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Toward N-heterocyclic carbene stabilized zinc sulfides

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Contents:

Experimental Procedures:

General

All reactions were performed in an inert atmosphere glovebox (Innovative Technology, Inc.). Solvents were dried using a Grubbs-type solvent purification system[S1] manufactured by Innovative Technologies, Inc., degassed (freeze-pump-thaw method), and stored under an atmosphere of nitrogen prior to use. $S(SiMe_3)_2$, $Zn(OAc)_2$, $Cd(OAc)_2$, $Hg(OAc)_2$ and 4-dimethylaminopyridine (DMAP) were purchased from Sigma-Aldrich and used as received. IPr was prepared according to a literature procedure.[S2] ^1H and $^{13}C\{^1H\}$NMR spectra were recorded on 400, 500, 600 or 700 MHz Varian Inova instruments and were referenced externally to $SiMe_4$ (^1H, $^{13}C\{^1H\}$). Elemental analyses were performed by the Analytical and Instrumentation Laboratory at the University of Alberta. Melting points were measured in sealed glass capillaries under nitrogen by using a MelTemp apparatus and are uncorrected.

X-ray Crystallography

Crystals for X-ray diffraction studies were removed from a vial (in a glovebox) and immediately coated with a thin layer of hydrocarbon oil (Paratone-N). A suitable crystal was then mounted on a glass fiber and quickly placed in a low temperature stream of nitrogen on the X-ray diffractometer.[S3] All data were collected using a Bruker APEX II CCD detector/D8 or PLATFORM diffractometer using Mo Kα or Cu Kα radiation, with the crystals cooled to –80 °C or –100 °C. The data were corrected for absorption through Gaussian integration from the indexing of the crystal faces. Crystal structures were solved using intrinsic phasing (*SHELXT*)[S4] and refined using *SHELXL-2014*.[S5] The assignment of hydrogen atom positions were based on the sp^2 or sp^3 hybridization geometries of their attached carbon atoms and were given thermal parameters 20% greater than those of their parent atoms.

Synthesis of [(IPr)Zn(OAc)$_2$] (1)

To a vial containing Zn(OAc)$_2$ (0.138 g, 0.752 mmol) was added a 10 mL solution of IPr in toluene (0.298 g, 0.767 mmol) and the mixture was stirred. After a few minutes, a large amount of white precipitate began to form and the mixture was stirred for 16 h. The precipitate was allowed to settle, the toluene supernatant decanted (and discarded), and the remaining solid was dried *in vacuo* yielding **1** as a white solid (0.628 g, 85 %). ^{1}H NMR (C$_6$D$_6$, 499.8 MHz): δ 7.20 (t, 2H, $^3J_{HH}$ = 8.0 Hz, *p*-Ar*H*), 7.11 (d, 4H, $^3J_{HH}$ = 8.0 Hz, *m*-Ar*H*), 6.45 (s, 2H, NC*H*), 2.68 (septet, 4H, $^3J_{HH}$ = 7.0 Hz, C*H*(CH$_3$)$_2$), 1.58 (broad s, 6H, O$_2$CC*H*$_3$), 1.51 (d, 12H, $^3J_{HH}$ = 7.0 Hz, CH(C*H*$_3$)$_2$), 1.03 (d, 12H, $^3J_{HH}$ = 7.0 Hz, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, 125.7 MHz): δ 146.1 (Ar*C*), 134.1 (Ar*C*), 130.6 (N*C*H), 124.2 (Ar*C*), 124.0 (Ar*C*), 29.2 (*C*H(CH$_3$)$_2$), 25.5 (CH(*C*H$_3$)$_2$), 22.9 (CH(*C*H$_3$)$_2$), 20.8 (O$_2$C*C*H$_3$); N*C*N and O$_2$*C*CH$_3$ resonances were not observed. M.p. stable >250 °C. Anal. Calcd. for $C_{31}H_{42}ZnN_2O_4$: C 65.09, H 7.40, N 4.90. Found: C 64.86, H 7.44, N 4.85.

Synthesis of [(IPr)Cd(OAc)$_2$] (2)

To a vial containing Cd(OAc)$_2$ (0.188 g, 0.816 mmol) was added a 10 mL solution of IPr in toluene (0.298 g, 0.834 mmol) and the mixture was stirred. After *ca.* 30 minutes, a large amount of white precipitate began to form and the mixture was stirred for another 16 h. The precipitate was allowed to settle, the toluene supernatant decanted (and discarded), and the resulting solid was dried *in vacuo* yielding **2** as a white solid (0.505 g, 90 %). ^{1}H NMR (CDCl$_3$, 400.0 MHz): δ 7.52 (t, 2H, $^3J_{HH}$ = 7.9 Hz, *p*-Ar*H*), 7.34 (s, 2H, NC*H*), 7.32 (broad m, 4H, *m*-Ar*H*), 2.51 (septet, 4H, $^3J_{HH}$ = 6.9 Hz, C*H*(CH$_3$)$_2$), 1.62 (s, 6H, O$_2$CC*H*$_3$), 1.33 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$), 1.20 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, 125.7 MHz): δ 181.7 (N*C*N), 180.6 (O$_2$*C*CH$_3$), 145.6 (Ar*C*), 133.5 (Ar*C*), 131.0 (N*C*H), 124.6 (Ar*C*), 124.4 (Ar*C*), 29.0 (*C*H(CH$_3$)$_2$), 25.3 (CH(*C*H$_3$)$_2$), 22.6 (CH(*C*H$_3$)$_2$), 20.8 (O$_2$C*C*H$_3$). M.p. stable >250 °C. Elemental analyses were performed on several different samples. In all cases the CHN values were systematically low.

Synthesis of [(IPr)Hg(OAc)$_2$] (3)

To a vial containing Hg(OAc)$_2$ (0.202 g, 0.634 mmol) was added a 10 mL solution of IPr in toluene (0.252 g, 0.648 mmol) and the mixture stirred. After *ca.* 30 minutes, a large amount of white precipitate began to form and the mixture was stirred for another 16 h. The precipitate was allowed to settle, the toluene supernatant decanted (and discarded), and the resulting solid was dried *in vacuo* yielding **3** as a white solid (0.415 g, 93 %). ^{1}H NMR (CDCl$_3$, 400.0 MHz): δ 7.55 (t, 2H, $^3J_{HH}$ = 7.8 Hz, *p*-Ar*H*), 7.43 (s, 2H, satellites: $^4J_{H\text{-}Hg}$ = 32.2 Hz, NC*H*), 7.35 (d, $^3J_{HH}$ = 7.8, 4H, *m*-Ar*H*), 2.51 (septet, 4H, $^3J_{HH}$ = 6.9 Hz, C*H*(CH$_3$)$_2$), 1.67 (s, 6H, O$_2$CC*H*$_3$), 1.35 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$), 1.20 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, 125.7 MHz): δ 176.7 (O$_2$*C*CH$_3$), 145.5 (Ar*C*), 132.4 (Ar*C*), 131.7 (N*C*H), 125.3 (Ar*C*), 124.7 (Ar*C*), 29.1 (*C*H(CH$_3$)$_2$), 25.1 (CH(*C*H$_3$)$_2$), 23.3 (CH(*C*H$_3$)$_2$), 22.7 (O$_2$C*C*H$_3$); an N*C*N resonance was not observed. M.p. stable >250 °C. Anal. Calcd. for $C_{31}H_{42}HgN_2O_4$: C 52.64, H 5.99, N 3.96. Found: C 51.95, H 5.99, N 3.90.

Synthesis of [(IPr)Zn(SSiMe$_3$)$_2$] (4)

To a vial containing a slurry of [(IPr)Zn(OAc)$_2$] (0.142 g, 0.248 mmol) in 5 mL of Et$_2$O was added S(SiMe$_3$)$_2$ (104.7 µL, 0.496 mmol). After *ca.* 5 minutes of stirring, all of the solids in the reaction mixture had dissolved. The reaction mixture was left to stir for 45 minutes and the solvent was removed *in vacuo*, affording **4** as a white solid (0.162 g, 98 %). ^{1}H NMR (C$_6$D$_6$, 400.0 MHz): δ 7.22 (t, 2H, *p*-Ar*H*), 7.11 (d, 4H, $^3J_{HH}$ = 8.0 Hz, *m*-Ar*H*), 6.43 (s, 2H, NC*H*), 2.83 (septet, 4H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 1.55 (d, 12H, $^3J_{HH}$ = 6.8 Hz CH(C*H*$_3$)$_2$), 0.98 (d, 12H, $^3J_{HH}$ = 7.2 Hz CH(C*H*$_3$)$_2$), 0.33 (s, 18H, Si(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz): δ 181.2 (N*C*N), 146.0 (Ar*C*), 134.4 (Ar*C*), 131.0 (Ar*C*), 124.6 (Ar*C*), 123.8 (Ar*C*), 29.0 (*C*H(CH$_3$)$_2$), 25.8 (CH(*C*H$_3$)$_2$), 23.4 (CH(*C*H$_3$)$_2$), 6.6 (Si(*C*H$_3$)$_3$). M.p.: 138-142 °C. Anal. Calcd. for $C_{33}H_{54}N_2S_2Si_2Zn$: C 59.65, H 8.19, N 4.22, S 9.65. Found: C 59.28, H 7.94, N 4.24, S 9.87. *Crystals of **4** were grown from Et$_2$O, however their quality only allowed the determination of atomic connectivity in this complex. Additionally, in the attempted growth of crystals of **4** by storing saturated toluene solution of **4** layered with hexanes in a −30 °C freezer (in a glovebox) overnight, we observed very small batches of crystalline [IPrH]$_2$[Zn$_3$(μ_3-S)(μ_2-SSiMe$_3$)$_3$(SSiMe$_3$)$_3$] (**6**) on a few occasions. The formation of **6** presumably arises from the partial hydrolysis of **4** by adventitious water.*

Synthesis of [(IPr)Zn(SSiMe$_3$)$_2$(DMAP)] (5)

Compound **4** was prepared as described above from [(IPr)Zn(OAc)$_2$] (0.191 g, 0.343 mmol) and S(SiMe$_3$)$_2$ (144 µL, 0.343 mmol) in 4 mL of Et$_2$O and used *in situ*. A 2 mL Et$_2$O solution of DMAP (0.043 g, 0.350 mmol) was then added to the solution of **4** and the immediate formation of a white precipitate was observed. The reaction mixture was stirred for one hour, after which the precipitate was allowed to settle and the supernatant decanted. The remaining solid was dried under vacuum and washed with 2 × 2 mL of hexanes. The solid was dissolved in 1 mL of fluorobenzene and stored at −35 °C for 2 days to afford a white precipitate. The supernatant was decanted and the resulting solid dried to afford [(IPr)Zn(SSiMe$_3$)$_2$(DMAP)] (**5**) as a white solid (0.148 g, 55 %). Crystals of **5** suitable for X-ray crystallographic analysis were grown by storing a fluorobenzene solution in a −30 °C freezer for 3 weeks. ^{1}H NMR (C_6D_6, 400.0 MHz): δ 8.61 (br s, 2H, *o*-DMAP-Ar*H*), 7.23 (t, 2H, *p*-Ar*H*), 7.02 (d, 4H, *m*-Ar*H*), 6.46 (s, 2H, NC*H*), 5.85 (d, 2H, $^3J_{HH}$ = 4.0 Hz, *m*-DMAP-Ar*H*), 3.00 (septet, 4H, $^3J_{HH}$ = 4.0 Hz, C*H*(CH$_3$)$_2$), 2.06 (br s, 6H, DMAP-N(C*H*$_3$)$_2$), 1.57 (d, 12H, $^3J_{HH}$ = 4.0 Hz, CH(C*H*$_3$)$_2$), 1.03 (d, 12H, $^3J_{HH}$ = 4.0 Hz, CH(C*H*$_3$)$_2$), 0.39 (s, 18H, Si(C*H*$_3$)$_3$). Mp: 212 °C (decomp.). ^{13}C{^{1}H} NMR (C_6D_6, 125.7 MHz): δ 163.4 (N*C*N), 162.5 (*p*-DMAP-*C*), 146.2 (Ar*C*), 130.6 (Ar*C*), 130.1 (ArC), 128.3 (Ar*C*), 124.1 (ArC), 106.1 (*m*-DMAP-*C*), 38.1 (DMAP-N(*C*H$_3$)$_2$), 28.9 (*C*H(CH$_3$)$_2$), 26.4 (CH(*C*H$_3$)$_2$), 24.0 (CH(*C*H$_3$)$_2$), 6.7 (Si(*C*H$_3$)$_3$).

NMR Spectroscopic Data

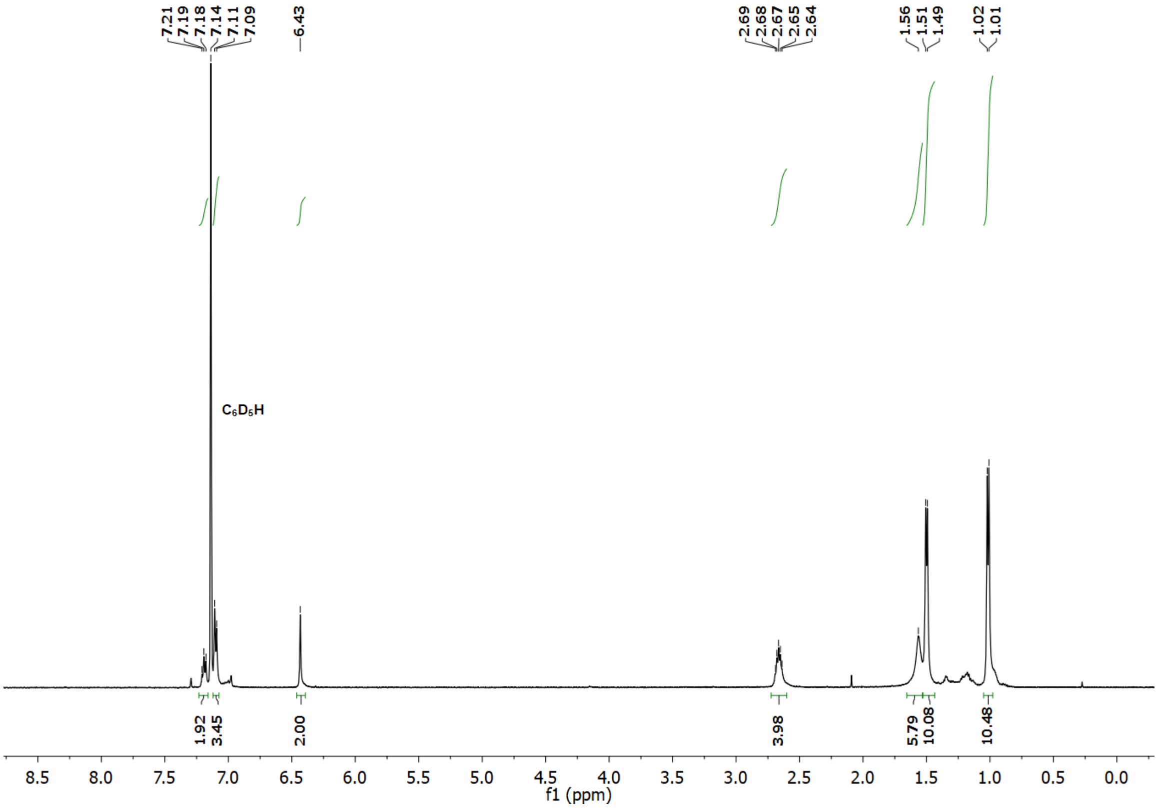

Figure S1. ^{1}H NMR spectrum of [(IPr)Zn(OAc)$_2$] (**1**) in C_6D_6.

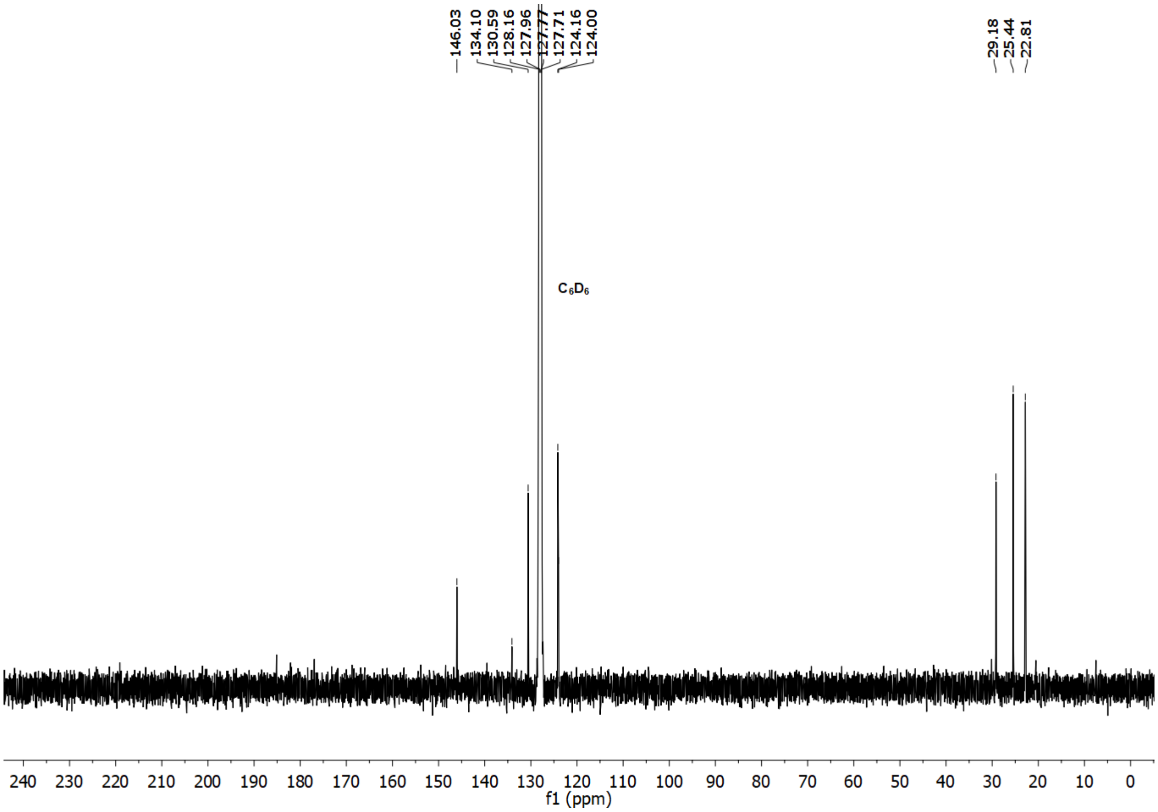

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of $[(IPr)Zn(OAc)_2]$ (**1**) in C_6D_6.

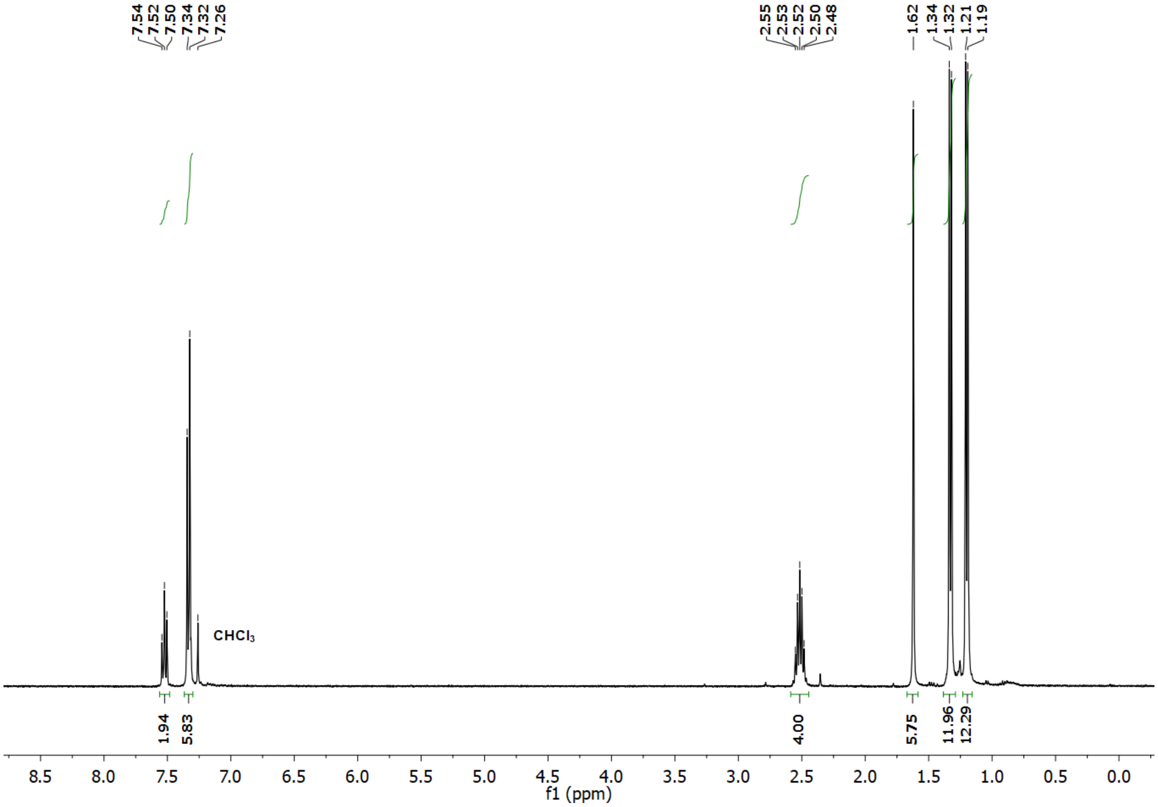

Figure S3. ^{1}H NMR spectrum of [(IPr)Cd(OAc)$_2$] (**2**) in CDCl$_3$.

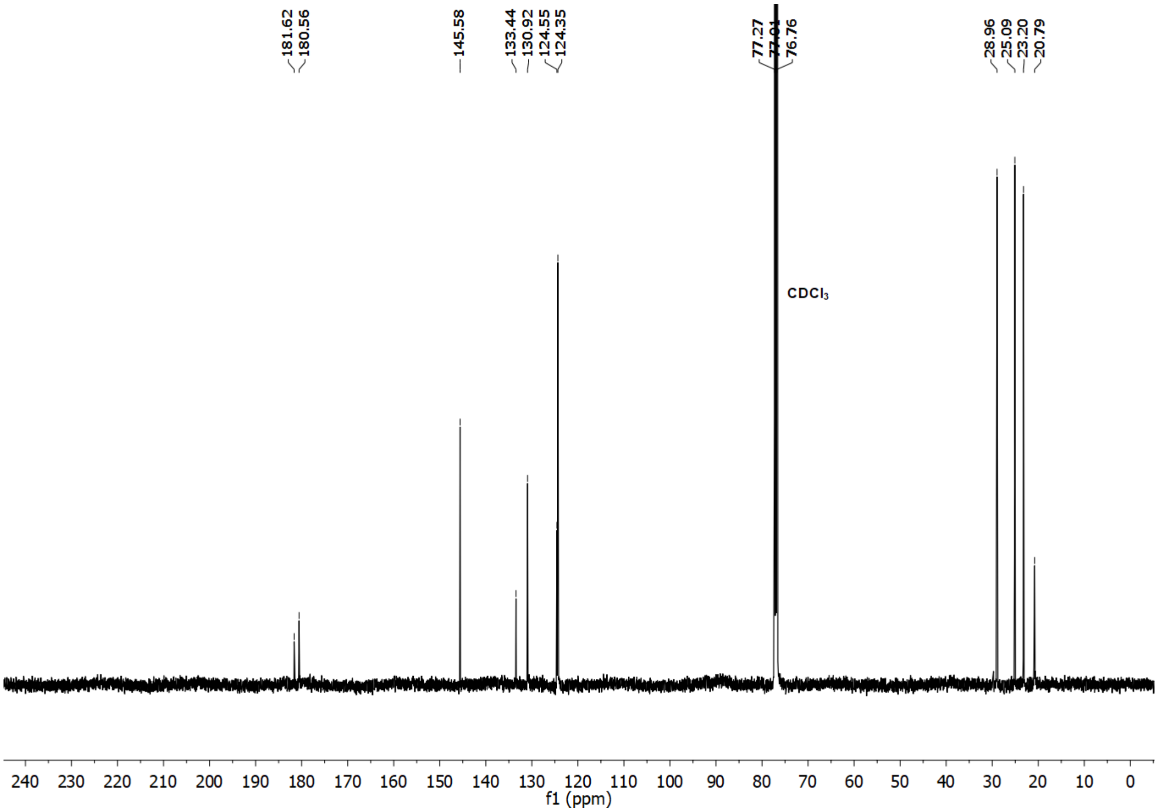

Figure S4. $^{13}C\{^1H\}$ NMR spectrum of [(IPr)Cd(OAc)$_2$] (**2**) in $CDCl_3$.

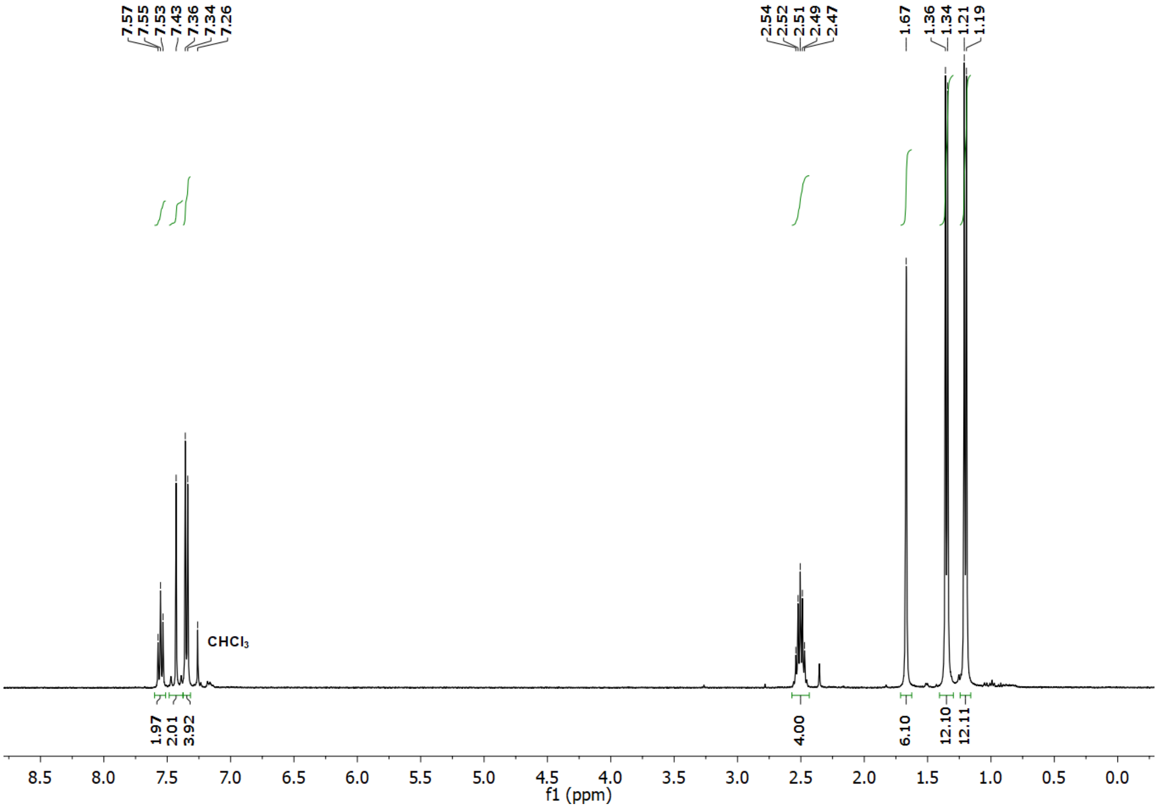

Figure S5. ^{1}H NMR spectrum of [(IPr)Hg(OAc)$_2$] (**3**) in CDCl$_3$.

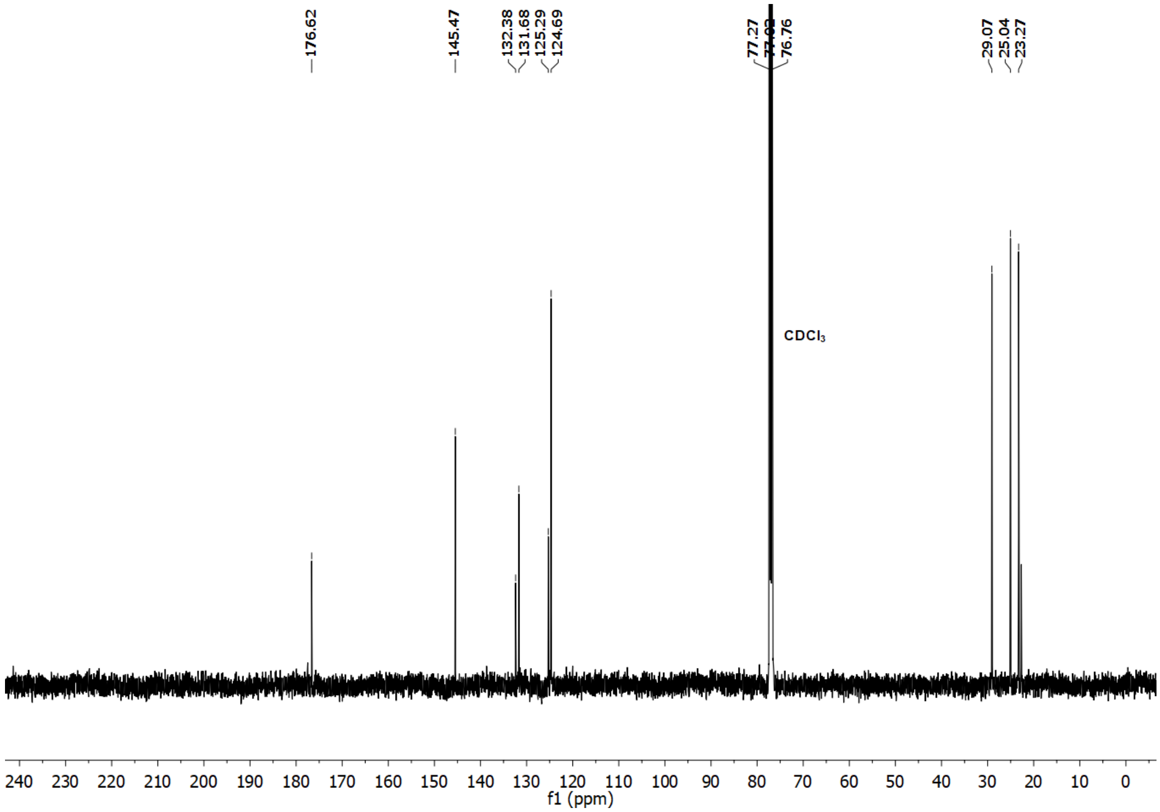

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of [(IPr)Hg(OAc)$_2$] (**3**) in CDCl$_3$.

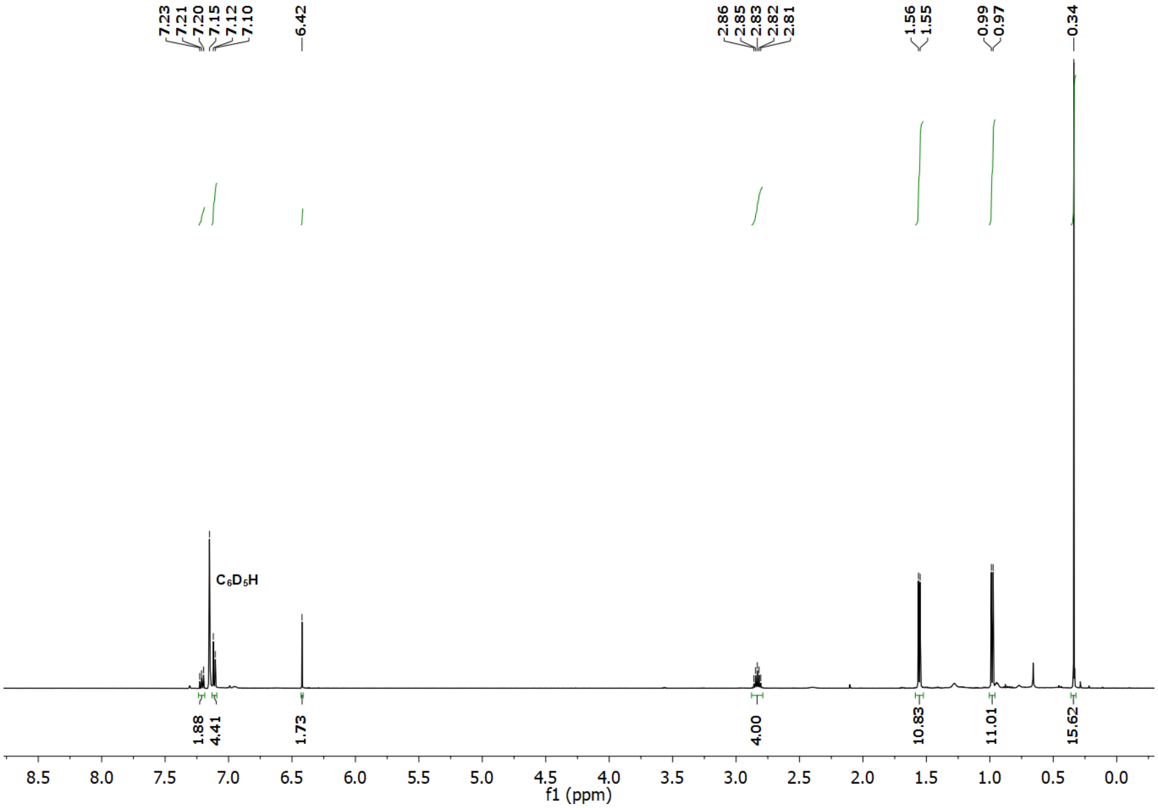

Figure S7. ^{1}H NMR spectrum of [(IPr)Zn(SSiMe$_3$)$_2$] (**4**) in C_6D_6.

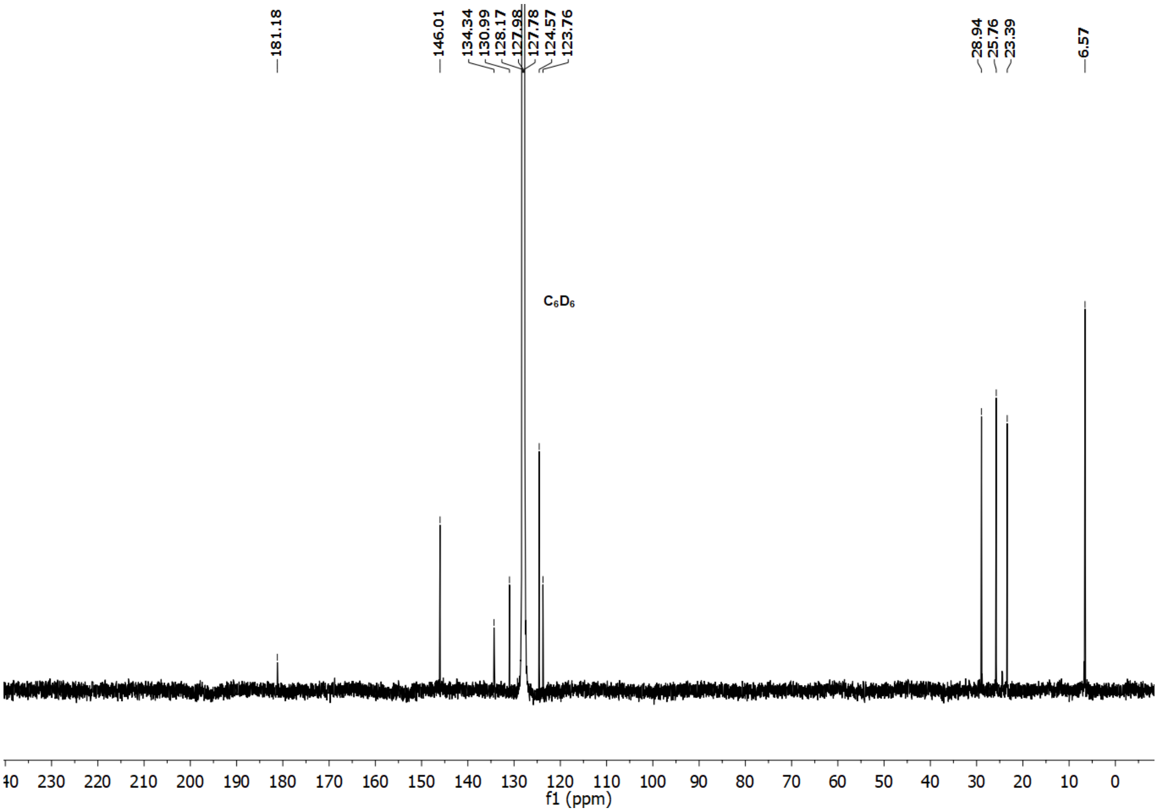

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of $[(IPr)Zn(SSiMe_3)_2]$ (**4**) in C_6D_6.

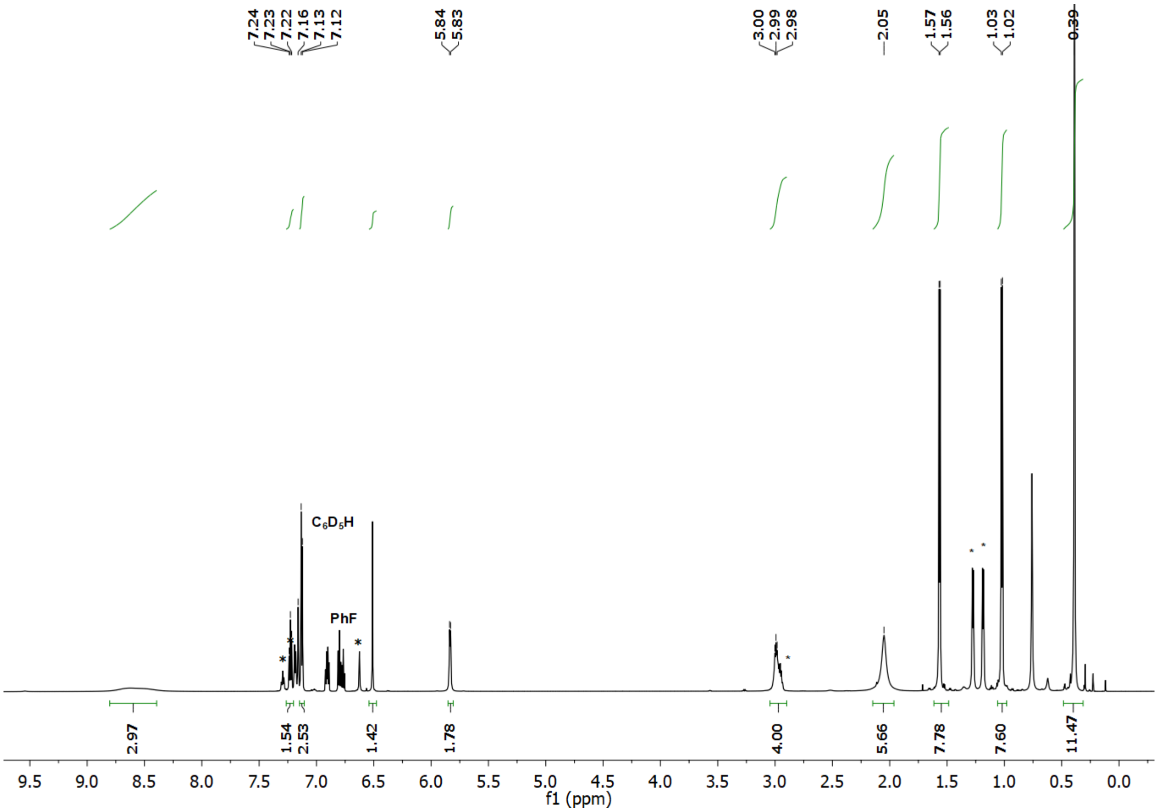

Figure S9. ^{1}H NMR spectrum of [(IPr)Zn(SSiMe$_3$)$_2$(DMAP)] (**5**) in C_6D_6. [* denotes free IPr resonances]

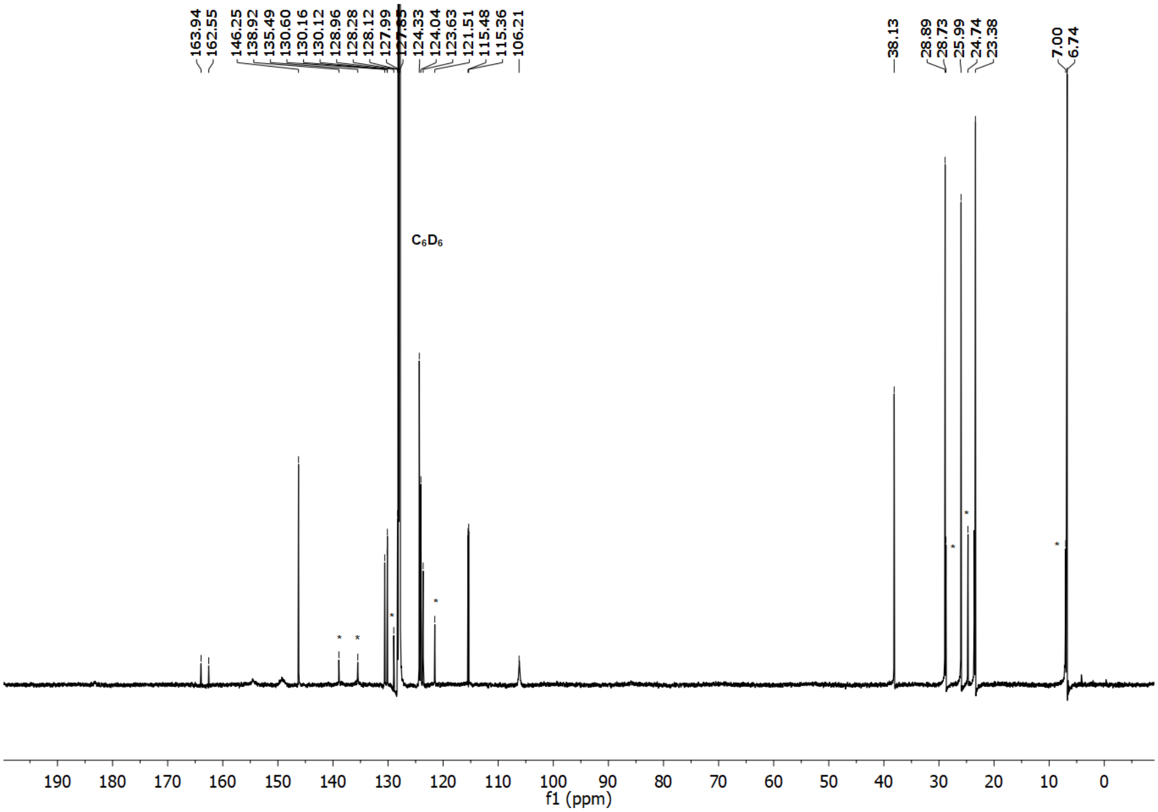

Figure S10. $^{13}C\{^1H\}$ NMR spectrum of [(IPr)Zn(SSiMe$_3$)$_2$(DMAP)] (**5**) in C_6D_6. [* denotes free IPr resonances]

X-Ray Crystallographic Data

Table S1. Crystallographic Experimental Details for [(IPr)Zn(SSiMe$_3$)$_2$(DMAP)] (**5**)

A. Crystal Data	
formula	$C_{46}H_{69}FN_4S_2Si_2Zn$
formula weight	882.72
crystal dimensions (mm)	0.29 × 0.14 × 0.12
crystal system	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell parameters[a]	
a (Å)	10.100 (3)
b (Å)	12.363 (4)
c (Å)	21.191 (7)
α (deg)	89.824 (5)
β (deg)	85.218 (5)
γ (deg)	69.150 (5)
V (Å^3)	2463.2 (14)
Z	2
ρ_{calcd} (g cm^{-3})	1.190
μ (mm^{-1})	0.670

B. Data Collection and Refinement Conditions

diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–100
scan type	ω scans (0.3°) (20 s exposures)
data collection 2θ limit (deg)	51.65
total data collected	18595 ($-12 \leq h \leq 12$, $-15 \leq k \leq 15$, $-25 \leq l \leq 25$)
independent reflections	9384 (R_{int} = 0.0637)
number of observed reflections (*NO*)	6330 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	intrinsic phasing (*SHELXT-2014*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–2014*[d])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	1.0000–0.7160
data/restraints/parameters	9384 / 5[e] / 531
goodness-of-fit (*S*)[f] [all data]	0.993
final *R* indices[g]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0687
wR_2 [all data]	0.2017
largest difference peak and hole	1.268 and –1.261 e Å^{-3}

[a] Obtained from least-squares refinement of 5376 reflections with 4.50° < 2θ < 44.92°.

[b] Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c] Sheldrick, G. M. *Acta Crystallogr.* **2015**, *A71*, 3–8. (*SHELXT-2014*)

[d] Sheldrick, G. M. *Acta Crystallogr.* **2015**, *C71*, 3–8. (*SHELXL-2014*)

[e] The C–F distance of the disordered fluorobenzene molecules was restrained to be 1.350(5) Å. Additionally, the C–C distance (C11S–C12S, C12S–C13S, C11S–C13S’) was restrained to by 1.390(5) Å.

[f] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.1174P)^2]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$).

[g] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table S2. Crystallographic Experimental Details for $[IPrH]_2[Zn_3(\mu_3\text{-}S)(\mu_2\text{-}SSiMe_3)_3(SSiMe_3)_3]$ (**6**)

A. Crystal Data

formula	$C_{79}H_{136}N_4S_7Si_6Zn_3$
formula weight	1730.98
crystal dimensions (mm)	0.42 × 0.09 × 0.07
crystal system	monoclinic
space group	$P2_1/c$ (No. 14)
unit cell parameters[a]	
a (Å)	15.6474 (3)
b (Å)	20.7512 (3)
c (Å)	30.1314 (5)
β (deg)	92.7671 (9)
V (Å^3)	9772.3 (3)
Z	4
ρ_{calcd} (g cm^{-3})	1.177
μ (mm^{-1})	3.248

B. Data Collection and Refinement Conditions

diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	Cu Kα (1.54178) (microfocus source)
temperature (°C)	–100
scan type	ω and ϕ scans (1.0°) (5 s exposures)
data collection 2θ limit (deg)	150.07
total data collected	69438 ($-18 \le h \le 19$, $-25 \le k \le 25$, $-37 \le l \le 37$)
independent reflections	19762 (R_{int} = 0.0392)
number of observed reflections (*NO*)	16044 [$F_o^2 \ge 2\sigma(F_o^2)$]
structure solution method	intrinsic phasing (*SHELXT-2014*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–2014*[d])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.8864–0.5630
data/restraints/parameters	19762 / 7[e] / 953
goodness-of-fit (S)[f] [all data]	1.040
final R indices[g]	
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0363
wR_2 [all data]	0.0956
largest difference peak and hole	0.586 and –0.425 e Å^{-3}

[a] Obtained from least-squares refinement of 9880 reflections with 5.18° < 2θ < 147.78°.

[b] Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c] Sheldrick, G. M. *Acta Crystallogr.* **2015**, *A71*, 3–8. (*SHELXT-2014*)

[d] Sheldrick, G. M. *Acta Crystallogr.* **2015**, *C71*, 3–8. (*SHELXL-2014*)

[e] The C12–C17A and C12–C17B distances were restrained by use of the *SHELXL* **SAME** instruction during refinement. Likewise, the C17A–C18A, C17A–C19A, C17B–C18B, and C17B–C19B distances were also restrained.

[f] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0054P)^2 + 6.7722P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[g] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

References

S1. A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics*, 1996, **15**, 1518.
S2. L. Jafarpour, E. D. Stevens, S. P. Nolan, *J. Organomet. Chem.*, 2000, **606**, 49.
S3. H. Hope, *Prog. Inorg. Chem.*, 1994, **41**, 1.
S4. G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2015, **71**, 3.
S5. G. M. Sheldrick, *Acta Crystallogr., Sect. C*, 2015, **71**, 3.