2424 Inorg. Chem. **2001,** *40,* 2424−2426

Synthesis of the Titanium Compound $[(MeC_5H_4)TiCl(\mu\text{-}NSiMe_3)]_2$ with Migration of a $SiMe_3$ Group and Preparation of $Cp_2ZrCl(\eta^2\text{-}NHNCHSiMe_3\}$[†]

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Received January 3, 2001

Introduction

Diazoalkanes have been attracting wide interest as versatile reagents in synthetic organic and organometallic chemistry because of their high reactivity and variety of coordination modes possible for metal complexes.[1] Complexes containing the diazoalkyl ligand C-bonded to a metal are obtained by the reaction of a lithiated diazomethane with metal halides.[2] The α-metalated diazoalkanes would be potential precursors for the metal carbene or carbyne complexes.[3] Early transition metals especially in their higher oxidation states have the ability to form extremely strong bonds with N donors.[4] The η^2-N_2- and terminal-bonded η^1-N-metal diazoalkane complexes[5] are known. One well-defined coordination mode obtained for the CN_2 ligand at the dinuclear center is the μ-η^1 binding using only the terminal N atom.[6]

Boche and co-workers[7] calculated the energies of lithiated CH_2N_2 derivatives and found that the N-lithiated N-isocyano amide (C≡N−NHLi) is the most stable Li isomer. However, in the case of trimethylsilyl diazomethane, the most stable isomer (in the crystalline state obtained from ether solution) is the N-lithiated nitrile imide ($Me_3SiC{\equiv}N{-}NLi$), which cocrystallized with the lithium salt of the bis(trimethylsilyl)triazene in diethyl ether.[8] However, only C−Li attachments and no N−Li ones were found in the solid-state structure of the THF complex of lithiated trimethylsilyl diazomethane.[9]

Herein we present the synthesis of an imido-bridged dinuclear titanium complex and the formation of an η^2-hydrazonato zirconium complex.

Results and Discussion

The reaction of a THF solution of $(MeC_5H_4)TiCl_3$ with an equivalent amount of $Me_3SiCLiN_2$ at −78 °C resulted in the formation of reddish brown crystals of the imido-bridged dinuclear complex $[(MeC_5H_4)TiCl(\mu\text{-}NSiMe_3)]_2$ (**1**, eq 1). The

$$(MeC_5H_4)TiCl_3 + Me_3SiCLiN_2 \xrightarrow[-78\ °C]{THF} \underset{\mathbf{1}}{[(MeC_5H_4)TiCl(\mu\text{-}NSiMe_3)]_2} \quad (1)$$

mechanism for the formation of **1** is not clear. One intermediate might be a terminal nitrogen atom μ-η^1 binding a dinuclear titanium center (μ-η^1-metal diazoalkane complexes are known,[5] and the imido dinuclear titanium complex is accessible and stable in the sterically less demanding RR′Ti system),[10] which then undergoes rearrangement of the trimethsilyl group from carbon to the terminal nitrogen atom. The elimination of a CN group leads to the imido dinuclear complex **1**. However, we were not able to identify any CN species. Furthermore, an intermolecular migration of a Me_3Si moiety could also be possible. Me_3SiCl formed in the first step under the condition reported could then go on to react with other nitrogen-containing species to yield compound **1**. This result is in contrast to those obtained from the reaction of diazo derivatives with a wide variety of other metal compounds, which lead to the formation of metal carbene complexes concurrent with the liberation of N_2 or metal complexes with retention of N_2. No reaction was observed when $(MeC_5H_4)_2TiCl_2$ was treated with $Me_3SiCLiN_2$ under the same conditions. Meanwhile, Bergman et al.[11] reported on the synthesis of an η^2-N_2-titanium diazoalkane complex $Cp^*_2Ti(\eta^2\text{-}N_2CHSiMe_3)$ ($Cp^* = Me_5C_5$) from the reaction of $Cp^*_2Ti(C_2H_4)$ with Me_3SiCHN_2. An η^3-N,N,O-titanium compound $Cp_2Ti(\eta^3\text{-DEDM})$ (DEDM = EtO_2CCN_2)[12] was prepared from the reaction of $Cp_2Ti(CO)_2$ with DEDM. Furthermore, we were not able to isolate the imido-bridged dinuclear complex from

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[†] Dedicated to Professor Karl Heinz Büchel on the occasion of his 70th birthday.

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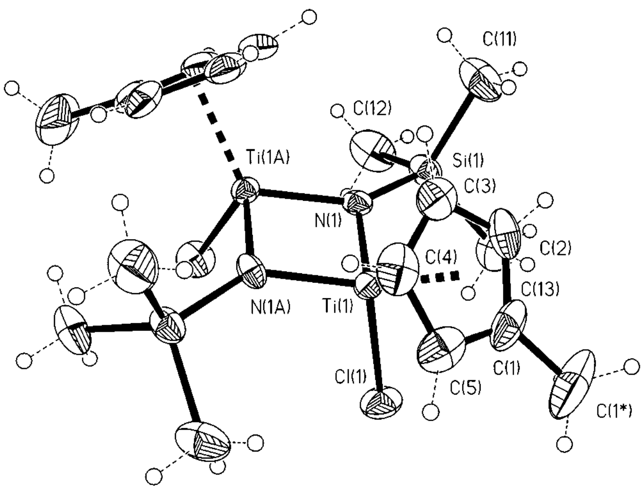

Figure 1. Molecular structure of **1**.

the reaction of Cp^*TiCl_3 with $Me_3SiCLiN_2$. However, the direct reaction of Cp_2ZrHCl with Me_3SiCHN_2 in toluene at room temperature produced the η^2-hydrazonato complex $Cp_2ZrCl(\eta^2\text{-}NHNCHSiMe_3)$ (**2**, eq 2) in high yield. The intermediate

$$Cp_2ZrHCl + Me_3SiCHN_2 \xrightarrow{\text{toluene}} \underset{\textbf{2}}{Cp_2ZrCl(\eta^2\text{-}NHNCHSiMe_3)} \quad (2)$$

for the formation of **2** should be the diazoalkane molecule that coordinates to the electrophilic zirconium(IV) using the more basic terminal nitrogen atom.[13] Hydrozirconation of the zirconium-bonded dinitrogen leads to the insertion of a diazoalkane into the zirconium hydrogen bond and the formation of **2**.

Compounds **1** (reddish brown) and **2** (colorless) are crystalline solids. **1** is stable above the melting point (242 °C), while **2** starts to decompose at 143 °C. The IR spectrum of **2** shows absorptions at 3381 and 3080 cm^{-1}, assignable to the N$-$H and NC$-$H stretching frequency, respectively. In solution the ^1H NMR spectrum of **2** gives two resonances (0.13 and 0.07) for the hydrogen atoms of the Me_3Si group, an additional two (6.01 and 5.63) for the hydrogen atoms of the Cp groups, and two resonances (6.84 and 6.82) for the hydrogen atom of the NH group; however, only a singlet (1.06) was found for the NC$-$H proton. This phenomenon is indicative for the electronic delocalization over the C$-$N$-$N unit, which leads to an easy interconversion in solution of the cis and trans isomer.

The molecular structures of **1** and **2** are shown in Figures 1 and 2. Details of the data collection, structure solution, and refinement are given in Table 1.

Compound **1** crystallizes in the tetragonal space group $R\bar{4}2_1c$, and **2** crystallizes in the monoclinic space group $P2_1/c$. The selected bond lengths and angles for **1** and **2** are presented in Table 2. The central core of **1** contains a planar four-memberd $Ti_2(\mu\text{-}N)_2$ ring, with each titanium bonded to a MeC_5H_4 group and a terminal chlorine atom. The $Ti_2(\mu\text{-}N)_2$ plane is distorted with slight difference in Ti$-$(μ-$NSiMe_3$) bond lengths (1.916(2) and 1.878(2) Å) of 0.038 Å. The Ti$-$(μ-$NSiMe_3$) and Ti···Ti (2.7758(10) bond lengths as well as the (μ-$NSiMe_3$)$-$Ti$-$(μ-$NSiMe_3$) angles (85.94(11)°) are typical for imido-bridged titanium dimers.[14] The $SiMe_3$ groups are slightly bent out of the $Ti_2(\mu\text{-}N)_2$ plane toward the same side where the chlorine atoms are oriented, which minimizes the steric repulsion between the MeC_5H_4 and $SiMe_3$ groups. The X-ray structure analysis of **2** revealed that the diazoalkane ligand is bound to zirconium in a side-on fashion through the two nitrogen atoms.

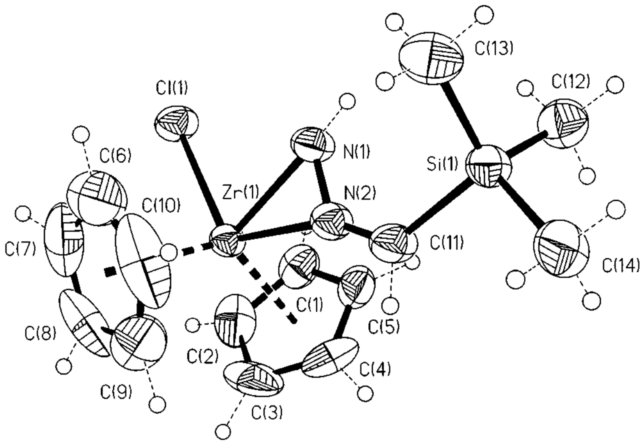

Figure 2. Molecular structure of **2**.

Table 1. Crystallographic Data for **1** and **2**

	1	2
empirical formula	$C_{18}H_{32}Cl_2N_2Si_2Ti_2$	$C_{14}H_{21}ClN_2SiZr{\cdot}C_7H_8$
fw	499.34	372.08 + 92.14
cryst size (mm)	0.8 × 0.4 × 0.4	0.6 × 0.5 × 0.4
cryst syst	tetragonal	monoclinic
space group	$P\bar{4}2_1c$	$P2_1/c$
a (Å)	13.4571(15)	13.0530(13)
b (Å)	13.4571(15)	17.627(3)
c (Å)	13.724(2)	10.477(2)
α (deg)	90	90
β (deg)	90	109.425(12)
γ (deg)	90	90
V (Å^3)	2485.4(6)	2273.3(7)
Z	4	4
ρ_c (g mm^{-3})	1.334	1.356
μ (mm^{-1})	0.960	0.661
F(000)	1040	960
2θ range (deg)	7.32$-$44.92	7.02$-$45.04
no. data: measd, unique	3699, 1622 (R_{int} = 0.0256)	2966, 2956 (R_{int} = 0.0699)
R,[a] wR2[b] ($I > 2\sigma(I)$)	0.0304, 0.0779	0.0305, 0.0772
R,[a] wR2[b] (all data)	0.0312, 0.0804	0.0334, 0.0820
GOF, S[c]	1.123	1.052
no. refined params	122	247
no. restraints	0	0
largest diff peak, hole (e Å^{-3})	+0.529, $-$0.251	+0.692, $-$0.372

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)]^{1/2}$. [c] $S = [\sum w(F_o^2 - F_c^2)^2/\sum(n - p)]^{1/2}$.

Table 2. Selected Bond Distance (Å) and Angles (deg) for **1** and **2**

1		2	
Ti(1)$-$N(1A)	1.878(2)	Zr$-$N(1)	2.142(3)
Ti(1)$-$N(1)	1.916(2)	Zr$-$N(2)	2.193(3)
Ti(1)$-$Ti(1A)	2.7758(10)	N(1)$-$N(2)	1.331(4)
Ti(1)$-$Cl(1)	2.2831(11)	N(2)$-$C(11)	1.293(4)
N(1)$-$Si(1)	1.758(2)	Si$-$C(11)	1.866(3)
N(1)$-$Ti(1A)	1.878(2)	Zr$-$Cl	2.5299(9)
N(1A)$-$Ti(1)$-$N(1)	85.94(11)	N(1)$-$Zr$-$N(2)	35.72(10)
Ti(1A)$-$N(1)$-$Ti(1)	94.05(11)	N(2)$-$N(1)-Zr	74.2(2)
N(1A)$-$Ti(1)$-$Cl(1)	105.69(8)	N(1)$-$N(2)-Zr	70.1(2)
N(1)$-$Ti(1)$-$Cl(1)	104.11(8)	N(2)$-$C(11)-Si	129.2(3)
Si(1)$-$N(1)$-$Ti(1A)	135.18(15)	N(2)$-$Zr$-$Cl	122.20(7)
Si(1)$-$N(1)$-$Ti(1)	130.14(14)	N(1)$-$Zr$-$Cl	86.48(7)

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The bond lengths of Zr−N(1) (2.142(3) Å), Zr−N(2) (2.193(3) Å), N(1)−N(2) (1.331(4) Å), and C(11)−N(2) (1.293(4) Å) are comparable to those found in $Cp_2Zr(\eta^2\text{-}NHNCPh_2)$ (Zr−N(1) 2.103(3) Å, Zr−N(2) 2.283(3) Å, N(1)−N(2) 1.338(4) Å, and C(17)−N(2) 1.307(4), Å, respectively).[13] The difference between Zr−N(1) and Zr−N(2) (0.051 Å) is less pronounced than that in $Cp_2ZrCl(\eta^2\text{-}NHNCPh_2)$ (0.180 Å). The N(1)−N(2) bond distance is shorter than expected for a N−N single bond (N−N 1.434(4) Å in $Cp_2Zr(\eta^2\text{-}N_2Ph_2)\cdot py$ (py = pyridine))[15] but longer than a N═N double bond (N═N 1.254 Å in MeN═NMe).[16] The C(11)−N(2) distance of 1.293(4) Å is between a C−N single bond (C−N 1.474(4) Å in MeN═NMe) and a C−N double bond (C═N 1.269(35) Å in $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NHNCPh_2)]$).[17] The partial N−N and C−N double bond character indicates an electronic delocalization over the C−N−N unit, in agreement with the ^1H NMR spectrum.

In summary we have shown that the reaction of methylcyclopentadienyltitanium trichloride with lithiated trimethylsilyl diazomethane leads to the imido-bridged dinuclear titanium complex. The mechanism for the formation of **1** is not known. This is an interesting example of a migration of a trimethylsilyl group when a diazo derivative is reacted with a transition metal compound. Obviously, during the reaction an elimination of a CN group occurs. Moreover, the less sterically hindered and strong Lewis acidic titanium center is important for the formation of **1**. For compound **2** an electronic delocalization over the C−N−N unit leads to an easy interconversion of the isomer ($ZrN(H)-N{=}CHSiMe_3$) from cis to trans in solution, in agreement with the two resonances for $SiMe_3$, Cp, and NH groups, respectively, in the ^1H NMR spectrum.

Experimental Section

General Procedures. All experimental manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. Samples prepared for spectral measurements as well as for reactions were manipulated in a glovebox. Solvents were dried using conventional procedures, distilled under nitrogen, and degassed prior to use. Deuterated NMR solvents were treated with K/Na alloy, distilled, and stored under nitrogen.

Physical Measurements. The NMR spectra were recorded on Bruker AM 250 and Bruker AM 200 spectrometers with $SiMe_4$ as an external standard. Mass spectra were recorded on a Finnigan MAT 8230 mass spectrometer using the EI-MS method. The most intensive peak of an isotope distribution is tabulated. IR spectra are recorded on Bio-Rad FTS-7 spectrometer as Nujol mulls between KBr plates. Elemental analyses were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry, University of Göttingen.

Synthesis of 1. $(MeC_5H_4)TiCl_3$ (0.93 g, 4.0 mmol) in THF (20 mL) was added dropwise to the freshly prepared $Me_3SiCLiN_2$ (4 mmol) in THF (20 mL) at −78 °C. The reaction mixture turned reddish brown immediately. Stirring was continued for 1 h at this temperature. The reaction mixture slowly warmed to room temperature and was stirred for an additional 12 h. Removal of the solvent in vacuo gave a deep-brown solid, which was extracted with toluene (20 mL). After filtration and concentration (to 8 mL), the deep-brown solution was kept at −20 °C for some weeks. Reddish brown crystals of **1** (0.08 g) were obtained. After concentration of the filtrate (to 5 mL) and addition of hexane (10 mL), the solution was kept at −20 °C for 2 days. An additional crop of **1** (0.14 g) was formed. Total yield, 0.22 g (22%); mp, 242 °C. Anal. Calcd for $C_{18}H_{32}Cl_2N_2Si_2Ti_2$ (499.35): C, 43.3; H, 6.5; N, 5.6. Found: C, 43.7; H, 6.5; N, 5.8. IR (Nujol): $\tilde{\nu}$ 1589 s, 1406 m, 1261 s, 1094 vs, 1022 vs, 802 vs, 658 m, 451 m cm^{-1}. EI-MS (*m*/*e* (%)): 498 (32) (M^+), 483 (100) ($M^+ - Me$). ^1H NMR (250 MHz, C_6D_6): δ 6.40−6.37, 5.55−5.53 (m, 8H, C_5H_4), 2.17 (s, 6H, MeC_5), 0.04 (s, 18H, $SiMe_3$). ^{13}C NMR (100 MHz, C_6D_6): δ 114.45, 112.47 (C_5H_4), 15.86 (MeC_5), 3.81 ($SiMe_3$).

Synthesis of 2. Me_3SiCHN_2 (2 m in hexane, 1 mL, 2.0 mmol) was added to a suspension of Cp_2ZrHCl (0.52 g, 2.0 mmol) in toluene (40 mL) at room temperature. After the solid dissolved the solution turned light-yellow within 10 min. Stirring was continued overnight. After concentration (to 5 mL) in vacuo, the light-yellow solution was kept at −20 °C for 1 week. Colorless crystals of **2** were obtained in 93% yield (0.69 g); dec point, 143 °C. The lattice toluene was removed in vacuo. Anal. Calcd for $C_{14}H_{21}ClN_2SiZr$ (372.10): C, 45.2; H, 5.7. Found: C, 45.2; H, 5.6. IR (Nujol): $\bar{\nu}$ 3310 m, 3080 m, 1535 s, 1247 s, 1046 s, 1025 m, 1012 s, 830 vs, 800 vs, 750 m, 692 m, 657 m, 589 m, 482 s cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 6.84, 6.82 (ds, 1H, NH), 6.01, 5.87 (ds, 10H, C_5H_5), 1.06 (s, 1H, CH), 0.13, 0.67 (ds, 9H, Si Me_3).

X-ray Structure Determination of 1 and 2. Single crystals of **1** and **2** suitable for X-ray structural analysis were obtained from toluene by keeping the reaction mixture at −20 °C for 2 months and at 0 °C for 1 week, respectively. The crystals of **1** and **2** were removed from the flask under nitrogen gas and mounted on a glass fiber in a rapidly cooled perfluoropolyether suspension. Data for the structure were collected at 203(2) K on a Stoe-Siemens-AED2 four-circle diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å), performing $2\theta/\omega$ scans. The structures were solved by direct methods (SHELXS-90)[18] and refined with all data by full-matrix least-squares on F^2.[19] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of N−H bonds and those of C−H bonds were added in idealized positions. Other details of the data collection, structure solution, and refinement are listed in Table 1.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supporting Information Available: Tables of crystal data, fractional coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC010007X

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