight). Comparison with authentic material revealed it to be $[Cp_2ZrO]_3$ (**7a**) [6]. This zirconocene oxide product may originate from an oxidation of the original dicyclopentadienylzirconium by the nitroso reagent with extrusion of the conjugated diene. We have noticed that the amount of **7a** formed is somewhat dependent on the reaction conditions, and so a full mechanistic description of the formation of this product upon reacting of **1a** with **6** must await further detailed experimental studies.

From the pentane extract we recovered the addition product **8a** of (butadiene)zirconocene with two equivalents of 2-methyl-2-nitrosopropane (M^+: $m/e = 448.1667$ found, 448.1663 calculated) in 30% yield. The reaction between the (butadiene)hafnocene system **1b** and Me_3CNO (**7**) proceeds analogously. We iso-



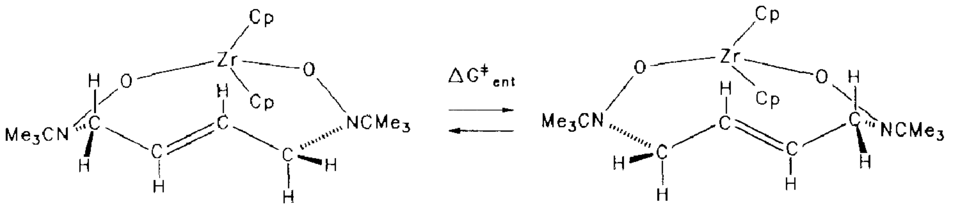
M = Zr(a), Hf(b)

lated the products $(Cp_2HfO)_3$ (**7b**) [6] and $Cp_2\overline{HfON(R)CH_2CH{=}CHCH_2N(R)O}$ (**8b**) in 36% and 29% yield, respectively.

The ^{13}C NMR spectra of complexes **8** are quite simple at ambient temperature. In CS_2/benzene-d_6 solvent $Cp_2\overline{ZrON(R)CH_2CH{=}CHCH_2N(R)O}$ (**8a**, $R = CMe_3$) exhibits signals at δ 112.8 (^1J(CH) 171 Hz, Cp), 135.8 (d, ^1J(CH) 153 Hz) and 54.8 (t, ^1J(CH) 133 Hz, CH_2–CH=), 59.4 (s) and 26.0 (q, ^1J(CH) 126 Hz, t-butyl). The ^1H NMR spectrum (CS_2/benzene-d_6, ambient temperature) also exhibits only one Cp resonance (δ 6.00) and a single N–CMe_3 signal (δ 0.96). However, the allylic hydrogens of the CH_2–CH= moiety are diastereotopic (δ 2.40 and 3.17, CH_2; δ 5.39, =CH). From these spectral data we assign an overall C_2 molecular symmetry to the nine-membered metallacycle **8a**. The hafnium complex **8b** exhibits almost identical ^1H and ^{13}C NMR spectra. This complex also appears to have a chiral metallacyclic structure, exhibiting a *trans*-C=C double bond in the medium-sized heterocyclic ring system (see Scheme 1).

It is a typical feature of many chiral nine-membered ring systems possessing an endocyclic *trans*-configurated carbon–carbon double bond that enantiomerization can be observed by dynamic NMR spectroscopy at high temperature. For *trans*-cyclononene the activation energy $\Delta G^{\ddagger}_{ent}$ (263 K) is ca. 19 kcal/mol for this process [7]. Similar values have been obtained for this type of conformational equilibration from the variable temperature ^1H NMR spectra of the metallacycles **5** (M = Zr, $R = CH_3$, $M'L_n = Cr(CO)_5$, $Mo(CO)_5$, or $W(CO)_5$; $\Delta G^{\ddagger}_{ent}(323\ K) = 16.6 \pm 0.4$ kcal/mol; R = Ph, $M'L_n = W(CO)_5$: $\Delta G^{\ddagger}_{ent}(350\ K) = 17.0 \pm 0.4$ kcal/mol) [3]. Complexes **8a** and **8b** both show dynamic NMR spectra. ^1H NMR spectra at high temperatures were recorded in xylene-d_{10} solvent at 80 MHz. Coalescence of the ^1H NMR signals of the diastereotopic $CH_2CH{=}CHCH_2$ protons was observed above 120 °C. From these spectra identical barriers to enantiomerization $\Delta G^{\ddagger}_{ent}$ (393 K) of ca. 19.5 ± 0.5 kcal/mol were estimated for the zirconium- and hafnium-containing metallacyclic heteroatom-containing *trans*-cyclononene systems **8a** and **8b**, respectively.

The operation of a second dynamic process for complexes **8a** and **8b** was revealed by recording their ^{13}C NMR spectra at low temperatures. In CS_2/benzene-d_6 solvent the single ^{13}C NMR t-butyl methyl resonance at δ 26.0 splits into three separate signals at δ 29.9, 27.6, and 18.9 (intensity 1/1/1, 50 MHz, T 163 K). All the other ^{13}C NMR signals of **8a** remain completely unchanged, including the signal



Scheme 1: Schematic representation of the conformational equilibration taking place with complexes **8**.

of the quaternary carbon atom of the nitrogen-bonded t-butyl group (observed at δ 59.3 in 9/1 CS_2/benzene-d_6 at T 163 K). Similarly, the line shape of the ^{13}C NMR signals of **8b** is not altered when the temperature is lowered from ambient to 175 K, except for the $NC(CH_3)_3$ resonance (δ 26.0 in 9/1 CS_2/benzene-d_6), which splits into three signals (δ 30.0, 28.0, 19.1 at 175 K, see Fig. 1). From the temperature dependent ^{13}C NMR methyl resonances we have estimated identical Gibbs-activation energies $\Delta G^{\ddagger}_{rot}(190\ K) \approx 8.2 \pm 0.5$ kcal/mol for the molecular rearrangement process responsible for these spectral dynamics of the zirconium complex **8a** and the hafnium complex **8b**.

We think that hindered $N{-}CMe_3$ rotation is responsible for the observed splitting of the $N{-}C(CH_3)_3$ resonance into three separate lines at low temperature.

A simple N–C rotational process could in principle be responsible for the observed t-butyl methyl group inequivalency. In that case, an unusual structure for complexes **8** containing sp^2-hybridized nitrogen centers in the ring system would have to be assumed. It is conceivable that such a special structure could benefit from an electronic stabilization by the Lewis-acidic early transition metal center e.g. via a heteroallene-type N=O=Zr interaction [8].

A more conventional interpretation based on the assumption of ordinary tetrahedral geometry of the ring nitrogens would attribute the observed phenomenon to operation of two dynamic processes, namely inversion at nitrogen and hindered N–C(t-butyl) rotation. The observed overall rate in this case would correspond to the process having the lower activation energy barrier. N(sp^3)-inversion barriers have been reported to span a wide range, depending on the specific substitution pattern [9]. However, the $\Delta G^{\ddagger}_{rot}$-value observed here for complexes **8** is much lower than typical $\Delta G^{\ddagger}_{inv}$ activation barriers for hydroxylamine systems $R^1R^2NOR^3$ (e.g. $R^1 = R^2 = PhCH_2$, $R^3 = H$: $\Delta G^{\ddagger}_{inv}(257\ K) = 12.8 \pm 0.2$ kcal/mol; $R^1 = CHMe_2$, $R^2 = PhCH_2$, $R^3 = COCH_3$: $\Delta G^{\ddagger}_{inv}(244\ K) = 12.0 \pm 0.2$ kcal/mol; $R^1 = CH_3$, $R^2 = PhCH_2$, $R^3 = CH_3$: $E_a(257\ K) = 12.4 \pm 0.5$ kcal/mol in CS_2-solution) [10]. Thus, complexes **8** probably represent cases in which the barrier to nitrogeninversion (interconverting C_2-symmetric enantiomers) is higher than that for the nitrogen-t-butyl rotational process [11]. The few unambiguously assigned $\Delta G^{\ddagger}_{rot}$-values due to hindered $N{-}CMe_3$ rotation in t-butyl amines are of exactly the same magnitude as those observed for the metallacyclic N-t-butyl substituted hydroxylamine derivatives described here (**8**: $\Delta G^{\ddagger}_{rot}$ (190 K) = 8.2 ± 0.5 kcal/mol vs. e.g. $\Delta G^{\ddagger}_{rot}(151\ K) = 8.3 \pm 0.3$ kcal/mol for $PhCH_2(Me_3C)NCl$) [12]. We thus believe that, regardless of the nitrogen hybridization present in **8**, the line shape in the NMR spectra at low temperature is determined by the rate of the hindered N–C(t-butyl) rotational process for these organometallic hydroxylamine derivatives.

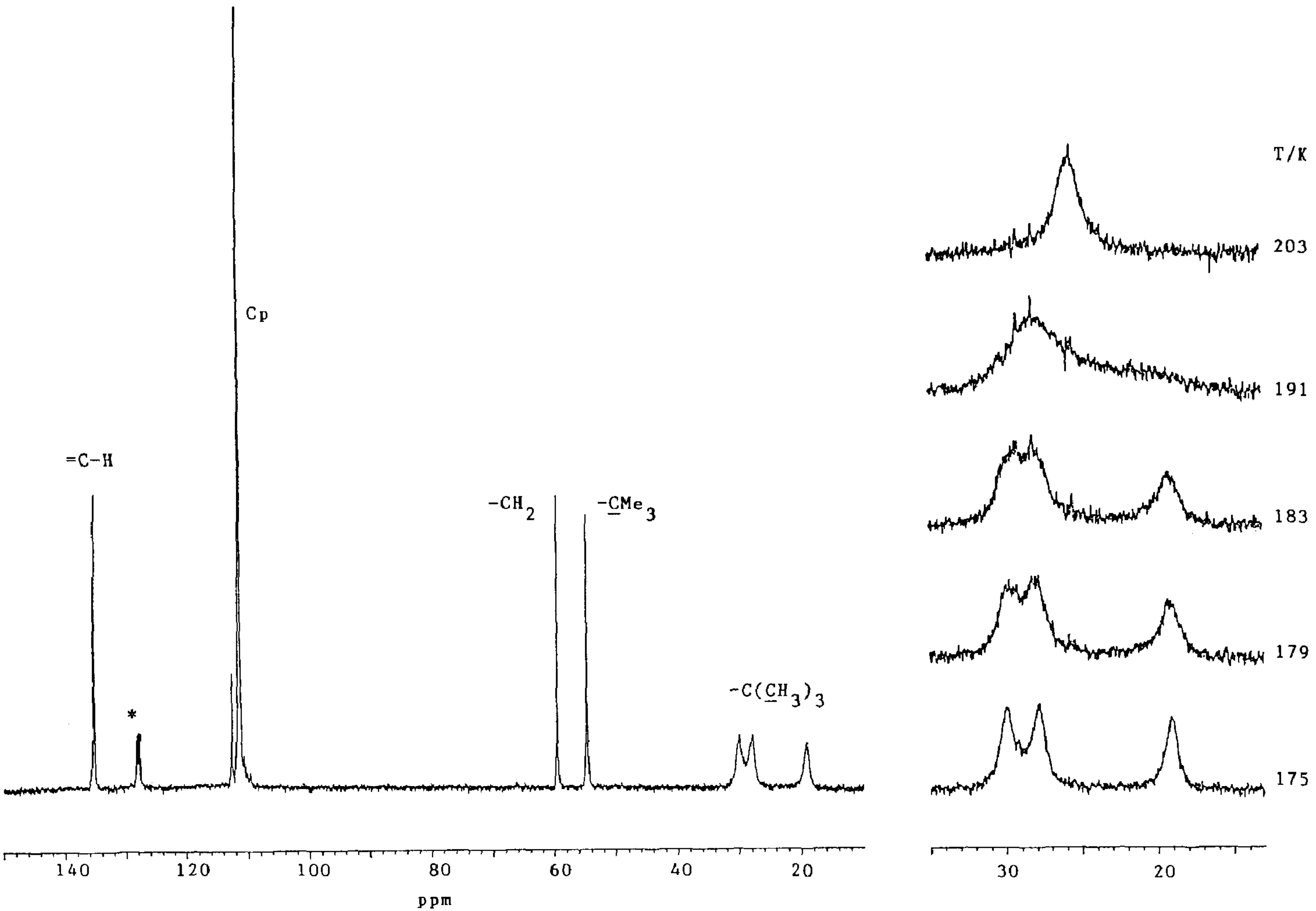


Fig. 1. ^{13}C NMR spectrum of **8b** in CS_2/C_6D_6 (9/1) at $T = 175$ K (left). Dynamic NMR spectra of the $C(CH_3)_3$ section are shown at different temperatures (right).

Experimental

Reactions were carried out under argon by Schlenk techniques. Solvents were dried and freshly distilled from potassium/benzophenone prior to use. Deuterated solvents benzene-d_6, toluene-d_8, and *o*-xylene-d_{10} were dried over sodium/potassium alloy, then distilled and stored under argon. The following spectrometers were used: NMR, Bruker WM 400 (^{13}C 100.6 MHz, low temperature), Bruker WP 200 SY (^{1}H 200.1 MHz, ^{13}C 50.3 MHz), and Bruker WP 80 (^{1}H 80 MHz, high temperature); IR, Nicolet 5DXC FT IR spectrometer; MS, CH 7/Varian MAT (low resolution, EI, 70 eV), and 8200 Finnigan MAT (exact mass determinations). Elemental analyses were performed at the Institut für Anorganische Chemie der Universität Würzburg. Melting points are uncorrected. (Butadiene)dicyclopentadienyl-zirconium (**1a**) and -hafnium (**1b**) [13] and 2-methyl-2-nitrosopropane [14] were prepared by published procedures.

Synthesis of $Cp_2\overline{MON(Bu^t)(CH_2CH{=}CHCH_2N(Bu^t)O}$, *M = Zr (**8a**), Hf (**8b**)*

1. M = Zr (**8a**): Toluene (20 ml) was added to a mixture of 2-methyl-2-nitrosopropane (700 mg, 8.04 mmol) and $Zr(\eta\text{-}C_4H_6)(\eta\text{-}C_5H_5)_2$ (990 mg, 3.59 mmol). The blue solution was stirred in the dark at room temperature for 90 min to give a green solution. The solvent was removed and a pentane extract of the residue filtered and reduced to dryness. A further pentane extraction, filtration and solvent removal, followed by drying in vacuo afforded (**8a**) as a green powder (480 mg, 30%), m.p. 92–94° (dec.). MS. M^+ $m/z = 455\text{–}448$, rel. intensity found (calcd.): 0.01 (0.02), 0.06 (0.07), 0.08 (0.09), 0.34 (0.35), 0.10 (0.10), 0.42 (0.43), 0.44 (0.48), 1.00 (1.00); exact mass $m/z = 448.1667$ (found), 448.1663 (calcd. for $C_{22}H_{34}N_2O_2Zr$). $[M - C_5H_5]^+$ $m/z = 390\text{–}383$, rel. intensity found (calcd.): 0.01 (0.01), 0.05 (0.06), 0.06 (0.07), 0.32 (0.35), 0.07 (0.07), 0.35 (0.40), 0.38 (0.42), 1.00 (1.00); IR (KBr): ν(NO) 1261 cm^{-1}. ^{1}H NMR (CS_2/benzene-d_6): δ 6.00 (s, 10H, Cp), 5.39 (m, 2H =CH), 3.17, 2.40 (m, 2H each, CH_2), 0.96 (s, 18H, t-butyl). ^{13}C NMR (toluene-d_8, ambient temperature, ^1J(CH) in Hz): δ 26.0 (q, 126, CH_3), 54.8 (t, 133, CH_2), 59.4 (s, $C(CH_3)_3$), 112.8 (d, 171, Cp), 135.8 (d, 153, =CH). The white residue from the first pentane extraction was identified as $[Zr(\mu\text{-}O)(\eta\text{-}C_5H_5)_2]_3$ (425 mg, 50%) by comparison of its ^{1}H NMR spectrum (benzene-d_6, δ 6.21, Cp) with that of an authentic sample prepared by the published procedure [6].

2. M = Hf (**8b**): By the procedure described above, 2-methyl-2-nitrosopropane (370 mg, 4.25 mmol) and $Hf(\eta\text{-}C_4H_6)(\eta\text{-}C_5H_5)_2$ (750 mg, 2.07 mmol) gave **8b** as a green powder (320 mg, 29%). m.p. 112–113°. Anal. Found: C, 49.63; H, 6.72; N, 5.03. $C_{22}H_{34}N_2O_2Hf$ calcd.: C, 49.21; H, 6.38; N, 5.22%. MS. M^+ $m/z = 540\text{–}534$, rel. intensity found (calcd.): 0.03 (0.03), 0.23 (0.24), 1.00 (1.00), 0.53 (0.54), 0.84 (0.81), 0.53 (0.50), 0.13 (0.13); exact mass $m/z = 538.2102$ (found), 538.2088 (calcd.). $[M - C_5H_5]^+$ $m/z = 475\text{–}469$, rel. intensity found (calcd.): 0.02 (0.02), 0.19 (0.19), 1.00 (1.00), 0.56 (0.51), 0.84 (0.80), 0.60 (0.51), 0.15 (0.13); exact mass $m/z = 473.1698$ (found), 473.1697 (calcd.). IR (KBr): ν(NO) 1262 cm^{-1}. ^{1}H NMR (benzene-d_6): δ 5.98 (s, 10H, Cp), 5.32 (m, 2H, =CH), 3.13, 2.41 (m, 2H each, CH_2), 1.00 (s, 18H, t-Bu). ^{13}C NMR (benzene-d_6, ambient temperature, ^1J(CH) in Hz): δ 26.0 (q, 125, CH_3), 55.0 (t, 134, CH_2), 59.6 (s, $C(CH_3)_3$), 111.6 (d, 172, Cp), 135.4 (d, 154, =CH). The white residue was identified as $[Hf(\mu\text{-}O)(\eta\text{-}C_5H_5)_2]_3$ (240 mg, 36%) by comparison of its ^{1}H NMR spectrum (benzene-d_6, δ 6.18, Cp) [6].

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