

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 $(\text{MeC}_5\text{H}_4)_2\text{ZrCl}_2$ with K (Na) or NaNH_2 in liquid ammonia/toluene at -78°C led to the pentanuclear zirconium cluster $\{[(\text{MeC}_5\text{H}_4)\text{Zr}]_5(\mu_5 - \text{N})(\mu_3 - \text{NH})_4(\mu - \text{NH}_2)_4\}$ (**1**) and the alkali metal aggregate $[(\text{MeC}_5\text{H}_4)\text{M}]_n$ ($\text{M} = \text{K}$ (**2**) or Na). Reaction of Cp_2^*TiCl with NaNH_2 in liquid ammonia/toluene at -78°C yielded $\text{Cp}_2^*\text{TiNH}_2$ (**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.

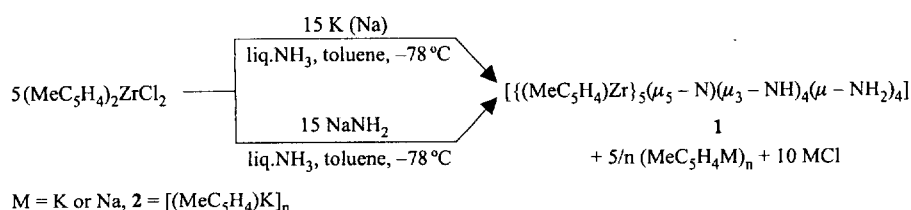
Key words: ammonolysis, zirconium, titanium, metal aggregate.

the reaction of Cp^*TiMe_3 with excess of ammonia to yield $[(\text{Cp}^*\text{Ti})_3(\mu_3 - \text{N})(\mu - \text{NH})_3]$ [27] and the reaction of L_2TiCl_2 ($\text{L} = p\text{-MeC}_6\text{H}_4\text{C}(\text{NSiMe}_3)_2$) with NaNH_2 in liquid ammonia/toluene to obtain $[(\text{LTi})_6(\mu_3 - \text{N})_2(\mu_3 - \text{NH})_6 \cdot 6(\text{C}_7\text{H}_8)]$ [28]. Furthermore, we recovered the square pyramidal zirconium cluster $\{[(\text{MeC}_5\text{H}_4)\text{Zr}]_5(\mu_5 - \text{N})(\mu_3 - \text{NH})_4(\mu - \text{NH}_2)_4\}$ by the reaction of $(\text{MeC}_5\text{H}_4)_2\text{ZrCl}_2$ 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 $\text{L}'\text{ZrCl}_2$ ($\text{L}' = (\text{tBuNP})_2(\text{tBuN})_2$) 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 $\{[(\text{MeC}_5\text{H}_4)\text{Zr}]_5(\mu_5 - \text{N})(\mu_3 - \text{NH})_4(\mu - \text{NH}_2)_4\}$ (**1**, Scheme 1) [29]. Treatment of $(\text{MeC}_5\text{H}_4)_2\text{ZrCl}_2$ with 3 equivalents of alkali metal or alkali metal amide led to the ammonolysis of two Zr-Cl bonds and one $(\text{MeC}_5\text{H}_4)\text{-Zr}$ bond of the starting material and the formation of **1** and



Scheme 1

$[(\text{MeC}_5\text{H}_4)\text{M}]_n$ ($\text{M} = \text{K}, \text{Na}$; **2**, $\text{M} = \text{K}$). 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 $\mu_5\text{-N}$ 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 $(\text{MeC}_5\text{H}_4)_2\text{ZrCl}_2$ 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 $(\text{MeC}_5\text{H}_4)_2\text{ZrCl}_2$ in toluene, a white precipitate was formed immediately. Equation (1) represents the initial coordination of ammonia molecules to form the zirconium chloride

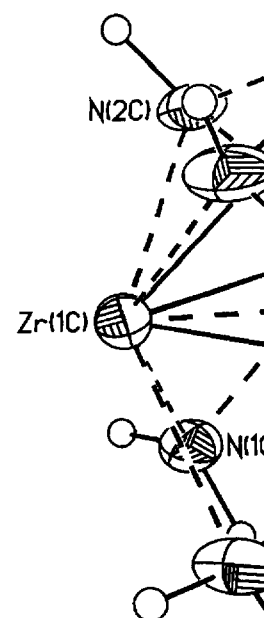
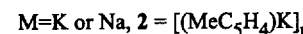
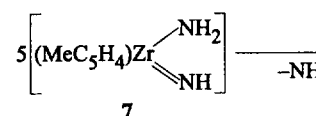
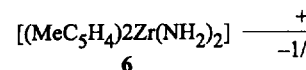
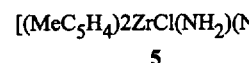
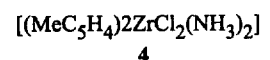
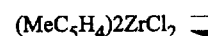


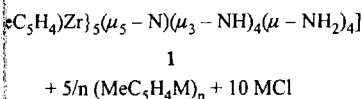
Fig. 1. Central core of **1**



monia to yield $[(Cp^*Ti)_3(\mu_3 - N)(\mu_3 - NH)_4(\mu - NH_2)_4)]$ (1, Scheme 2). The synthesis of **1** was carried out by the reaction of $(MeC_5H_4)_2ZrCl_2$ with KH in liquid ammonia. The reaction of $(MeC_5H_4)_2ZrCl_2$ with KH in liquid ammonia is an effective two phase reaction for the cleavage of zirconium(IV) chloride bonds.

Discussion

The synthesis and X-ray structural analysis of **1** are shown in Scheme 2. The central core of **1** consists of five zirconium atoms and four nitrogen atoms. The zirconium atoms are arranged in a square pyramidal core with a fifth zirconium atom at the center. The nitrogen atoms are arranged in a tetrahedral core with a fifth nitrogen atom at the center. The zirconium atoms are bridged by nitrogen atoms. The zirconium atoms are also bridged by nitrogen atoms. The zirconium atoms are also bridged by nitrogen atoms.



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The reaction of $(MeC_5H_4)_2ZrCl_2$ with KH in liquid ammonia is an effective two phase reaction for the cleavage of zirconium(IV) chloride bonds. Equation (1) represents the reaction of $(MeC_5H_4)_2ZrCl_2$ with KH in liquid ammonia to form the zirconium chloride

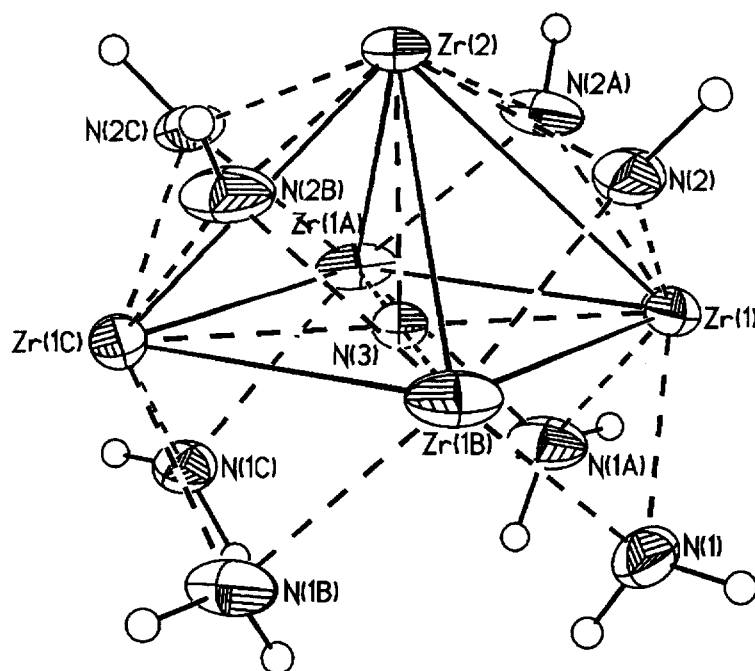
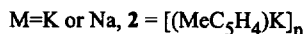
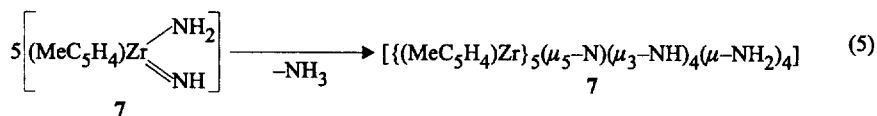
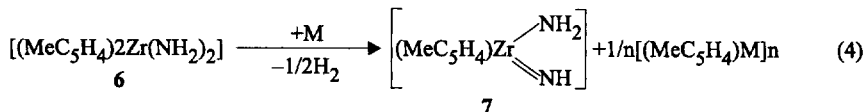
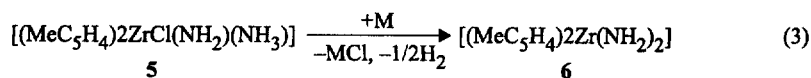
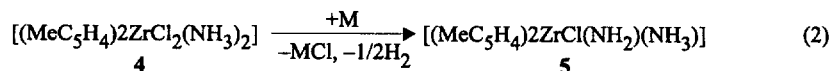
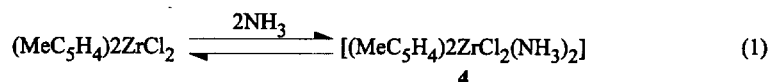


Fig. 1. Central core of $[(MeC_5H_4)_5Zr_5(\mu_5 - N)(\mu_3 - NH)_4(\mu - NH_2)_4]$ (1) (50% probability ellipsoids)

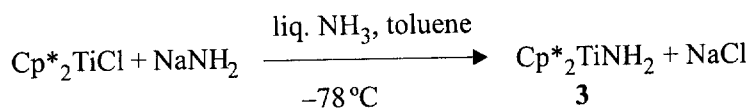


Scheme 2

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 $(\text{MeC}_5\text{H}_4)\text{M}$ which under aggregation leads to stable $[(\text{MeC}_5\text{H}_4)\text{M}]_n$ (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 $(\text{MeC}_5\text{H}_4)_2\text{ZrCl}_2$ with NaNH_2 in liquid ammonia/toluene leads also to **1** and $[(\text{MeC}_5\text{H}_4)\text{Na}]_n$ 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 $(\text{MeC}_5\text{H}_4)_2\text{ZrCl}_2$ with 1, 1.5, and 2 equivalents of $\text{K}(\text{Na})$ 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 $(\text{MeC}_5\text{H}_4)_2\text{ZrCl}_2$ with $\text{K}(\text{Na})$ in liquid ammonia/toluene in a 1:0.5 molar ratio at -78°C .

In comparison, treatment of Cp_2^*TiCl 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 $\text{Cp}_2^*\text{TiNH}_2$ (**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 $\text{CpTiCl}(\text{NH}_2)$. 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 $\text{TiCl}(\text{NH}_2)_2$ [31]. Compound **3** has been previously prepared from the reaction of Cp_2^*TiMe with NH_3 and structurally characterized by Brady *et al.* [32].



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 collection

Index ranges

Reflections collected

Independent reflections

Refinement method

Data / restraints / para

Goodness-of-fit on F^2 Final *R* indices [$I > 2\sigma(I)$]*R* indices (all data)

Largest difference peak

Compound **2** is a color very sensitive to moisture, EI mass spectrum of **2** from $[\text{MeC}_5\text{H}_4^+]$ were observed. at $\delta 5.47\text{--}5.40$ ppm for the nance at $\delta 2.17$ ppm corresponds the cyclopentadienyl ring. [33]. Characterization of **2** (analysis) shows that nearly removed while evaporating

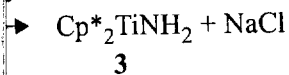
TABLE 1

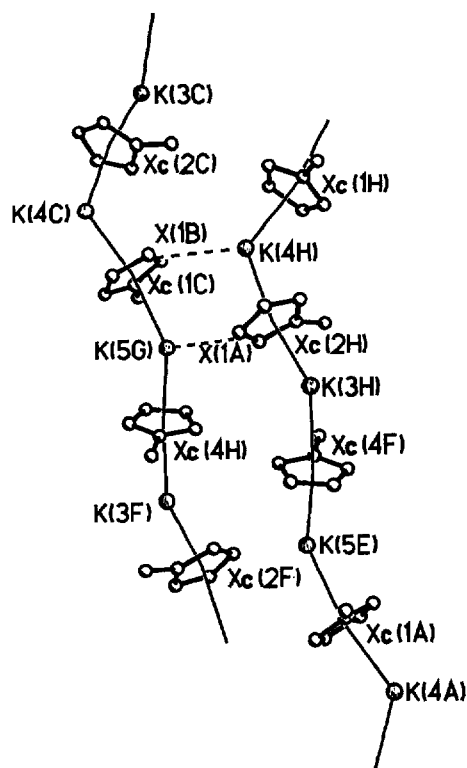
Crystal data and structure refinement for **2**

Empirical formula	C ₆ H ₇ K
Formula weight	118.22
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	C2/c
Unit cell dimensions	$a = 33.959(7) \text{ \AA}$ $b = 10.607(2) \text{ \AA}$ $\beta = 120.65(3)^\circ$ $c = 17.998(4) \text{ \AA}$
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 ≤ h ≤ 34, 0 ≤ k ≤ 12, 0 ≤ l ≤ 21
Reflections collected	33764
Independent reflections	4657 [$R(\text{int}) = 0.0563$]
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%) [MeC₅H₄⁺] were observed. The ¹H NMR spectrum of **2** shows a multiplet at δ 5.47–5.40 ppm for the protons of the C₅H₄ group and a singlet resonance at δ 2.17 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*.

resulted in the isolation of the product was obtained. Equivalents of zirconium atom in **4** withdraws to a more acidic hydrogen of addition of an alkali metal from the zirconium of **4** and the eqs. (2) and (3). Subsequently mediate **7** with concomitant loss as (MeC₅H₄)M which under eq. (4). The amidoimidozirconium forms the pentamer under NH₃ (Eq. (5)). Treatment of ammonia/toluene leads also to **1** ates, while NH₃ is formed intermediate in the formation of **1**, 1.5, and 2 equivalents of K leads also to the formation of %, respectively. Furthermore, the reaction of (MeC₅H₄)₂ZrCl₂ 1:0.5 molar ratio at –78°C. with an equivalent of NaNH₂ in slowly warming to room temperature(III) amide Cp₂*TiNH₂ (**3**, sharp contrast to that obtained ammonia at –36°C, which leads Ti-Cl bond and the formation that this reaction at room the second Cp-Ti bond with the has been previously prepared and structurally characterized by



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 $[(\text{Me}_3\text{SiC}_5\text{H}_4)\text{K}]_n$ (2.78 Å) [33] and in $[(\text{C}_5\text{Me}_5)\text{K} \cdot 2\text{py}]_n$ (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 $[(\text{C}_5\text{Me}_5)\text{K} \cdot 2\text{py}]_n$ (138°) and smaller than that in $[(\text{Me}_3\text{SiC}_5\text{H}_4)\text{K}]_n$ (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 the MeC_5H_4 rings, respectively. The Xc and X are used to the reality and are only used to calculate

Compound **3** is a black solid. The IR spectrum of **3** shows the NH_2 stretching frequency at 3400 cm^{-1} . The ^1H NMR spectrum of **3** shows unresolved resonances. The molecular ion peak of **3** appears at m/z 317 [35], which is assigned to the molecular ion $[(\text{MeC}_5\text{H}_4)\text{M}]_n^+$.

In conclusion we have shown that the formation of Ti-Cl bonds is achieved by treatment of **1** with transition metals or alkali metal amides. The reaction of **1** is thought to proceed via a zwitterionic intermediate. The Ti-Cl bond is preferentially formed by the equivalent of NaNH_2 . The reaction is dependent on the solubility of the organic amide. The reaction preferentially occurs at the ammonia/toluene two phase system.

Synthesis of $[(\text{MeC}_5\text{H}_4)\text{M}]_n$ 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 MeC₅H₄ rings and the centers of the adjacent carbon atoms in the MeC₅H₄ 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 NH₂ 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⁺ - NH₂ - 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 Cp₂*TiCl is treated with one equivalent of NaNH₂. 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 [(MeC₅H₄)M]_n (M = K (**2**) or Na). Method A: Ammonia (80 mL) was condensed onto a suspension of (MeC₅H₄)₂ZrCl₂ (2.56 g, 8.0 mmol) and potassium (0.94

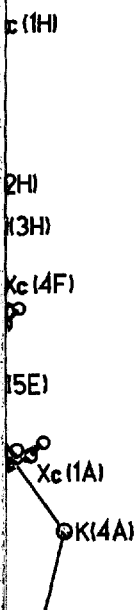


Figure of 2

Fig. 2. Selected bond lengths and angles for compound **2**. Compound **2** crystallizes in the triclinic system. The structural analysis of this aggregate shows a zig-zag chain made up of a repeating sequence of MeC₅H₄ rings.

The K-C bond length (2.81 Å) is comparable to those in [(C₅Me₅)K · 2py]_n (2.79 Å). The K-K bond length (3.25 Å) indicates an additional zig-zag chain of MeC₅H₄ rings, which results in a distortion of the chain and as a consequence a zig-zag chain. The K-C-K angle (126.9° to 135.7°, av 130.9°) is smaller than that of [(C₅Me₅)K · 2py]_n (138°) and smaller than that of [(C₅Me₅)K · 2py]_n. The K-K-K and K-Xc-K angles as well as the K-C-K angles are 133.0°, 160.0° and 5.60 Å,

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 $(\text{MeC}_5\text{H}_4)_2\text{ZrCl}_2$ (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 $[(\text{MeC}_5\text{H}_4)\text{Na}]_n$ were obtained in 53% (0.52 g) and 55% (0.28 g) yields, respectively.

Compound **2**: Mp: 250°C . IR (Nujol): $\tilde{\nu} = 3047(\text{m}), 1615(\text{w}), 1555(\text{w}), 1261(\text{w}), 1261(\text{m}), 1234(\text{w}), 1037(\text{s}), 1025(\text{s}), 966(\text{w}), 927(\text{m}), 891(\text{m}), 852(\text{m}), 782(\text{vs}), 723(\text{vs}), 638(\text{s})\text{ cm}^{-1}$. EI-MS: $m/z(\%) 79(100)[\text{MeC}_5\text{H}_4^+], 39(20)[\text{K}^+]$. $^1\text{H NMR}$ (250 MHz, toluene- d_8 , 100°C): $\delta 5.47 - 5.40(\text{m}, 4\text{H}, \text{C}_5\text{H}_4), 2.17(\text{s}, 3\text{H}, \text{MeC}_5)$. Elemental analysis for $(\text{C}_6\text{H}_7\text{K})_n$ (118.23 \times 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): $\tilde{\nu} = 3437(\text{w}), 1653(\text{w}), 1536(\text{m}), 1262(\text{w}), 1155(\text{w}), 1064(\text{m}), 1024(\text{s}), 970(\text{m}), 800(\text{m}), 722(\text{s}), 617(\text{s}), 599(\text{s}), 571(\text{m}), 491(\text{s}), 428(\text{s})\text{ cm}^{-1}$. $^1\text{H NMR}$ (200 MHz, C_6D_6): $\delta 2.50 - 1.97(\text{br m}), 1.82, 1.79, 1.76, 1.66, 1.15(\text{br s})$. EI-MS: $m/z(\%) 334(53)[\text{M}^+], 317(100)[\text{M}^+ - \text{NH}_3]$. Elemental analysis for $\text{C}_{20}\text{H}_{32}\text{NTi}$ (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 $\text{MoK}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$), 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
under stirring over 4 h. During this
e. The reaction mixture was filtered
temperature for four weeks. Colorless
ngle 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
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
 $[\text{MeC}_5\text{H}_4]\text{Na}]_n$ were obtained in 53%

7(m), 1615(w), 1555(w), 1261 (w),
m), 891(m), 852 (m), 782 (vs), 723
, 39 (20) $[\text{K}^+]$. ^1H NMR (250 MHz,
(s, 3 H, MeC_5). Elemental analysis
H: 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),
e (s), 617 (s), 599 (s), 571 (m), 491
- 1.97 (br m), 1.82, 1.79, 1.76, 1.66,
00) $[\text{M}^+ - \text{NH}_3]$. Elemental analysis
ound: C 70.9, H 9.4, N 3.6.

f **2** was removed from the flask un-
pidly cooled perfluoropolyether [35].
uber four-circle-diffractometer cou-
with graphite-monochromated $\text{MoK}\alpha$
ms. The structure was solved by di-
ainst F^2 on all data by full-matrix
m atoms were refined anisotropically
gen atoms bonded to carbon were
ositions and refined using a riding
tion, and refinement are listed in Ta-
actors) 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)

te Deutsche Forschungsgemein-
rie for financial support of this

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Theoretical Sim

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Dorota

Presented by P

Summary. Theoretical simulation of the vibrational spectrum of salicylaldehyde in the liquid phase taking into account an adiabatic approximation for the O-H stretching and the low-frequency intramolecular torsions of the potential energy surface. The influence of the O-H stretching vibration and the low-frequency intramolecular stretching vibrations in the hydro-

In this letter we present the vibrational spectrum of salicylaldehyde in the liquid phase taking into account an adiabatic approximation for the O-H stretching and the low-frequency intramolecular torsions of the potential energy surface. The present model is based on the study of hydrogen-bonded systems with weak and medium-strong hydrogen bonds. The model is based on the work of Maréchal [1, 2] and the torsional spectra of hydrogen-bonded systems [3-6].

For a three-atomic hydrogen-bonded system, ν_b ; and q , ν the coordinates of the O-H stretching (b) and the remaining modes are denoted by q and ν .

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

Key words: salicylaldehyde