Alkali-metal-mediated zincation (AMMZn) meets *N*-heterocyclic carbene (NHC) chemistry: Zn–H exchange reactions and structural authentication of a dinuclear Au(I) complex with a NHC anion

David R. Armstrong,[a] Sharon E. Baillie, [a] Victoria L. Blair,[a] Nicolas G. Chabloz,[a] Josefina Diez,[b] Joaquin Garcia-Alvarez,[b] Alan R. Kennedy,[a] Stuart D. Robertson[a] and Eva Hevia*[a]

[a] Dr. D. R. Armstrong, Dr. S. E. Baillie, Dr. V. L. Blair, N. G. Chabloz, Dr. A. R. Kennedy, Dr. S. D. Robertson and Dr. E. Hevia,

WestCHEM, Department of Pure and Applied Chemistry,

University of Strathclyde, Glasgow, G1 1XL, U.K.

E-mail: eva.hevia@strath.ac.uk

[b] Dr. J. Garcia-Alvarez, Dr. J. Diez

Departamento de Química Orgánica e Inorgánica, Instituto Universitario de Química Organometálica "Enrique Moles" (Unidad Asociada al CSIC), Facultad de Química, Universidad de Oviedo, E-33071 Oviedo, Spain

Crystallography. All data were measured at low temperature using Oxford Diffraction diffractometers. Refinements to convergence on F^2 were performed with SHELXL-97.[1] Final models for structures **2** and **4** included models for disorder in multiple THF groups and also (for **4**) a disordered butyl fragment. Reflection data for compound **5** had a low average intensity, and the count statistics were further compromised by the presence of other non-indexed diffraction peaks. Numerous samples of **5** were measured, but no better dataset was achieved. Thus the structure of **5** is of lower quality than the others presented here.

Table S1. Selected crystallographic and refinement parameters.

Compound	**2**	**3**	**4**	**5**	**6**
Formula	$C_{47}H_{77}N_2NaO_3Zn$	$C_{35}H_{54}N_2Zn$	$C_{71}H_{127}N_2NaO_7Zn_2$	$C_{39}H_{63}LiN_2Zn$	$C_{45}H_{50}Au_2ClN_2P$
Formula weight	806.47	568.17	1274.48	632.22	1079.22
Crystal system	orthorhombic	triclinic	monoclinic	orthorhombic	triclinic
Space Group	$P2_12_12_1$	P-1	$P2_1/c$	Pbca	P-1
λ Å	0.71073	1.5418	0.71073	0.71073	1.5418
a Å	11.9480(6)	9.7795(5)	12.5177(2)	21.8628(13)	9.2833(3)
b Å	15.8780(8)	10.1033(5)	33.2445(6)	22.1892(11)	14.4759(3)
c Å	24.9404(11)	20.1669(8)	18.2146(6)	31.9347(14)	16.9188(4)
α °	90	90.336(4)	90	90	68.109(2)
β °	90	103.989(4)	100.694(2)	90	81.380(2)
γ °	90	118.932(5)	90	90	86.270(2)
Volume Å^3	4731.5(4)	1674.40(14)	7448.3(2)	15492.1(14)	2085.74(9)
Temp. *K*	123(2)	123(2)	123(2)	123(2)	150(2)
Z	4	2	4	16	2
Refls. Collected	30717	11997	106036	43518	46765
Refls. Unique	10854	6087	17954	13585	8371
Refls. Obs.	7909	5646	14402	5496	7267
Rint	0.0552	0.0312	0.0636	0.3604	0.0487
Goodness of Fit	1.011	1.094	1.178	0.915	1.051
R[I>2σ(I)], *F*	0.0557	0.0425	0.0781	0.0897	0.0311
Rw, F^2	0.1010	0.0989	0.1585	0.2639	0.0804

[1] G. M. Sheldrick, *Acta Crystallogr.*, **2008**, *A64*, 112.

General Experimental Conditions All reactions were performed under a protective argon atmosphere using standard Schlenk techniques. Hexane and THF were dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use. [(TMEDA)Na(TMP)Zn(*t*Bu)$_2$] (**1**),[2] **IPr**,[3] **IBu**,[4] Zn*t*Bu$_2$,[1] and [ClAu(PPh$_3$)][5] were prepared according to literature procedures. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer operating at 400.13 MHz for ^{1}H, 100.62 MHz for ^{13}C and 155.50 MHz for ^{7}Li. Elemental analyses was carried out using a Perkin Elmer 2400 elemental analyzer.

Synthesis of (THF)$_3$Na[:C{[N(2,6-*i*Pr$_2$C$_6$H$_3$)]$_2$CHCZn(*t*Bu$_2$)}] (**2**) To a solution of [(TMEDA)Na(TMP)Zn(*t*Bu)$_2$] (**1**) (2.30 g, 5 mmol) in hexane (30 mL) 1,3-bis-(2,6-diisopropylphenyl)imidazole-2-ylidene (1.95 g, 5 mmol) was added and the resulting cream suspension was stirred for 30 minutes after which all volatiles were removed. THF (10 mL) and gentle heat gave a clear tan solution which was transferred to the freezer (-28 °C), which overnight deposited a crop of colourless crystals (3.46 g, 86%). Anal. Calcd for $C_{43}H_{69}N_2NaO_2Zn$: C, 70.33; H, 9.47; N, 3.81. Found: C, 70.45; H, 9.95; N 3.79. ^{1}H NMR (400.03 MHz, 298 K, d$_8$-THF) δ (ppm)[6] 0.73 (18H, s, C(C*H*$_3$)$_3$), 1.12 (6H, d, CH(C*H*$_3$)$_2$), 1.15 (6H, d, CH(C*H*$_3$)$_2$), 1.18 (6H, d, CH(C*H*$_3$)$_2$), 1.23 (6H, d, CH(C*H*$_3$)$_2$), 1.77 (8H, m, C*H*$_2$ (THF)), 2.95 (2H, septet, C*H*(CH$_3$)$_2$), 3.16 (2H, septet, C*H*(CH$_3$)$_2$), 3.62 (8H, m, OC*H*$_2$ (THF)), 6.66 (1H, s, imidazole backbone C*H*), 7.19-7.25 (5H, overlapping m, ArC*H*), 7.32 (1H, t, *p*-C*H*). ^{13}C {^{1}H} NMR (100.62 MHz, 298 K, d$_8$-THF) δ (ppm) 22.4 (*C*CH$_3$), 23.6 (CH(*C*H$_3$)$_2$), 24.6 (CH(*C*H$_3$)$_2$), 25.1 (CH(*C*H$_3$)$_2$), 26.0 (CH(*C*H$_3$)$_2$), 26.4 (*C*H$_2$ (THF)), 28.7 (*C*H(CH$_3$)$_2$), 28.8 (*C*H(CH$_3$)$_2$), 34.5 (C*C*H$_3$), 68.2 (O*C*H$_2$ (THF)), 123.9 (Ar*C*H), 123.9 (Ar*C*H), 127.6 (Ar*C*H), 128.6 (Ar*C*H), 129.9 (imidazole backbone *C*H), 140.7 (Ar*C*), 145.4 (Ar*C*), 146.5 (Ar*C*), 147.5 (Ar*C*), 159.5 (Zn*C*), 201.4 (C:).

Synthesis of (THF)$_3$Na[:C{[N(*t*Bu)]$_2$CHCZn(*t*Bu$_2$)}] (**2^{IBu}**) This compound was prepared using the same experimental procedure described for **2**, by reacting [(TMEDA)Na(TMP)Zn(*t*Bu)$_2$] (**1**) (0.23 g, 0.5 mmol) in hexane (5 mL) with 1,3-ditertbutlyl-imidazole-2-ylidene (0.09 g, 0.5 mmol). Addition of 1 mL of THF and storing the resulting solution in the freezer (-28 °C) over 24 hour led to the isolation

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6. The integration of the THF resonances in the ^{1}H NMR spectrum **2** with respect to those belonging to the *t*Bu groups and the metallated NHC fragment, show that only two molecules are present whereas the crystal structure of **2** contains three solvating THF molecules. This deficiency of THF in the ^{1}H NMR spectrum is due to removal of some of the sodium-bound THF when crystals of **2** are dried under vacuum. The loss of this THF molecule is also shown in the data obtained for CHN analysis.

of **2**$^{\mathbf{IBu}}$ in a 63% yield (0.187 g). Anal. Calcd for $C_{19}H_{37}N_2NaZn$:[7] C, 59.76; H, 9.77; N, 7.34. Found: C, 59.23; H, 10.01; N 7.59. ^{1}H NMR (400.03 MHz, 298 K, d_8-THF) δ (ppm)[8] 0.91 (18H, s, Zn-C(C*H*$_3$)$_3$), 1.46 (9H, s, NC(C*H*$_3$)$_3$), 1.48 (9H, s, NC(C*H*$_3$)$_3$), 1.73 (8H, m, C*H*$_2$ (THF)), 3.58 (8H, m, OC*H*$_2$ (THF)), 6.34 (1H, s, imidazole backbone C*H*). ^{13}C {^{1}H} NMR (100.62 MHz, 298 K, d_8-THF) δ (ppm) 21.4 (Zn-*C*(*C*H$_3$)$_3$), 26.4 (*C*H$_2$ (THF)), 32.0 (NC(*C*H$_3$)$_3$), 33.2 (NC(*C*H$_3$)$_3$), 35.7 (Zn-C (*C*H$_3$)$_3$), 54.1 (N*C*(CH$_3$)$_3$), 55.7 (N*C*(CH$_3$)$_3$), 68.2 (O*C*H$_2$ (THF)), 118.2 (imidazole backbone *C*H), 153.7 (Zn*C*), 195.2 (C:).

Synthesis of [Ipr.Zn*t*Bu$_2$] (3) To a solution of Zn*t*Bu$_2$ (1.26 g, 7 mmol) in hexane (35 mL) was added **IPr** (2.73 g, 7 mmol), giving a pale yellow suspension. After stirring for 30 minutes THF (10 mL) was charged, giving a clear yellow solution which deposited a crop of crystals after storage in the freezer overnight: 3.01 g, 76%. Crystals suitable for X-ray determination were crystallised from methylcyclohexane solution. Anal. Calcd for $C_{35}H_{54}N_2Zn$: C, 73.96; H, 9.58; N, 4.93. Found: C, 73.76; H, 10.12; N 4.99. ^{1}H NMR (400.03 MHz, 298 K, C_6D_6) δ (ppm) 0.96 (12H, d, CH(C*H*$_3$)$_2$), 1.10 (18H, s, C(C*H*$_3$)$_3$), 1.35 (12H, d, CH(C*H*$_3$)$_2$), 3.06 (4H, septet, C*H*(CH$_3$)$_2$), 6.63 (2H, s, imidazole backbone C*H*), 7.12 (4H, d, *m*-C*H*), 7.19 (2H, t, *p*-C*H*). ^{13}C {^{1}H} NMR (100.62 MHz, 298 K, C_6D_6) δ (ppm) 22.6 (*C*H(CH$_3$)$_2$), 23.7 (*C*(CH$_3$)$_3$), 26.0 (CH(*C*H$_3$)$_2$), 28.5 (*C*H(CH$_3$)$_2$), 34.1 (CH(*C*H$_3$)$_2$), 123.3 (imidazole backbone *C*H), 124.6 (*m*-*C*H), 130.1 (*p*-*C*H), 136.2 (*i*-*C*), 144.8 (*o*-*C*). Carbene C could not be detected.

[Na(THF)$_6$]$^+$ [*t*Bu$_2$Zn:C{[N(2,6-*i*Pr$_2$C$_6$H$_3$)]$_2$CHCZn(*t*Bu$_2$)}]$^-$ (4) To a solution of [IPr.Zn*t*Bu$_2$] (**3**) (0.57 g, 1 mmol) in hexane (10 mL) was added [(TMEDA)Na(TMP)Zn(*t*Bu)$_2$] (**1**) (0.46 g, 1 mmol) and the off-white suspension was stirred for 15 minutes. THF (5 mL) was added and the straw solution was frozen in liquid nitrogen before transferral to the freezer (-28 °C). A crop of colourless crystals was deposited overnight (0.36 g, 30%).[9] Anal. Calcd for $C_{59}H_{106}N_2NaO_4Zn_2$: C, 66.77; H, 10.07; N, 2.64. Found: C, 66.14; H, 10.45; N 2.93. ^{1}H NMR (400.03 MHz, 298 K, d_8-THF) δ (ppm) 0.50 (18H, s, C(C*H*$_3$)$_3$), 0.74 (18H, s, C(C*H*$_3$)$_3$), 1.10 (6H, d, CH(C*H*$_3$)$_2$), 1.14 (6H, d, CH(C*H*$_3$)$_2$), 1.23 (6H, d, CH(C*H*$_3$)$_2$), 1.27 (6H, d, CH(C*H*$_3$)$_2$), 1.77 (16H, m, C*H*$_2$ (THF)), 3.23 (2H, septet, C*H*(CH$_3$)$_2$), 3.38 (2H, septet, C*H*(CH$_3$)$_2$), 3.62 (16H, m, OC*H*$_2$ (THF)), 6.88 (1H, s, imidazole backbone C*H*), 7.16-7.26

[7] . CHN analysis results are consitent with the lack of THF molecules in the isolated solid, which were probably removed under vacumm when **2**$^{\mathbf{IBu}}$ was dried.

[8] The integration of the THF resonances in the ^{1}H NMR spectrum **2** with respect to those belonging to the *t*Bu groups and the metallated NHC fragment, show that only two molecules are present whereas the crystal structure of **2** contains three solvating THF molecules. This deficiency of THF in the ^{1}H NMR spectrum is due to removal of some of the sodium-bound THF when crystals of **2** are dried under vacuum.

[9]. NMR analysis of the filtrate showed that **4** is the only organometallic species present in solution suggesting that its formation is quantitative.

(6H, overlapping m, ArC*H*). ^{13}C {^{1}H} NMR (100.62 MHz, 298 K, d$_8$-THF) δ (ppm) 22.1 (*C*CH$_3$), 23.0 (CH(*C*H$_3$)$_2$), 23.1 (*C*CH$_3$), 24.2 (CH(*C*H$_3$)$_2$), 26.1 (CH(*C*H$_3$)$_2$), 26.4 (*C*H$_2$ (THF)), 26.8 (CH(*C*H$_3$)$_2$), 28.8 (*C*H(CH$_3$)$_2$), 28.9 (*C*H(CH$_3$)$_2$), 34.9 (C*C*H$_3$), 35.4 (C*C*H$_3$), 68.2 (O*C*H$_2$ (THF)), 124.4 (Ar*C*H), 124.6 (Ar*C*H), 127.6 (Ar*C*H), 128.7 (Ar*C*H), 131.4 (imidazole backbone *C*H), 139.3 (Ar*C*), 143.6 (Ar*C*), 144.9 (Ar*C*), 146.0 (Ar*C*), 160.8 (Zn*C*), 187.8 (C:).

Synthesis of [IPrLiZn*t*Bu$_3$] (5) A solution of Zn*t*Bu$_2$ (0.18 g, 1 mmol) in hexane (5 mL) was added to **IPr** (0.39 g, 1 mmol) and the pale yellow suspension stirred for 90 minutes before *t*BuLi (0.6 mL of a 1.7 M solution in pentane) was added giving a clear solution which was transferred to the freezer. A crop of crystals was formed after 3 days: 0.52 g, 82%. Anal. Calcd for C$_{39}$H$_{63}$LiN$_2$Zn: C, 74.06; H, 10.05; N, 4.43. Found: C, 73.74; H, 10.53; N 4.29.^{1}H NMR (400.03 MHz, 298 K, C$_6$D$_6$) δ (ppm)[10] 0.96 (12H, d, CH(C*H*$_3$)$_2$), 1.95 (27H, s, C(C*H*$_3$)$_3$), 1.26 (12H, d, CH(C*H*$_3$)$_2$), 2.64 (4H, br, C*H*(CH$_3$)$_2$), 6.47 (2H, s, imidazole backbone C*H*), 7.07 (4H, d, *m*-C*H*). 7.21 (2H, t, *p*-C*H*). ^{13}C {^{1}H} NMR (100.62 MHz, 298 K, C$_6$D$_6$) δ (ppm) 23.1 (*C*H(CH$_3$)$_2$), 24.6 (*C*H(CH$_3$)$_2$), 28.4 (*C*CH$_3$), 28.6 (CH(*C*H$_3$)$_2$), 34.2 (C*C*H$_3$), 123.4 (imidazole backbone *C*H), 124.3 (*m*-*C*H), 130.4 (*p*-*C*H), 136.0 (*i*-*C*H), 145.2 (*o*-*C*H). Carbene *C* could not be detected. ^{7}Li NMR (155.50 MHz, C$_6$D$_6$) δ -0.10 (s).

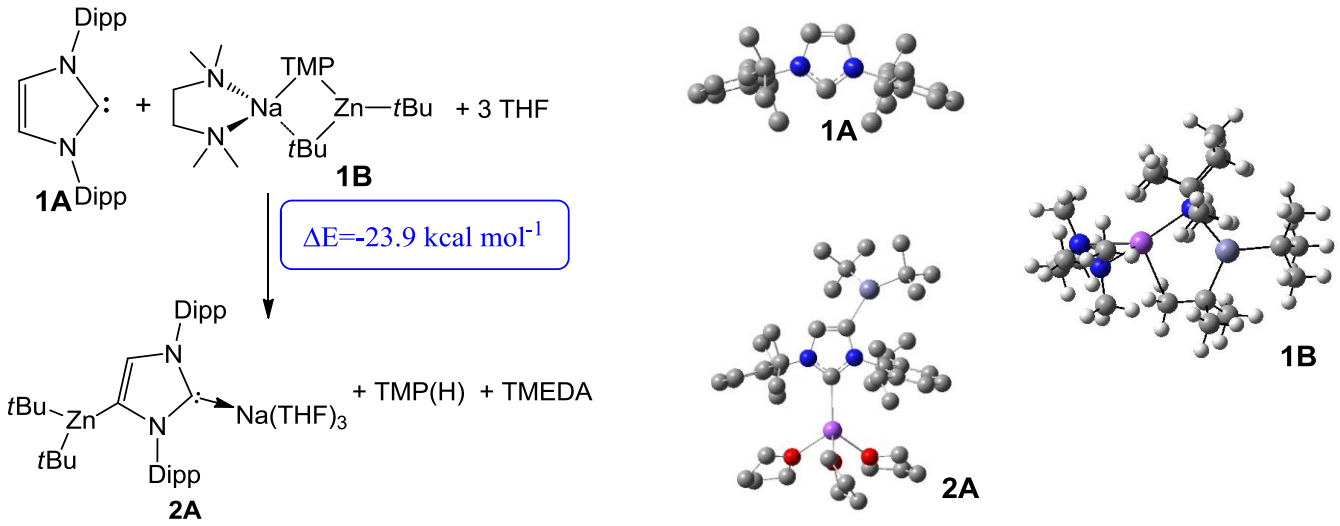
Synthesis of [ClAu:C{[N(2,6-*i*Pr$_2$C$_6$H$_3$)]$_2$CHCAu(PPh$_3$)}] (6). A solution of the sodium zincate **2** (0.403 g, 0.5 mmol) dissolved in 20 mL of THF was treated with [ClAu(PPh$_3$)] (0.496 g, 1 mmol) and stirred at room temperature for 1 h to yield a colourless solution. This solution was then evaporated to dryness and the solid residue extracted with diethyl ether (20 mL) and filtered off (Kieselguhr). The obtained solution was then concentrated to *ca.* 2 mL and supported on silica gel, and the resulting solid was transferred onto a silica gel column packed in hexane. The elution of this column with hexane-ethyl acetate (1:1) afforded compound **6** (0.329 g, 61%) which could be recrystallised as colourless crystals suitablesuitable for X-ray diffraction analysis by slow diffusion of hexane into a saturated solution of the complex in dichloromethane. Anal. Calcd for Au$_2$C$_{45}$H$_{50}$ClN$_2$P: C, 50.08; H, 4.67; N, 2.60. Found: C, 50.14; H, 4.70; N 2.63. IR (KBr, cm^{-1}): *v* 536, 692, 759, 802, 1021, 1100, 1261, 1384, 1436, 1647, 2862, 2923, 2961. ^{31}P{^{1}H} NMR (121.5 MHz, 298 K, 85% solution H$_3$PO$_4$ as a reference, CDCl$_2$) δ (ppm): *δ* 42.6 (s, Au-*P*Ph$_3$). ^{1}H NMR (400.03 MHz, 298 K, CDCl$_2$) δ (ppm): *δ* 1.17 (d, 6H, CH(C*H*$_3$)$_2$), 1.27 (d, 6H, CH(C*H*$_3$)$_2$), 1.32 (d, 6H, CH(C*H*$_3$)$_2$), 1.37 (d, 6H, , CH(C*H*$_3$)$_2$), 2.74 (m, 4H,

[10] As similarly described for **2**, integration of the THF resonances in the ^{1}H NMR with respect to those belonging to the *t*Bu groups and the metallated NHC fragment, show that only four molecules are present whereas the crystal structure of **4** contains six solvating THF molecules. This deficiency of THF in the ^{1}H NMR spectrum is due to removal of some of the sodium-bound THF when crystals of **4** are dried under vacuum The loss of 2 molecules of THF is also observed in the results from CHN analysis

C*H*(CH_3)$_2$), 6.91 (s1H, s, imidazole backbone C*H*), 7.27-7.64 (m, 6H, overlapping, ArC*H*). ^{13}C {^{1}H} NMR (100.62 MHz, 298 K, CD_2Cl_2) δ (ppm)): δ 23.8 (CH(*C*H_3)$_2$), 24.4 (CH(*C*H_3)$_2$), 28.5 (*C*H(CH_3)$_2$), 123.8 (d, $^3J_{CP}$ = 8.0 Hz, N*C*H=C-AuPPh_3), 126.7-146.0 (m, CH_{arom}, C_{arom} and NCH=*C*-Au), 172.8 (s, N_2*C*-Au).

Computational Details

Density Functional Theory (DFT) calculations[11] were performed using the Gaussian computational package G03.[12] In this series of calculations the geometries of the molecules and ions were optimised by employing the B3LYP density functionals[13,14] and the 6-311G** basis set.[15,16] The charge distributions were obtained from a Natural Bond Orbital analysis.[17]



Scheme S1: DFT study on the energy of the reaction of model systems **1A** and **1B** to afford **2A**

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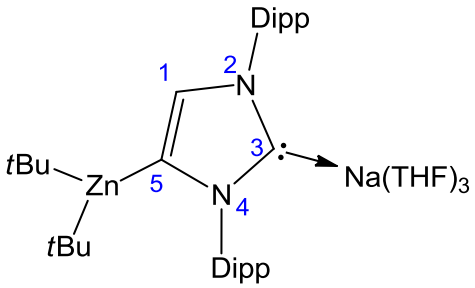
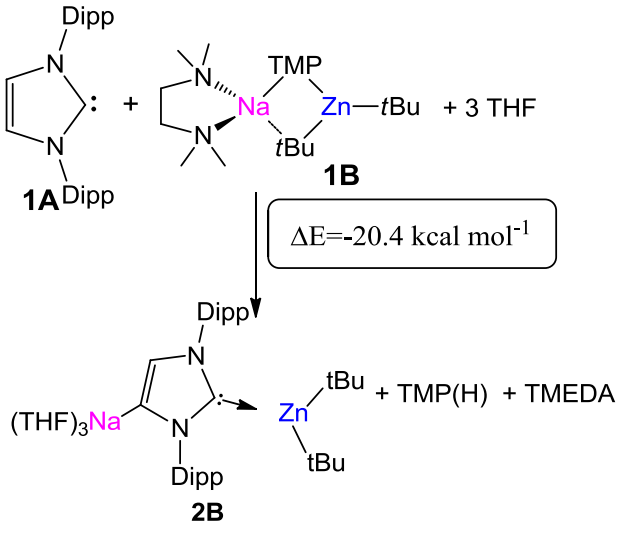
[17]. NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, and F.Weinhold.

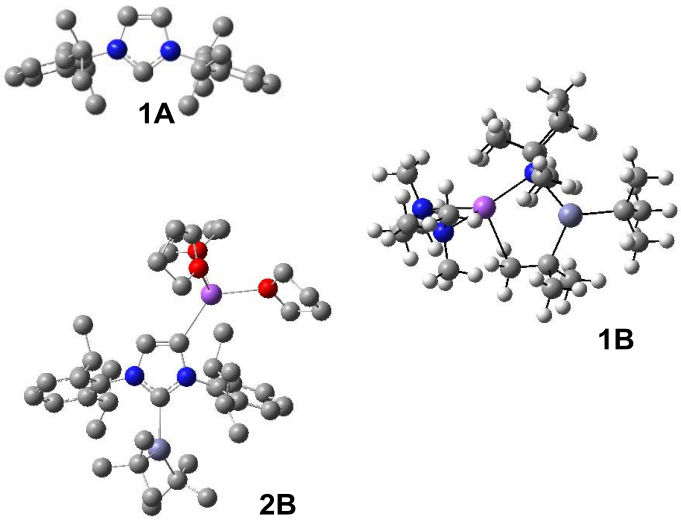
Table S2: Comparison of the calculated bond distances (Å) for model **2A** with those from the X-ray crystallographic data of **2**.

	2	**2A**
C_1-N_2	1.403(4)	1.404
C_3-N_2	1.359(4)	1.362
C_1-C_5	1.338(4)	1.364
C_5-N_4	1.416(4)	1.424
C_3-N_4	1.379(4)	1.373
Zn-C_5	2.058(3)	2.127
Zn-C_{tBu}	2.033(3), 2.056(3)	2.051, 2.073
Na-C_3	2.501(3)	2.500

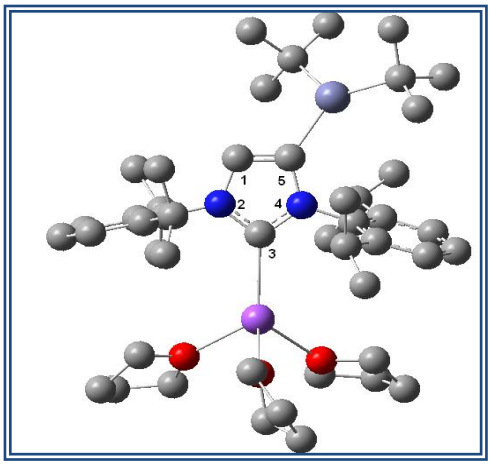


Switching the positions of $ZntBu_2$ and $\{Na(THF)_3\}^+$ in 2A: Formation of $tBu_2Zn:C\{[N(tBu)]_2CHC(THF)_3Na\}$ (2B)





Geometry optimisation of 2A



E = -4114.727393 a.u.

Principal bond lengths (Å)

N_2-C_1	1.404
N_2-C_3	1.362
C_1-C_5	1.364
N_4-C_5	1.424
N_4-C_3	1.373
N_2-C	1.436
N_4-C	1.439
C_5-Zn	2.127
Zn-C_{tbu}	2.051 2.073
C_3-Na	2.500
Na-O	2.369 2.376 2.369

Bond Indices and Charges

N_2-C_1	1.04	C_1	-0.13	N_4-C_5	1.06	C_5	-0.38
N_2-C_3	1.26	N_2	-0.46	N_4-C_3	1.24	N_4	-0.47
N_2-C_{Ph}	0.94	C_3	-0.06	N_4-$C_{Ph'}$	0.95	$C_{Ph'}$	+0.18
C_1-C_5	1.67	C_{Ph}	+0.16	C_5-Zn	0.22	Zn	+1.49
Zn-C_{tbu}	0.32	C_{tbu}	-0.57	C_3-Na	0.06	Na	+0.90
C_{tbu}-C_{Me}	1.03 1.03 1.03	C_{Me}	-0.59 -0.59 -0.59				
Zn-$C_{tbu'}$	0.28	$C_{tbu'}$	-0.58				
$C_{tbu'}$-C_{Me}	1.03 1.03 1.03	C_{Me}	-0.59 -0.59 -0.59				
Na-O	0.01 0.01 0.01	O	-0.66 -0.66 -0.64				

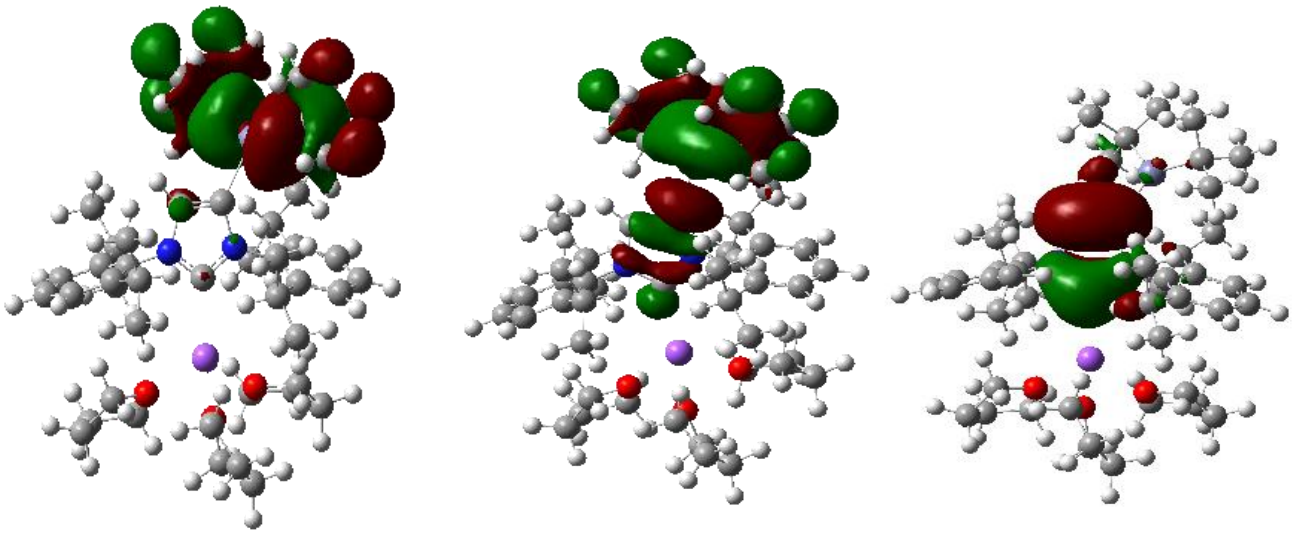
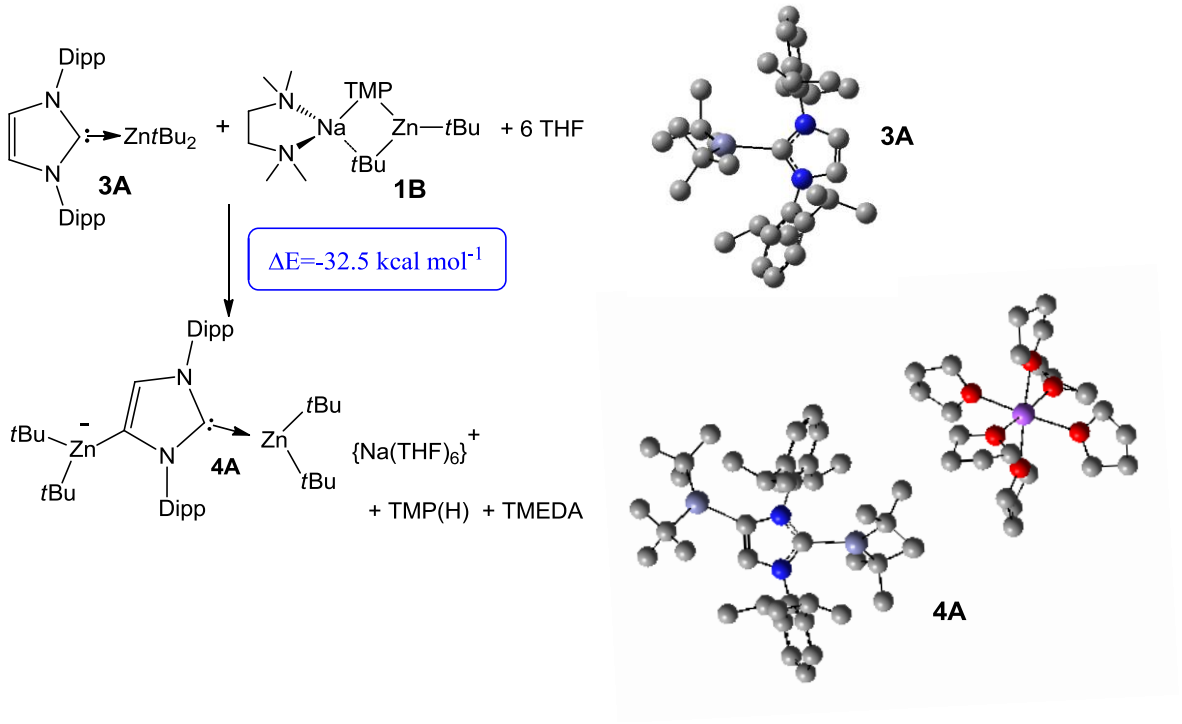


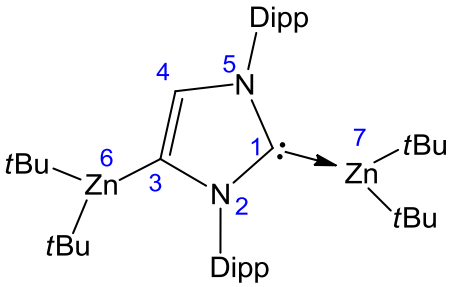
Figure S1. Representation of molecular orbitals HOMO, HOMO-1 and HOMO-2 of **2A**



Scheme S2: DFT study on the energy of the reaction of model systems **1B** and **3A** to afford **4A**

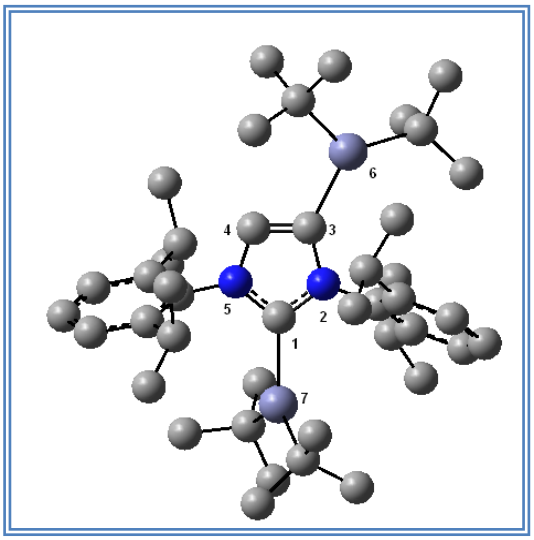
Table S3: Comparison of the calculated bond distances (Å) for the anion of model **4A** with those from the X-ray crystallographic data of the anion of **4**.

	4	**4A**
C_1-N_2	1.367(4)	1.372
C_3-N_2	1.423(4)	1.425
C_3-C_4	1.362(4)	1.361
C_4-N_5	1.394(4)	1.400
N_5-C_1	1.359(4)	1.361
Zn_6-C_3	2.058(3)	2.135
Zn_7-C_1	2.114(3)	2.140
Zn_6-C_{tBu}	2.058(4), 2.075(9)	2.054, 2.069
Zn_7-C_{tBu}	2.030(4), 2.047(4)	2.063, 2.071



Geometry optimisation of anion present in 4A

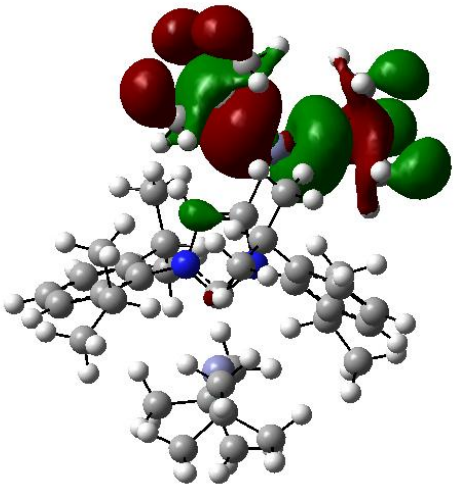
Principal bond lengths (Å) and bond angles (°)



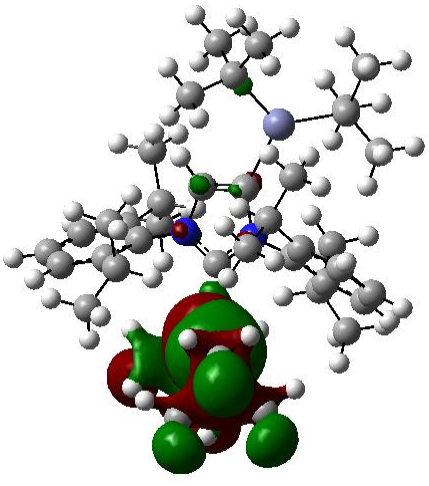
C_1-N_2	1.372	N_5-C_1-N_2	103.2
N_2-C_3	1.425	C_1-N_2-C_3	114.1
C_3-C_4	1.361	N_2-C_3-C_4	101.8
C_4-N_5	1.400	C_3-C_4-N_5	110.5
N_3-C_1	1.361	C_4-N_5-C_1	110.3
C_1-Zn_7	2.140	N_2-C_1-Zn_7	130.0
N_2-C	1.443	N_5-C_1-Zn_7	126.6
C_3-Zn_6	2.135	N_2-C_3-Zn_6	140.5
N_5-C	1.443	C_4-C_3-Zn_6	117.7
Zn_6-C(^{t}Bu)	2.054	C(^{t}Bu)-Zn_6-C(^{t}Bu)	128.4
Zn_6-C(^{t}Bu)	2.069	C(^{t}Bu)-Zn_7-C(^{t}Bu)	121.2
Zn_7-C(^{t}Bu)	2.063		
Zn_7-C(^{t}Bu)	2.071		

Charges and Bond Indices

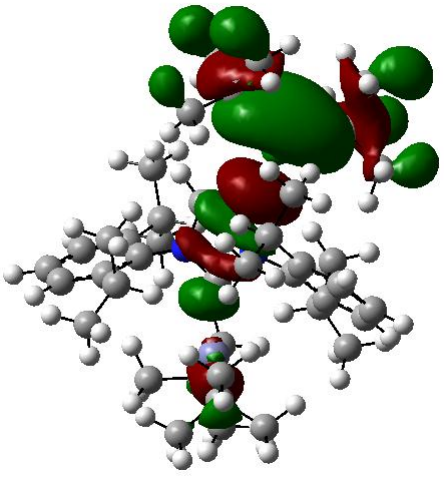
C_1-N_2	1.25	C_1	-0.05
N_2-C_3	1.05	N_2	-0.45
C_3-C_4	1.68	C_3	-0.39
C_4-N_5	1.05	C_4	-0.13
N_3-C_1	1.25	N_5	-0.44
C_1-Zn_7	0.22	Zn_6	+1.50
N_2-C	0.94	C(^{t}Bu)	-0.58 -0.58
C_3-Zn_6	0.22	C(Me)	-0.59 -0.59 -0.59 -0.59 -0.59 -0.59
N_5-C	0.94	Zn_7	+1.49
Zn_6-C(^{t}Bu)	0.28	C(^{t}Bu)	-0.58 -0.58
Zn_6-C(^{t}Bu)	0.31	C(Me)	-0.59 -0.59 -0.60 -0.59 -0.59 -0.60
Zn_7-C(^{t}Bu)	0.31		
Zn_7-C(^{t}Bu)	0.29		



HOMO



HOMO-1



HOMO-2

Figure S2. Representation of molecular orbitals HOMO, HOMO-1 and HOMO-2 of the anion of **4A**

NMR spectra of compounds 2-6

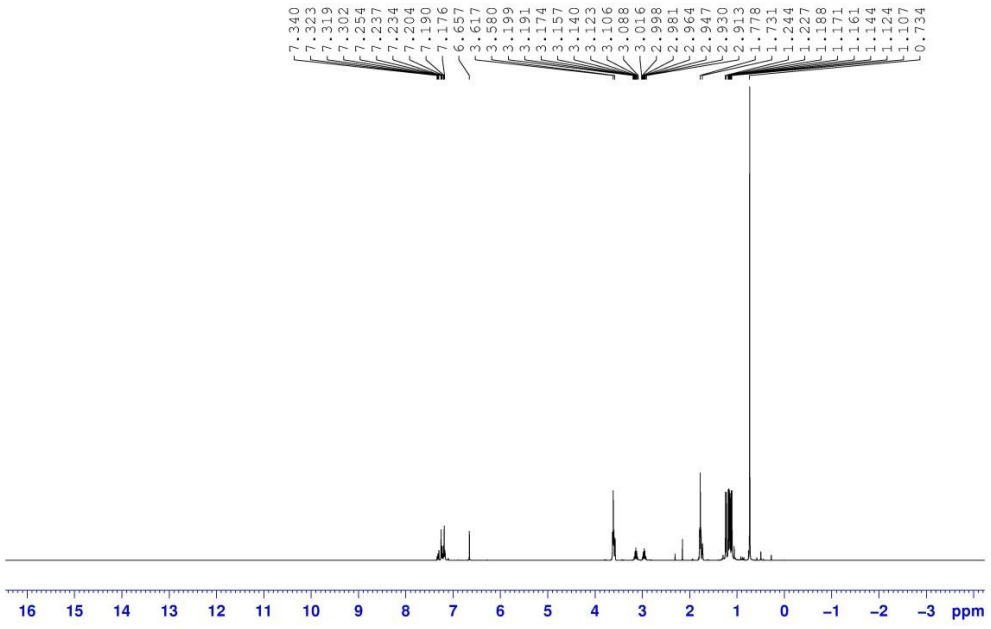


Figure S3: ^{1}H NMR spectrum of (THF)$_3$Na[:C{[N(2,6-*i*Pr$_2$C$_6$H$_3$)]$_2$CHCZn(*t*Bu$_2$)}] (**2**) in d$_8$-THF

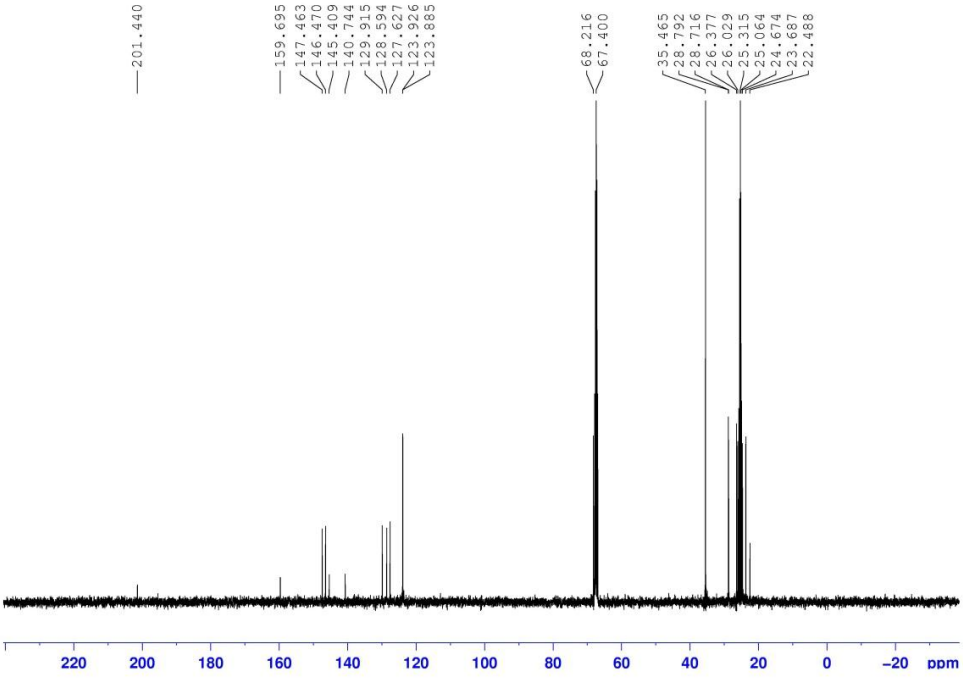


Figure S4: ^{13}C {^{1}H} NMR spectrum of (THF)$_3$Na[:C{[N(2,6-*i*Pr$_2$C$_6$H$_3$)]$_2$CHCZn(*t*Bu$_2$)}] (**2**) in d$_8$-THF

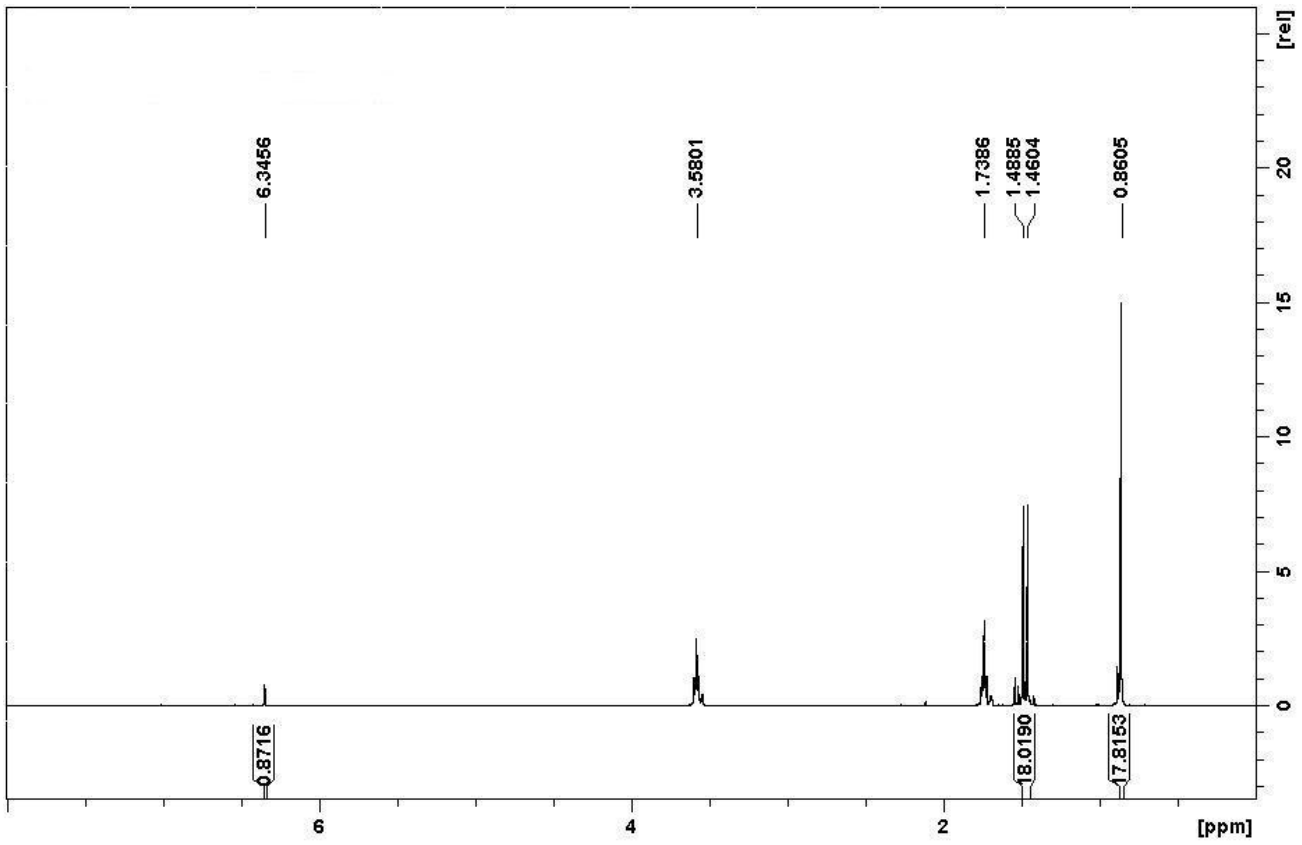


Figure S5: ^{1}H NMR spectrum of $(THF)_3Na[:C\{[N(tBu)]_2CHCZn(tBu_2)\}]$ (**2**^{IBu}) in d_8-THF

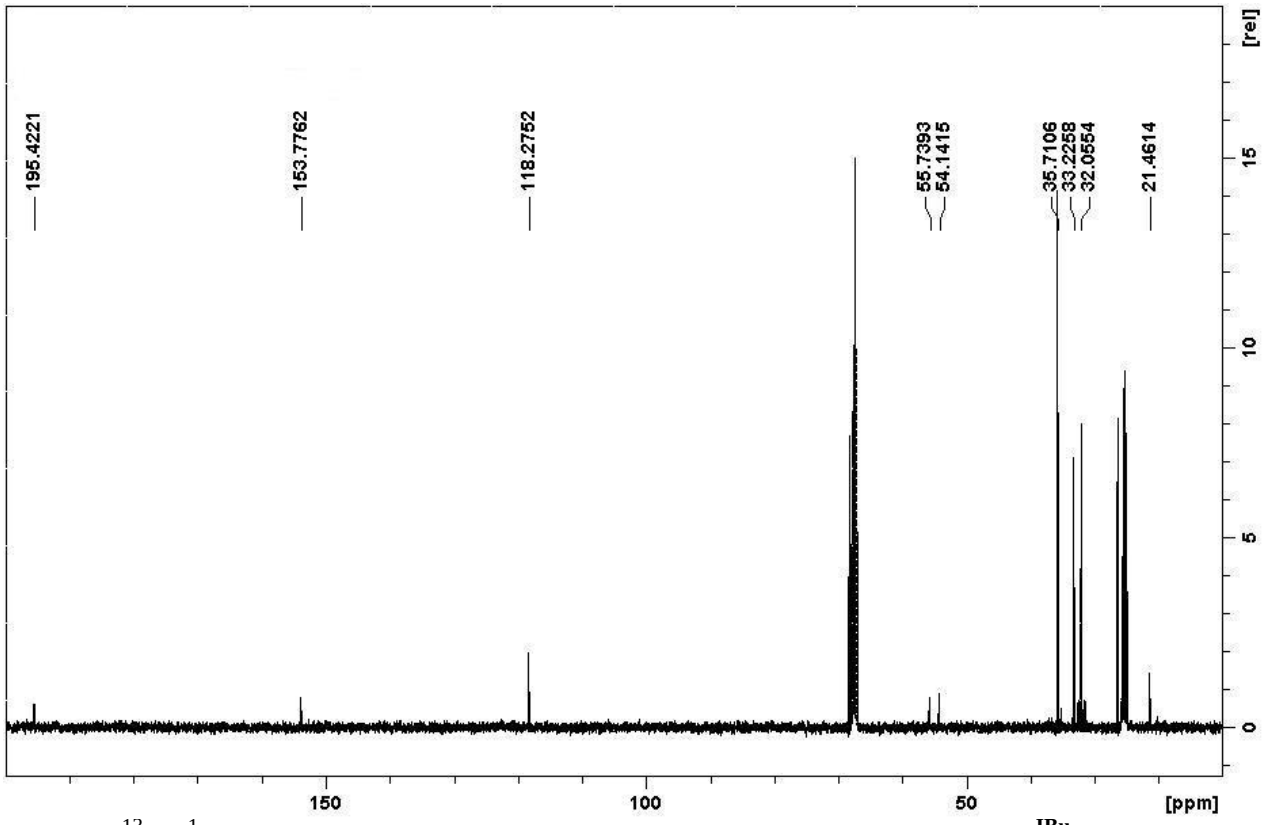


Figure S6: ^{13}C $\{^{1}$H$\}$ NMR spectrum of $(THF)_3Na[:C\{[N(tBu)]_2CHCZn(tBu_2)\}]$ (**2**^{IBu}) in d_8-THF

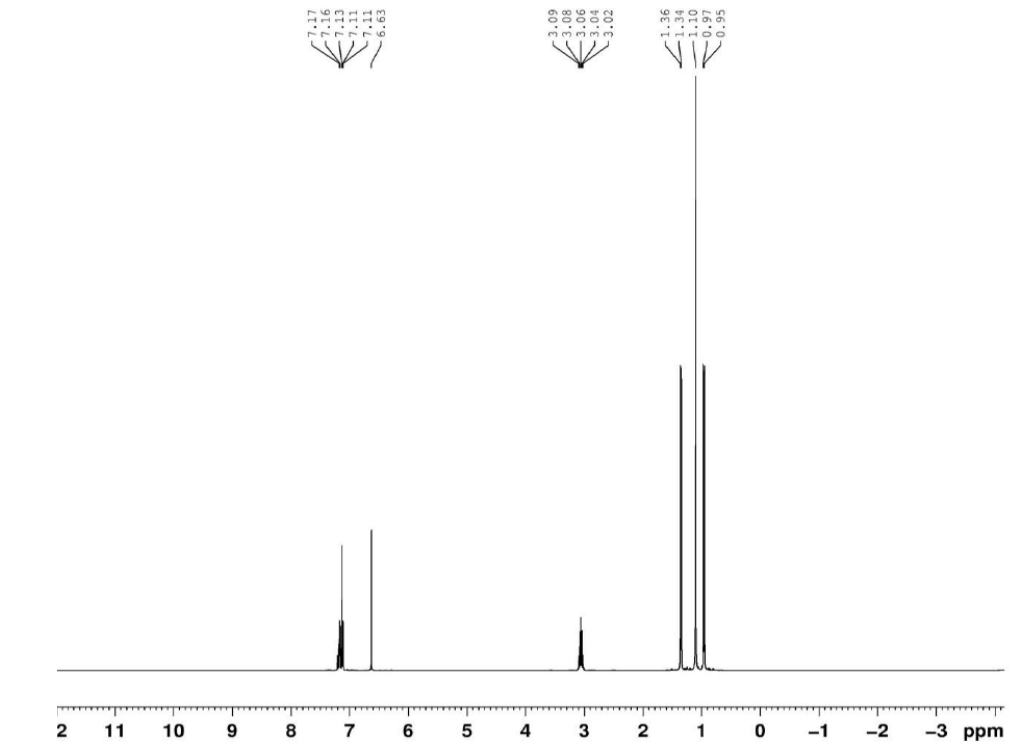


Figure S7: ^{1}H NMR spectrum of [IPr.Zn*t*Bu$_2$] (**3**) in C_6D_6

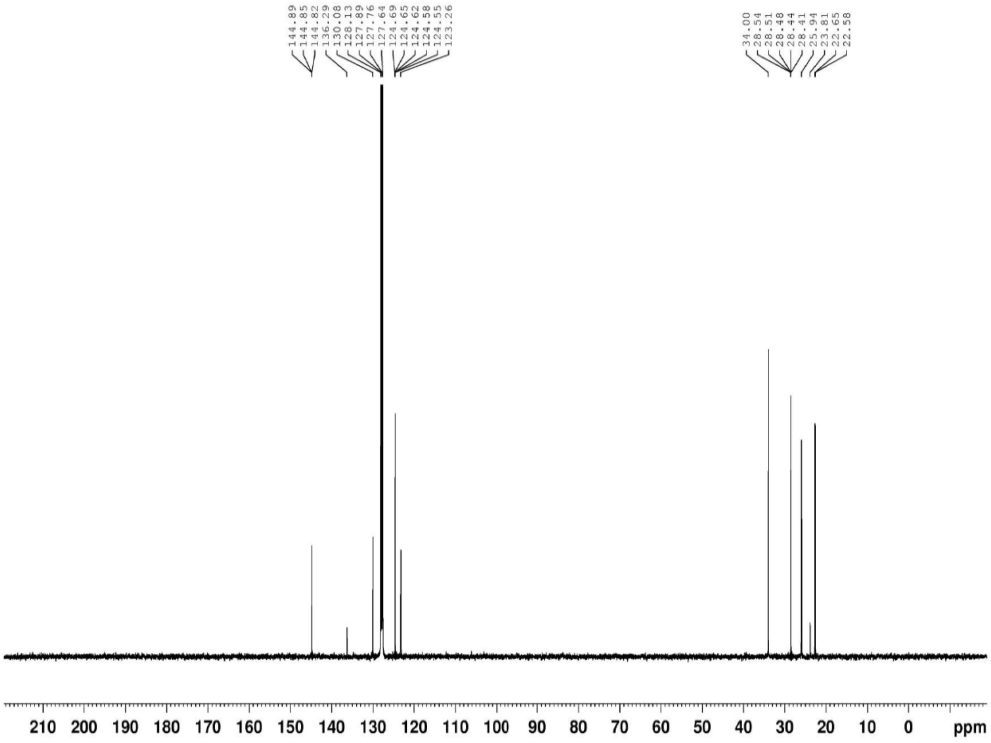


Figure S8: ^{13}C {^{1}H} NMR spectrum of [IPr.Zn*t*Bu$_2$] (**3**) in C_6D_6

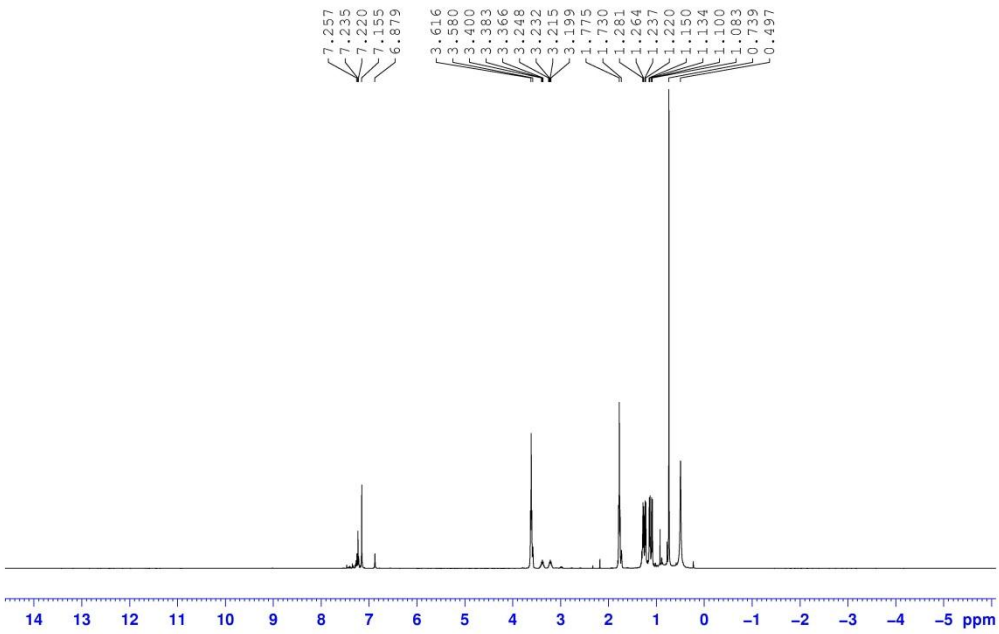


Figure S9: ^{1}H NMR spectrum of $Na(THF)_6]^+$ [tBu$_2$Zn:C{[N(2,6-iPr$_2$C$_6$H$_3$)]$_2$CHCZn(tBu$_2$)}]$^-$ (**4**) in d_8-THF

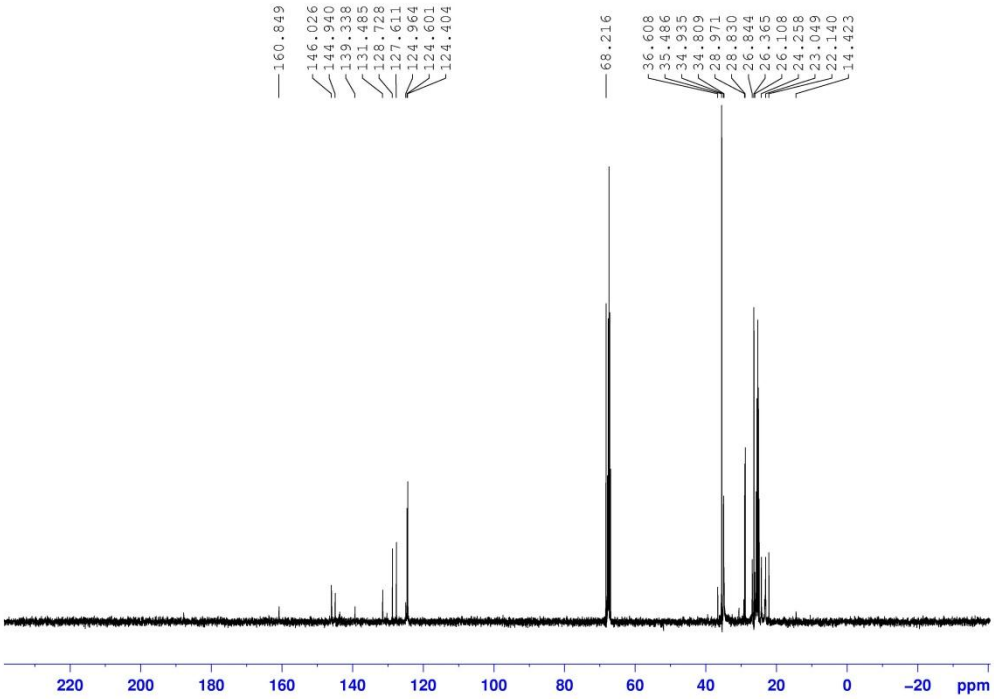


Figure S10: ^{13}C {^{1}H} NMR spectrum of $Na(THF)_6]^+$ [tBu$_2$Zn:C{[N(2,6-iPr$_2$C$_6$H$_3$)]$_2$CHCZn(tBu$_2$)}]$^-$ (**4**) in d_8-THF

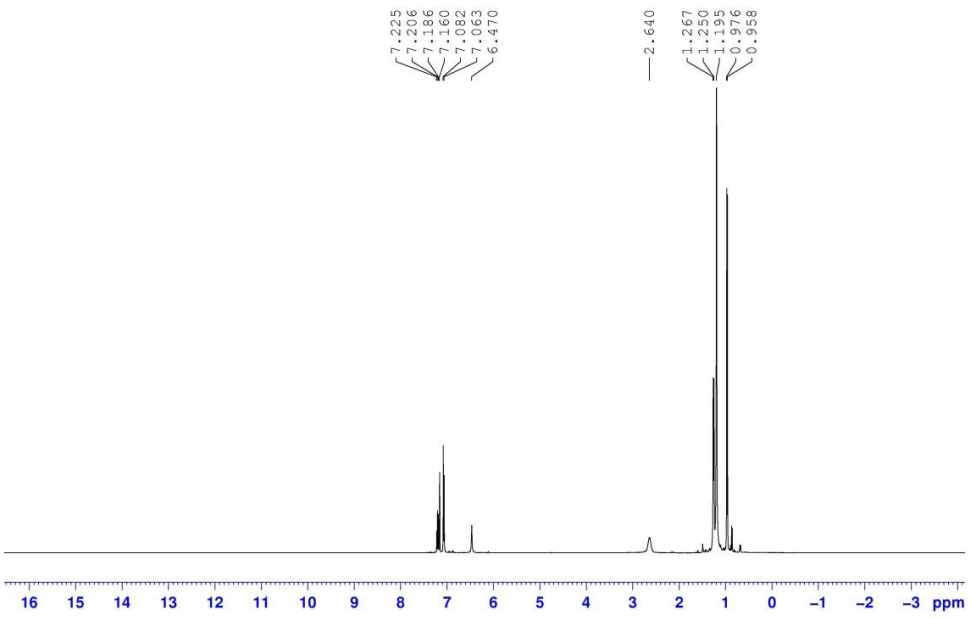


Figure S11: ^{1}H NMR spectrum of [IPr.LiZn*t*Bu$_3$] (**5**) in d$_8$-THF

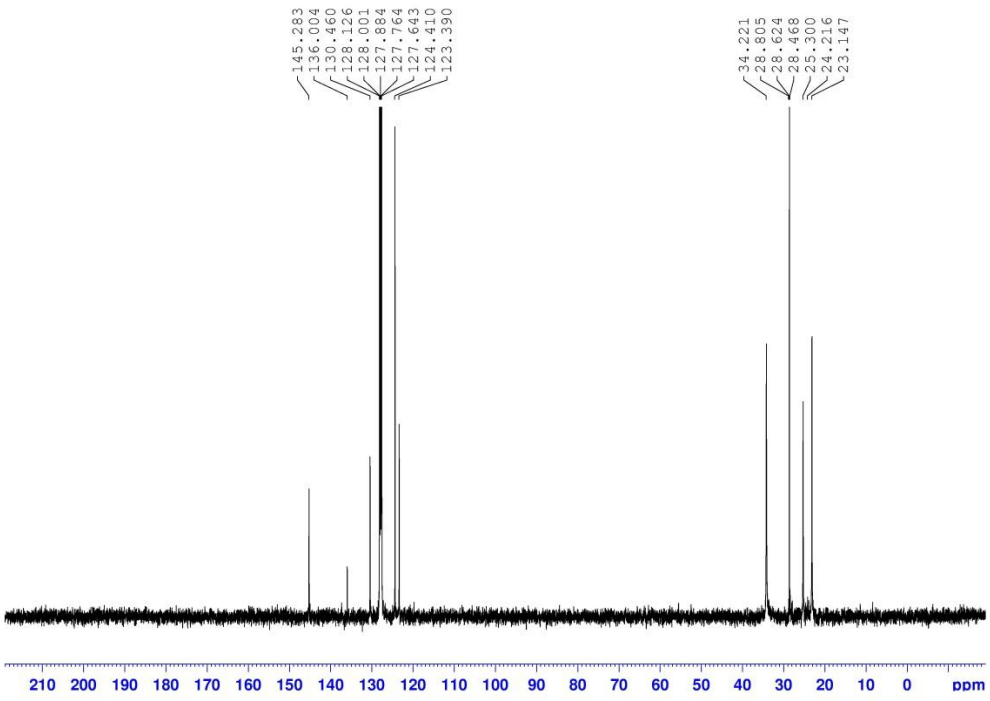


Figure S12: ^{13}C {^{1}H} NMR spectrum of [IPr.LiZn*t*Bu$_3$] (**5**) in d$_8$-THF

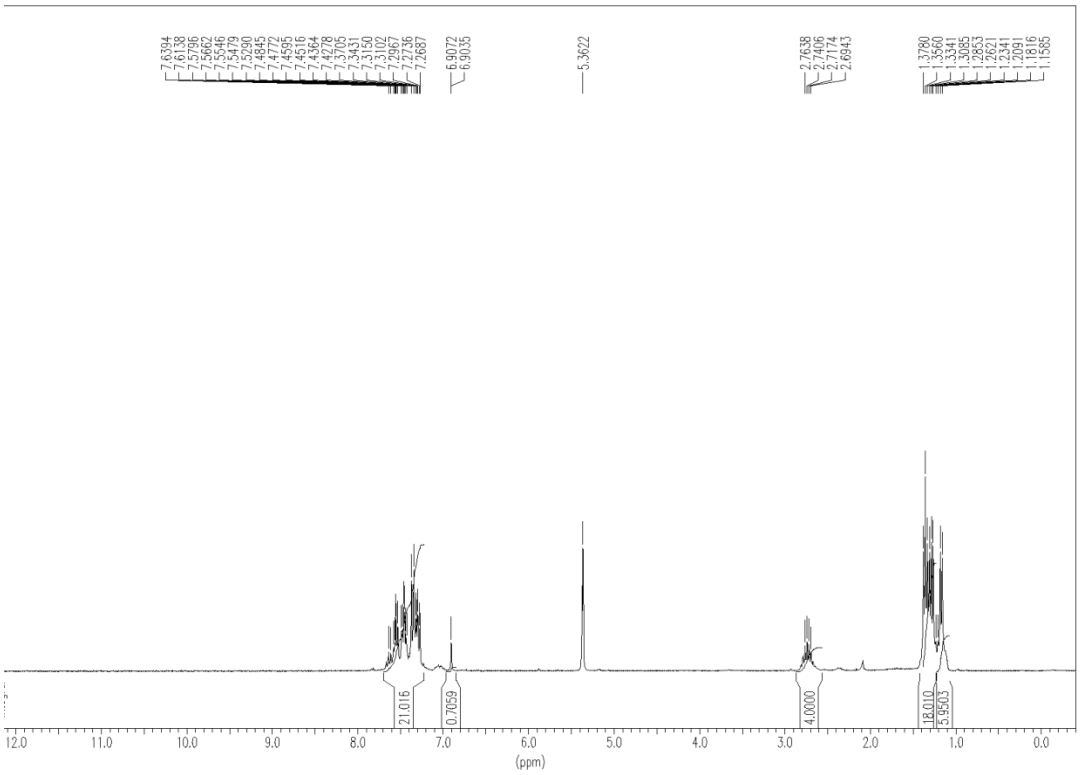


Figure S13: ^{1}H NMR spectrum of [ClAu:C{[N(2,6-*i*Pr$_2$C$_6$H$_3$)]$_2$CHCAu(PPh$_3$)] (**6**) in CDCl$_2$

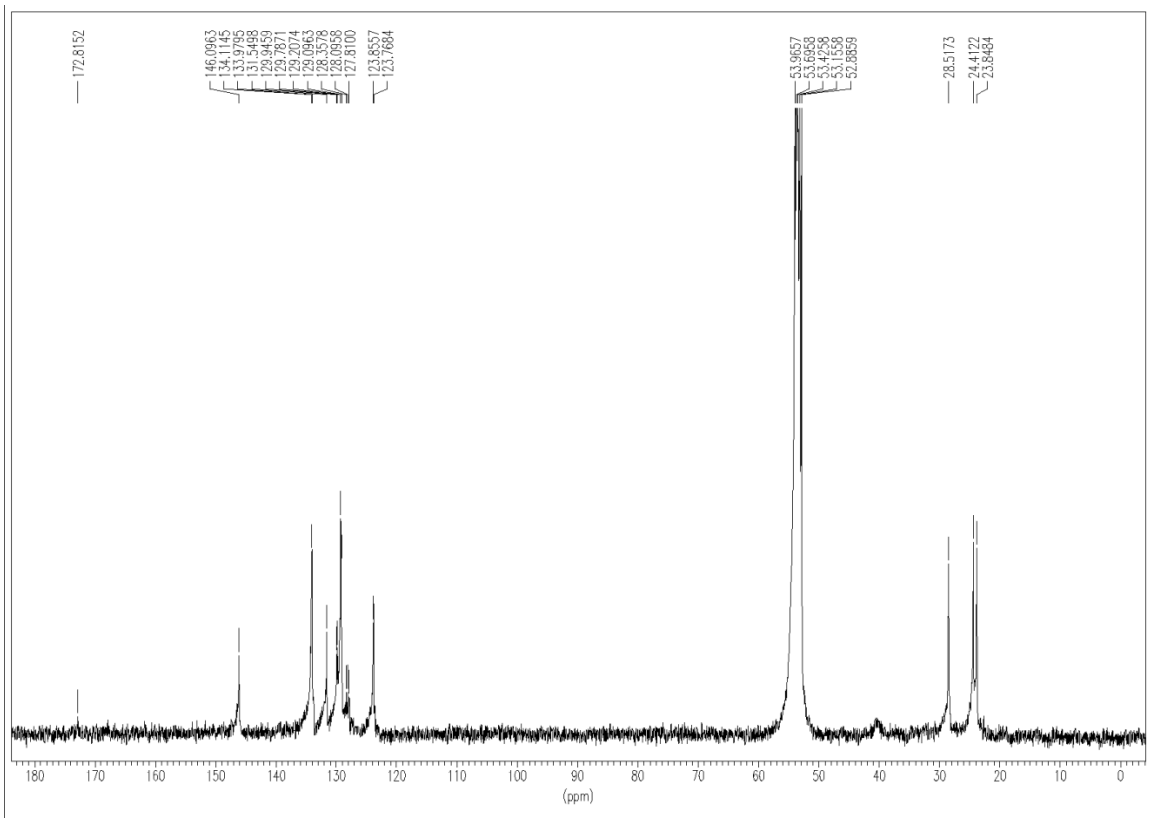


Figure S14: ^{13}C {^{1}H} NMR spectrum of [ClAu:C{[N(2,6-*i*Pr$_2$C$_6$H$_3$)]$_2$CHCAu(PPh$_3$)] (**6**) in CDCl$_2$

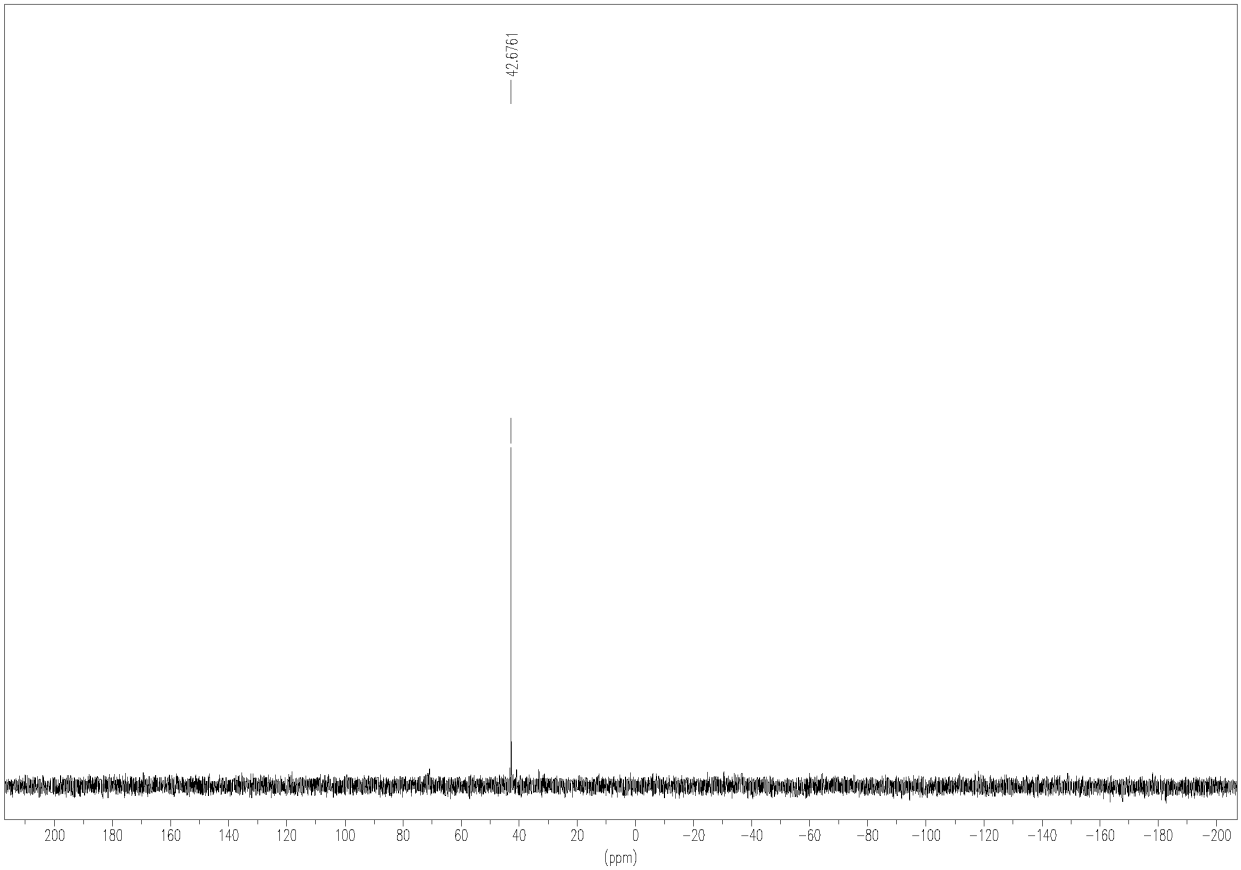


Figure S15: ^{31}P {^{1}H} NMR spectrum of [ClAu:C{[N(2,6-*i*$Pr_2C_6H_3$)]$_2$CHCAu(PPh_3)] (**6**) in $CDCl_2$

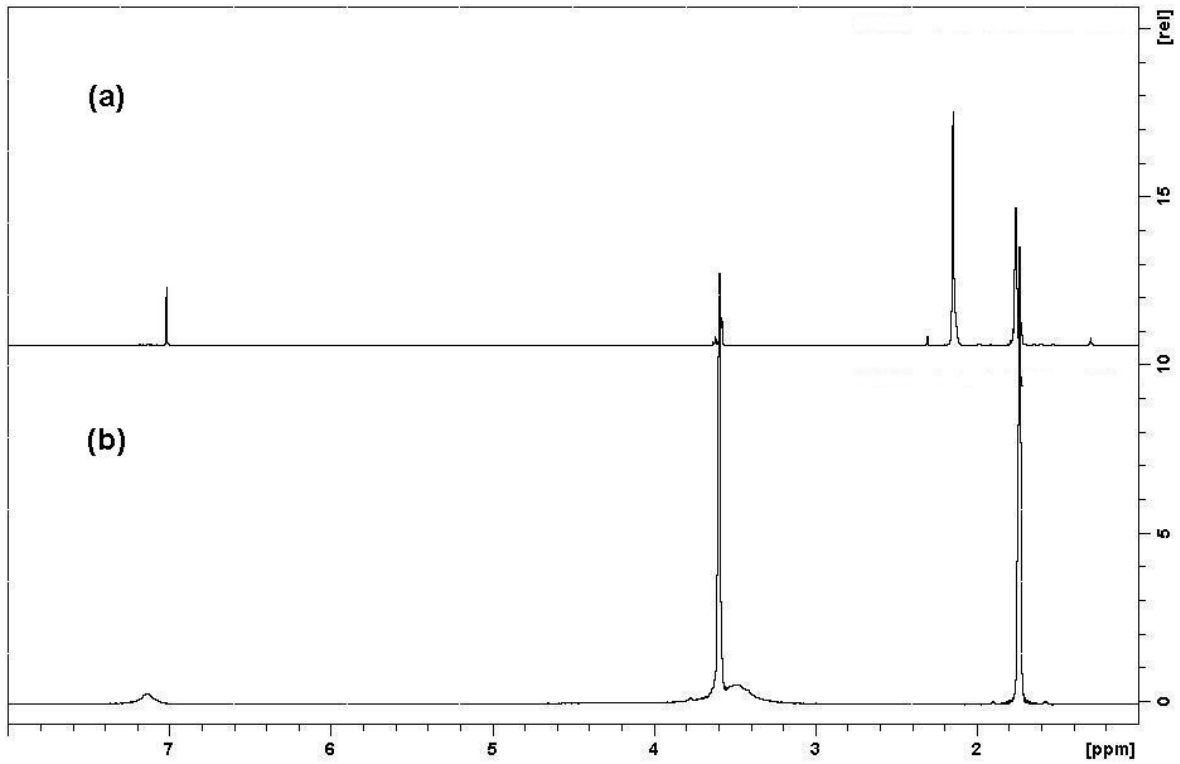


Figure S16: (a) ^{1}H NMR spectrum of free **IAd** in d_8-THF. (b) ^{2}H NMR of reaction crude of the reaction of **IAd** with sodium zincate **1** followed by *in situ* treatment with CD_3OD in d_8-THF.

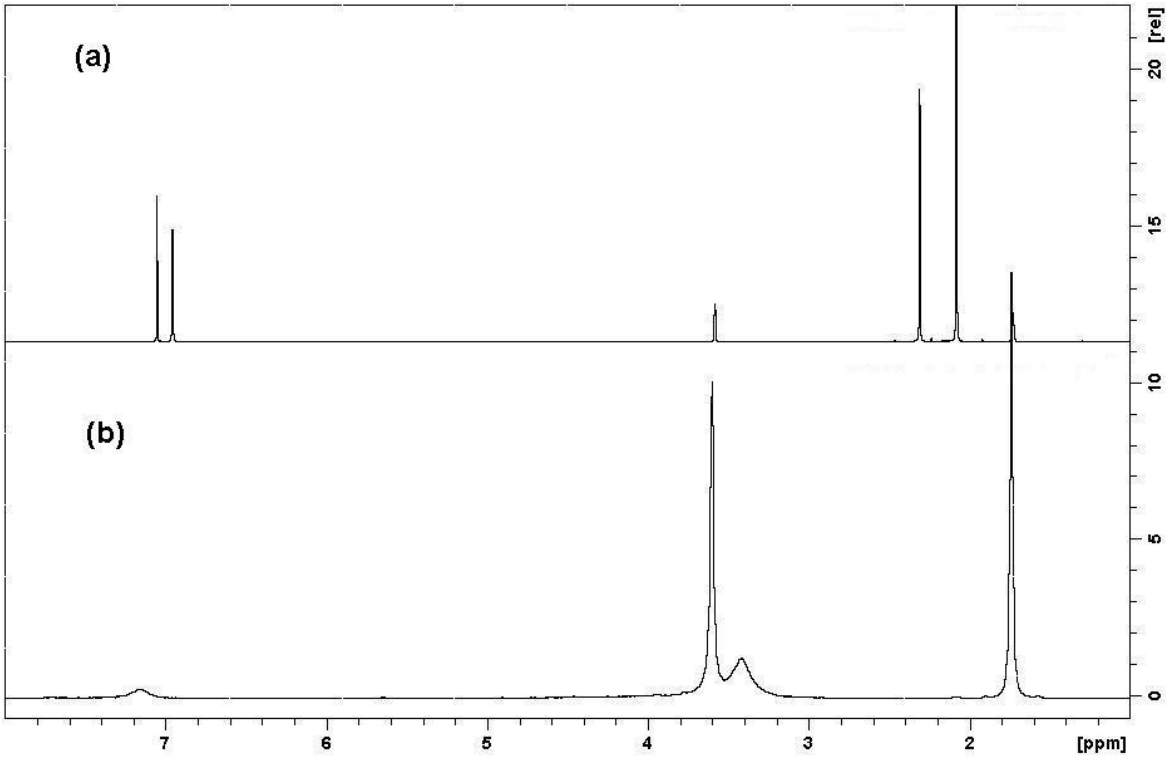


Figure S17: (a) ^{1}H NMR spectrum of free **IMes** in d_8-THF. (b) ^{2}H NMR of reaction crude of the reaction of **IMes** with sodium zincate **1** followed by *in situ* treatment with CD_3OD in d_8-THF.