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Ammonolysis of M-Cl Bonds of Organozirconium(IV) and Titanium(III) Chlorides in a Liquid Ammonia/Toluene Two Phase System[(*)]

by

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Summary. Treatment of $(MeC_5H_4)_2ZrCl_2$ with K (Na) or $NaNH_2$ in liquid ammonia/toluene at −78 °C led to the pentanuclear zirconium cluster $[\{(MeC_5H_4)Zr\}_5(\mu_5-N)(\mu_3-NH)_4(\mu-NH_2)_4]$ (**1**) and the alkali metal aggregate $[(MeC_5H_4)M]_n$ (M = K (**2**) or Na). Reaction of Cp^*_2TiCl with $NaNH_2$ in liquid ammonia/toluene at −78 °C yielded $Cp^*_2TiNH_2$ (**3**).

Thin layers of MN compounds have many applications as technologically important materials due to their unique combination of properties [1–6]. An important discipline of inorganic and organometallic transition metal chemistry involves the preparation of solid-state materials via solution methods using molecular precursors [7, 8]. The ready availability and high reactivity of ammonia renders this small molecule attractive as a nitrogen source. In recent years several polynuclear early transition metal complexes containing nitrogen have been obtained via solution ammonolysis of precursor alkyl or dialkylamido organometallic derivatives [9–13]. Generally, complete ammonolysis of early transition metal halides in liquid ammonia is very difficult to achieve [14–24]. Furthermore, it has been demonstrated that the metal ions of high oxidation state (e.g. VCl_4) are more readily ammonolysed than the same metal ions of low oxidation state (e.g. VCl_3) [25, 26].

We are interested in studying the derivatives with amido, imido, and nitrido groups formed during the reaction of early transition metal precursors with NH_3 or other nitrogen-containing compounds. We reported already on

[(*)] Dedicated to Professor Adam Bielański on the occasion of his 90th birthday.

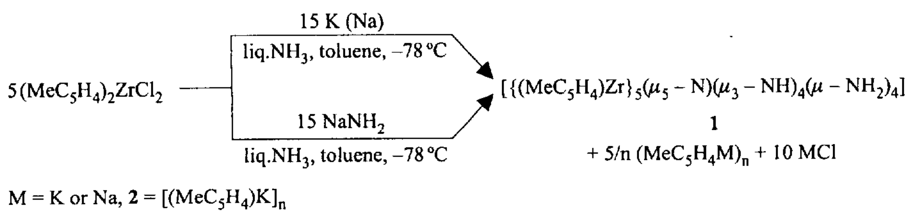
Key words: ammonolysis, zirconium, titanium, metal aggregate.

the reaction of Cp^*TiMe_3 with excess of ammonia to yield $[(Cp^*Ti)_3(\mu_3-N)(\mu-NH)_3]$ [27] and the reaction of $L_2TiCl_2(L = p-MeC_6H_4C(NSiMe_3)_2)$ with $NaNH_2$ in liquid ammonia/toluene to obtain $[(LTi)_6(\mu_3-N)_2(\mu_3-NH)_6 \cdot 6(C_7H_8)]$ [28]. Furthermore, we recovered the square pyramidal zirconium cluster $[\{(MeC_5H_4)Zr\}_5(\mu_5-N)(\mu_3-NH)_4(\mu-NH_2)_4]$ by the reaction of $(MeC_5H_4)_2ZrCl_2$ with K (Na or $NaNH_2$) in liquid ammonia/toluene [29]. The first (NH) bridged dinuclear zirconium complex supported by the bis(*tert*-butylamido)cyclodiphosph(III)azane ligand has been prepared by treatment of $L'ZrCl_2$ ($L' = (tBuNP)_2(tBuN)_2$) with KH in liquid ammonia/toluene [30].

Herein we report on liquid ammonia/toluene as an effective two phase system for the complete ammonolysis of M–Cl bonds of zirconium(IV) chloride and also of titanium(III) chloride.

Results and Discussion

We have previously communicated the synthesis and X-ray structural characterization of $[\{(MeC_5H_4)Zr\}_5(\mu_5-N)(\mu_3-NH)_4(\mu-NH_2)_4]$ (**1**, Scheme 1) [29]. Treatment of $(MeC_5H_4)_2ZrCl_2$ with 3 equivalents of alkali metal or alkali metal amide led to the ammonolysis of two Zr–Cl bonds and one (MeC_5H_4)–Zr bond of the starting material and the formation of **1** and



Scheme 1

$[(MeC_5H_4)M]_n$ (M = K, Na; **2**, M = K). The central core of **1** consists of five Zr atoms forming a square pyramid. The four triangular faces of this pyramid are capped by NH groups, the four edges of the base are bridged by NH_2 units, and in the center of the basal plane of the Zr_5 cluster there is a μ_5–N atom (Fig. 1). These three different N species in **1** can be regarded as amide (NH_2^-), imide (NH^{2-}) and nitride (N^{3-}) groups. Further studies have shown that compounds **1** and **2** were formed when $(MeC_5H_4)_2ZrCl_2$ was reacted with K in liquid ammonia/toluene at −78 °C under dinitrogen or argon gas, indicating that all the nitrogen atoms in **1** stem from NH_3. A possible mechanism for the formation of **1** and **2** is shown in Scheme 2.

When NH_3 was condensed onto a solution of $(MeC_5H_4)_2ZrCl_2$ in toluene, a white precipitate was formed immediately. Equation (1) represents the initial coordination of ammonia molecules to form the zirconium chloride

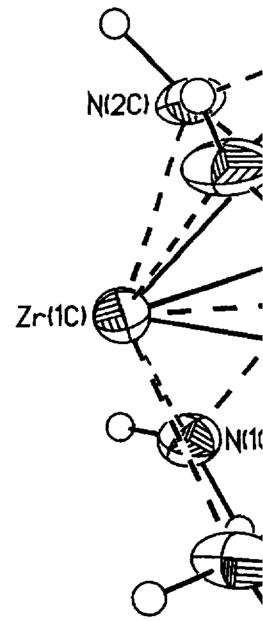
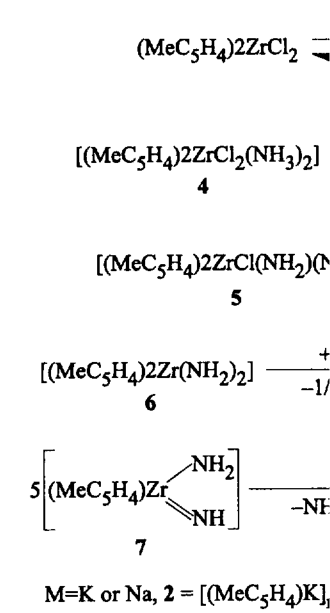


Fig. 1. Central core of [
(1)



nonia to yield $[(Cp^*Ti)_3(\mu_3 -$
$(L = p-MeC_6H_4C(NSiMe_3)_2)$
obtain $[(LTi)_6(\mu_3 - N)_2(\mu_3 -$
ered the square pyramidal zir-
$NH)_4(\mu - NH_2)_4]$ by the reac-
$H_2)$ in liquid ammonia/toluene
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$)_2)$ with KH in liquid ammo-

uene as an effective two phase
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$\mu_3-NH)_4(\mu-NH_2)_4]$ (**1**, Sche-
th 3 equivalents of alkali metal
s of two Zr–Cl bonds and one
1 and the formation of **1** and

$eC_5H_4)Zr\}_5(\mu_5 - N)(\mu_3 - NH)_4(\mu - NH_2)_4]$
1
$+ 5/n\ (MeC_5H_4M)_n + 10\ MCl$

he central core of **1** consists of
he four triangular faces of this
edges of the base are bridged
plane of the Zr_5 cluster there is
N species in **1** can be regarded
(N^{3-}) groups. Further studies
formed when $(MeC_5H_4)_2ZrCl_2$
ne at −78 °C under dinitrogen
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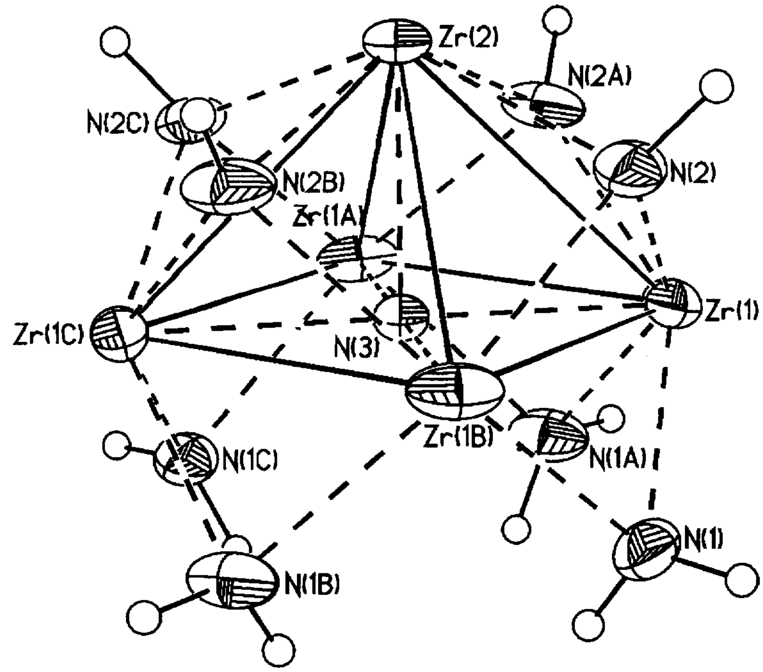

Fig. 1. Central core of $[\{(MeC_5H_4)Zr\}_5(\mu_5 - N)(\mu_3 - NH)_4(\mu - NH_2)_4]$ (**1**) (50% probability ellipsoids)

$$(MeC_5H_4)2ZrCl_2 \underset{}{\overset{2NH_3}{\rightleftharpoons}} \underset{\mathbf{4}}{[(MeC_5H_4)2ZrCl_2(NH_3)_2]} \quad (1)$$

$$\underset{\mathbf{4}}{[(MeC_5H_4)2ZrCl_2(NH_3)_2]} \xrightarrow[-MCl,\ -1/2H_2]{+M} \underset{\mathbf{5}}{[(MeC_5H_4)2ZrCl(NH_2)(NH_3)]} \quad (2)$$

$$\underset{\mathbf{5}}{[(MeC_5H_4)2ZrCl(NH_2)(NH_3)]} \xrightarrow[-MCl,\ -1/2H_2]{+M} \underset{\mathbf{6}}{[(MeC_5H_4)2Zr(NH_2)_2]} \quad (3)$$

$$\underset{\mathbf{6}}{[(MeC_5H_4)2Zr(NH_2)_2]} \xrightarrow[-1/2H_2]{+M} \underset{\mathbf{7}}{\left[(MeC_5H_4)Zr{\textstyle\genfrac{}{}{0pt}{}{NH_2}{NH}}\right]} + 1/n[(MeC_5H_4)M]n \quad (4)$$

$$5\underset{\mathbf{7}}{\left[(MeC_5H_4)Zr{\textstyle\genfrac{}{}{0pt}{}{NH_2}{NH}}\right]} \xrightarrow[-NH_3]{} \underset{\mathbf{7}}{[\{(MeC_5H_4)Zr\}_5(\mu_5\text{-}N)(\mu_3\text{-}NH)_4(\mu\text{-}NH_2)_4]} \quad (5)$$

M=K or Na, **2** = $[(MeC_5H_4)K]_n$

Scheme 2

adduct **4**. Removal of the solvents *in vacuo* resulted in the isolation of the starting material rather than an ammonolysis product was obtained. Equation (1) demonstrates this equilibrium. The zirconium atom in **4** withdraws electron density from the nitrogen atom leading to a more acidic hydrogen of the coordinated ammonia. Consequently, the addition of an alkali metal results in the displacement of a chlorine atom from the zirconium of **4** and the formation of the zirconium amides **5** and **6** (Eqs. (2) and (3)). Subsequently this leads to the amidoimidozirconium intermediate **7** with concomitant loss of a MeC_5H_4 group from the zirconium amide as $(MeC_5H_4)M$ which under aggregation leads to stable $[(MeC_5H_4)M]_n$ (Eq. (4)). The amidoimidozirconium intermediate **7** is unstable and very easily forms the pentamer under simultaneous elimination of one molecule of NH_3 (Eq. (5)). Treatment of $(MeC_5H_4)_2ZrCl_2$ with $NaNH_2$ in liquid ammonia/toluene leads also to **1** and $[(MeC_5H_4)Na]_n$ via the same intermediates, while NH_3 is formed instead of H_2 in Eqs. (2), (3), and (4).

Attempts to detect or isolate any intermediate in the formation of **1** failed. Treatment of $(MeC_5H_4)_2ZrCl_2$ with 1, 1.5, and 2 equivalents of K (Na) in liquid ammonia/toluene at −78 °C leads also to the formation of **1** in relatively low yields of 5%, 12%, and 14%, respectively. Furthermore, light yellow liquid products were formed in the reaction of $(MeC_5H_4)_2ZrCl_2$ with K(Na) in liquid ammonia/toluene in a 1:0.5 molar ratio at −78 °C.

In comparison, treatment of Cp^*_2TiCl with an equivalent of $NaNH_2$ in liquid ammonia/toluene at −78 °C then slowly warming to room temperature resulted in the formation of the titanium(III) amide $Cp^*_2TiNH_2$ (**3**, Scheme 3) in 27% yield. This result is in sharp contrast to that obtained from the reaction of Cp_2TiCl with liquid ammonia at −36 °C, which leads to the cleavage of the Cp–Ti rather than the Ti–Cl bond and the formation of $CpTiCl(NH_2)$. Furthermore, it was predicted that this reaction at room temperature would result in the cleavage of the second Cp–Ti bond with the formation of $TiCl(NH_2)_2$ [31]. Compound **3** has been previously prepared from the reaction of Cp^*_2TiMe with NH_3 and structurally characterized by Brady *et al.* [32].

$$Cp^*_2TiCl + NaNH_2 \xrightarrow[-78\,^{\circ}C]{\text{liq. } NH_3\text{, toluene}} \underset{\mathbf{3}}{Cp^*_2TiNH_2} + NaCl$$

Scheme 3

Crystal da

Empirical formula
Formula weight
Temperature
Wavelength
Crystal system
Space group
Unit cell dimensions
Volume
Z
Density (calculated)
Absorption coefficient
$F(000)$
Crystal size
θ range for data collecti
Index ranges
Reflections collected
Independent reflections
Refinement method
Data / restraints / para
Goodness-of-fit on F^2
Final R indices [$I > 2\sigma($
R indices (all data)
Largest difference peak

Compound **2** is a colo
very sensitive to moisture,
EI mass spectrum of **2** fra
$[MeC_5H_4^+]$ were observed.
at δ5.47–5.40 ppm for the
nance at δ2.17 ppm corres
the cyclopentadienyl ring.
[33]. Characterization of **2**
analysis) shows that nearly
removed while evaporating

esulted in the isolation of the
product was obtained. Equa-
rconium atom in **4** withdraws
g to a more acidic hydrogen of
addition of an alkali metal re-
om the zirconium of **4** and the
qs. (2) and (3)). Subsequently
ediate **7** with concomitant loss
e as $(MeC_5H_4)M$ which under
q. (4)). The amidoimidozirco-
ily forms the pentamer under
NH_3 (Eq. (5)). Treatment of
nonia/toluene leads also to **1**
ates, while NH_3 is formed in-

nediate in the formation of **1**
, 1.5, and 2 equivalents of K
eads also to the formation of
%, respectively. Furthermore,
e reaction of $(MeC_5H_4)_2ZrCl_2$
:0.5 molar ratio at −78 °C.
th an equivalent of $NaNH_2$ in
wly warming to room temper-
um(III) amide $Cp^*_2TiNH_2$ (**3**,
arp contrast to that obtained
nmonia at −36 °C, which leads
Ti–Cl bond and the formation
ted that this reaction at room
e second Cp–Ti bond with the
has been previously prepared
d structurally characterized by

→ $Cp^*_2TiNH_2$ + NaCl
3

TABLE 1

Crystal data and structure refinement for **2**

Empirical formula	C_6H_7K
Formula weight	118.22
Temperature	133(2) K
Wavelength	0.71073 C
Crystal system	monoclinic
Space group	$C2/c$
Unit cell dimensions	a = 33.959(7) Å
	b = 10.607(2) C β = 120.65(3)°
	c = 17.998(4) Å
Volume	5577.3(19) $Å^3$
Z	36
Density (calculated)	1.267 Mg/m^3
Absorption coefficient	0.725 mm^{-1}
$F(000)$	2232
Crystal size	0.3 × 0.3 × 0.2 mm^3
θ range for data collection	2.04–24.71°
Index ranges	$-39 \leqslant h \leqslant 34$, $0 \leqslant k \leqslant 12$, $0 \leqslant l \leqslant 21$
Reflections collected	33764
Independent reflections	4657 [R(int) = 0.0563]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4657 / 255 / 312
Goodness-of-fit on F^2	1.062
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0531$, $wR2 = 0.1397$
R indices (all data)	$R1 = 0.0631$, $wR2 = 0.1473$
Largest difference peak and hole	1.093 and −0.590 e $Å^{-3}$

Compound **2** is a colorless crystalline solid melting at 220 °C. It is very sensitive to moisture, decomposition occurs immediately in air. In the EI mass spectrum of **2** fragments at m/z 39 (62%) [K^+] and 79 (100%) [$MeC_5H_4^+$] were observed. The ^1H NMR spectrum of **2** shows a multiplet at δ5.47–5.40 ppm for the protons of the C_5H_4 group and a singlet resonance at δ2.17 ppm corresponding to the protons of the methyl group of the cyclopentadienyl ring. Dissolving **2** in THF leads to the THF solvate [33]. Characterization of **2** (by ^1H NMR spectrum, EI-MS and elemental analysis) shows that nearly all the coordinated or lattice THF molecules are removed while evaporating the solvent *in vacuo*.

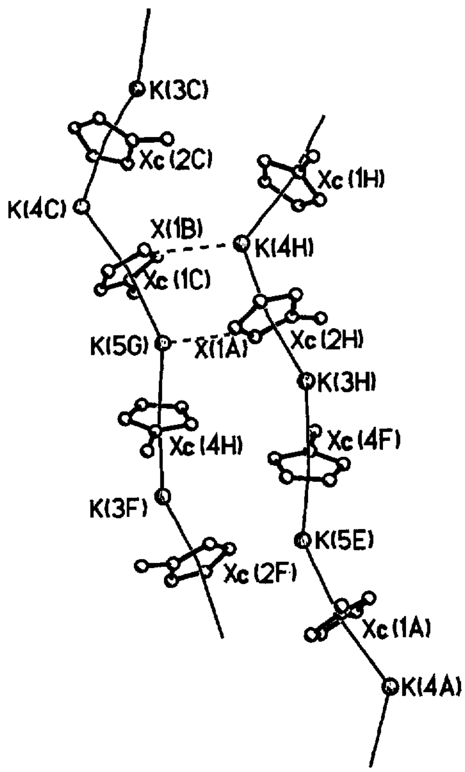

Fig. 2. Molecular structure of **2**

The molecular structure of **2** is shown in Fig. 2. Selected bond lengths and angles for **2** are presented in Table 2. Compound **2** crystallizes in the monoclinic space group $C2/c$. The X-ray structural analysis of this aggregate reveals that **2** contains units of a parallel arranged one-dimensional infinite "supersandwich complex". The units are made up of a repeating sequence of potassium atoms and η^5-methylcyclopentadienyl rings.

The K–Xc distance (2.78 Å to 2.86 Å, av 2.81 Å) is comparable to those found in $[(Me_3SiC_5H_4)K]_n$ (2.78 Å) [33] and in $[(C_5Me_5)K \cdot 2py]_n$ (2.79 Å) [34]. The K–X distance (3.21 Å to 3.28 Å, av 3.25 Å) indicates an additional weak bonding relationship between potassium atoms and the neighboring cyclopentadienyl units of the other chain, which results in a distortion of the geometry around each potassium atom and as a consequence a zig-zag chain structure of **2**. The Xc–K–Xc angle (126.9° to 135.7°, av 130.9°) is similar to that found in $[(C_5Me_5)K \cdot 2py]_n$ (138°) and smaller than that in $[(Me_3SiC_5H_4)K]_n$ (150.7°). The average K–K–K and K–Xc–K angles as well as the K···K distance within the chains are 133.0°, 160.0° and 5.60 Å, respectively.

Selected di

K(4H)-Xc(1H)
K(3H)-Xc(2H)
K(5G)-Xc(1C)
K(4C)-Xc(1C)
K(4H)-X(1B)
K(3C)-K(4C)
K(4C)-K(5G)
Xc(2C)-K(4C)-
Xc(1C)
Xc(2H)-K(4H)-
Xc(1B)
Xc(4H)-K(5G)-
Xc(1C)
Xc(1C)-K(5G)-

(*) Xc and X represent the centers of t
MeC_5H_4 rings, respectively. The Xc an
to the reality and are only used to calcu

Compound **3** is a black
The IR spectrum of **3** show
the NH_2 stretching frequen
the ^1H NMR spectrum of **3**
unresolved resonances. Th
of **3** appears at m/z 317 [
assigned to the molecular i

In conclusion we have s
Cl bonds is achieved by t
metals or alkali metal ami
1 is thought to proceed vi
The Ti–Cl bond is preferen
equivalent of $NaNH_2$. The
solubility of the organic a
preferentially occurs at th
ammonia/toluene two pha

Synthesis of [(MeC₅H₄)M]ₙ
condensed onto a suspension of

TABLE 2

Selected distances (Å) and angles (°) for **2**[(*)]

K(4H)–Xc(1H)	2.79	K(4H)–Xc(2H)	2.82
K(3H)–Xc(2H)	2.78	K(3H)–Xc(4F)	2.86
K(5G)-Xc(1C)	2.84	K(5G)-Xc(4H)	2.78
K(4C)–Xc(1C)	2.79	K(4C)–Xc(2C)	2.82
K(4H)–X(1B)	3.28	K(5G)–X(1A)	3.21
K(3C)–K(4C)	5.58	K(3H)–K(4H)	5.58
K(4C)–K(5G)	5.60	K(3H)–K(5E)	5.61
Xc(2C)–K(4C)–Xc(1C)	126.9	Xc(2H)–K(4H)–Xc(1H)	126.9
Xc(2H)-K(4H)–Xc(1B)	110.1	Xc(1H)–K(4H)–Xc(1B)	120.1
Xc(4H)–K(5G)–Xc(1C)	135.7	Xc(4H)–K(5G)–X(1A)	110.5
Xc(1C)–K(5G)–X(1A)	135.7		

(*) Xc and X represent the centers of the MeC_5H_4 rings and the centers of the adjacent carbon atoms in the MeC_5H_4 rings, respectively. The Xc and X positions are artificially calculated points. They do not correspond to the reality and are only used to calculate the distances given in Table 2.

Compound **3** is a black crystalline solid with a melting point of 202 °C. The IR spectrum of **3** shows a broad absorption at 3437 cm^{-1}, assignable to the NH_2 stretching frequencies. Due to the paramagnetism of titanium(III), the ^1H NMR spectrum of **3** recorded at room temperature shows broad and unresolved resonances. The most intensive peak in the EI mass spectrum of **3** appears at m/z 317 [$M^+ - NH_2 - H$], and the signal at 334 (53%) is assigned to the molecular ion.

In conclusion we have shown that the complete ammonolysis of the M–Cl bonds is achieved by treatment of organometallic chlorides with alkali metals or alkali metal amide in liquid ammonia/toluene. The formation of **1** is thought to proceed via the zirconium amide and imide intermediates. The Ti–Cl bond is preferentially cleaved when Cp_2^*TiCl is treated with one equivalent of $NaNH_2$. The two phase system ammonia/toluene increases the solubility of the organic and inorganic components, so that the reaction preferentially occurs at the interface. Therefore we assume that the liquid ammonia/toluene two phase system is important for the above reactions.

Experimental

*Synthesis of [(MeC_5H_4)M]$_n$ (M = K (**2**) or Na).* Method A: Ammonia (80 mL) was condensed onto a suspension of $(MeC_5H_4)_2ZrCl_2$ (2.56 g, 8.0 mmol) and potassium (0.94

g, 24 mmol) in toluene (80 mL) at −78 °C and stirred for 1 h. The excess of ammonia was allowed to evaporate from the reaction mixture under stirring over 4 h. During this period the mixture slowly warmed to room temperature. The reaction mixture was filtered and the light yellow solution was kept at room temperature for four weeks. Colorless crystals of **1** were obtained in 25% yield (0.40 g). Single crystals of **2** suitable for X-ray structural analysis were obtained from toluene by keeping the filtrate for two months at room temperature. The residue was extracted with THF (30 mL). After filtration and concentration to 10 mL, the resulting light yellow solution was stored at room temperature for four weeks. Colorless crystals of **2** were formed in 40% yield (0.38 g). Method B: In a procedure similar to method A, ammonia (50 mL) was condensed onto a solution of $(MeC_5H_4)_2ZrCl_2$ (1.61 g, 5.0 mmol) in toluene (60 mL) at −78 °C. $NaNH_2$ (0.59 g, 15.1 mmol) was added to the resulting mixture. **1** and $[(MeC_5H_4)Na]_n$ were obtained in 53% (0.52 g) and 55% (0.28 g) yields, respectively.

Compound **2**: Mp: 250 °C. IR (Nujol): $\tilde{\nu}$ = 3047(*m*), 1615(w), 1555(w), 1261 (w), 1261 (m), 1234 (w), 1037 (s), 1025 (s), 966 (w), 927 (m), 891(m), 852 (m), 782 (vs), 723 (vs), 638 (s) cm^{-1}. EI-MS: *m*/*z*(%)79(100)$[MeC_5H_4^+]$, 39 (20) $[K^+]$. ^1H NMR (250 MHz, toluene-d_8, 100 °C): δ5.47 − 5.40 (m, 4 H, C_5H_4), 2.17 (s, 3 H, MeC_5). Elemental analysis for $(C_6H_7K)_n$ (118.23×n): calcd: C 61.0, H 6.0; found: C 60.2, H 6.5.

Synthesis of **3**: In a procedure similar to method A for the preparation of **2** ammonia (40 mL) was condensed onto a suspension of Cp_2^*TiCl (1.06 g, 3.0 mmol) and $NaNH_2$ (0.12 g, 3.1 mmol) in toluene (60 mL) under stirring at −78 °C. After filtration and partial removal of the solvent *in vacuo*, the resulting deep brown solution was kept at 0 °C for 3 weeks. Black crystals of **3** were obtained in a 27% yield (0.27 g).

Compound **3**: Mp: 202 °C. IR (Nujol): $\tilde{\nu}$ = 3437 (w), 1653 (w), 1536 (m), 1262 (w), 1155 (w), 1064 (m), 1024 (s), 970 (m), 800 (m), 722 (s), 617 (s), 599 (s), 571 (m), 491 (s), 428 (s) cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ2.50 − 1.97 (br m), 1.82, 1.79, 1.76, 1.66, 1.15 (br s). EI-MS: *m*/*z* (%): 334 (53) $[M^+]$, 317 (100) $[M^+ - NH_3]$. Elemental analysis for $C_{20}H_{32}NTi$ (334.4): calcd: C 71.8, H 9.6, N 4.2; found: C 70.9, H 9.4, N 3.6.

X-ray structural determination of **2**. A crystal of **2** was removed from the flask under argon gas and mounted on a glass fiber in a rapidly cooled perfluoropolyether [35]. Diffraction data were collected on a Stoe-Siemens-Huber four-circle-diffractometer coupled to a Siemens CCD area detector at 133(2) K with graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å), performing φ and ω scans. The structure was solved by direct methods using SHELXS-97 [36] and refined against F^2 on all data by full-matrix least-squares with SHELXL-97 [37]. All non-hydrogen atoms were refined anisotropically with similarity and rigid bond restraints. All hydrogen atoms bonded to carbon were included in the models at geometrically calculated positions and refined using a riding model. Details of the data collection, structure solution, and refinement are listed in Table 1. Crystallographic data (excluding structure factors) for the structure **2** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 161811. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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ed for 1 h. The excess of ammonia
ınder stirring over 4 h. During this
e. The reaction mixture was filtered
ıperature for four weeks. Colorless
ıgle crystals of **2** suitable for X-ray
eeping the filtrate for two months
THF (30 mL). After filtration and
ion was stored at room temperature
ı 40% yield (0.38 g). Method B: In
was condensed onto a solution of
L) at −78 °C. $NaNH_2$ (0.59 g, 15.1
$[eC_5H_4)Na]_n$ were obtained in 53%

7(m), 1615(w), 1555(w), 1261 (w),
m), 891(m), 852 (m), 782 (vs), 723
, 39 (20) $[K^+]$. ^1H NMR (250 MHz,
(s, 3 H, MeC_5). Elemental analysis
I: C 60.2, H 6.5.

A for the preparation of **2** ammonia
Cl (1.06 g, 3.0 mmol) and $NaNH_2$
ng at −78 °C. After filtration and
g deep brown solution was kept at
a 27% yield (0.27 g).

(w), 1653 (w), 1536 (m), 1262 (w),
2 (s), 617 (s), 599 (s), 571 (m), 491
– 1.97 (br m), 1.82, 1.79, 1.76, 1.66,
00) $[M^+ - NH_3]$. Elemental analysis
ound: C 70.9, H 9.4, N 3.6.

f **2** was removed from the flask un-
pidly cooled perfluoropolyether [35].
Iuber four-circle-diffractometer cou-
ith graphite-monochromated $Mo_{K\alpha}$
ns. The structure was solved by di-
ainst F^2 on all data by full-matrix
n atoms were refined anisotropically
ogen atoms bonded to carbon were
positions and refined using a riding
ion, and refinement are listed in Ta-
ctors) for the structure **2** reported
ge Crystallographic Data Centre as
s of the data can be obtained free of
ambridge CB2 1EZ, UK (fax: (+44)

e Deutsche Forschungsgemein-
rie for financial support of this

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Theoretical Sir
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Marek BOCZAR, Mar
Dorota

Presented by I

Summary. Theoretical simula
hyde taking into account an adi
and the low-frequency intramo
tortions of the potential energ
the O–H stretching vibration a
stretching vibrations in the hyc

In this letter we presen
trum of salicylaldehyde ir
taking into account an adi
stretching and the low-freq
resonance interaction betw
present model is based on
tra of hydrogen-bonded s
and medium-strong hydro
Maréchal [1, 2] and the t
spectra of hydrogen-bond
[3–6].

For a three-atomic hyd
ν_b; and q, ν the coordinat
C–H stretching (b) and the
remaining modes are deno

(*) Dedicated to Professor
(**) Corresponding author.

Key words: salicylaldehyc