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Articles

Synthesis of a Dinuclear Complex with a $Zr_2(\mu\text{-NH})_2$ Core in a Two-Phase System[†]

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Treatment of an equivalent amount of $ZrCl_4$ with $[(PN\mathit{t}Bu)_2(\mathit{t}BuNLi\cdot THF)_2]$ in toluene affords the bis(*tert*-butylamido)cyclodiphosph(III)azane zirconium complex $LZrCl_2$ (**1**; L = $(PN\mathit{t}Bu)_2(\mathit{t}BuN)_2$). Ammonolysis of compound **1** has been carried out in the two-phase system liquid ammonia/toluene at −78 °C in the presence of 2 equiv of KH to yield the imido (NH) bridged dinuclear zirconium derivative $[(\eta^3\text{-L})Zr(\mu\text{-NH})]_2$ (**2**). The molecular structure of $[(\eta^3\text{-L})Zr(\mu\text{-NH})]_2$ (**2**) has been determined by X-ray diffraction.

Introduction

Particular attention has been focused on the chemistry of group 4 metal imido complexes since the discovery of C−H bond activation by zirconium imido compounds in 1988.[1] In recent years, considerable progress has been achieved using metal imido compounds, such as C−H bond activation,[2] catalytic hydroamination of alkynes and allenes,[3] dihydrogen activation,[4] [2 + 2] cycloaddition,[5] mediate addition of carbonyl compounds,[6] synthesis and new reactions of heterometallic complexes,[7] and metal nitride film deposition.[8] A variety of group 4 metal imido complexes supported by ligands such as cyclopentadienyl, bulky amides, bis(amidophosphine), amidinates, tetraazaanulene, chloro, siloxy, and alkoxy has been successfully prepared.[9] Imido-bridged dinuclear complexes such as $[Cp_2Zr(\mu\text{-NAr}')]_2$ (Ar′ = 4-$\mathit{t}BuC_6H_4$),[1a,6b] $[(Me_2N)_2Zr(\mu\text{-N}\mathit{t}Bu)]_2$,[10] $[CpTiCl(\mu\text{-NPh})]_2$, $[CpTiCl(\mu\text{-NPh})_2TiCp_2]$,[11] $[(\eta^8\text{-}C_8H_8)M(\mu\text{-NAr})]_2$ (M = Zr, Hf, Ar = 2,6-$\mathit{i}Pr_2C_6H_3$), and $[(MeC_5H_4)ZrCl(\mu\text{-NAr})]_2$[12] are available with sterically less demanding ligands, and thus steric bulk often prevents the formation of imido-bridged dinuclear compounds. Consequently, under these conditions the terminal imido monomers are formed, such as $(Me_4taa)M{=}NAr$ (M = Zr, Hf, Me_4taaH_2 = tetramethyldibenzotetraaza[14]annulene),[5a,13] and $(P_2N_2)Zr{=}N\mathit{t}Bu$ (P_2N_2 = $PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh$).[14] The NH-bridged dinuclear titanium compound $[Cp^*TiMe(\mu\text{-NH})]_2$ (Cp^* = C_5Me_5)[15] and amido−imido−nitrido zirconium clusters[16]

[†] Dedicated to Professor Hartmut Fuess on the occasion of his 60th birthday.

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with μ_3-NH groups have been reported. However, to the best of our knowledge, so far no imido(NH)-bridged dinuclear zirconium complex has been detected or isolated.

In this context, we are interested in studying the derivatives with amido, imido, and nitrido groups formed during the reaction of early-transition-metal precursors with nitrogen-containing compounds. In 1990 the first terminal titanium imido complex $Ph_2P(S)N{=}TiCl_2\cdot 3C_5H_5N$ was structurally characterized.[17] Moreover, we have prepared the imido complexes $[(Me_3SiC_5H_4)TiCl(\mu\text{-}N\textit{t}Bu)]_2$, $[Cp'TiCl(\mu\text{-}NSnMe_3)]_2$ (Cp′ = Cp*, $Me_3SiC_5H_4$),[18] $[CpTiCl(\mu\text{-}N\textit{t}Bu)]_2$, $[CpTi(NH\textit{t}Bu)(\mu\text{-}N\textit{t}Bu)]_2$,[19] $[(MeC_5H_4)TiF(\mu\text{-}NPh)]_2$, $[(Me_3SiC_5H_4)TiF(\mu\text{-}N\textit{t}Bu)]_2$,[20] $[(\textit{t}BuNH)_2M(\mu\text{-}N\textit{t}Bu)]_2$, $[Cp^*M(NHPh)(\mu\text{-}NPh)]_2$ (M = Zr, Hf), and $Cp^*Zr{=}NAr(NHAr)\cdot C_5H_5N$.[21] We reported already on the reaction of Cp^*TiMe_3 with excess ammonia[22] to yield $[(Cp^*Ti)_3(\mu_3\text{-}N)(\mu\text{-}NH)_3]$ and furthermore on the reaction of L'_2TiCl_2 (L′ = $p\text{-}MeC_6H_4C(NSiMe_3)_2$) with $NaNH_2$ in liquid ammonia and toluene[23] to obtain $[(L'Ti)_6(\mu_3\text{-}N)_2(\mu_3\text{-}NH)_6\cdot 6C_7H_8]$. More recently, from the reaction of $(MeC_5H_4)_2ZrCl_2$ with K (Na or $NaNH_2$) in liquid ammonia and toluene,[24] we recovered the square-pyramidal zirconium cluster $[\{(MeC_5H_4)Zr\}_5(\mu_5\text{-}N)(\mu_3\text{-}NH)_4(\mu\text{-}NH_2)_4]$. Herein we describe the synthesis of the first NH-bridged dinuclear zirconium complex supported by the bis(*tert*-butylamido)cyclodiphosph(III)azane ligand.

Results and Discussion

Treatment of $ZrCl_4$ with $L(Li\cdot THF)_2$ in toluene at 80 °C results in the formation of colorless crystals of $LZrCl_2$ (**1**) in 66% yield. Further reaction of **1** with KH (1:2 molar ratio) in liquid ammonia and toluene at −78 °C yields $[(\eta^3\text{-}L)Zr(\mu\text{-}NH)]_2$ (**2**; eq 1). It is assumed that the

$$\underset{\mathbf{1}}{2LZrCl_2} \xrightarrow[\text{liq } NH_3\text{, toluene, } -78\ ^\circ C]{4KH} \underset{\mathbf{2}}{[(\eta^3\text{-}L)Zr(\mu\text{-}NH)]_2} + 4KCl + 4H_2 \quad (1)$$

formation of **2** proceeds via two possible intermediates. The in situ formation of the amide (NH_2^-) from the reaction of KH with ammonia[25] leads to the diamide intermediate $[LZr(NH_2)_2]$, which after inter- or intramolecular elimination of ammonia is converted to **2**. The other proposed intermediate is the zirconium amido hydride $[LZr(NH_2)H]$, which undergoes an inter- or intramolecular hydrogen elimination to yield **2**. Recently an imido *ansa*-zirconium dihydride was prepared from a liquid ammonia/toluene system.[24] Meanwhile, Bercaw et al.[26] reported on the ammonolysis of $Cp^*_2MH_2$ (M = Ti, Zr) that did not lead to the imido compound; instead, the amido complex $Cp^*_2M(NH_2)H$ was formed, due to the steric bulk of the Cp* ligand. Obviously, the in situ formation of the amide and the liquid ammonia/toluene two-phase system as well as the organic ligand are important for the generation of **2**. The KH has two functions in this reaction: first, to react with the zirconium chloride to form KCl, and second, to generate a Zr−H or $Zr{-}NH_2$ species as an intermediate.

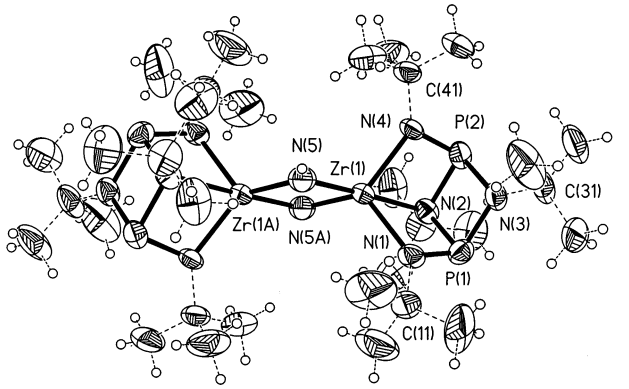

Figure 1. Molecular structure of **2** (50% probability ellipsoids).

Compounds **1** and **2** are colorless crystalline solids. The melting point of **1** is 170 °C, while compound **2** decomposes above 220 °C. The IR spectrum of **2** shows a broad absorption at 3378 cm^{-1}, assignable to the N−H stretching frequency. The most intense peak in the EI mass spectrum of **1** appears at *m*/*e* 493 ($M^+ - Me$), and the signal at 508 (7%) is assigned to the molecular ion. The EI mass spectrum of **2** shows peaks corresponding to M^+ (*m*/*e* 904, 38%) and $M^+ - \textit{t}Bu - Me$ (*m*/*e* 832, 83%).

The molecular structure of **2** is shown in Figure 1. Compound **2** crystallizes in the monoclinic space group $P2_1/c$. The central core of **2** contains an ideally planar (centrosymmetrical) four-membered $Zr_2(\mu\text{-}N)_2$ ring. The $(\mu\text{-}NH){-}Zr{-}(\mu\text{-}NH)$ angle (78.7(3)°; Table 2) is smaller, while the bond lengths of $Zr{-}(\mu\text{-}NH)$ (from 2.039(8) to 2.057(8) Å, average 2.048 Å) and Zr···Zr (3.168(2) Å) are similar to those found in $[(Me_2N)_2Zr(\mu\text{-}N\textit{t}Bu)]_2$ ($(\mu\text{-}N\textit{t}Bu){-}Zr{-}(\mu\text{-}N\textit{t}Bu)$, 83.10(5)°; $Zr{-}(\mu\text{-}N\textit{t}Bu)$, 2.060 Å; Zr···Zr, 3.092(1) Å),[10] $[Cp_2Zr(\mu\text{-}NAr')]_2$ ($(\mu\text{-}NAr'){-}Zr{-}(\mu\text{-}NAr')$, 80.56(7)°; $Zr{-}(\mu\text{-}NAr')$, 2.096 Å; Zr···Zr, 3.198(1) Å),[6b] and in $[(MeC_5H_4)ZrCl(\mu\text{-}NAr)]_2$ ($(\mu\text{-}NAr){-}Zr{-}(\mu\text{-}NAr)$, 96.98°; $Zr{-}(\mu\text{-}NAr)$, 2.016 Å; Zr···Zr, 3.087(2) Å),[12] respectively. The coordination sphere of each zirconium is completed by the η^3-bis(*tert*-butylamido)cyclodiphosph(III)azane ligand.

The bond lengths of Zr(1)−N(1) (2.116(7) Å) and Zr(1)−N(4) (2.129(7) Å) are comparable to those found in $[(MeSiN\textit{t}Bu)_2(N\textit{t}Bu)_2]ZrCl_2$ (2.075(3) and 2.089(3) Å).[27] The sums of the angles at N(1) and N(4) are 359.1 and 359.2°, respectively. The approximately triangular-planar coordination environment indicates that the N(1)

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Table 1. Crystallographic Data for 2

empirical formula	$C_{32}H_{74}N_{10}P_4Zr_2$
fw	905.45
cryst size (mm)	$0.9\times 0.9\times 0.6$
cryst syst	monoclinic
space group	$P2_1/c$
a (Å)	13.618(7)
b (Å)	18.426(7)
c (Å)	18.479(8)
β (deg)	90.25(3)
V (Å^3)	4637(3)
Z	4
ρ_c (g cm^{-3})	1.297
μ(mm^{-1})	0.620
F(000)	1904
2θ range (deg)	7.28−47.50
no. of data: measd, unique	6971, 6913 ($R_{int} = 0.0614$)
R1,[a] wR2[b] ($I > 2\sigma(I)$)	0.0859, 0.2027
R1, wR2 (all data)	0.1078, 0.2203
goodness of fit, S[c]	1.107
no. of refined params	457
no. of restraints	0
largest diff peak/hole (e Å^{-3})	+1.418/−1.109

[a] $R1 = \sum||F_o| - |F_c|/\sum|F_o|$. [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 Lengths (Å) and Bond Angles (deg) for $[(\eta^3\text{-L})Zr(\mu\text{-NH})]_2$ (2)

Bond Lengths			
Zr(1)−N(5)	2.039(8)	Zr(1)−N(5A)	2.057(8)
Zr(1)−N(1)	2.116(7)	Zr(1)−N(4)	2.129(7)
Zr(1)−N(2)	2.399(7)	Zr(1)−Zr(1A)	3.168(2)
P(1)−N(1)	1.686(8)	P(2)−N(4)	1.689(8)
P(1)−N(3)	1.733(8)	P(2)−N(3)	1.726(8)
P(1)−N(2)	1.789(8)	P(2)−N(2)	1.781(8)

Bond Angles			
N(5)−Zr(1)−N(5A)	78.7(3)	Zr(1)−N(5)−Zr(1A)	101.3(3)
N(5)−Zr(1)−N(1)	113.5(3)	N(5A)−Zr(1)−N(1)	119.4(3)
N(5)−Zr(1)−N(4)	114.5(3)	N(5A)−Zr(1)−N(4)	121.1(3)
N(5)−Zr(1)−N(2)	176.4(3)	N(5A)−Zr(1)−N(2)	97.8(3)
N(1)−Zr(1)−N(2)	67.9(3)	N(4)−Zr(1)−N(2)	67.5(3)
C(11)−N(1)−P(1)	119.7(7)	P(1)−N(1)−Zr(1)	104.4(3)
C(11)−N(1)−Zr(1)	135.0(6)	P(2)−N(4)−Zr(1)	104.1(3)
C(41)−N(4)−P(2)	118.6(6)	C(41)−N(4)−Zr(1)	136.3(6)

and N(2) atoms are nearly sp^2-hybridized. Therefore, the N(1) and N(2) atoms donate their lone-pair electrons into the empty d orbitals of zirconium as three-electron donors, which is in agreement with the bonding situation in $[(MeSiN\textit{t}Bu)_2(N\textit{t}Bu)_2]ZrCl_2$. The bond lengths of P(1)−N(1) (1.686(8) Å), P(1)−N(3) (1.733(8) Å), and P(1)−N(2) (1.789(8) Å) are similar to those found in $[(\eta^3\text{-L})In]_2$ (1.670(3), 1.723(3), and 1.801(3) Å, respectively).[28]

A smaller (μ-N)−Zr−(μ-N) angle was also found in the imido-bridged complex $[(Me_4taa)Zr(1)(\mu\text{-NAr})_2Zr(2)(NHAr)_2]$,[29] in which the ($\mu$-N)−Zr(1)−($\mu$-N) angle (75.0(10)°) is smaller than (μ-N)−Zr(2)−(μ-N) (85.7(11)°), due to the more sterically demanding Me_4taa group at Zr(1). Furthermore, the imido bridge (μ-NR) has to bend more if R is a bulky group. The (μ-NAr)−Zr−(μ-NAr) angles (96.98°) in $[(MeC_5H_4)ZrCl(\mu\text{-NAr})]_2$[12] are obviously larger than those in $[Cp_2Zr(\mu\text{-NAr}')]_2$ (80.56(7)°).[1a] Therefore, compound **2**, with a bulky ligand on zirconium and smaller imido (NH) bridges, has smaller (μ-NH)−Zr−(μ-NH) angles.

Conclusion

We have shown that the ligand on zirconium and the method of preparation are important for the synthesis of the first NH-bridged dizirconium compound. Moreover, the liquid ammonia/toluene two-phase system and the bis(*tert*-butylamido)cyclodiphosph(III)azane ligand are obviously essential for obtaining **2**. Because of the bulk of the ligand and the smaller imido (NH) bridges on zirconium, the molecular structure of **2** has smaller (μ-NH)−Zr−(μ-NH) angles compared to those found in other organoimido-bridged zirconium dimers. The nearly planar coordination geometry at the amido nitrogen atoms suggests that two nitrogen atoms are functioning as three-electron donors for each zirconium.

Experimental Section

General Data. 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.

The NMR spectra were recorded on Bruker AM 250 or MSL 500 NMR spectrometer with $SiMe_4$ as external standard. Mass spectra were recorded on a Finnigan MAT 8230 or Varian MAT CH 5 mass spectrometer using the EI-MS method. The most intensive peak of an isotope distribution is tabulated. IR spectra are recorded on a 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 $LZrCl_2$ (1). A suspension of $ZrCl_4$ (3.26 g, 14.0 mmol) and $[(PN\textit{t}Bu)_2(\textit{t}BuNLi\cdot THF)_2]$[30] (7.0 g, 13.9 mmol) in toluene (100 mL) was stirred for 48 h at 80 °C. After filtration and concentration in vacuo to 20 mL the resulting light yellow solution was stored at 0 °C for 1 week. Colorless crystals of **1** (3.9 g) were obtained. After concentration of the filtrate to 10 mL, storage at −20 °C for 3 days gave an additional crop of **1** (0.8 g). Total yield: 4.7 g (66%). Mp: 170 °C. IR (Nujol): $\tilde{\nu}$ 1392 (m), 1220 (m), 1186 (vs), 1084 (w), 1027 (s), 1003 (m), 946 (s), 868 (s), 824 (vs), 781 (s), 724 (w), 584 (m), 538 (w), 479 (m) cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6): δ 1.41 (s, 18 H, *t*Bu), 1.27 (s, 18 H, *t*Bu). ^{13}C NMR (126 MHz, C_6D_6): δ 59.39, 59.28 (CMe_3), 55.02, 54.92, 54.83 (CMe_3), 33.47, 33.49 ($C\textit{Me}_3$), 29.85, 29.80, 29.75 ($C\textit{Me}_3$). ^{31}P NMR (202 MHz, C_6D_6): δ 103.43. EI-MS: *m/e* (%) 508 (7) (M$^+$), 493 (100) (M$^+$ − Me). Anal. Calcd for $C_{16}H_{36}Cl_2N_4P_2Zr$ (508.6): C, 37.8; H, 7.1; N, 11.0. Found: C, 38.5; H, 7.4; N, 11.0.

Synthesis of $[LZr(\mu\text{-NH})]_2$ (2). Ammonia (50 mL) was condensed onto a suspension of **1** (1.02 g, 2.0 mmol) and KH (0.17 g, 4.2 mmol) in toluene (80 mL) at −78 °C and stirred for 1 h. Then the excess ammonia was allowed to evaporate from the reaction mixture over a period of 4 h. During this time the mixture was slowly warmed to room temperature. The resulting solution was filtered. The colorless solution was concentrated in vacuo to 15 mL and stored at 0 °C for 1 week. Colorless crystals of **2** (0.10 g) were obtained. After concentration of the filtrate to 5 mL the solution was kept at −20 °C for 3 days. An additional crop of **2** (0.15 g) was formed. Total yield: 0.25 g (28%). Dec pt: 220 °C. IR (Nujol): $\tilde{\nu}$ 3378 (w), 1589 (w), 1360 (s), 1192 (vs), 1135 (w), 1079 (w), 1032 (m), 997 (s), 956 (m), 859 (s), 813 (s), 775 (s), 678 (w), 641 (w), 580 (vs), 517 (s), 477 (m), 431 (m) cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6): δ 8.84, 7.99, 7.72 (br. s, NH), 1.58, 1.45, 1.40, 1.23 (s,

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*t*Bu). ^{13}C NMR (126 MHz, C_6D_6): δ 52.37, 52.26, 52.14 (*C*Me$_3$), 51.57, 51.47 (*C*Me$_3$), 33.24, 31.16 (C*Me*$_3$), 31.94, 31.88, 31.83 (C*Me*$_3$). EI-MS: *m*/*e* (%) 904 (38) (M$^+$), 847 (46) (M$^+$ − *t*Bu), 832 (83) (M$^+$ − *t*Bu − Me), 58 (100) (*t*BuH$^+$). Anal. Calcd for $C_{32}H_{74}N_{10}P_4Zr_2$ (905.4): C, 42.5; H, 8.2; N, 15.5. Found: C, 42.3; H, 8.4; N, 15.5.

X-ray Analysis of 2. Single crystals of **2** suitable for X-ray structural analysis were obtained from toluene by keeping the reaction mixture at 0 °C for 1 week. The crystal of **2** was 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 200(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 structure was solved by direct methods (SHELXS-90)[31] and refined with all data by full-matrix least squares on F^2.[32] 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.

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

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