Two-Coordinate Terminal Zinc Hydride Complexes: Synthesis, Structure and Preliminary Reactivity Studies

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ELECTRONIC SUPPLEMENTARY INFORMATION

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Contents

1. Syntheses

General considerations. All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. Diethyl ether and pentane were distilled over Na/K alloy (25:75), while THF, hexane, toluene and benzene were distilled over molten potassium. ^{1}H, $^{13}C\{^{1}H\}$, $^{29}Si\{^{1}H\}$, $^{11}B\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR spectra were recorded on either Bruker AvanceIII 400 or Bruker DPX300 spectrometers and were referenced to the resonances of the solvent used, external $SiMe_4$, $BF_3(OEt_2)$ or $CFCl_3$. IR spectra were recorded for solid samples protected from the atmosphere by Nujol films, or as Nujol mulls using an Agilent Cary 630 attenuated total reflectance (ATR) spectrometer. Mass spectra were recorded on an Agilent Techonlogies 5975D inert MSD with a solid state probe. Melting points were determined in sealed glass capillaries under dinitrogen, and are uncorrected. Microanalyses were carried out at the Science Centre, London Metropolitan University. L'ZnBr(THF),[1] L*ZnBr,[1] L†ZnBr,[1] L'CdI,[1] L*HgI,[1] L"K[2] and (BoN)(Me_3Si)NK (BoN = B(DipNCH)$_2$)[3] were prepared by literature procedures. All other reagents were used as received.

Synthesis of L"ZnBr. L"K (0.500 g, 0.729 mmol) was dissolved in THF (20 mL) and added to a suspension of $ZnBr_2$ (0.172 g, 0.766 mmol) in THF (10mL) at -80 °C. The reaction mixture was warmed to room temperature, then stirred for 18 hrs, affording a yellow solution. Volatiles were removed from the mixture *in vacuo*, and the residue extracted with warm hexane (50 mL). The extract was filtered and volatiles removed from the filtrate *in vacuo* affording the title compound as

a colourless powder (0.392 g, 65 %). NB: recrystallisation from diethyl ether at 5 °C yielded crystals of the compound suitable for X-ray diffraction. M.p. 219-220 °C; ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 1.41 (s, 27 H, OC(CH_3)$_3$), 1.89 (s, 3H, *p*-CH_3), 6.63 (s, 2H, Ph_2C*H*), 6.84 (s, 2H, *m*-Ar*H*) 7.05-7.35 (m, 20H, Ar*H*); ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): δ = 21.3 (*p*-*C*H_3), 32.1 (OC(*C*H_3)$_3$), 52.5 (*C*HPh_2), 74.3 (O*C*(CH_3)$_3$), 126.5, 128.6, 128.7, 128.8, 128.9, 130.4, 130.7, 130.8, 142.0, 143.8, 145.3 (Ar-*C*); ^{29}Si{^{1}H} NMR (80 MHz, C_6D_6, 298 K): δ = -87.6; IR ν/cm^{-1} (Nujol): 3370 (s), 1600 (m), 1444 (s), 1364 (m), 1293 (w), 1240 (w), 1181 (s), 930 (m), 831 (w), 700 (s); MS/EI *m/z* (%): 685.6 (L"H$^+$, 11), 439.3 (L"H$_2$-Si(OBu^t)$_3^+$, 100), 167.2 (Ph_2CH^+, 69). NB: L"ZnBr consistently co-crystallised with *ca.* 5% of protonated ligand (L"H) which could not be removed after repeated recrystallisations. Therefore a satisfactory microanalysis could not be obtained.

Synthesis of (BoN)(Me$_3$Si)NZnBr(THF). (BoN)(Me$_3$Si)NK (1.80 g, 3.79 mmol) was dissolved in THF (30 mL) and the solution added to a suspension of $ZnBr_2$ (940 mg, 4.17 mmol) in THF (20 mL) at -80 °C. The reaction mixture was warmed to room temperature and stirred for 18 hrs, affording a green solution. Volatiles were removed *in vacuo* and the residue extracted with hexane (30 mL). The pale green extract was filtered and the filtrate concentrated (to *ca.* 10 mL), affording colourless crystals of the title compound overnight (1.62 g, 62 %). M.p.: 134-135 °C; ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = -0.03 (s, 9H, Si(CH_3)$_3$), 1.18 (d, J = 6.9 Hz, 12H, CH(CH_3)$_2$), 1.30 (m, 4H, THF-CH_2), 1.36 (d, J = 6.9 Hz, 12H, CH(CH_3)$_2$), 3.46 (sept, J = 6.9 Hz, 4H, C*H*(CH_3)$_2$), 3.60 (m, 4H, THF-OCH_2), 5.98 (s, 2H, {N(Dip)C(*H*)}$_2$), 7.15-7.33 (m, 6H, Ar*H*); ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): δ = 4.8 (Si(*C*H_3)$_3$), 23.4 (CH(*C*H_3)$_2$), 25.4 (THF-*C*H_2), 25.7 (CH(*C*H_3)$_2$), 28.8 (*C*H(CH$_3$)$_2$), 68.8 (THF-O*C*H$_2$), 118.0 ({N(Dip)*C*(H)}), 124.0, 125.6, 129.3, 148.1 (Ar-*C*); ^{29}Si{^{1}H} NMR (80 MHz, C_6D_6, 298 K): δ = -1.92; ^{11}B{^{1}H} NMR (128 MHz, C_6D_6, 298 K): δ = 24.3; IR ν/cm^{-1} (Nujol): 3056 (w), 1576 (w), 1457 (s), 1370 (s), 1138 (m), 1073 (m), 1024 (s), 986 (m), 880(s), 825 (s), 752 (s), 648 (s); MS/EI *m/z* (%): 617.4 ((BoN)(Me$_3$Si)NZnBr$^+$, 24.3), 475.5 ((BoN)(Me$_3$Si)NH$^+$, 100), 403.4 ((BoN)NH$_2^+$, 48.5); anal. calc. for $C_{33}H_{53}BBrN_3OSiZn$: C 57.28 %, H 7.72 %, N 6.07 %, found: C 57.01 %, H 7.85 %, N 5.94 %.

Synthesis of L"ZnEt. A solution of ethyl magnesium bromide, freshly prepared from bromoethane (0.054 mL, 0.724 mmol) and magnesium turnings (0.022 g, 0.957 mmol) in diethyl ether (10 mL) was added to a solution of L"ZnBr (0.50 g, 0.638 mmol) in diethyl ether (10 mL) at room temperature. The reaction mixture was then stirred for 18 hrs to afford a pale yellow solution. Volatiles were removed *in vacuo* and the residue extracted with warm hexane (20 mL). The pale yellow extract was filtered and concentrated to *ca.* 10 mL. Storage of the solution at -30 °C

overnight afforded the title compound as colourless crystals. (0.278 g, 56 %). M.p. 233-234 °C; ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = -0.62 (q, J = 8.0 Hz, 2H, ZnCH_2CH$_3$), 0.82 (t, J = 8.0 Hz, 3H, ZnCH$_2$CH_3), 1.43 (s, 27H, OC(CH_3)$_3$), 1.91 (s, 3H, *p*-CH_3), 6.76 (s, 2H, Ph$_2$CH), 6.85 (s, 2H, *m*-ArH) 7.00-7.43 (m, 20H, ArH); ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): δ = -0.1 (ZnCH$_2$CH$_3$), 11.4 (ZnCH$_2$$CH_3$), 21.3 (*p*-$CH_3$), 32.2 (OC($CH_3$)$_3$), 52.1 ($CHPh_2$), 73.4 (O$C$(CH$_3$)$_3$), 126.3, 127.0, 128.5, 129.0, 129.2, 129.4, 130.4, 130.6, 131.1, 141.7, 145.7, 146.0 (Ar-C); ^{29}Si{^{1}H} NMR (80 MHz, C_6D_6, 298 K): δ = -88.0; IR ν/cm^{-1} (Nujol): 1598 (w), 1493 (m), 1445 (m), 1184 (s), 1140 (w), 1080 (s), 942 (m),799 (s), 747 (m), 700 (s), 621 (w); MS/EI *m/z* (%): 777.5 (L"ZnEt$^+$, 4), 685.5 (L"$^+$, 8), 167.1 (Ph$_2$CH$^+$, 100); anal. calc. for $C_{47}H_{59}NO_3SiZn$: C 72.42%, H 7.63%, N 1.80%, found: C 72.36%, H 7.73%, N 1.82%.

Synthesis of L'ZnH (5). L'ZnBr(THF) (1.0 g, 1.46 mmol) was dissolved in THF (30 mL) and added to a suspension of NaH (0.046 g, 1.9 mmol) in THF (10 mL) at -80 °C. The reaction mixture was warmed to room temperature and stirred for 24 hrs, affording a yellow solution. Volatiles were removed *in vacuo* and the residue extracted with pentane (50 mL). The pale yellow extract was filtered and the filtrate concentrated (to *ca.* 20 mL), affording colourless crystals of **5** overnight (0.69 g, 78 %). M.p.: >260 °C; ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 0.33 (s, 9H, Si(CH_3)$_3$), 0.97 (d, J = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.85 (s, 1H, ZnH), 2.50 (sept, J = 6.9 Hz, 1H, ArCH(CH$_3$)$_2$), 6.22 (s, 2H, Ph$_2$CH), 6.88-7.27 (m, 22H, ArH); ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): δ = 2.1 (Si(CH$_3$)$_3$), 23.1 (CH(CH$_3$)$_2$), 32.7 (CH(CH$_3$)$_2$), 52.5 (CHPh$_2$), 125.4, 125.5, 127.5, 128.8, 129.1, 140.5, 141.2, 143.6, 143.7 (Ar-C); ^{29}Si{^{1}H} NMR (80 MHz, C_6D_6, 298 K): δ = -2.88; IR ν/cm^{-1} (Nujol): 1902 (m, Zn-H), 1598 (m), 1492 (m), 1161 (m), 1129 (m), 1030 (m), 934 (s), 894 (m), 821 (s), 756 (s), 737 (m), 699 (s); MS/EI *m/z* (%): 603.5 (M$^+$, 7), 539.5 (L'H$^+$, 100), 466.4 (L'H-SiMe$_3^+$, 35), 167.2 (Ph$_2$CH$^+$, 49); anal. calc. for $C_{38}H_{41}NSiZn$: C 75.41%, H 6.83%, N 2.31%, found: C 75.30%, H 6.91%, N 2.35%.

Synthesis of L*ZnH (6). L*ZnBr (0.40 g, 0.54 mmol) was dissolved in THF (10 mL) and added to a suspension of NaH (0.04 g, 1.62 mmol) in THF (10 mL) at -80 °C. The reaction solution was warmed to room temperature and stirred for 24 hrs, affording a yellow solution. Volatiles were removed *in vacuo* and the residue extracted with pentane (30 mL). The pale yellow extract was filtered and the filtrate concentrated (to *ca.* 5 mL), affording **6** as a colourless crystalline solid overnight (0.19 g, 66%). M.p.: 223-225 °C; ^{1}H NMR (300 MHz, C_6D_6, 298 K): 1.23 (d, J = 7.2 Hz, 18H, SiCH(CH_3)$_2$), 1.48 (sept, J = 7.5 Hz, 3H, SiCH(CH$_3$)$_2$), 1.85 (s, 1H, ZnH), 1.91 (s, 3H, *p*-CH_3), 6.38 (s, 2H, Ph$_2$CH), 6.85 (s, 2H, *m*-ArH), 6.93-7.31 (m, 20H, ArH); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 298 K): δ = 15.5 (SiCH(CH$_3$)$_2$), 20.0 (SiCH(CH$_3$)$_2$), 21.3 (*p*-CH$_3$), 53.0 (CHPh$_2$),

126.6, 128.8, 129.4, 130.2, 130.5, 142.7, 144.8, 145.1 (Ar-*C*); $^{29}Si\{^1H\}$ NMR (80 MHz, C_6D_6): δ = 0.67; IR *v*/cm^{-1} (Nujol): 1892 (m, Zn-H), 1598 (m), 1129 (w), 1075 (w), 1031 (w), 1000 (w), 901 (m), 879 (m), 840 (m), 745 (m), 700 (s); MS/EI *m/z* (%): 659.5 (M^+, 7), 616.5 (M^+-Pr^i, 49), 552.5 (L*-Pr^{i+}, 36), 167.2 (Ph_2CH^+, 100); anal. calc for $C_{42}H_{49}NSiZn$: C 76.28%, H 7.47%, N 2.12%, found: C 76.39%, H 7.50%, N 2.14%.

Synthesis of {L*Zn(μ-OH)}$_2$. During one synthesis of **6** a low yield (*ca.* 5%) of {L*Zn(μ-OH)}$_2$ was obtained after work-up. The compound presumably formed due to the presence of adventitious water in the reaction mixture. M.p.: 207-209 °C; ^1H NMR (400 MHz, C_6D_6, 298 K): δ = -0.64 (s, 2H, O*H*), 1.23 (d, *J* = 7.2 Hz, 36H, SiCH(C*H*$_3$)$_2$), 1.35 (sept, *J* = 8 Hz, 6H, SiC*H*(CH$_3$)$_2$), 1.89 (s, 6H, *p*-C*H*$_3$), 6.57 (s, 4H, Ph$_2$C*H*), 6.96 (s, 4H, *m*-Ar*H*), 7.05-7.36 (m, 40H, Ar*H*); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 298 K): δ = 15.5 (Si*C*H(CH$_3$)$_2$), 19.9 (SiCH(*C*H$_3$)$_2$), 21.1 (*p*-*C*H$_3$), 51.3 (*C*HPh$_2$), 126.5, 126.9, 128.6, 129.1, 129.9, 130.4, 131.0, 141.5, 146.0, 148.4 (Ar-*C*); $^{29}Si\{^1H\}$ NMR (80 MHz, C6D6): δ = 1.06; IR *v*/cm^{-1} (Nujol): 3347 (w), 1598 (m), 1127 (w), 1075 (w), 1030 (w), 880 (s), 761 (w), 699 (s); MS/EI *m/z* (%): 595.5 (L*H$^+$, 19), 552.4 (L*H-Pr^{i+}, 556), 167.2 (Ph_2CH^+, 100); anal. calc for $C_{84}H_{98}N_2O_2Si_2Zn_2$: C 74.48%, H 7.29%, N 2.07%, found: C 74.70%, H 7.45%, N 2.22%.

Synthesis of L†ZnH (7). L†ZnBr (0.30 g, 0.39 mmol) was dissolved in THF (10 mL) and added to a suspension of NaH (0.03 g, 1.17 mmol) in THF (10 mL) at -80 °C. The reaction solution was warmed to room temperature and stirred for 24 hrs, affording a yellow solution. Volatiles were removed *in vacuo* and the residue extracted with pentane (30 mL). The pale yellow extract was filtered and concentrated (to *ca.* 5 mL), affording **7** as a colourless crystalline solid overnight (0.25 g, 71%). M.p.: 187-189 °C; ^1H NMR (300 MHz, C_6D_6, 298 K): δ = 0.97 (d, *J* = 6.9 Hz, 6H, ArCH(C*H*$_3$)$_2$), 1.23 (d, *J* = 7.5 Hz, 18H, SiCH(C*H*$_3$)$_2$), 1.48 (sept, *J* = 7.8 Hz, 3H, SiC*H*(CH$_3$)$_2$), 1.87 (s, 1H, Zn*H*), 2.52 (sept, *J* = 6.6 Hz, 1H, ArC*H*(CH$_3$)$_2$), 6.39 (s, 2H, Ph$_2$C*H*), 6.89 (s, 2H, *m*-ArH), 6.96-7.32 (m, 20H, Ar*H*); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 298 K): δ = 15.5 (Si*C*H(CH$_3$)$_2$), 20.0 (SiCH(*C*H$_3$)$_2$), 24.3 (ArCH(*C*H$_3$)$_2$), 33.8 (Ar*C*H(CH$_3$)$_2$), 53.2 (*C*HPh$_2$), 126.6, 128.8, 129.4, 130.2, 130.4, 142.6, 144.9, 145.1 (Ar-*C*); $^{29}Si\{^1H\}$ NMR (80 MHz, C6D6): δ = 6.26; IR *v*/cm^{-1} (Nujol): 1898 (m, Zn-H), 1600 (m), 1129 (w), 1076 (w), 1031 (w), 917 (w), 744 (w), 702 (s); MS/EI *m/z* (%): 687.5 (M^+, 4), 644.4 (M^+-Pr^i, 24), 580.4 (L†H-Pr^{i+}, 28) 167.1 (Ph_2CH^+, 100); anal. calc. for $C_{44}H_{53}NSiZn$: C 76.66%, H 7.75%, N 2.03%, found: C 76.55%, H 7.81%, N 2.15%.

Synthesis of L'Zn(OCH$_2$Ph). To a solution of L'ZnH (0.02 g, 0.033 mmol) in C_6D_6 (0.5 mL) in a J. Young's NMR tube was added benzaldehyde (3.5 mg, 0.033 mmol). The reaction mixture was

monitored by ^{1}H NMR spectroscopy which showed essentially complete conversion (*ca.* 98%) to the title compound in less than 5 mins. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = -0.10 (s, 9H, Si(C*H*-$_3$)$_3$), 1.00 (d, J = 6.9 Hz, 6H, CH(CH_3)$_2$), 2.55 (sept, J = 6.9 Hz, 1H, C*H*(CH$_3$)$_2$), 4.19 (s, 2H, ZnOCH_2), 6.59 (s, 2H, Ph$_2$C*H*), 9.89-7.50 (m, 25H, Ar*H*).

N.B. A single crystal of {L'Zn(O=CHPh)(μ-OCH$_2$Ph)}$_2$ was isolated from the reaction mixture by layering it with pentane. Details of its X-ray crystal structure can be found below.

N.B. Treatment of a C_6D_6 solution of L'Zn(OCH$_2$Ph) with 1 equiv. of HSi(OEt)$_3$ led to the clean regeneration of L'ZnH, and the formation of (EtO)$_3$SiOCH$_2$Ph, as determined by a ^{1}H NMR spectroscopic analysis. This result implies related alkoxide intermediates are involved in the reactions catalysed by **7** mentioned below.

Synthesis of L'Zn{OCH(Ph)(CF$_3$)}. To a solution of L'ZnH (0.02 g, 0.033 mmol) in C_6D_6 (0.5 mL) in a J. Young's NMR tube was added trifluoroacetophenone (5.7 mg, 0.033 mmol). The reaction mixture was monitored by ^{1}H NMR spectroscopy which showed essentially complete conversion (*ca.* 98%) to the title compound in less than 5 mins. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 0.12 (s, 9H, Si(CH_3)$_3$), 0.93 (d, J = 6.9 Hz, 6H, CH(CH_3)$_2$), 2.46 (sept, J = 6.9 Hz, 1H, C*H*(CH$_3$)$_2$), 5.31 (q, $J_{H\text{-}F}$ = 6.3 Hz, 1H, ZnOC*H*(Ph)(CF$_3$)), 6.18 (s, 2H, Ph$_2$C*H*), 6.95-7.27 (m, 25H, Ar*H*); ^{19}F NMR (282 MHz, C_6D_6, 298 K): -78.15 (d, $J_{F\text{-}H}$ = 6.8 Hz, CF_3).

Catalysis Studies

All reaction samples were prepared in J. Young's NMR tubes on a Schlenk line, under an atmosphere of nitrogen gas. A stock solution of L†ZnH **7** (44.3 mg, 0.0643 mmol) in d_6-benzene (10.06 mL) containing an internal standard of tetrakis(trimethylsilyl)silane (104.7 mg, 0.3263 mmol) was prepared and stored in a Schlenk flask fitted with a J. Youngs tap. For each reaction, 0.50 mL of this stock solution was syringed into a NMR tube under nitrogen, then the hydride and carbonyl substrates (20 equiv. of each) added *via.* micropipette. The samples were then sealed, vigorously shaken, and initial ^{1}H NMR spectra recorded (t ≤ 10 min). The reactions were then monitored periodically (*ca.* every 30 min.), until the catalyst, or intermediate in the catalytic cycle, had fully decomposed to protonated ligand, L†H, as determined *via* monitoring of C*H*Ph$_2$ resonances. At this point conversion of substrate to product had ceased. It should be noted that in control experiments, no reaction was observed between catalyst **7** and either (EtO)$_3$SiH or HBpin.

Hydrosilylation of benzaldehyde and acetophenone with triethoxylsilane

Conversions were determined by the ratio of the ^{1}H NMR spectroscopic integrals for the unreacted (CH$_3$C***H$_2$***O)$_3$SiH and (CH$_3$C***H$_2$***O)$_{4-n}$Si(OR)$_n$ (R = CH$_2$Ph or CH(Me)Ph) product resonances, and

were confirmed by integration against the signal for the $(TMS)_4Si$ internal standard. Product resonance chemical shifts were confirmed by comparison to literature values.[4] Control reactions in the absence of **7** were also performed and monitored by ^1H NMR spectroscopy. No reaction was observed in all cases. Results are summarised below. Note that the product mixtures, $(CH_3CH_2O)_{4-n}Si(OR)_n$, for the hydrosilylation of the carbonyl substrates with triethoxysilane have been observed on previous occasions.[4]

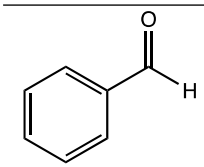
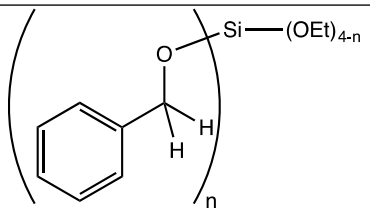
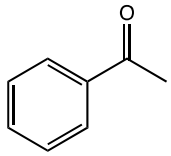
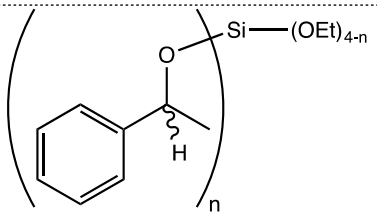
		catalyst 7, 5 mol%		
Substrate	**Product**	**Conversion**	**Time**	**TOF (h^{-1})**
		47 %	1 h	19
		NB: catalyst was fully decomposed after 1 h. No further conversion was observed.		
		75 %	> 72 h	< 0.21
		NB: a negligible amount of catalyst was observed to persist (ca. 5%), however conversion became negligible after time stated		

Table S1 – Results for the hydrosilylation (using triethoxysilane) of benzaldehyde and acetophenone utilising **7** as a catalyst (5 mol%).

Hydroboration of benzaldehyde and acetophenone with with pinacol borane

Conversions were determined by the ratio of the integrals of the ^1H NMR spectroscopic signals for the carbonyl precursor (PhC**H**O or Ph(C***H***$_3$)CO) and product (BOC***H***) resonances, and were confirmed by integration against the signal for the $(TMS)_4Si$ internal standard. Product resonance chemical shifts were confirmed by comparison to literature values.[5] Control reactions in the absence of **7** were also performed and monitored by ^1H NMR spectroscopy. No reaction was observed in all cases. Results are summarised below.

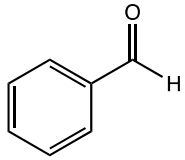
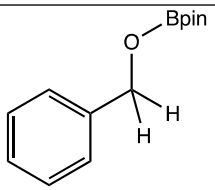
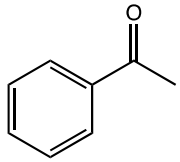
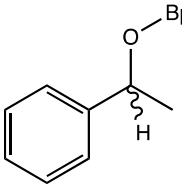
		catalyst 7, 5 mol%		
Substrate	**Product**	**Conversion**	**Time**	**TOF (h^{-1})**
		45 %	< 10 min	> 54
		NB: catalyst was fully decomposed before first ^1H NMR spectrum could be run. No further conversion was observed.		
		68 %	> 24 h	< 0.57
		NB: a negligible amount of catalyst was observed to persist (ca. 5%), however conversion became negligible after time stated		

Table S2 – Results for the hydroboration (using pinacol borane) of benzaldehyde and acetophenone utilising **7** as a catalyst (5 mol%).

2. X-Ray Crystallography

Crystals of **5**-**7**, L"ZnEt, L"ZnBr, (BoN)(Me_3Si)NK(THF), (BoN)(Me_3Si)NZnBr(THF), {L*Zn(μ-OH)}$_2$, and {L'Zn(O=CHPh)(μ-OCH_2Ph)}$_2$ suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were carried out with either a Bruker Apex X8 diffractometer using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å), or the MX1 beamline of the Australian Synchrotron (λ = 0.7109 Å). The software package Blu-Ice[6] was used for synchrotron data acquisition, while the program XDS[7] was employed for synchrotron data reduction. All structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX97[8]) using all unique data. Hydrogen atoms are typically included in calculated positions (riding model), except for the hydride ligands of **5**-**7**, which were refined isotropically with the Zn-H distance constrained for **5** and **6**, and the positional parameters for **7** freely refined. The absolute structure factors for (BoN)(Me_3Si)NK(THF) and {L'Zn(O=CHPh)(μ-OCH_2Ph)}$_2$ are 0.36(9) and 0.009(9), respectively. Crystal data, details of data collections and refinements (including structural diaorder) for all structures can be found in their CIF files and are summarized in Table S3.

Table S3. Crystal data for **5-7**, L"ZnEt **1S**, L"ZnBr **2S**, (BoN)(Me_3Si)NK(THF) **3S**, (BoN)(Me_3Si)NZnBr(THF) **4S**, {L*Zn(μ-OH)}$_2$ **5S**, and {L'Zn(O=CHPh)(μ-OCH_2Ph)}$_2$ **6S**.

Identification code	5	6	7	1S	2S	3S	4S
Empirical formula	$C_{38}H_{41}NSiZn$	$C_{42}H_{48.98}Br_{0.02}NSiZn$	$C_{44}H_{53}NSiZn$	$C_{47}H_{59}NO_3SiZn$	$C_{45}H_{54}BrNO_3SiZn$	$C_{33}H_{53}BKN_3OSi$	$C_{33}H_{53}BBrN_3OSiZn$
Formula weight	605.18	662.86	689.33	779.41	830.26	585.78	691.96
Crystal system	Triclinic	Triclinic	Orthorhombic	Tetragonal	Tetragonal	Orthorhombic	Monoclinic
Space group	P-1	P-1	Pbca	P-42_1c	$I4_1$/a	$P2_12_12_1$	$P2_1$/c
a (Å)	9.9787(14)	14.0869(4)	18.699(4)	21.1923(12)	20.9835(10)	11.5483(8)	15.203(3)
b (Å)	11.6997(14)	15.8901(5)	10.648(2)	21.1923(12)	20.9835(10)	15.6266(11)	11.974(2)
c (Å)	14.992(2)	17.1769(5)	37.755(8)	18.9615(15)	37.613(3)	19.1969(12)	19.965(4)
α (°)	88.800(3)	72.1010(10)	90.00	90.00	90.00	90.00	90.00
β (°)	85.337(4)	81.4480(10)	90.00	90.00	90.00	90.00	100.30(3)
γ (°)	72.292(3)	81.0360(10)	90.00	90.00	90.00	90.00	90.00
V (Å^3)	1661.9(4)	3593.29(18)	7517(3)	8515.9(10)	16561.1(17)	3464.3	3576.1(12)
Z	2	4	8	8	16	4	4
T (K)	123(2)	123(2)	100(2)	123(2)	123(2)	123(2)	123(2)
ρ_{calc} (g/cm^3)	1.209	1.225	1.218	1.216	1.332	1.123	1.285
μ (mm^{-1})	0.801	0.768	0.716	0.645	1.627	0.216	1.866
F(000)	640	1411	2944	3328	6944	1272	1456
2Θ range for data collection/°	6.44 to 51	5.86 to 51	5.9 to 51	6.08 to 55	5.90 to 51	6.1 to 52.3	6.34 to 55
Reflections collected	21733	48757	51283	27597	20894	39016	42912
Unique reflections	6161	13370	6982	9704	7690	6861	8212
R_{int}	0.0840	0.0223	0.1145	0.0543	0.0780	0.1013	0.0487
R_1 [I>=2σ (I)]	0.0650	0.0395	0.0711	0.0543	0.0597	0.0739	0.0327
wR_2 [all data]	0.1691	0.1139	0.2061	0.1477	0.1364	0.2236	0.0739
Largest diff. peak/hole / e Å^{-3}	0.60/-0.74	1.04/-1.11	0.47/-1.56	0.96/-0.53	1.03/-0.68	0.55/-1.15	0.60/-0.41
CCDC no.	1488971	1488967	1488970	1488964	1488968	1488963	1488965

Table S3 (contd.). Crystal data for **5**-**7**, L"ZnEt **1S**, L"ZnBr **2S**, (BoN)(Me_3Si)NK(THF) **3S**, (BoN)(Me_3Si)NZnBr(THF) **4S**, {L*Zn(μ-OH)}$_2$ **5S**, and {L'Zn(O=CHPh)(μ-OCH_2Ph)}$_2$ **6S**.

Identification code	**5S**	**6S**.(pentane)$_{1.5}$
Empirical formula	$C_{84}H_{98}N_2O_2Si_2Zn_2$	$C_{55.75}H_{62}NO_2SiZn$
Formula weight	1354.56	871.52
Crystal system	Triclinic	Orthorhombic
Space group	P-1	$Pna2_1$
a (Å)	13.390(3)	27.289(6)
b (Å)	14.317(3)	12.855(3)
c (Å)	20.067(4)	28.084(6)
α (°)	80.79(3)	90.00
β (°)	79.66(3)	90.00
γ (°)	71.54(3)	90.00
V (Å^3)	3567.7(12)	9852(3)
Z	2	8
T (K)	100(2)	100(2)
ρ_{calc} (g/cm^3)	1.261	1.175
μ (mm^{-1})	0.755	0.563
F(000)	1440	3708
2Θ range for data collection/°	5.92 to 51	5.98 to 51
Reflections collected	50036	68711
Unique reflections	13231	18296
R_{int}	0.0575	0.0877
R_1 [I>=2σ (I)]	0.0385	0.0543
wR_2 [all data]	0.1023	0.1377
Largest diff. peak/hole / e Å^{-3}	0.74/-1.01	0.83/-0.448
CCDC no.	1488966	1488969

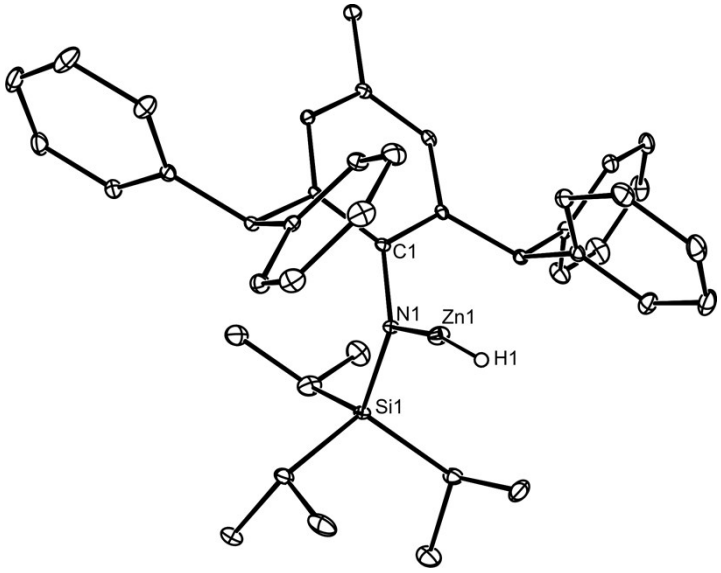


Fig. S1 Molecular structure of L*ZnH **6** (25% thermal ellipsoids; hydrogen atoms, except H(1), omitted). Selected bond lengths (Å) and angles (º): Zn(1)-N(1) 1.8652(18), Zn(1)-H(1) 1.531(8), N(1)-Zn(1)-H(1) 170.8(8), C(1)-N(1)-Si(1) 123.89(14).

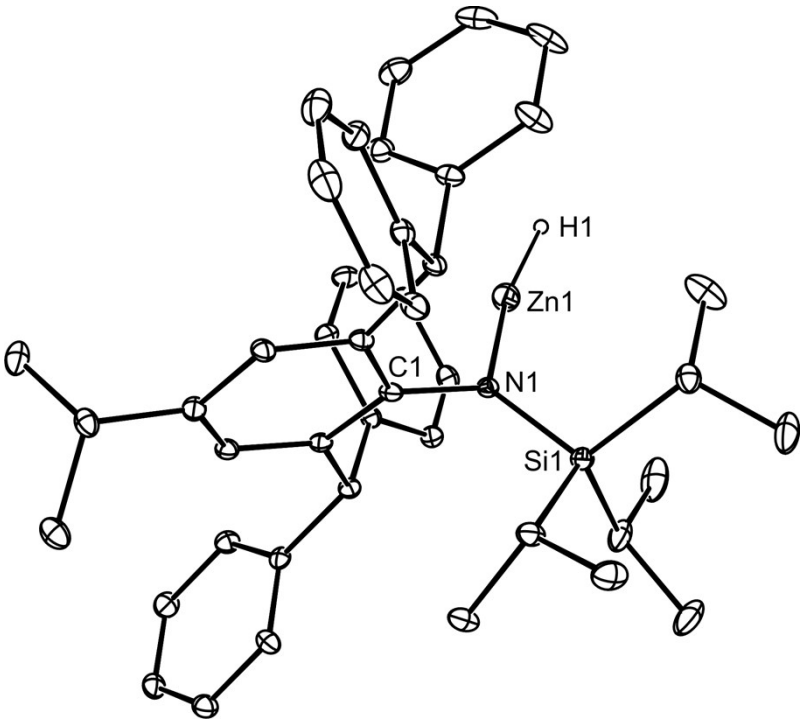


Fig. S2 Molecular structure of L†ZnH **7** (25% thermal ellipsoids; hydrogen, except H(1), atoms omitted). Selected bond lengths (Å) and angles (º): Zn(1)-N(1) 1.868(3), Zn(1)-H(1) 1.50(5), N(1)-Zn(1)-H(1) 166.9(18), C(1)-N(1)-Si(1) 124.1(3).

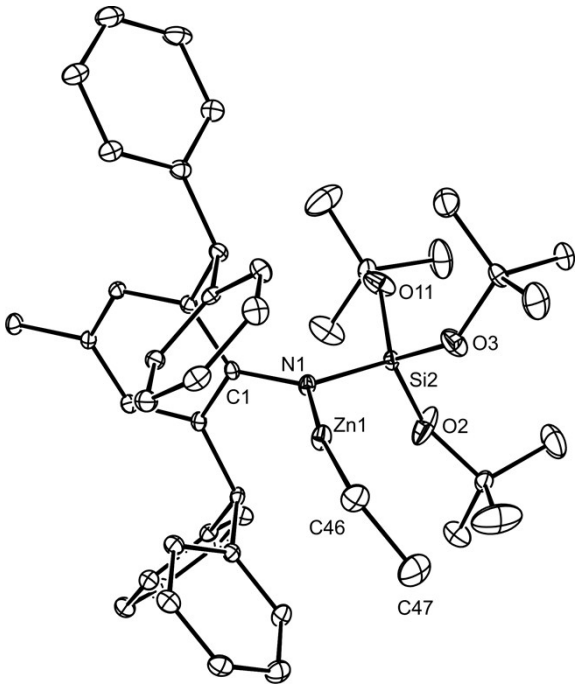


Fig. S3 Molecular structure of L"ZnEt **1S** (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (º): Zn(1)-N(1) 1.866(3), Zn(1)-C(46) 1.929(4), N(1)-Zn(1)-C(46) 171.13(19), C(1)-N(1)-Si(2) 125.3(2).

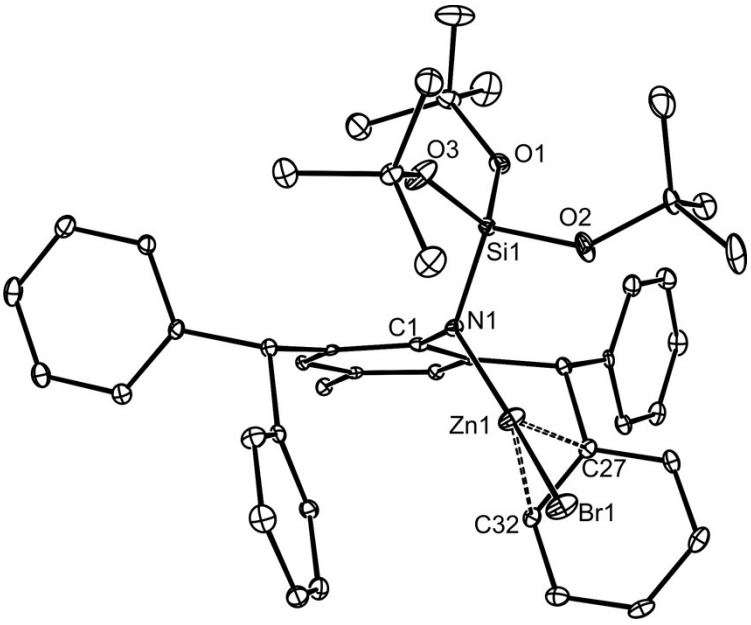


Fig. S4 Molecular structure of L"ZnBr **2S** (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (º): Zn(1)-N(1) 1.864(3), Zn(1)-Br(1) 2.2392(7), Zn(1)-C(27) 2.716(3), Zn(1)-C(32) 2.788(3), N(1)-Zn(1)-Br(1) 157.34(11), C(1)-N(1)-Si(1) 124.5(3).

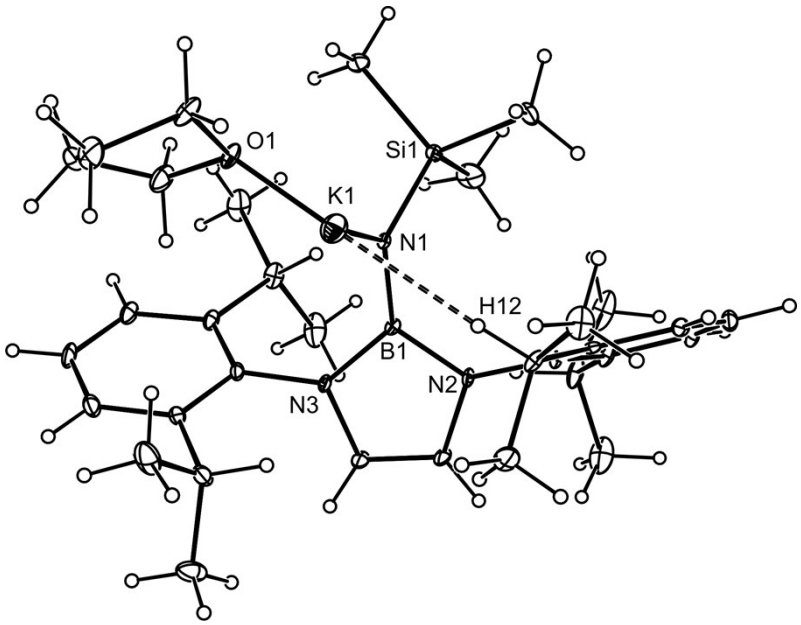


Fig. S5 Molecular structure of (BoN)(Me_3Si)NK(THF) **3S** (25% thermal ellipsoids). Selected bond lengths (Å) and angles (º): Si(1)-N(1) 1.734(4), N(1)-B(1) 1.435(6), K(1)-N(1) 1.847(4), K(1)-O(1) 1.902(3), K(1)-H(12) 2.60(1), N(1)-K(1)-O(1) 108.45(16), B(1)-N(1)-Si(1) 125.9(3).

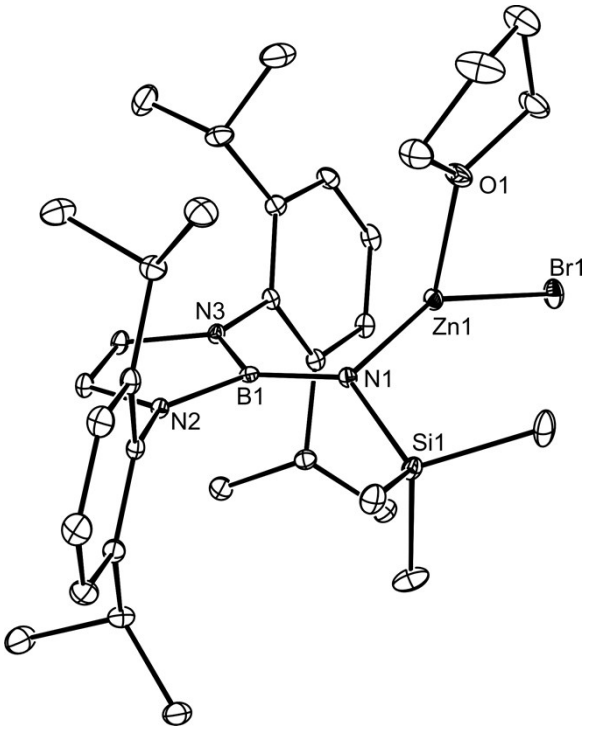


Fig. S6 Molecular structure of (BoN)(Me_3Si)NZnBr(THF) **4S** (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (º): Zn(1)-N(1) 1.8921(16), Zn(1)-O(1) 2.0658(16), B(1)-N(1) 1.423(3), N(1)-Zn(1)-O(1) 106.56(7), N(1)-Zn(1)-Br(1) 147.30(5), O(1)-Zn(1)-Br(1) 101.02(4), B(1)-N(1)-Si(1) 129.33(14).

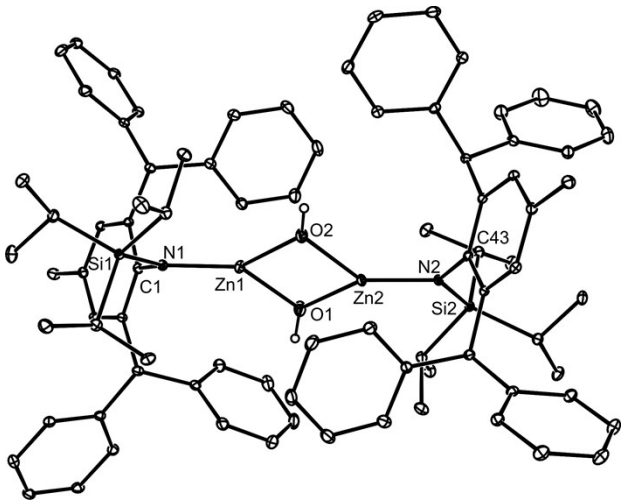


Fig. S7 Molecular structure of {L*Zn(μ-OH)}$_2$ **5S** (25% thermal ellipsoids; hydrogen atoms, except hydroxyl protons, omitted). Selected bond lengths (Å) and angles (º): Zn(1)-N(1) 1.8957(18), Zn(1)-O(1) 1.9280(18), Zn(1)-O(2) 1.9693(17), Zn(2)-N(2) 1.8838(17), Zn(2)-O(1) 1.9173(17), Zn(2)-O(2) 1.9577(17), N(1)-Zn(1)-O(1) 140.77(7), N(1)-Zn(1)-O(2) 139.21(7), N(2)-Zn(2)-O(1) 139.47(7), N(2)-Zn(2)-O(2) 139.29(7), O(1)-Zn(1)-O(2) 78.77(7), O(1)-Zn(2)-O(2) 79.31(7).

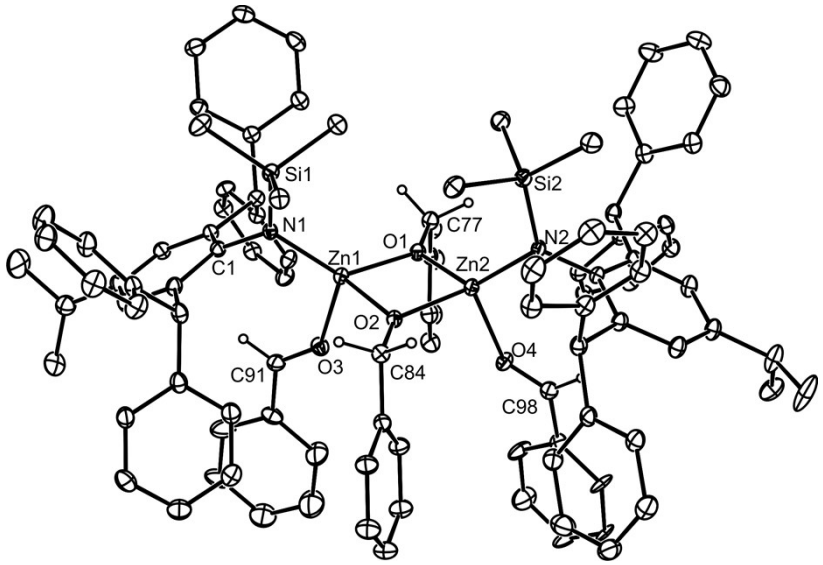
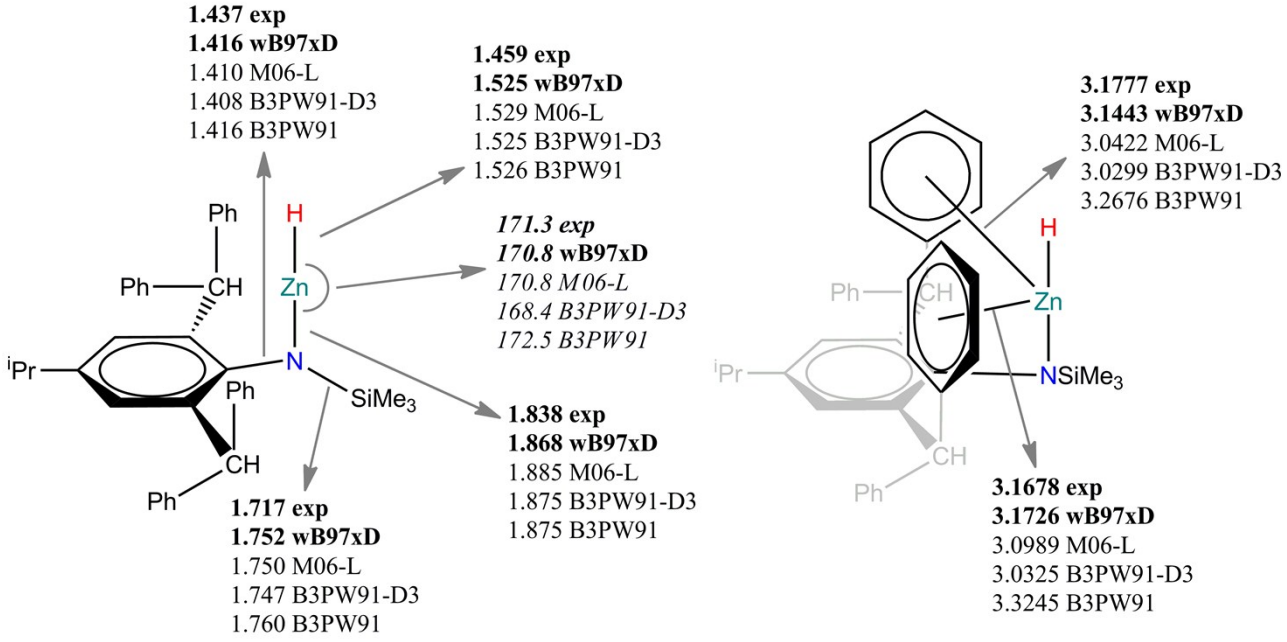


Fig. S8 Molecular structure of {L'Zn(O=CHPh)(μ-OCH$_2$Ph)}$_2$ **6S** (25% thermal ellipsoids; hydrogen atoms, except methylene and alkoxy protons, omitted). Selected bond lengths (Å) and angles (º): Zn(2)-N(2) 1.909(4), Zn(2)-O(2) 1.964(3), Zn(2)-O(1) 1.975(3), Zn(2)-O(4) 2.114(3), Zn(1)-N(1) 1.913(4), Zn(1)-O(1) 1.970(3), Zn(1)-O(2) 1.978(3), Zn(1)-O(3) 2.112(3), N(1)-Zn(1)-O(1) 131.36(15), N(1)-Zn(1)-O(2) 128.94(14), O(1)-Zn(1)-O(2) 80.24(13), N(1)-Zn(1)-O(3) 108.54(14), O(1)-Zn(1)-O(3) 102.24(13), N(2)-Zn(2)-O(2) 131.31(15), N(2)-Zn(2)-O(1) 127.85(15), O(2)-Zn(2)-O(1) 80.46(13), N(2)-Zn(2)-O(4) 107.69(14), O(2)-Zn(2)-O(4) 101.05(13), O(1)-Zn(2)-O(4) 102.89(13).

3. Computational Studies

Calculations were carried out with Gaussian 09 program[9] using the long-range corrected hybrid density functional that includes empirical atom–atom dispersion corrections and denoted as wB97xD.[10] For the Zn atom the large triple-zeta basis set, denoted as Def2-TZVPD, is used which is built on Karlsruhe's segmented contracted basis sets.[11] The Si atom was treated with the corresponding Stuttgart-Dresden RECP (relativistic effective core potential) in combination with its adapted basis sets,[12] and augmented by an extra polarization function.[13] For all the remaining atoms the 6-31G(d,p) basis set was used.[14] Geometry optimizations were carried out without any symmetry restrictions. It should be noted that we have performed benchmark calculations by using different type of functionals, as B3PW91,[15] B3PW91-GD3BJ,[15,16] M06-L,[17] and wB97xD, by keeping constantly the same basis set combination. The final functional of choice, wB97xD, was based on the better match found for a selection of some critical bond distances and angles with respect to those of the X-ray available structure (see scheme S1 below). Next, we proceeded into the theoretical estimation of the ^{1}H magnetic isotropic shielding tensor of the hydride in complex **5'** (with the $SiMe_4$ being the reference compound) on the wB97xD gas-phase optimized geometries, by using the Gauge Including Atomic Orbitals (GIAO) method.[18] Natural population analysis (NPA) was performed using Weinhold's methodology.[19] Finally, Chemcraft is used for the visualization of the molecular orbitals.[20]



Scheme S1. Selected bond distances (in angstroms) and angles (in degrees) using different DFT methods. The notation **exp** stands for the corresponding X-ray derived value.

Table S4. Cartesian coordinates of optimized structures along with relevant ^{1}H magnetic isotropic shielding tensors.

5' (B3PW91)

1	1.243785000	-1.634694000	-5.805180000
1	-3.490465000	2.957864000	-4.992751000
1	2.960762000	0.129188000	-5.446550000
6	1.135829000	-0.926480000	-4.988018000
6	2.099241000	0.063035000	-4.788360000
6	-3.604820000	2.112213000	-4.319583000
1	-5.753120000	2.055907000	-4.494311000
1	-1.490171000	1.929136000	-3.976809000
1	-0.721435000	-1.775347000	-4.312543000
6	-4.873009000	1.608127000	-4.040986000
6	0.033169000	-1.010921000	-4.141603000
6	-2.474231000	1.533473000	-3.742467000
6	1.950397000	0.959460000	-3.733658000
1	2.695281000	1.732955000	-3.567170000
6	-0.131992000	-0.114395000	-3.075376000
6	-5.002545000	0.519785000	-3.178306000
6	-2.590408000	0.442718000	-2.874282000
6	0.846410000	0.869773000	-2.881101000
1	-5.985872000	0.113598000	-2.956140000
6	-3.871901000	-0.053740000	-2.602946000
1	-1.867766000	-3.612798000	-2.189753000
6	-1.383236000	-0.207404000	-2.204816000
1	0.733521000	1.574327000	-2.061656000
1	-1.608381000	-1.275061000	-2.126504000
1	3.136918000	-1.886386000	-2.022128000
1	1.034995000	-4.591108000	-1.461078000
1	-3.982255000	-0.899985000	-1.929108000
6	-2.107275000	-3.636450000	-1.121666000
1	-2.499219000	-4.634498000	-0.892415000
30	1.825143000	-1.711467000	-1.262789000
1	-2.913864000	-2.920138000	-0.933899000
1	-2.269388000	2.088548000	-1.018360000
6	0.703856000	-4.624423000	-0.416356000
1	0.273620000	-5.617964000	-0.248168000
6	-1.129621000	0.288041000	-0.784293000
1	4.535910000	1.524276000	-0.173309000
6	-1.625282000	1.520823000	-0.351487000
7	0.199059000	-1.742573000	-0.330099000
1	1.587314000	-4.532748000	0.224301000
14	-0.587017000	-3.288668000	-0.032395000
1	6.137767000	-0.333596000	0.224737000
6	4.223782000	0.644787000	0.383538000
6	-0.311724000	-0.485421000	0.075938000
6	5.123381000	-0.394030000	0.608447000
1	-2.514366000	3.751422000	0.527268000
1	2.219874000	1.379319000	0.694410000
6	2.916442000	0.563982000	0.869943000
6	-1.322652000	2.043238000	0.905773000
1	-0.172005000	4.564324000	0.770370000
6	4.708632000	-1.516903000	1.325330000
6	-1.904119000	3.371096000	1.357681000
1	5.400385000	-2.335923000	1.503063000
6	0.055165000	0.071428000	1.328823000
1	-1.844728000	-4.346318000	1.847740000
6	-1.196294000	-3.467874000	1.757406000
6	2.488549000	-0.555742000	1.595481000
6	-0.814126000	4.412549000	1.643909000

6	-0.461893000	1.306006000	1.722933000
1	-3.633546000	2.486110000	2.354370000
6	3.406345000	-1.593908000	1.813347000
1	-1.259422000	5.377569000	1.910487000
1	-1.783284000	-2.591599000	2.053026000
1	-0.374189000	-3.586219000	2.470047000
1	0.826669000	-1.717595000	2.151040000
6	-2.829962000	3.197117000	2.569961000
6	1.085359000	-0.655114000	2.188343000
1	-3.286198000	4.152636000	2.852399000
1	3.092986000	-2.466786000	2.381771000
1	-0.175793000	4.101911000	2.478458000
1	-0.180070000	1.696212000	2.697262000
1	-2.277064000	2.821762000	3.438181000
6	1.049041000	-0.248629000	3.659027000
1	2.758769000	1.059390000	3.603004000
1	-0.674981000	-1.471428000	4.066953000
6	1.967546000	0.644228000	4.220472000
6	0.048759000	-0.777119000	4.486376000
6	1.887982000	1.000274000	5.567526000
6	-0.032876000	-0.424894000	5.830558000
1	2.614426000	1.694133000	5.982578000
1	-0.815310000	-0.851403000	6.452857000
6	0.888829000	0.467890000	6.378177000
1	0.829343000	0.742093000	7.427898000

5' (B3PW91-GD3BJ)

1	1.615836000	-1.578903000	-5.541370000
1	-3.178840000	3.078976000	-4.950067000
1	3.302749000	0.139022000	-4.925593000
6	1.423408000	-0.897128000	-4.718143000
6	2.370595000	0.067314000	-4.373914000
6	-3.354985000	2.197226000	-4.340211000
1	-5.483382000	2.191745000	-4.677983000
1	-1.275241000	1.952623000	-3.840506000
1	-0.504647000	-1.747602000	-4.270938000
6	-4.647501000	1.700573000	-4.188225000
6	0.234508000	-0.997671000	-4.000883000
6	-2.281754000	1.565212000	-3.714308000
6	2.119675000	0.923948000	-3.306146000
1	2.853952000	1.672693000	-3.024505000
6	-0.031910000	-0.139535000	-2.926848000
6	-4.860534000	0.565604000	-3.406294000
6	-2.486048000	0.429661000	-2.926844000
6	0.927784000	0.821341000	-2.585445000
1	-5.864205000	0.167730000	-3.285051000
6	-3.786940000	-0.062421000	-2.782275000
1	-2.225872000	-3.418346000	-1.965239000
6	-1.354613000	-0.252906000	-2.185098000
1	0.729456000	1.487941000	-1.751861000
1	-1.585866000	-1.319876000	-2.150124000
1	3.105857000	-2.006761000	-1.965002000
1	0.683847000	-4.540824000	-1.700157000
1	-3.953186000	-0.944909000	-2.169970000
6	-2.329035000	-3.414450000	-0.875600000
1	-2.839203000	-4.338673000	-0.583054000
30	1.804199000	-1.730579000	-1.219911000
1	-2.974393000	-2.575850000	-0.592748000
1	-2.388716000	1.994052000	-0.981539000
6	0.498424000	-4.639582000	-0.624817000
1	0.057390000	-5.627102000	-0.454131000
6	-1.207739000	0.219136000	-0.750331000

1	4.180863000	1.425574000	-0.612961000
6	-1.747188000	1.428671000	-0.311011000
7	0.161981000	-1.767390000	-0.315105000
1	1.463648000	-4.610907000	-0.107812000
14	-0.653480000	-3.279822000	0.001058000
1	5.877671000	-0.349383000	-0.241048000
6	3.953918000	0.580467000	0.029990000
6	-0.385766000	-0.541173000	0.107784000
6	4.906910000	-0.411678000	0.240738000
1	-2.706540000	3.616482000	0.614922000
1	1.954602000	1.266095000	0.473817000
6	2.698884000	0.492493000	0.636226000
6	-1.472175000	1.932220000	0.959935000
1	-0.368965000	4.452499000	0.821553000
6	4.598789000	-1.496481000	1.061579000
6	-2.074222000	3.239358000	1.429509000
1	5.331007000	-2.282372000	1.222236000
6	-0.044460000	0.002599000	1.366289000
1	-1.696459000	-4.381437000	1.988069000
6	-1.025593000	-3.527912000	1.843479000
6	2.381668000	-0.589862000	1.466028000
6	-0.991002000	4.287314000	1.706744000
6	-0.597122000	1.212643000	1.777420000
1	-3.754960000	2.302013000	2.451356000
6	3.348058000	-1.583071000	1.666888000
1	-1.437420000	5.244570000	1.996836000
1	-1.524253000	-2.639629000	2.246284000
1	-0.119361000	-3.710128000	2.429215000
1	0.793121000	-1.758498000	2.189601000
6	-2.965111000	3.030090000	2.658849000
6	1.038335000	-0.694204000	2.169818000
1	-3.435096000	3.970469000	2.966747000
1	3.109378000	-2.427792000	2.308170000
1	-0.333672000	3.965826000	2.521966000
1	-0.326038000	1.603619000	2.753533000
1	-2.379953000	2.654811000	3.505436000
6	1.104583000	-0.217727000	3.607093000
1	2.673860000	1.218487000	3.300649000
1	-0.464770000	-1.546063000	4.231326000
6	1.979100000	0.791039000	4.017340000
6	0.221419000	-0.763376000	4.544094000
6	1.968553000	1.247407000	5.334576000
6	0.208782000	-0.310636000	5.859896000
1	2.656009000	2.032365000	5.637352000
1	-0.482887000	-0.747575000	6.574783000
6	1.083336000	0.699512000	6.259964000
1	1.076308000	1.053785000	7.286708000

5' (M06-L)

1	1.425603000	-1.851914000	-5.529372000
1	-3.214235000	3.143674000	-4.913533000
1	3.159839000	-0.117893000	-5.128421000
6	1.279108000	-1.102735000	-4.756249000
6	2.252378000	-0.130945000	-4.532265000
6	-3.390402000	2.256626000	-4.310625000
1	-5.516173000	2.247276000	-4.658561000
1	-1.311092000	2.015719000	-3.808239000
1	-0.639052000	-1.882382000	-4.158925000
6	-4.680986000	1.755225000	-4.167942000
6	0.122098000	-1.123134000	-3.983783000
6	-2.318689000	1.623197000	-3.686852000
6	2.061259000	0.810566000	-3.525965000

1	2.819510000	1.565933000	-3.336621000
6	-0.090112000	-0.176002000	-2.974353000
6	-4.892984000	0.614897000	-3.396562000
6	-2.519201000	0.480097000	-2.908552000
6	0.901479000	0.787132000	-2.748785000
1	-5.895681000	0.211336000	-3.283201000
6	-3.820009000	-0.014075000	-2.774230000
1	-2.025923000	-3.495709000	-2.077020000
6	-1.385361000	-0.213879000	-2.179188000
1	0.755047000	1.523536000	-1.959697000
1	-1.659247000	-1.272960000	-2.116418000
1	3.147362000	-1.956303000	-1.995570000
1	0.945008000	-4.460981000	-1.580618000
1	-3.986227000	-0.905071000	-2.170369000
6	-2.194930000	-3.510266000	-0.995316000
1	-2.656352000	-4.471804000	-0.746309000
30	1.832369000	-1.718893000	-1.252144000
1	-2.927550000	-2.730521000	-0.759833000
1	-2.365106000	2.055113000	-0.960594000
6	0.666228000	-4.565856000	-0.525245000
1	0.273846000	-5.579125000	-0.398391000
6	-1.184593000	0.270660000	-0.753721000
1	4.245925000	1.517852000	-0.505410000
6	-1.717060000	1.479416000	-0.300766000
7	0.187702000	-1.726482000	-0.331590000
1	1.583596000	-4.493052000	0.069860000
14	-0.595465000	-3.258545000	-0.010889000
1	5.920486000	-0.289538000	-0.187895000
6	4.005729000	0.651898000	0.106197000
6	-0.354531000	-0.497531000	0.095766000
6	4.945539000	-0.358049000	0.285633000
1	-2.672344000	3.662497000	0.645184000
1	2.015838000	1.351841000	0.564571000
6	2.748839000	0.558939000	0.705260000
6	-1.442907000	1.972326000	0.973114000
1	-0.334603000	4.501581000	0.896877000
6	4.621099000	-1.465635000	1.066626000
6	-2.045567000	3.270852000	1.459272000
1	5.343857000	-2.265289000	1.203616000
6	-0.018651000	0.033900000	1.364999000
1	-1.758724000	-4.303995000	1.944803000
6	-1.075467000	-3.459637000	1.809727000
6	2.411853000	-0.547388000	1.495400000
6	-0.970195000	4.310833000	1.767001000
6	-0.572950000	1.241197000	1.783762000
1	-3.737418000	2.328089000	2.462188000
6	3.366271000	-1.558430000	1.661577000
1	-1.416444000	5.261712000	2.076591000
1	-1.592266000	-2.562071000	2.167750000
1	-0.210103000	-3.627300000	2.458506000
1	0.818509000	-1.737729000	2.172918000
6	-2.940045000	3.045470000	2.677038000
6	1.057630000	-0.667595000	2.176605000
1	-3.403444000	3.981226000	3.007066000
1	3.112290000	-2.426094000	2.269256000
1	-0.320116000	3.973801000	2.582842000
1	-0.308545000	1.627228000	2.767446000
1	-2.359810000	2.649940000	3.519049000
6	1.088537000	-0.231030000	3.628688000
1	2.729675000	1.147331000	3.436132000
1	-0.564822000	-1.502190000	4.145888000
6	1.987433000	0.723792000	4.109313000
6	0.143865000	-0.761628000	4.513827000

6	1.943008000	1.137603000	5.439127000
6	0.095688000	-0.349881000	5.840611000
1	2.651962000	1.880384000	5.795442000
1	-0.645071000	-0.775970000	6.512122000
6	0.997447000	0.604034000	6.308997000
1	0.963904000	0.925750000	7.346162000

5' (wB97xD)

1	1.582946000	-1.550284000	-5.631296000
1	-3.293023000	3.088752000	-4.872161000
1	3.285795000	0.161233000	-5.042734000
6	1.408450000	-0.869434000	-4.804086000
6	2.363524000	0.090502000	-4.475585000
6	-3.429407000	2.177282000	-4.298130000
1	-5.549952000	2.075741000	-4.658964000
1	-1.347196000	2.024486000	-3.788494000
1	-0.510141000	-1.715393000	-4.326384000
6	-4.694775000	1.610788000	-4.178475000
6	0.234129000	-0.967273000	-4.065753000
6	-2.332074000	1.579079000	-3.684000000
6	2.131734000	0.947178000	-3.405672000
1	2.871027000	1.695140000	-3.136802000
6	-0.011431000	-0.112902000	-2.984880000
6	-4.855517000	0.439906000	-3.442068000
6	-2.483673000	0.409259000	-2.937410000
6	0.954009000	0.846380000	-2.664158000
1	-5.836909000	-0.014648000	-3.346848000
6	-3.757775000	-0.153026000	-2.827677000
1	-2.350990000	-3.360648000	-1.874417000
6	-1.320090000	-0.247414000	-2.210612000
1	0.779772000	1.515817000	-1.827089000
1	-1.531170000	-1.317584000	-2.175072000
1	3.102551000	-2.082750000	-1.991121000
1	0.522508000	-4.604430000	-1.696067000
1	-3.886834000	-1.067426000	-2.254677000
6	-2.414942000	-3.312186000	-0.782725000
1	-2.976942000	-4.186749000	-0.438757000
30	1.803528000	-1.818379000	-1.237141000
1	-2.986223000	-2.418741000	-0.507596000
1	-2.322119000	2.005714000	-1.003387000
6	0.353713000	-4.693940000	-0.617168000
1	-0.144506000	-5.652126000	-0.438940000
6	-1.156851000	0.220600000	-0.769610000
1	4.246178000	1.493210000	-0.570307000
6	-1.685635000	1.434798000	-0.333002000
7	0.178706000	-1.793612000	-0.315731000
1	1.328919000	-4.728271000	-0.119331000
14	-0.702732000	-3.266326000	0.036204000
1	5.956876000	-0.263150000	-0.187936000
6	4.022261000	0.643895000	0.067828000
6	-0.344554000	-0.543314000	0.094533000
6	4.982533000	-0.338192000	0.283455000
1	-2.565483000	3.676413000	0.549845000
1	2.018181000	1.311201000	0.490859000
6	2.764895000	0.541797000	0.663041000
6	-1.412216000	1.941014000	0.934154000
1	-0.230870000	4.434981000	1.038745000
6	4.679658000	-1.424944000	1.101199000
6	-2.024808000	3.247464000	1.402958000
1	5.419847000	-2.200646000	1.270658000
6	0.002614000	0.004803000	1.349379000
1	-1.722263000	-4.326309000	2.057438000

6	-1.028283000	-3.495680000	1.892370000
6	2.449480000	-0.544760000	1.484871000
6	-0.959838000	4.263018000	1.836388000
6	-0.546951000	1.217492000	1.753677000
1	-3.819566000	2.307042000	2.206319000
6	3.425678000	-1.525085000	1.694579000
1	-1.422887000	5.221822000	2.091032000
1	-1.487324000	-2.590814000	2.305523000
1	-0.111642000	-3.704916000	2.452540000
1	0.868669000	-1.748407000	2.175893000
6	-3.040535000	3.004284000	2.527490000
6	1.091364000	-0.679717000	2.167296000
1	-3.518648000	3.941243000	2.831864000
1	3.192796000	-2.373319000	2.333400000
1	-0.415122000	3.913545000	2.719974000
1	-0.280472000	1.612266000	2.729562000
1	-2.548122000	2.574585000	3.406732000
6	1.126463000	-0.221627000	3.618190000
1	2.699132000	1.224294000	3.375520000
1	-0.450274000	-1.564402000	4.190412000
6	1.990369000	0.778534000	4.066754000
6	0.228555000	-0.785892000	4.528509000
6	1.953997000	1.208075000	5.391406000
6	0.189258000	-0.359380000	5.851180000
1	2.635479000	1.985999000	5.722125000
1	-0.515702000	-0.810262000	6.543044000
6	1.053151000	0.642576000	6.287878000
1	1.025085000	0.977121000	7.320227000

$\sigma^{5'}$= 30.72 ppm

$SiMe_4$

14	0.000000000	0.000000000	-0.000890000
6	0.000000000	-0.000201000	1.894180000
1	0.000000000	1.021317000	2.287623000
1	-0.884964000	-0.510561000	2.287152000
1	0.884964000	-0.510561000	2.287152000
6	0.000000000	-1.786800000	-0.631293000
1	-0.884927000	-2.326626000	-0.279730000
1	0.000000000	-1.817602000	-1.725437000
1	0.884927000	-2.326626000	-0.279730000
6	-1.547342000	0.893311000	-0.632071000
1	-1.573791000	1.929293000	-0.279506000
1	-1.573317000	0.909898000	-1.726255000
1	-2.457465000	0.396329000	-0.281681000
6	1.547342000	0.893311000	-0.632071000
1	2.457465000	0.396329000	-0.281681000
1	1.573317000	0.909898000	-1.726255000
1	1.573791000	1.929293000	-0.279506000

σ^{TMS}= 31.75 ppm

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