

Electronic Supplementary Information for:

Isolable zirconium hydride species in the reaction of amido complexes with amine–boranes

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Contents:

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- Experimental crystallographic data of compounds **1**, **2** and **4**. Tables for selected lengths and angles of compounds **1**, **2** and **4**.
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Experimental Details and Characterization Data:

General Considerations. All manipulations were carried out under argon atmosphere using Schlenk line or glovebox techniques. Hexane was distilled from Na/K alloy just before use. Dichloromethane was dried with P₂O₅ and distilled prior to use. NMR solvents were dried with Na/K alloy (C₆D₆) or calcium hydride (CDCl₃) and vacuum-distilled. Oven-dried glassware was repeatedly evacuated with a pumping system (ca. 1 × 10⁻³ Torr) and subsequently filled with inert gas. N,N-dimethylamine–borane (NHMe₂BH₃) and N-*tert*-butylamine-borane (NH₂*t*BuBH₃) were purchased from Aldrich and used as received. [Zr(η⁵-C₅Me₅)(NMe₂)₃] and [Zr(η⁵-C₅Me₅)Cl₂(NMe₂)₂] were prepared according to published procedures.¹

Samples for infrared spectroscopy were prepared as KBr pellets, and the spectra were obtained using a FT-IR Perkin-Elmer FRONTIER spectrophotometer. ¹H and ¹³C{¹H} NMR spectra were recorded on a Varian Mercury-300 or Unity-500 spectrometers. ¹¹B NMR spectra were obtained using a Bruker AV400 spectrometer. Chemical shifts (δ, ppm) in the ¹H and ¹³C{¹H} NMR spectra are given relative to residual protons or to carbon of the solvent. Chemical shifts (δ, ppm) in the ¹¹B NMR spectra are given relative to BF₃OEt₂ as external reference. Microanalyses (C, H, N) were performed in a Perkin Elmer CHNS/O 2400 or Leco CHNS-932 microanalyzers.

Synthesis of [Zr(η⁵-C₅Me₅)H(NMe₂BH₃)₂] (1). A 100 mL Schlenk tube was charged with [Zr(η⁵-C₅Me₅)(NMe₂)₃] (0.30 g, 0.84 mmol), NHMe₂BH₃ (0.30 g, 5.02 mmol), and hexane (40 mL). The reaction mixture was stirred at room temperature for 16 h to give a light brown solution. After filtration, the volatile components of the solution were removed under reduced pressure to afford **1** as a light brown solid (0.23 g, 80%). IR (KBr, cm⁻¹): $\tilde{\nu}$ 3038 (w), 2985 (m), 2948 (s), 2897 (s), 2870 (s), 2840 (w), 2829 (m), 2794 (w), 2781 (w), 2468 (s) (BH_{term}), 2424 (s) (BH_{term}), 2399 (s) (BH_{term}), 2320 (m)

(BH_{term}), 2058 (s) (BH_{bridging}), 2003 (w) (BH_{bridging}), 1870 (m) (BH_{bridging}), 1560 (s) (ZrH), 1458 (s), 1379 (m), 1295 (s), 1251 (s), 1174 (s), 1041 (m), 994 (vs), 981 (vs), 931 (m), 703 (w), 613 (w), 489 (w). ¹H NMR (300 MHz, C₆D₆, 20 °C): δ 6.76 (s br, 1H; Zr–H), 2.43 (s br, 6H; NMeMeBH₃), 2.38 (s br, 6H; NMeMeBH₃), 1.96 (s, 15H; C₅Me₅), 0.76 (q br, ¹J(H,B) = 88.5 Hz, 6H; NMe₂BH₃). ¹³C{¹H} NMR (75 MHz, C₆D₆, 20 °C): δ 120.4 (C₅Me₅), 51.9 (NMeMeBH₃), 51.2 (NMeMeBH₃), 12.7 (C₅Me₅). ¹¹B NMR (128 MHz, C₆D₆, 20 °C): δ –7.3 (q, ¹J(B,H) = 89.7 Hz; BH₃). Anal. Calcd (%) for C₁₄H₃₄B₂N₂Zr (M_w = 343.28): C 48.98, H 9.98, N 8.16. Found: C 48.81, H 10.01, N 7.77.

Synthesis of [Zr(η⁵-C₅Me₅)₃(μ₃-H)(μ-H)₃(μ-CH₂NMe)₂(NMe₂BH₃)] (2). A 100 mL Schlenk tube was charged with **1** (0.13 g, 0.38 mmol), [Zr(η⁵-C₅Me₅)(NMe₂)₃] (0.14 g, 0.39 mmol), and hexane (30 mL). The reaction mixture was stirred at room temperature for 3 days. After filtration, the resultant red solution was concentrated under reduced pressure to ca. 5 mL and was cooled to –35 °C for 7 days to give **2** as red crystals (0.080 g, 50%). IR (KBr, cm⁻¹): $\tilde{\nu}$ 2966 (s), 2907 (vs), 2866 (vs), 2831 (s), 2782 (m), 2427 (m) (BH_{term}), 2397 (m) (BH_{term}), 2372 (w) (BH_{term}), 2320 (w) (BH_{term}), 1862 (m) (BH_{bridging}), 1555 (s) (ZrH), 1443 (s), 1372 (s), 1247 (w), 1206 (m), 1157 (s), 1024 (m), 986 (s), 968 (s), 722 (m), 694 (w), 573 (w), 502 (w), 464 (m), 420 (w). ¹H NMR (500 MHz, C₆D₆, 20 °C): δ 3.53 (s, 3H; NMeMeBH₃), 3.13 (AB system, ²J(H,H) = 4.0 Hz, 1H; NMeCHH), 2.71 (s, 3H; NMeCH₂), 2.47 (s, 3H; NMeCH₂), 2.31 (AB system, ²J(H,H) = 5.0 Hz, 1H; NMeCHH), 2.16 (s, 15H; C₅Me₅), 2.15 (s, 3H; NMeMeBH₃), 2.03 (s, 15H; C₅Me₅), 2.00 (s, 15H; C₅Me₅), 1.71 (AB system, ²J(H,H) = 3.0 Hz, 1H; NMeCHH), 1.25 (AB system, ²J(H,H) = 5.0 Hz, 1H; NMeCHH), 0.94 (s br, 1H; Zr–H–Zr), 0.41 (s br, 1H; Zr–H–Zr), –2.01 (s br, 1H; Zr–H–Zr), one Zr–H–Zr and the NMe₂BH₃ resonance signals were not observed. ¹³C{¹H} NMR (125 MHz, C₆D₆, 20 °C): δ 118.7 (C₅Me₅),

117.9 (C_5Me_5), 115.6 (C_5Me_5), 64.1 (NMeCH₂), 61.20 (NMeCH₂), 61.17 (NMeCH₂), 50.8 (NMeMe), 49.3 (NMeCH₂), 44.3 (NMeMe), 13.2 (C_5Me_5), 12.6 (C_5Me_5), 11.9 (C_5Me_5), the assignment of signals was carried out by a ¹H-¹³C HSQC experiment. ¹¹B NMR (128 MHz, C₆D₆, 20 °C): δ -15.7 (m br; BH₃). Anal. Calcd (%) for C₃₆H₆₈BN₃Zr₃ ($M_w = 827.44$): C 52.26, H 8.28, N 5.08. Found: C 51.96, H 7.66, N 4.83.

Synthesis of [(NHMe₂)₂BH₂][{Zr(η⁵-C₅Me₅)Cl₂}₂(μ-H)₃] (3). A 100 mL Schlenk tube was charged with [Zr(η⁵-C₅Me₅)Cl₂(NMe₂)] (0.40 g, 1.22 mmol), NHMe₂BH₃ (0.071 g, 1.22 mmol), and hexane (30 mL). The reaction mixture was stirred at room temperature for 24 h to give a white solid and a colorless solution. The solid was isolated by filtration onto a glass frit and vacuum-dried to afford **3** (0.29 g, 68%). IR (KBr, cm⁻¹): $\tilde{\nu}$ 3188 (s) (NH), 2958 (m), 2908 (s), 2456 (m) (BH), 1457 (vs) (ZrH), 1380 (m), 1190 (m), 1158 (m), 1030 (w), 916 (w), 875 (w), 782 (m). ¹H NMR (300 MHz, C₆D₆, 20 °C): δ 5.35 (s br, 2H; NHMe₂), 4.35 (s br, 3H; Zr-H-Zr), 2.29 (s, 30H; C₅Me₅), 2.08 (s br, 12H; NHMe₂), the BH₂ resonance signal was not observed. ¹H NMR (300 MHz, CDCl₃, 20 °C): δ 5.46 (s br, 2H; NHMe₂), 3.96 (s br, 3H; Zr-H-Zr), 2.61 (d, ³J(H,H) = 6.0 Hz, 12H; NHMe₂), 2.11 (s, 30H; C₅Me₅), the BH₂ resonance signal was not observed. ¹³C{¹H} NMR (75 MHz, CDCl₃, 20 °C): δ 124.0 (C_5Me_5), 43.4 (NHMe₂), 12.6 (C_5Me_5). ¹¹B NMR (128 MHz, CDCl₃, 20 °C): δ -0.7 (m br, BH₂). Anal. Calcd (%) for C₂₄H₄₉BCl₄N₂Zr₂ ($M_w = 700.74$): C 41.14, H 7.05, N 4.00. Found: C 41.12, H 6.73, N 4.03.

Synthesis of [(NH₂*t*Bu)₂BH₂][{Zr(η⁵-C₅Me₅)Cl₂}₂(μ-H)₃] (4). A 100 mL Schlenk tube was charged with [Zr(η⁵-C₅Me₅)Cl₂(NMe₂)] (0.40 g, 1.22 mmol), NH₂*t*BuBH₃ (0.11 g, 1.26 mmol), and hexane (30 mL). The reaction mixture was stirred at room temperature for 24 h to give a white solid and a colorless solution. The solid was isolated by filtration onto a glass frit and vacuum-dried to afford **4** (0.24 g, 52%). IR (KBr, cm⁻¹): $\tilde{\nu}$

3191 (vs) (NH), 3114 (s) (NH), 2977 (s), 2909 (s), 2484 (m) (BH), 1589 (m) (NH₂tBu), 1463 (vs) (ZrH), 1379 (s), 1348 (s), 1236 (w), 1203 (m), 1156 (w), 1027 (w), 889 (w), 780 (m). ¹H NMR (300 MHz, C₆D₆, 20 °C): δ 5.04 (s br, 4H; NH₂CMe₃), 4.17 (s br, 3H; Zr–H–Zr), 2.28 (s, 30H; C₅Me₅), 1.01 (s, 18H; NH₂CMe₃), the BH₂ resonance signal was not observed. ¹H NMR (300 MHz, CDCl₃, 20 °C): δ 4.76 (s br, 4H; NH₂CMe₃), 3.84 (s br, 3H; Zr–H–Zr), 2.13 (s, 30H; C₅Me₅), 1.28 (s, 18H; NH₂CMe₃), the BH₂ resonance signal was not observed. ¹³C{¹H} NMR (75 MHz, CDCl₃, 20 °C): δ 124.6 (C₅Me₅), 54.3 (NH₂CMe₃), 28.4 (NH₂CMe₃), 12.7 (C₅Me₅). ¹¹B NMR (128 MHz, CDCl₃, 20 °C): δ –13.1 (m br, BH₂). Anal. Calcd (%) for C₂₈H₅₇BCl₄N₂Zr₂ (M_w = 756.84): C 44.44, H 7.59, N 3.70. Found: C 43.28, H 7.47, N 4.39. This ionic compound is inevitably contaminated by the analogous salt **3** (≤ 5% by ¹H NMR spectroscopy) even after crystallization and hence satisfactory elemental analysis could not be obtained.

X-ray structure determination of 1, 2, and 4. Crystals of **1**, **2** and **4** are colorless. While crystalline samples of **1** and **2** were grown from hexane solutions at –35 °C, crystals of **4**·CH₂Cl₂ were obtained from a dichloromethane solution at –15 °C. The crystals were removed from the Schlenks and covered with a layer of a viscous perfluoropolyether (Fomblin[®]Y). A suitable crystal was selected with the aid of a microscope, mounted on a cryoloop, and immediately placed in the low temperature nitrogen stream of the diffractometer. The intensity data sets were collected at 150 K on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit.

Crystallographic data for complexes are presented in Table S1. The structures were solved, using the WINGX package,² by intrinsic phasing methods (SHELXT)³ and refined by least-squares against F² (SHELXL-2014/7).⁴ In the crystallographic study of

compound **1**, all non-hydrogen atoms were anisotropically refined. The hydrogen atoms of the BH₃ moieties (H(1)a, H(1)b, H(1)c, H(2)a, H(2)b and H(2)c) and the hydrogen H(1) linked to zirconium atom were located in the difference Fourier map and refined isotropically, whereas the rest of the hydrogen atoms were positioned geometrically and refined by using a riding model.

Complex **2** crystallized in the chiral space group $P2_12_12_1$. All the non-hydrogen atoms were anisotropically refined. The hydrogen atoms of the BH₃ group (H(1)a, H(1)b and H(1)c) and the hydrogen atoms H(12), H(13) and H(31) bridging two zirconium atoms were located in the difference Fourier map and refined isotropically. Since **2** is a diamagnetic species, XHYDEX tool was employed to locate additional hydride groups, and H(123) was found in the difference Fourier map. Unfortunately the isotropic displacement parameter obtained for H(123) was not appropriate, so the U_{iso} was forced to be 0.05 Å². The angles around the zirconium atoms and the different values for the Zr(1)⋯Zr(2) and Zr(1)⋯Zr(3) distances (3.417(1) and 3.222(1) Å, respectively) rule out a μ -H hydride group bridging Zr(1) and Zr(2) instead of the μ_3 -H ligand. The hydrogen atoms of the methyl and methylene groups were placed geometrically and refined by using a riding model. Additionally FREE instruction was employed to delete the Zr(2)–C(5) bond from the connectivity array to avoid problems with the calculated hydrogen atoms bound to C(5).

Finally, compound **4** crystallized with a molecule of dichloromethane in the $Fddd$ space group. The solvent molecule presented disorder, which was treated conventionally by using the PART tool and allowing free refinement of the occupancy factors with the FVAR command. The final values of occupancy were 64 and 36%. All the non-hydrogen atoms were anisotropically refined. The hydrogen atoms linked to N(1) (H(11) and H(12)) and B(1) (H(10)), and those bridging the zirconium atoms (H(1) and

H(2)) were located in the difference Fourier map and refined isotropically. The rest of the hydrogen atoms were positioned geometrically and refined by using a riding model, except those of the solvent molecules which were not included. In addition, the position and the displacement parameters of C(100) and C(101) of the dichloromethane molecules were constrained to be identical.

References

- (1) A. M. Irigoyen, A. Martín, M. Mena, F. Palacios and C. Yélamos, *J. Organomet. Chem.*, 1995, **494**, 255–259.
- (2) L. J. Farrugia, *J. Appl. Crystallogr.*, 2012, **45**, 849–854.
- (3) G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2015, **71**, 3–8.
- (4) G. M. Sheldrick, *Acta Crystallogr., Sect. C*, 2015, **71**, 3–8.

Table S1.- Crystallographic data for complexes **1**, **2** and **4**.

| Compound | 1 | 2 | 4 ·CH ₂ Cl ₂ |
|--|--|---|---|
| Empirical formula | C ₁₄ H ₃₄ B ₂ N ₂ Zr | C ₃₆ H ₆₈ BN ₃ Zr ₃ | C ₂₉ H ₅₉ BCl ₆ N ₂ Zr ₂ |
| Formula weight | 343.27 | 827.40 | 841.73 |
| Temperature (K) | 150(2) | 150(2) | 150(2) |
| Wavelength (Å) | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Orthorhombic | Orthorhombic |
| Space group | <i>P2₁/n</i> | <i>P2₁2₁2₁</i> | <i>Fddd</i> |
| <i>a</i> (Å); α (°) | 8.641(1) | 11.414(1) | 16.301(2) |
| <i>b</i> (Å); β (°) | 26.129(1); 111.81(1) | 16.131(1) | 20.610(4) |
| <i>c</i> (Å); γ (°) | 8.690(1) | 21.261(2) | 48.31(4) |
| Volume (Å ³) | 1821.5(2) | 3914.5(6) | 16230(20) |
| Z | 4 | 4 | 16 |
| Density (calculated) (Mg/m ³) | 1.252 | 1.404 | 1.378 |
| Absorption coefficient (mm ⁻¹) | 0.594 | 0.811 | 0.929 |
| F(000) | 728 | 1720 | 6944 |
| Crystal size (mm ³) | 0.32 × 0.15 × 0.14 | 0.19 × 0.17 × 0.11 | 0.15 × 0.12 × 0.11 |
| Theta range for data collection | 3.12 to 27.50° | 3.09 to 27.50° | 3.19 to 27.52° |
| Index ranges | -11 to 11, -33 to 33, -11 to 11 | -14 to 14, -20 to 20, -27 to 27 | -21 to 20, -26 to 26, -62 to 62 |
| Reflections collected | 37262 | 74045 | 89620 |
| Independent reflections | 4175 [R(int) = 0.084] | 8992 [R(int) = 0.130] | 4669 [R(int) = 0.124] |
| Reflections [I>2σ(I)] | 2897 | 7064 | 3734 |
| Completeness to theta | 99.8% | 99.7% | 99.8% |
| Goodness-of-fit on F ² | 1.092 | 1.121 | 1.115 |
| Final R indices [I>2σ(I)] | R1 = 0.052, wR2 = 0.094 | R1 = 0.052, wR2 = 0.079 | R1 = 0.050, wR2 = 0.094 |
| R indices (all data) | R1 = 0.090, wR2 = 0.110 | R1 = 0.086, wR2 = 0.090 | R1 = 0.070, wR2 = 0.104 |
| Largest diff. peak and hole (e Å ⁻³) | 1.742 and -0.800 | 0.994 and -0.543 | 0.641 and -0.434 |

Table S2. Selected lengths (Å) and angles (°) for compound **1**.

| | | | |
|------------------|----------|------------------|----------|
| Zr(1)–N(1) | 2.306(3) | Zr(1)–N(2) | 2.353(3) |
| Zr(1)···B(1) | 2.680(5) | Zr(1)···B(2) | 2.359(5) |
| Zr(1)–H(1) | 1.83(4) | Zr(1)–H(1a) | 2.07(4) |
| Zr(1)–H(2a) | 2.14(4) | Zr(1)–H(2b) | 2.06(4) |
| N(1)–Zr(1)–N(2) | 90.5(1) | Zr(1)–N(1)–B(1) | 85.6(2) |
| Zr(1)–N(2)–B(2) | 71.3(2) | N(1)–Zr(1)–H(1) | 80(1) |
| N(1)–Zr(1)–H(1a) | 62(1) | N(2)–Zr(1)–H(1) | 88(1) |
| N(2)–Zr(1)–H(1a) | 85(1) | N(2)–Zr(1)–H(2a) | 56(1) |
| N(2)–Zr(1)–H(2b) | 58(1) | | |

Table S3. Selected lengths (Å) and angles (°) for compound **2**.

| | | | |
|------------------|-----------|------------------|----------|
| Zr(1)–N(1) | 2.317(6) | Zr(2)–N(2) | 1.984(6) |
| Zr(2)–N(3) | 2.191(6) | Zr(3)–N(3) | 2.232(6) |
| Zr(3)–C(5) | 2.446(7) | Zr(3)–C(7) | 2.307(7) |
| Zr(1)···B(1) | 2.657(10) | Zr(1)···Zr(2) | 3.417(1) |
| Zr(1)···Zr(3) | 3.222(1) | Zr(2)···Zr(3) | 3.066(1) |
| Zr(1)–H(1a) | 2.08(8) | Zr(1)–H(12) | 2.06(8) |
| Zr(1)–H(13) | 1.98(9) | Zr(1)–H(31) | 1.92(7) |
| Zr(1)–H(123) | 1.97(9) | Zr(2)–H(12) | 1.99(9) |
| Zr(2)–H(123) | 1.97(9) | Zr(3)–H(13) | 2.13(9) |
| Zr(3)–H(31) | 1.96(7) | Zr(3)–H(123) | 2.07(8) |
| Zr(1)–N(1)–B(1) | 84.6(5) | N(2)–Zr(2)–N(3) | 97.8(2) |
| Zr(2)–N(2)–C(5) | 92.6(4) | Zr(2)–N(2)–C(4) | 151.8(5) |
| C(4)–N(2)–C(5) | 115.3(6) | Zr(2)–N(3)–Zr(3) | 87.8(2) |
| Zr(2)–N(3)–C(6) | 117.5(5) | Zr(2)–N(3)–C(7) | 125.6(5) |
| C(6)–N(3)–C(7) | 116.0(6) | C(5)–Zr(3)–C(7) | 112.7(3) |
| C(5)–Zr(3)–N(3) | 75.3(2) | N(3)–Zr(3)–C(7) | 37.4(2) |
| Zr(3)–C(5)–N(2) | 128.2(5) | Zr(3)–N(3)–C(6) | 120.3(5) |
| Zr(3)–N(3)–C(7) | 74.1(4) | Zr(3)–C(7)–N(3) | 68.5(4) |
| N(1)–Zr(1)–H(1a) | 58(2) | N(1)–Zr(1)–H(12) | 126(2) |
| N(1)–Zr(1)–H(13) | 80(3) | N(1)–Zr(1)–H(31) | 135(2) |
| N(2)–Zr(2)–H(12) | 100(2) | N(3)–Zr(2)–H(12) | 131(2) |
| N(3)–Zr(3)–H(13) | 130(2) | N(3)–Zr(3)–H(31) | 113(2) |
| C(5)–Zr(3)–H(13) | 119(2) | C(5)–Zr(3)–H(31) | 65(2) |
| C(7)–Zr(3)–H(13) | 108(2) | C(7)–Zr(3)–H(31) | 129(2) |

Table S4. Selected lengths (Å) and angles (°) for compound **4**.

| | | | |
|-------------------|----------|-------------------|----------|
| Zr(1)–Cl(1) | 2.470(1) | Zr(1)–Cl(2) | 2.458(2) |
| Zr(1)···Zr(1)a | 3.106(3) | B(1)–N(1) | 1.595(5) |
| Zr(1)–H(1) | 1.80(4) | Zr(1)–H(2) | 1.91(3) |
| Cl(1)–Zr(1)–Cl(2) | 98.8(1) | B(1)–N(1)–C(1) | 118.1(3) |
| N(1)–B(1)–N(1)b | 105.6(4) | Cl(1)–Zr(1)–H(1) | 143(1) |
| Cl(1)–Zr(1)–H(2) | 92.2(5) | Cl(1)–Zr(1)–H(1)a | 80(1) |
| Cl(2)–Zr(1)–H(1) | 87(1) | Cl(2)–Zr(1)–H(2) | 141(1) |
| Cl(2)–Zr(1)–H(1)a | 86(1) | H(1)–Zr(1)–H(2) | 63(2) |
| H(1)–Zr(1)–H(1)a | 63(2) | | |

Symmetry code: (a) $-x + 3/4, -y + 3/4, z$; (b) $-x + 5/4, y, -z + 1/4$.

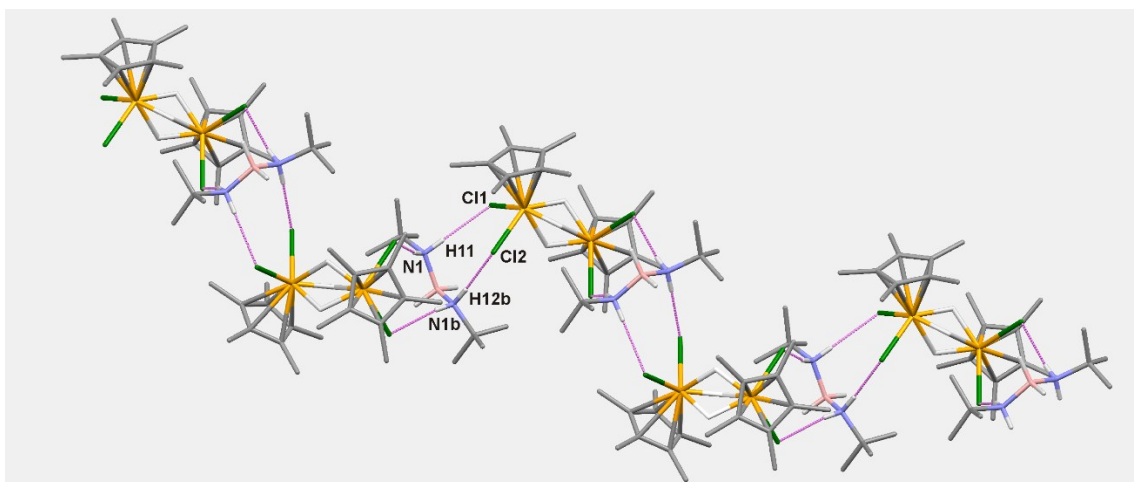


Fig. S1. Anion and cation fragments organized in a helical chain by hydrogen bonding interactions in the solid-state structure of compound **4**. Dichloromethane solvent molecules and hydrogen atoms of the methyl groups are not shown for clarity.

Table S5. Relevant hydrogen bonds for compound **4**.^a

| D–H···A | D···A/Å | H···A/Å | D–H···A/° |
|----------------------|----------|---------|-----------|
| N(1)–H(11)···Cl(1) | 3.338(4) | 2.47(4) | 169(3) |
| N(1)b–H(12)b···Cl(2) | 3.281(3) | 2.44(4) | 169(3) |

^aSymmetry transformation: (b) – x + 5/4, y, – z + 1/4. A = acceptor; D = donor.

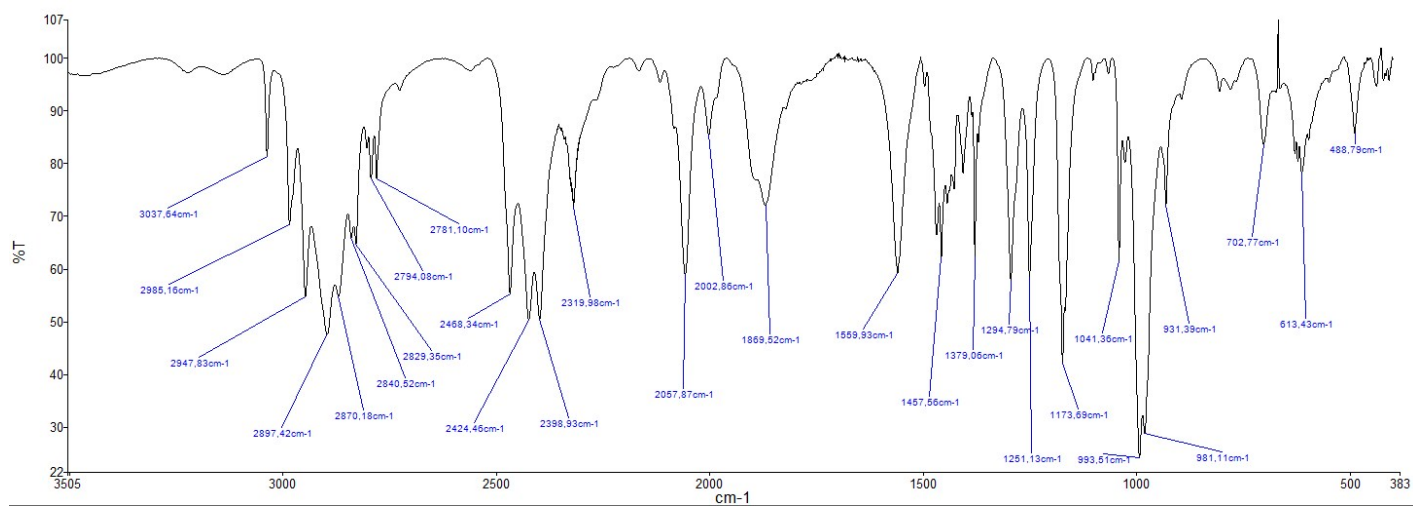


Figure S2. IR spectrum (KBr) of $[\text{Zr}(\eta^5\text{-C}_5\text{Me}_5)\text{H}(\text{NMe}_2\text{BH}_3)_2]$ (**1**).

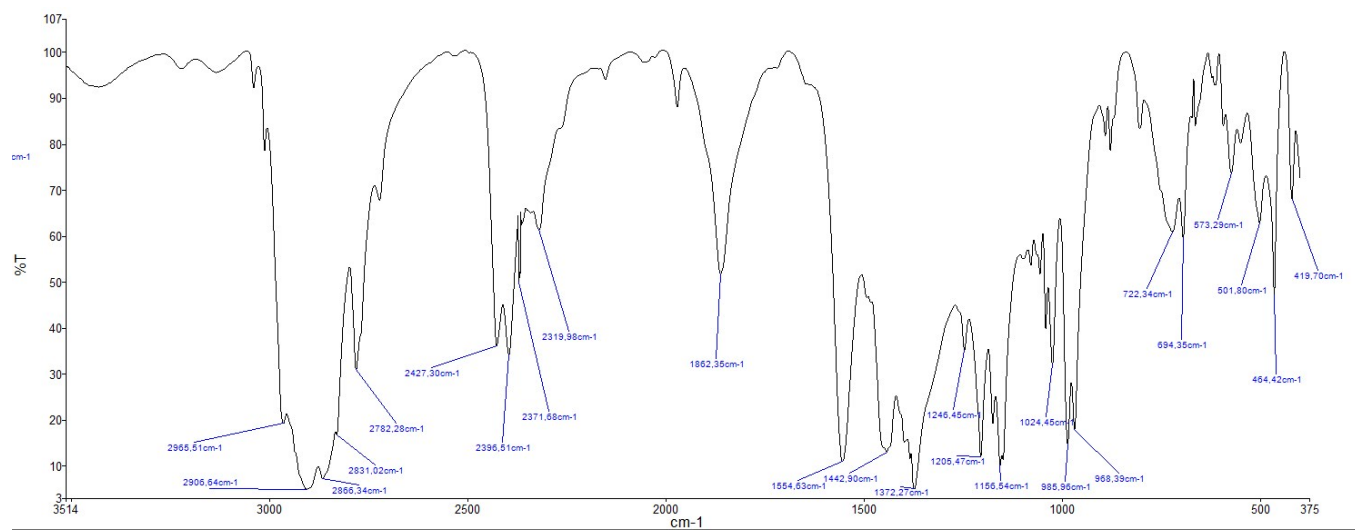


Figure S3. IR spectrum (KBr) of $[\{\text{Zr}(\eta^5\text{-C}_5\text{Me}_5)\}_3(\mu_3\text{-H})(\mu\text{-H})_3(\mu\text{-CH}_2\text{NMe})_2(\text{NMe}_2\text{BH}_3)]$ (**2**).

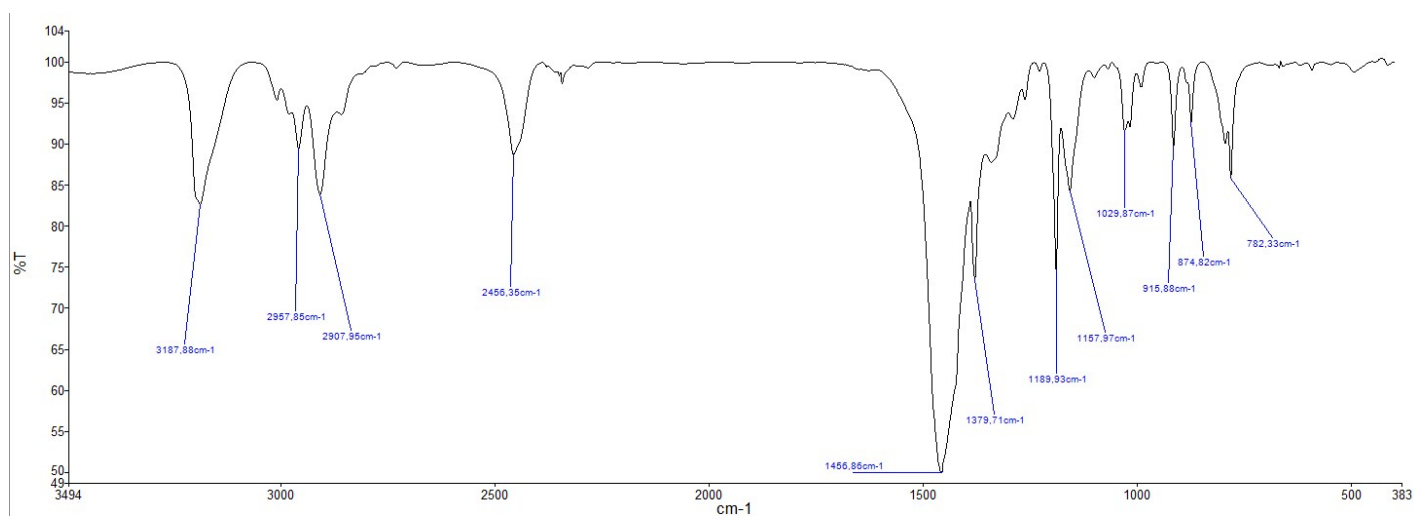


Figure S4. IR spectrum (KBr) of $[(\text{NHMe}_2)_2\text{BH}_2][\{\text{Zr}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2\}_2(\mu\text{-H})_3]$ (3).

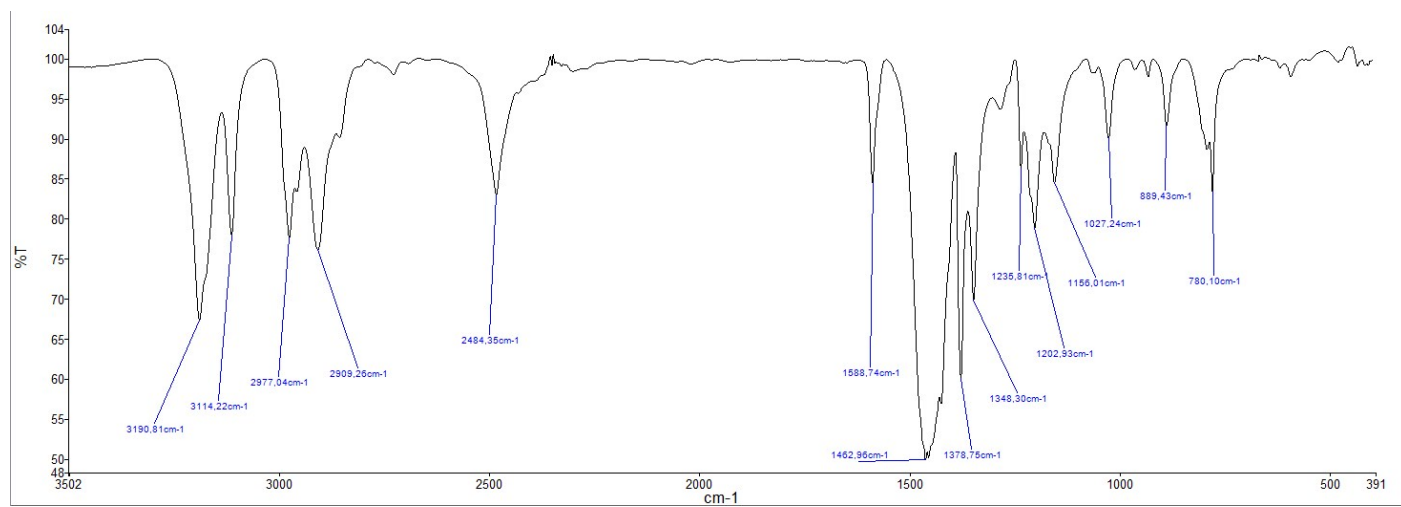


Figure S5. IR spectrum (KBr) of $[(\text{NH}_2t\text{Bu})_2\text{BH}_2][\{\text{Zr}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2\}_2(\mu\text{-H})_3]$ (4).

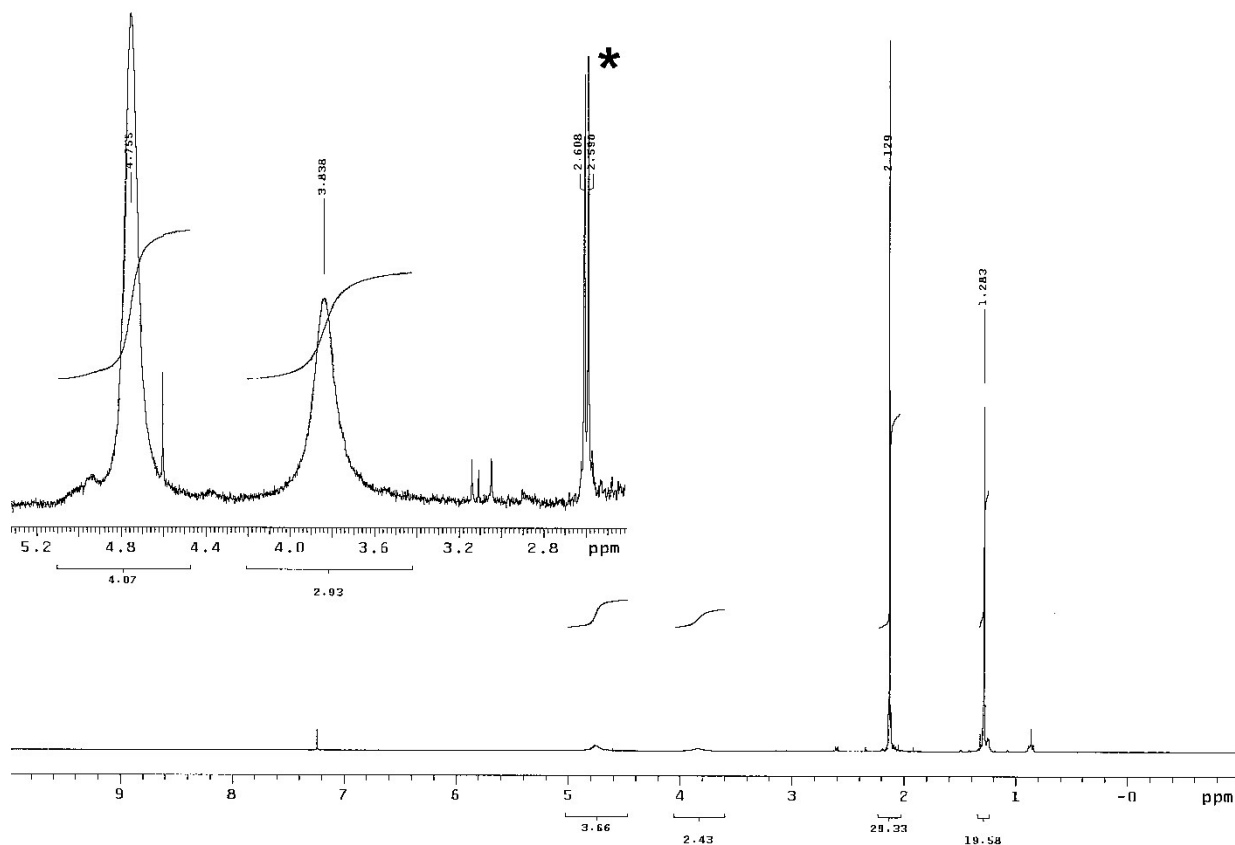


Figure S6. ^1H NMR spectrum (300 MHz, CDCl_3 , 20 $^\circ\text{C}$) of $[(\text{NH}_2t\text{Bu})_2\text{BH}_2][\{\text{Zr}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2\}_2(\mu\text{-H})_3]$ (**4**).

* Resonance for the $[(\text{NHMe}_2)_2\text{BH}_2]^+$ cation of compound **3**.

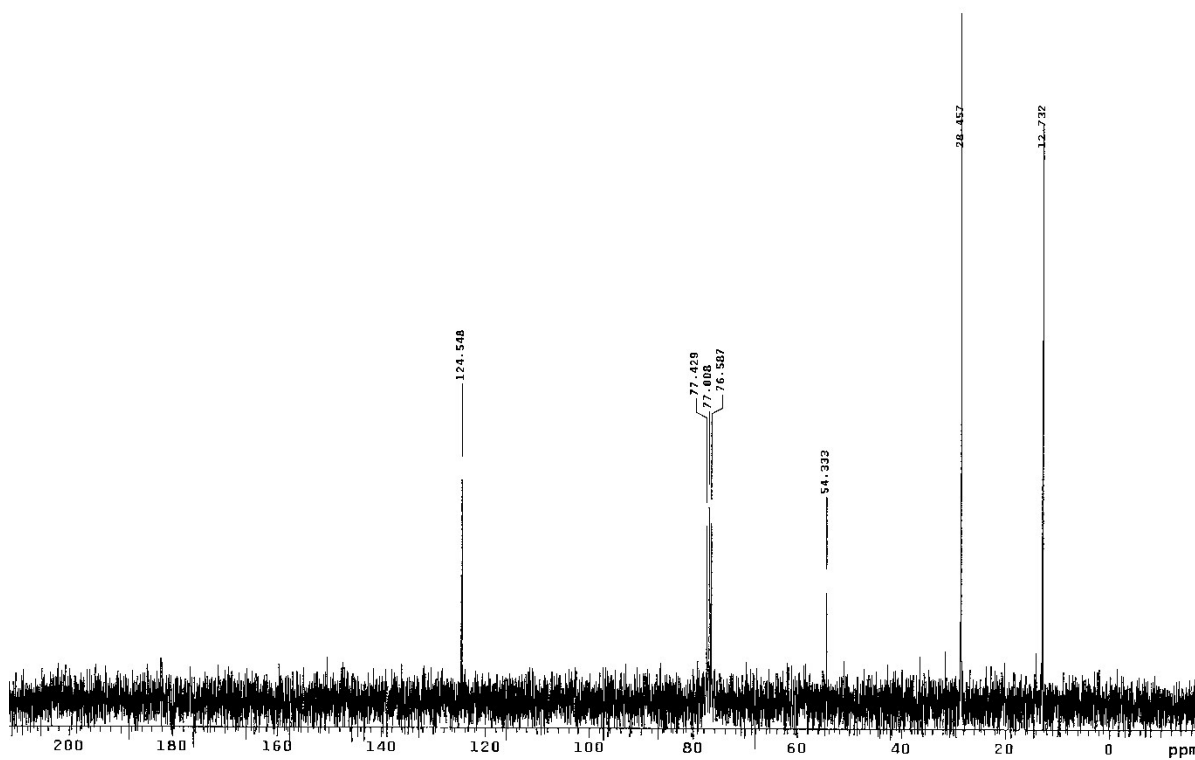


Figure S7. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (75 MHz, CDCl_3 , 20 $^\circ\text{C}$) of $[(\text{NH}_2t\text{Bu})_2\text{BH}_2][\{\text{Zr}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2\}_2(\mu\text{-H})_3]$ (**4**).