Electronic Supplementary Information

Intermediate Snapshot on the Insertion Reaction of Isocyanates into the Zn-Cp* Bond of Dizincocene $Cp^*_2Zn_2$

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Content

I. Experimental Section

All manipulations were carried out under a dry argon or nitrogen atmosphere using Schlenk line and glovebox techniques. All solvents were dried by Braun solvent drying system and degassed to use. Deuterated benzene was dried by refluxing with sodium/potassium under N_2 prior to use. The NMR (^{1}H, ^{13}C) spectra were recorded on Bruker Avance II 300 MHz spectrometer. Elemental analysis was performed at the *Elementaranalyse Labor* of the University of Duisburg-Essen. IR spectra were reported by a Bruker ALPHA-T FT-IR spectrometer equipped with a single-reflection ATR sampling module. Commercial reagents were purchased from Aldrich, Acros, or Alfa-Aesar Chemical Co. and used as received. $Cp^*_2Zn_2$ [1] was prepared according to the literature.

Synthesis of Cp*Zn-Zn(N(Dipp)C(Cp*)O) (2): A cooled solution (-10 °C) of DippNCO (100 mg, 0.5 mmol) in *n*-hexane (5 mL) was added to a cooled solution (-10 °C) of $Cp^*_2Zn_2$ (150 mg, 0.37mmol) in *n*-hexane (5 mL). The mixture was stirred at -3 °C for 2 days, filtered and the filtrate was concentrated to 2 mL. Colourless crystals formed upon storage at -30 °C for 24 h. Yield (153 mg, 68%). Melting point: 93 °C (dec.). Anal. Calcd (%) for $C_{33}H_{47}NOZn_2$ (Mr = 604.51): C, 65.57; H, 7.84; N, 2.32. Found: C, 65.90; H, 7.81; N, 2.24. ^{1}H NMR (300 MHz, C_6D_6): δ = 1.20 (d, $^3J_{HH}$ = 6.0 Hz, 6H, CHMe_2), 1.38 (d, $^3J_{HH}$ = 6.0 Hz, 6H, CHMe_2), 1.45 (s, 3H, C_5Me_5), 1.66 (s, 6H, C_5Me_5), 1.88 (s, 6H, C_5Me_5), 1.96 (s, 15H, C_5Me_5), 3.26 (sept, $^3J_{HH}$ = 6.0 Hz, 6H, C*H*Me$_2$), 7.19 (br, 3H, C_6H_3); ^{13}C NMR (75 MHz, C_6D_6): δ = 9.9 (C_5Me_5), 10.8 (C_5Me_5), 11.8 (C_5Me_5), 18.7 (C_5Me_5), 23.5 (CHMe_2), 23.9 (CHMe_2), 24.6 (CHMe_2), 28.2 (*C*HMe$_2$), 69.0 (C_5Me$_5$), 108.6 (C_5Me$_5$), 122.9 (C_6H$_3$), 125.4(C_6H$_3$), 136.0 (C_5Me$_5$), 139.1 (C_6H$_3$), 144.4 (C_6H$_3$), 148.5 (C_5Me$_5$), 172.3 (N*C*O). ATR-IR: *v* 2943, 2911, 2963, 1623, 1586, 1435, 1380, 1361, 1324, 1291, 1229, 971, 791, 750, 724, 616, 411 cm^{-1}.

Synthesis of Cp*Zn-Zn(N(*t*Bu)C(Cp*)O) (3): Pre-cooled solutions (-10 °C) of *t*-BuNCO (55 mg, 0.55 mmol) in *n*-hexane (5 mL) and $Cp^*_2Zn_2$ (150 mg, 0.37mmol) in *n*-hexane (5 mL) were combined at stirred at -3 °C for 48 h, filtered and the filtrate was concentrated to 2 mL. Colourless crystals formed upon storage at -30 °C for 24 h. Yield (100 mg, 53.7%). Melting point: 102 °C (dec.). Anal. Calcd (%) for $C_{25}H_{39}NOZn_2$ (Mr = 500.35): C, 60.01; H, 7.86; N, 2.80. Found: C, 60.51; H, 7.93; N, 2.78. ^{1}H NMR (300 MHz, C_6D_6): δ = 1.32 (s, 3H, C_5Me_5), 1.50 (s, 9H, CMe_3), 1.56 (s, 6H, C_5Me_5), 1.65 (s, 6H, C_5Me_5), 2.07 (s, 15H, C_5Me_5); ^{13}C NMR (75 MHz, C_6D_6): δ = 10.1 (C_5Me_5), 10.3 (C_5Me_5), 11.8 (C_5Me_5), 20.0 (C_5Me_5), 31.9 (CMe_3), 54.8 (*C*Me$_3$), 69.4 (C_5Me$_5$), 108.5 (C_5Me$_5$), 135.5 (C_5Me$_5$), 148.6 (C_5Me$_5$), 172.9 (N*C*O). ATR-IR: *v* 2950, 2912, 2860, 1626, 1526, 1438, 1383, 1356, 1315, 1288, 1206, 962, 793, 615 cm^{-1}.

II. NMR Spectra of 2 and 3

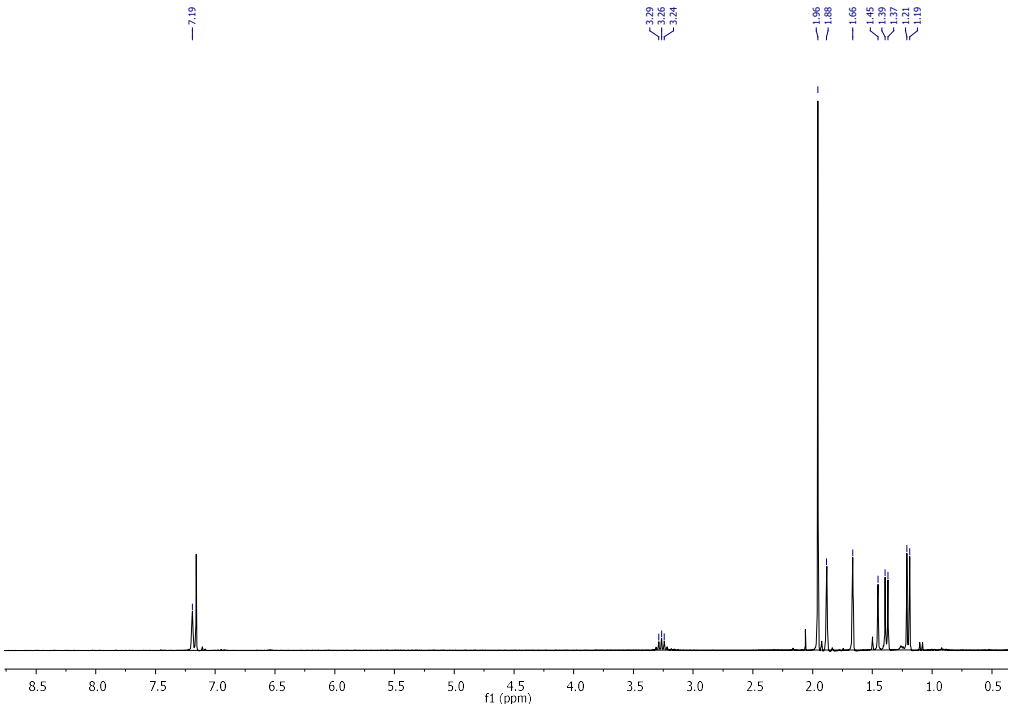


Figure S1. ^{1}H NMR spectrum of **2** in C_6D_6 at room temperature.

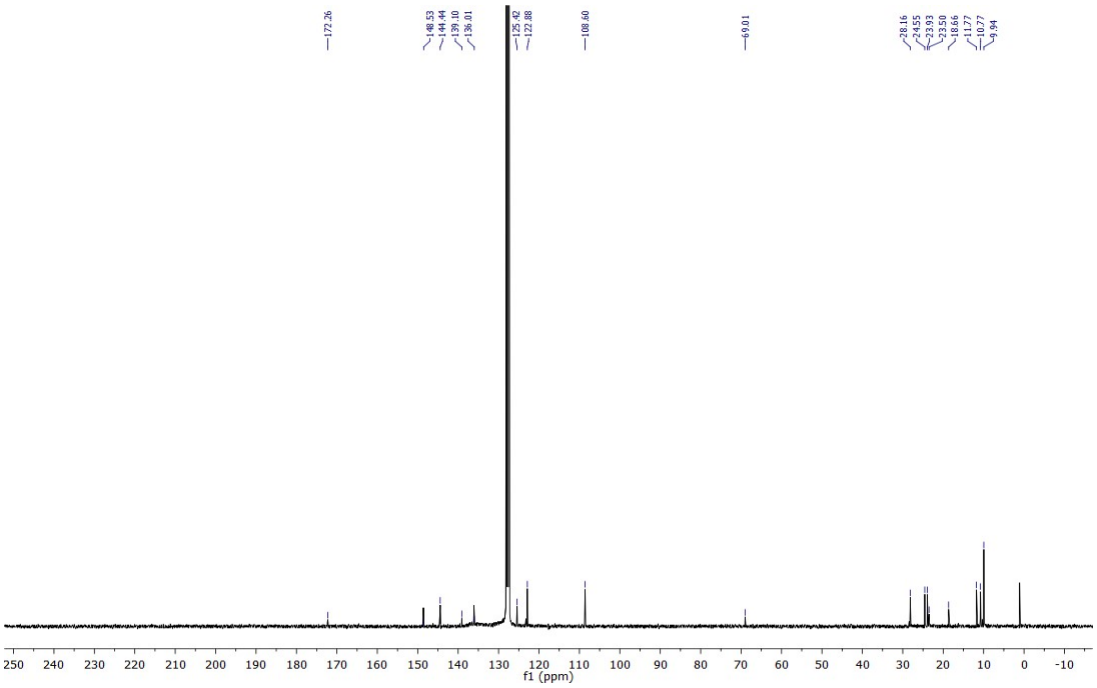


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in C_6D_6 at room temperature.

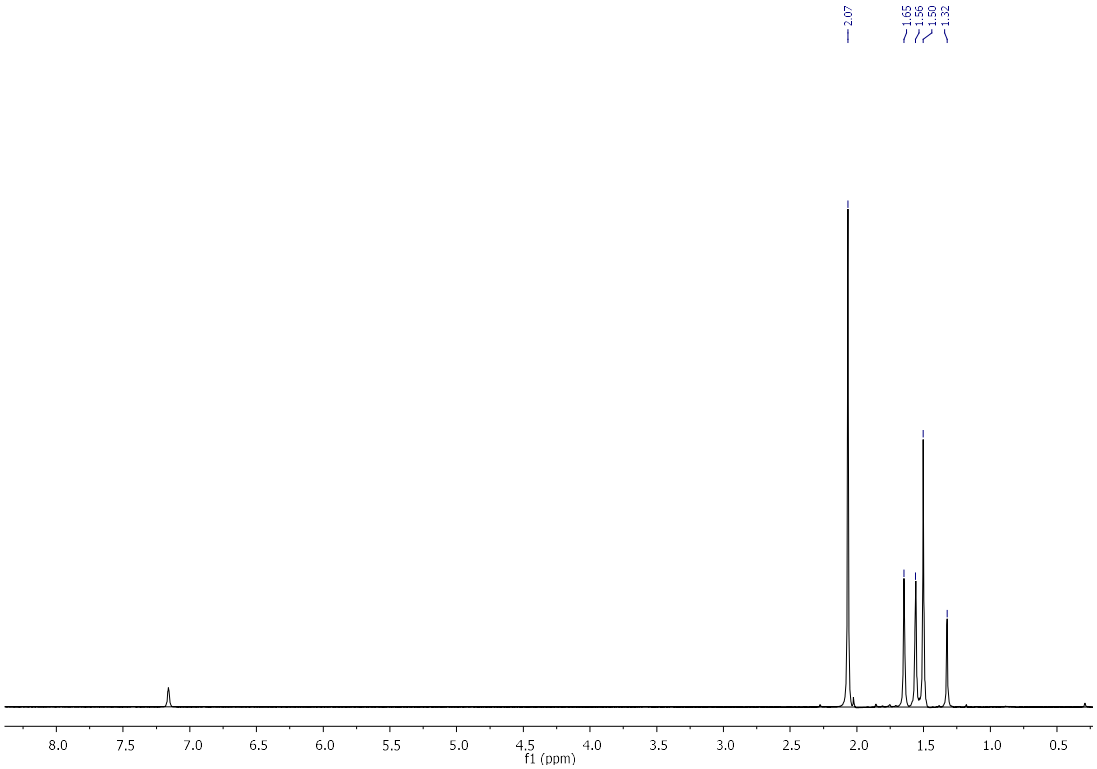


Figure S3. ^{1}H NMR spectrum of **3** in C_6D_6 at room temperature.

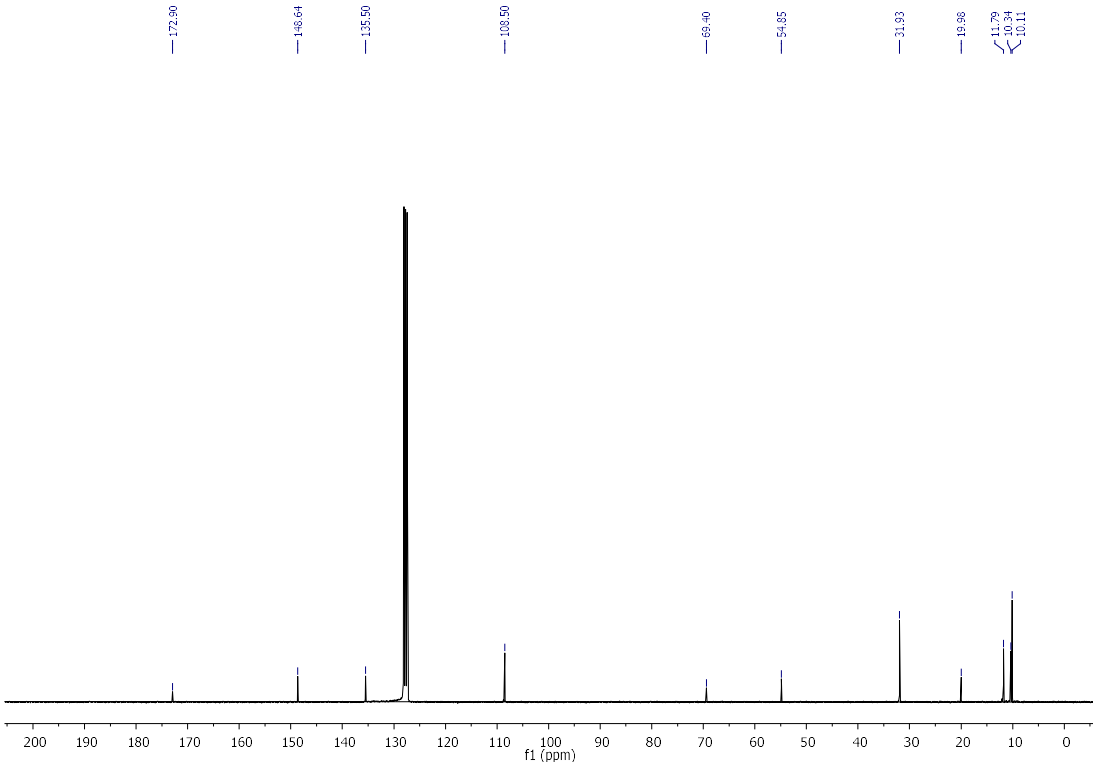


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6 at room temperature.

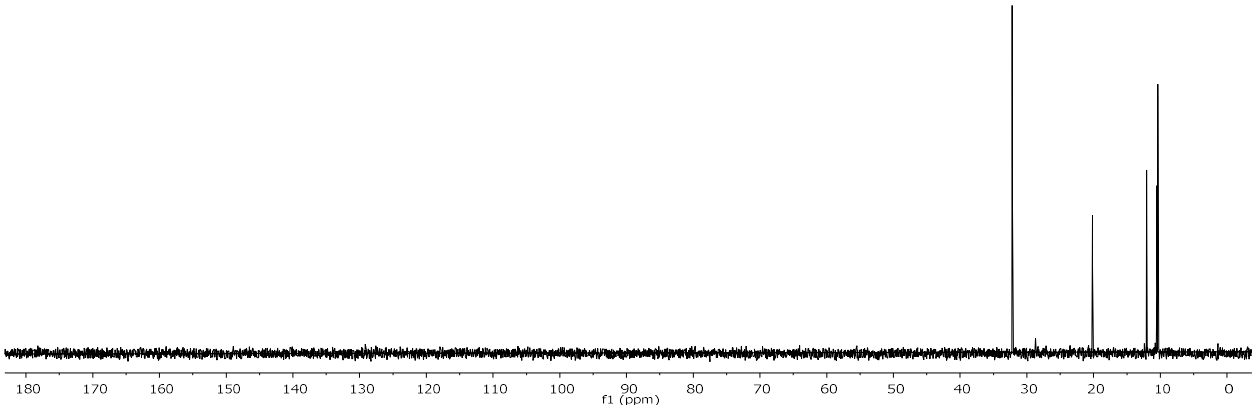


Figure S5. $^{13}C\{^{1}H\}$ NMR DEPT135 spectrum of **3** in toluene-d^8 at room temperature.

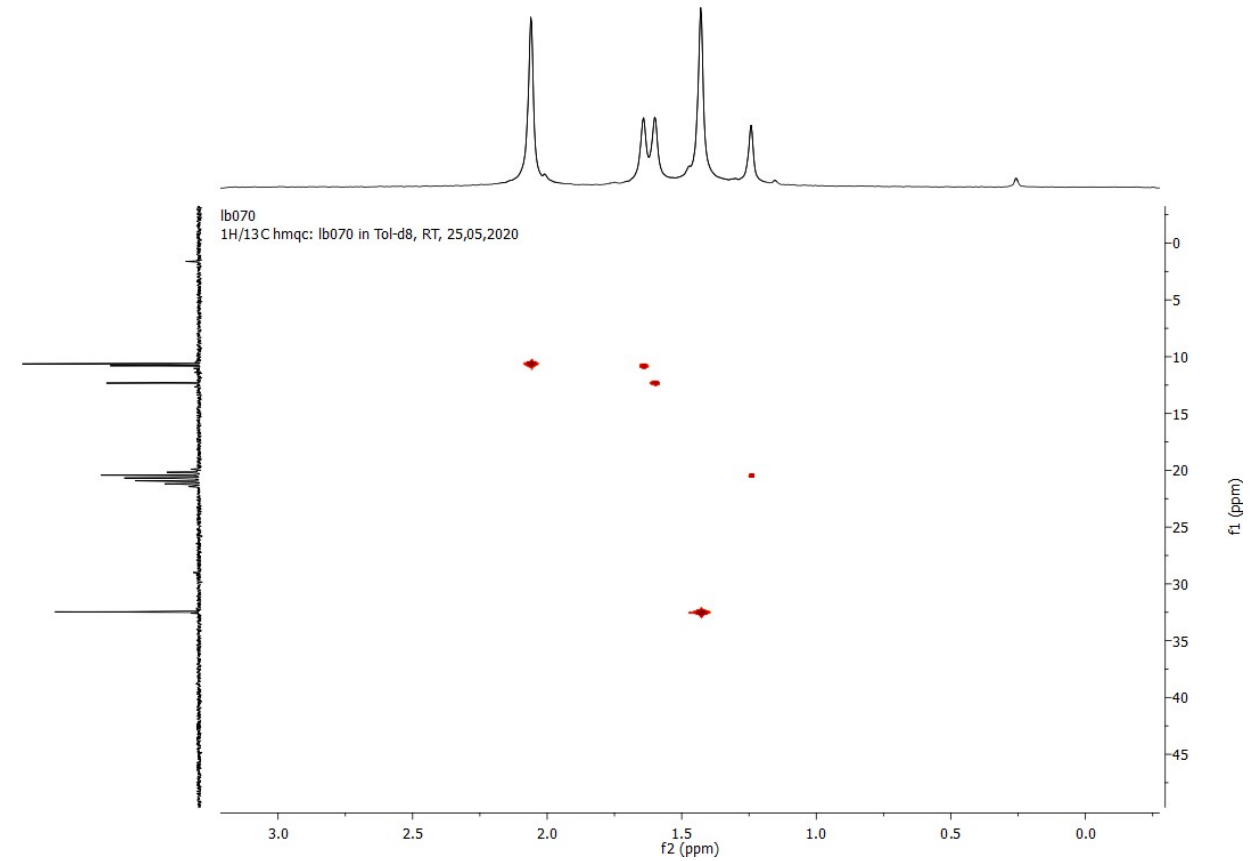


Figure S6. ^{1}H-^{13}C HMQC NMR spectrum of **3** in toluene-d^8 at room temperature.

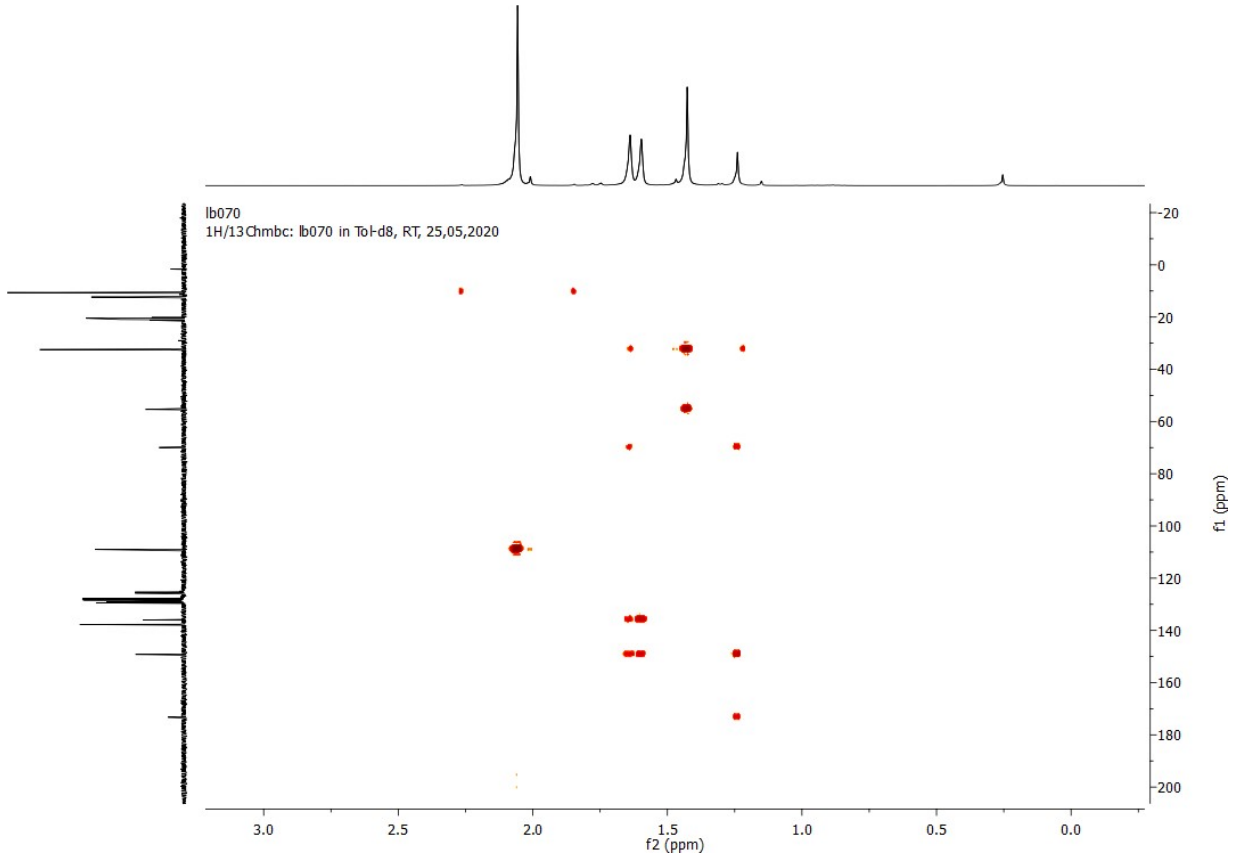
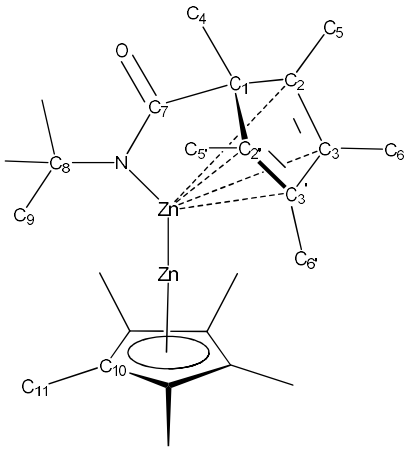


Figure S7. ^{1}H-^{13}C HMBC NMR spectrum of **3** in toluene-d^{8} at room temperature.

Scheme S1. Structural drawing of **3** with numbering all type carbon atoms for assignment of resonance in variable temperature NMR spectra.



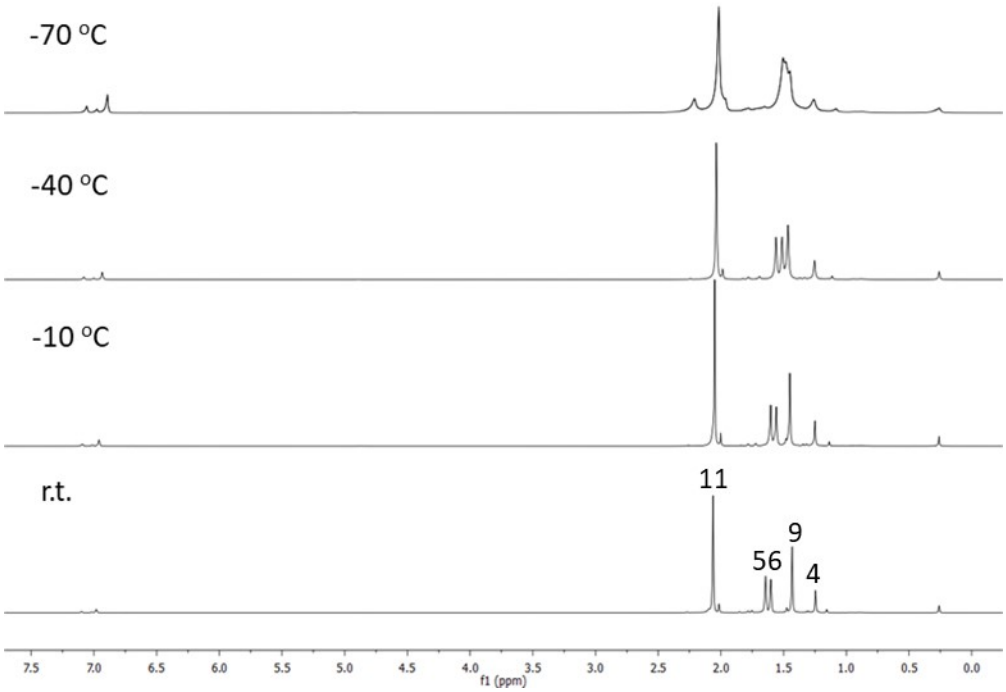


Figure S8. VT ^{1}H NMR spectra (-70 to 25 °C) of **3** in toluene-d^{8}.

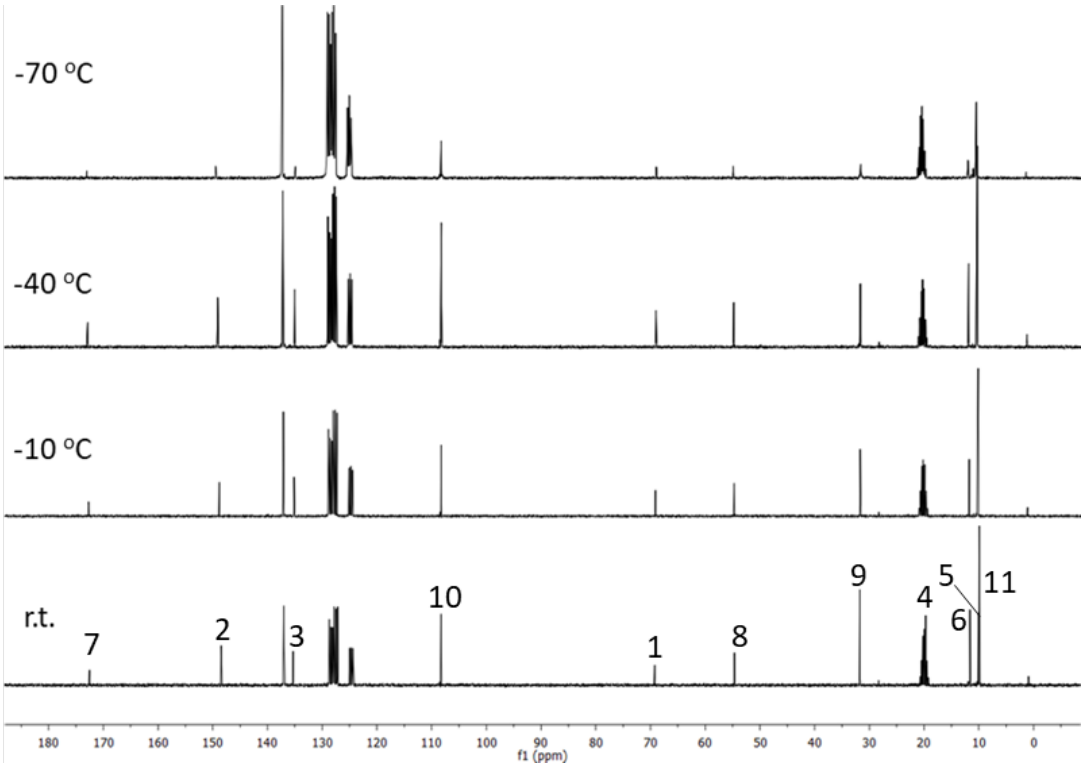


Figure S9. VT ^{13}C{^{1}H} NMR spectra (-70 to 25 °C) of **3** in toluene-d^{8}.

Scheme S2. Model drawings of compounds **2** and **3** (left) and homoleptic zinc(II) amidate complexes $Zn(OC(Cp^*)NR)_2$[2](middle) and *t*-BuNHC(O)Cp* (right).

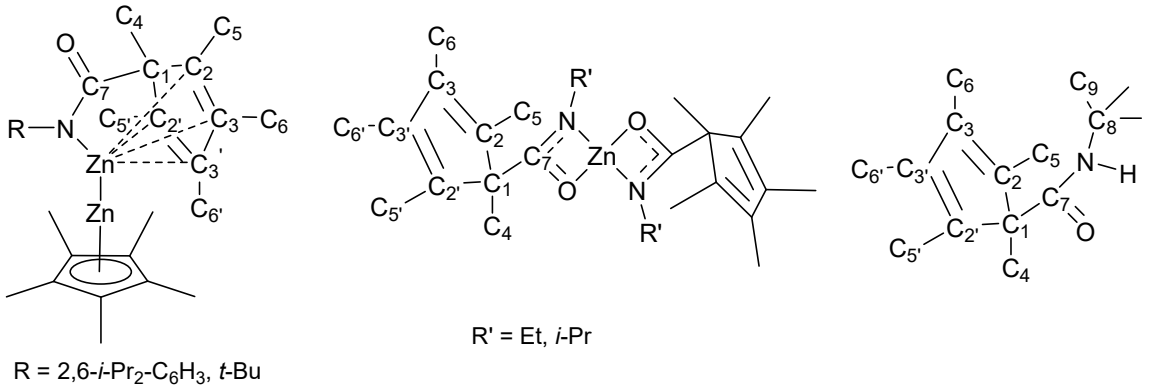


Table S1. ^{1}H NMR resonances of the tethered Cp* group of zinc(I) complexes **2** and **3**, homoleptic zinc(II) amidate complexes $Zn(OC(Cp^*)NR)_2$[2] and *t*-BuNHC(O)Cp*.

	2	**3**	$Zn(OC(Cp^*)NEt)_2$	$Zn(OC(Cp^*)N\textit{i}Pr)_2$	*t*-BuNHC(O)Cp*[a]
Me (C_4)	1.45	1.32	1.58	1.60	1.37
Me ($C_{5,5'}$)	1.88	1.65	1.96	1.99	1.80
Me ($C_{6,6'}$)	1.66	1.56	1.68	1.69	1.63

[a] *t*-BuNHC(O)Cp* was prepared by reacting Cp*K with *t*-BuNCO, followed by hydrolysis.

Table S2. ^{13}C NMR resonances of the tethered Cp* group of zinc(I) complexes **2** and **3**, homoleptic zinc(II) amidate complexes $Zn(OC(Cp^*)NR)_2$[2] and amide *t*-BuNHC(O)Cp*.

	2	**3**	$Zn(OC(Cp^*)NEt)_2$	$Zn(OC(Cp^*)N\textit{i}Pr)_2$	*t*BuNHC(O)Cp*
Me (C_4)	18.7	20.0	18.2	23.8	17.5
Me ($C_{5,5'}$)	10.8	10.3	10.3	10.2	10.6
Me ($C_{6,6'}$)	11.8	11.8	11.2	11.0	11.5
C_1	69.0	69.4	65.6	66.1	66.7
$C_{2,2'}$	148.5	148.6	140.1	140.1	140.6
$C_{3,3'}$	136.0	135.5	136.3	135.3	136.6
C_7 (NCO)	172.3	172.9	171.0	175.4	170.9

Table S2 summarizes ^{13}C NMR data of **2** and **3** as well as of two homoleptic amidate complexes $Zn(OC(Cp^*)NR)_2$ (R = Et, *i*-Pr),[2] which were formed in insertion reaction of isocyanates into Zn-Cp* bond and which do not contain any Zn-Cp* π-interaction to the tethered Cp* substituent. In addition, *t*-BuNHC(O)Cp* was also synthesized for comparison. Each of these compounds show three singlets which could be assigned to the ring-carbon atoms of the "activated" Cp* unit. The C_1 and $C_{3,3'}$ resonances in **2** and **3** are almost identical to those of $Zn(OC(Cp^*)NR)_2$ and *t*-BuNHC(O)Cp*, whereas the $C_{2,2'}$ resonances of **2** and **3** are significantly shifted to lower field. These findings can be explained by a polarization of the $C_{2,2'}$-$C_{3,3'}$ π bond and hence a decrease of the electron density of the Cp* ring due to preservation of the Zn-π interaction in solution.

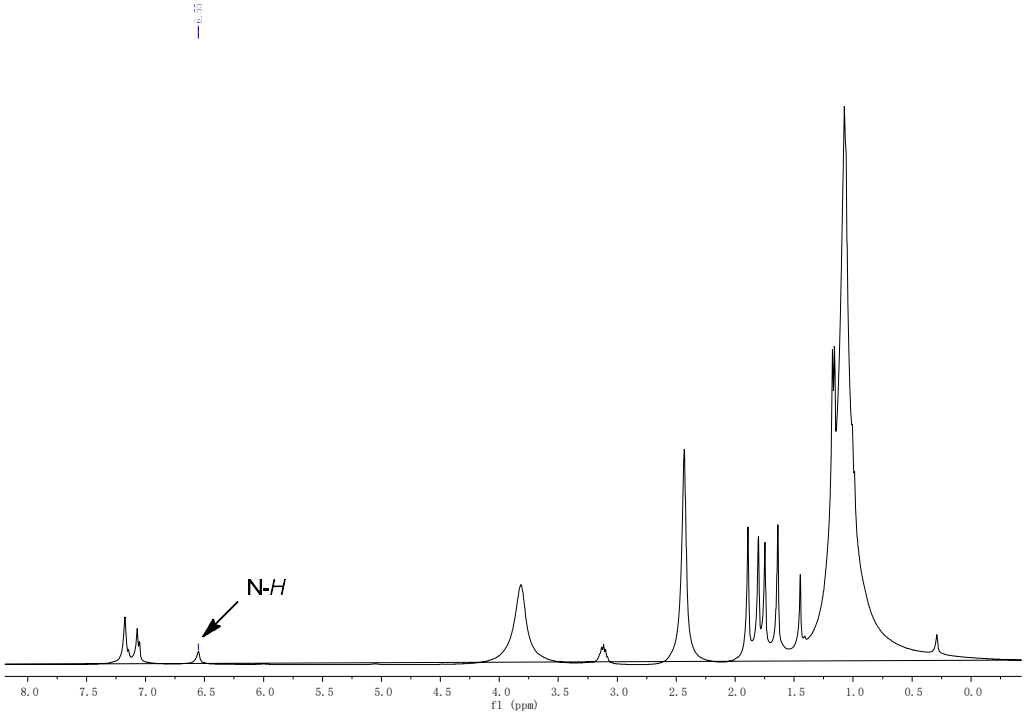


Figure S10. *In situ* reaction of **2** with isopropanol in C_6D_6 at ambient temperature. The singlet at 6.55 ppm assigned to N-*H* indicates the formation of amide Cp*C(O)NHDipp.

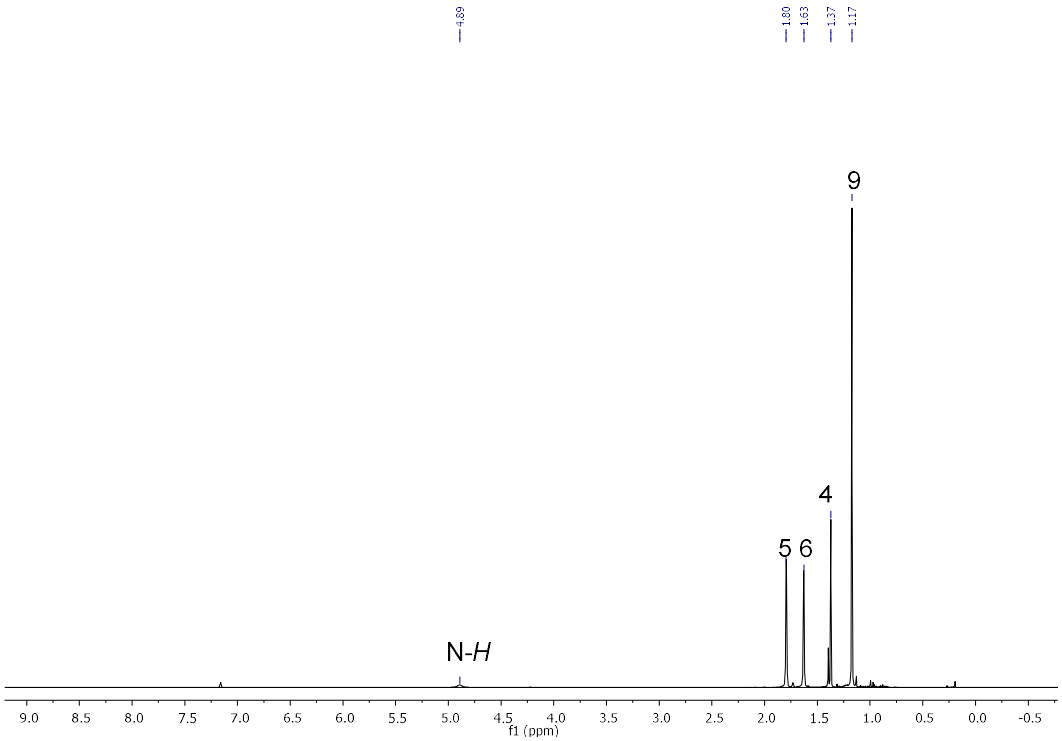


Figure S11. ^{1}H NMR spectrum of Cp*C(O)NH*t*-Bu in C_6D_6 at room temperature.

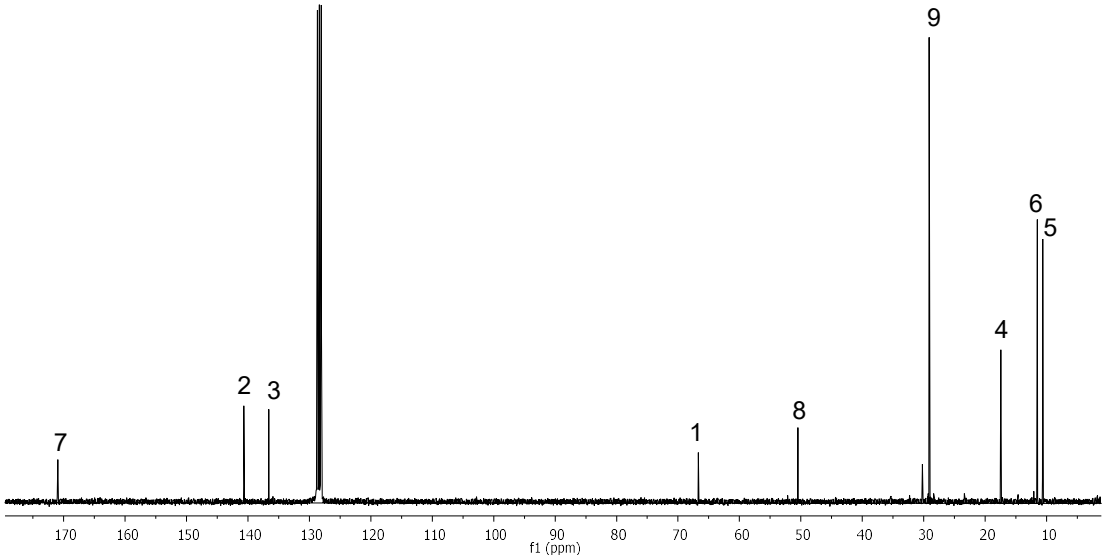


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of Cp*C(O)NH*t*-Bu in C_6D_6 at room temperature.

III. IR Spectra of 2 and 3

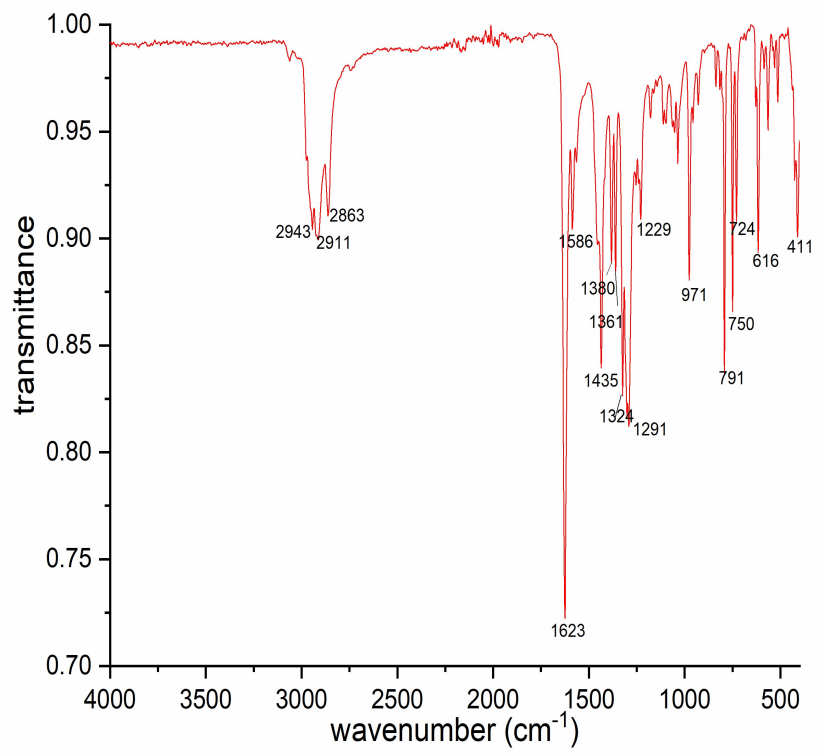


Figure S13. Infrared resonance spectrum of **2**.

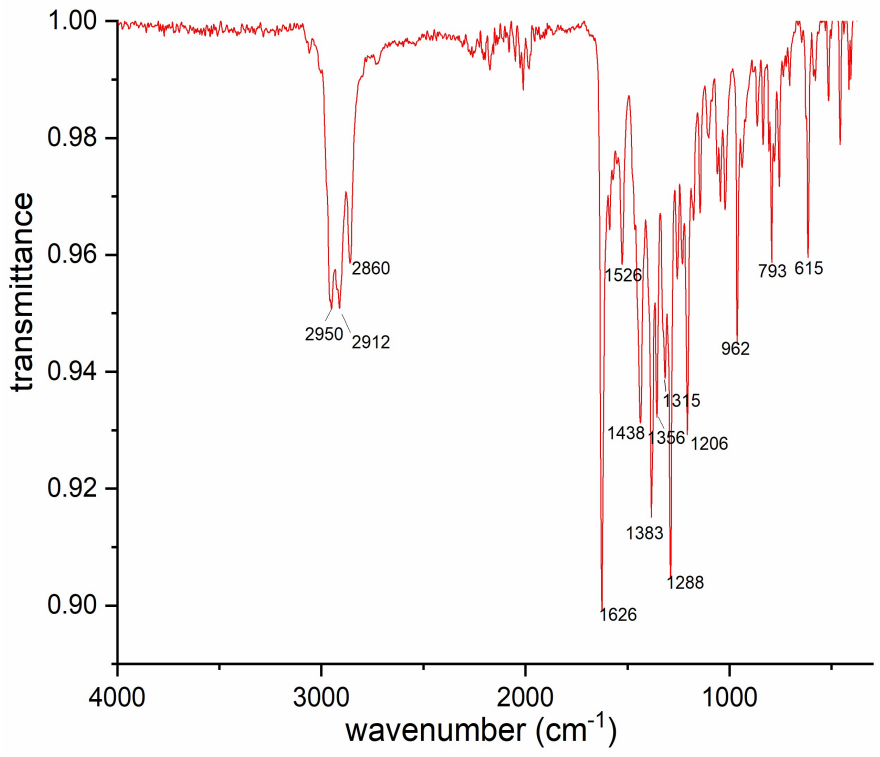


Figure S14. Infrared resonance spectrum of **3**.

IV. X-Ray Crystallographic Analysis of 2 and 3

Crystals of **2** and **3** were mounted on a suitable support under perfluorinated oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at T = 100(2) K during data collection. The structures were solved by direct methods (SHELXS-97)[3] and refined anisotropically by full-matrix least squares on F^2 (SHELXL-2014).[4-6] Absorption corrections were performed semi-empirically from equivalent reflections on the basis of multi-scans. Hydrogen atoms were refined using a riding model or rigid methyl groups.

Table S3. Crystal data and structure refinement of **2** and **3**.

Compound	**2**	**3**
Empirical formula	$C_{33}H_{47}NOZn_2$	$C_{25}H_{39}NOZn_2$
CCDC number	1992725	1992726
Formula weight	604.45	500.31
Temperature [K]	100(2)	100(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/m$
a [Å]	15.9994(14)	9.0241(10)
b [Å]	13.4294(12)	12.0224(13)
c [Å]	15.3641(13)	12.0743(13)
□ [°]	108.019(4)	110.467(5)
V [Å^3]	3139.3(5)	1227.3(2)
Z	4	2
□ [Mgm^{-3}]	1.279	1.354
□ [mm^{-1}]	1.552	1.969
F (000)	1280	528
Crystal size [mm]	0.850×0.298×0.120	0.402×0.310×0.218
□-max [°]	33.272	41.376
Index ranges	-24≤h≤24, -20≤k≤19, -23≤l≤20	-11≤h≤15, -22≤k≤22, -22≤l≤22
Total no. reflect. / unique	74019 / 11349	89099 / 7688
R_{int}	0.0364	0.0246
Data / restraints / param.	11349/0/348	7688/0/256
Goodness-of-fit on F^2	1.054	1.082
$R1$ [I>2□(I)]	0.0352	0.0241
$wR2$ [I>2□(I)]	0.0956	0.0611
$R1$ [all data]	0.0430	0.0374
$wR2$ [all data]	0.1000	0.0695
Largest diff. peak and hole max. / min. [e·Å^{-3}]	1.416/-0.913	0.827/-0.475

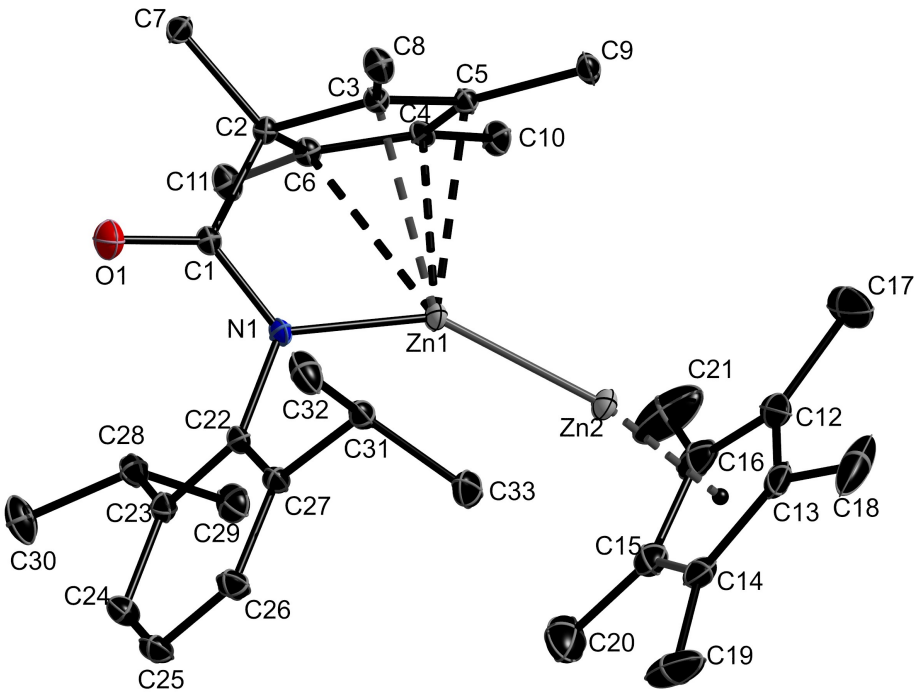


Figure S15. Molecular structure of **2** with thermal ellipsoids at 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond length (Å) and angels (°): Zn(1)-Zn(2) 2.2963(3), Zn(1)-C(2) 2.9329(13), Zn(1)-C(3) 2.7148(11), Zn(1)-C(4) 2.5272(13), Zn(1)-C(5) 2.5861(12), Zn(1)-C(6) 2.7988(13), Zn(1)-N(1) 1.9202(11), Zn(2)-C(13) 2.2124(15), Zn(2)-C(12) 2.2373(16), Zn(2)-C(14) 2.2446(15), Zn(2)-C(16) 2.2856(18), Zn(2)-C(15) 2.2911(16), O(1)-C(1) 1.2323(15), N(1)-C(1) 1.3489(16), C(1)-C(2) 1.5569(17); Cp^*_{centr}-Zn2-Zn1 165.89, C4-Zn1-Zn2 107.82(4), C5-Zn1-Zn2 105.21(3), N(1)-Zn(1)-Zn(2) 148.32(3), C(1)-N(1)-Zn(1) 120.46(8), O(1)-C(1)-N(1) 126.14(12), O(1)-C(1)-C(2) 121.12(11), N(1)-C(1)-C(2) 112.74(10).

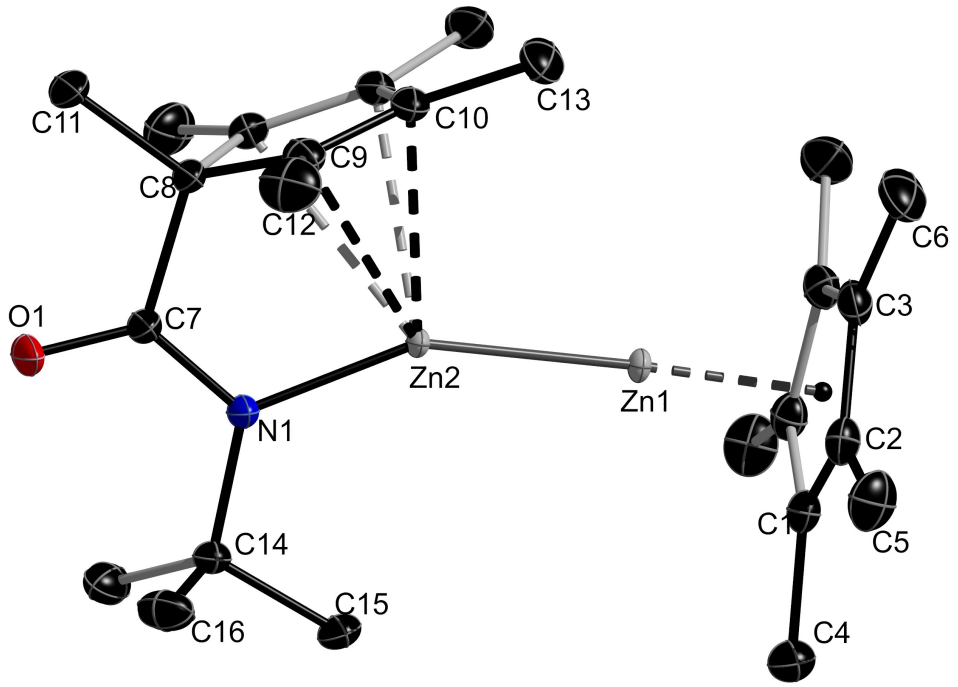
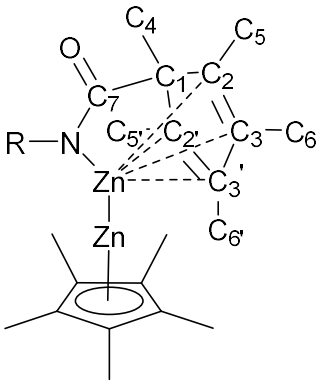
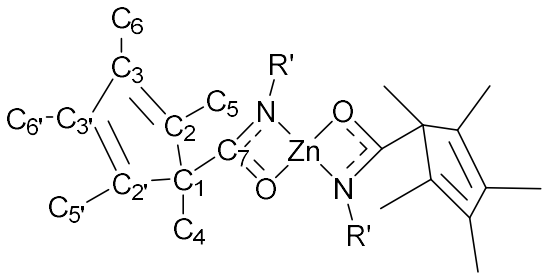


Figure S16. Molecular structure of **3** with thermal ellipsoids at 50% probability level. The hydrogen atoms are omitted for clarity. Atoms displayed in pale colours are generated by symmetry. Selected bond length (Å) and angels (°): Zn(1)-Zn(2) 2.3031(3), Zn(1)-C(2) 2.2602(7), Zn(1)-C(3) 2.2668(8), Zn(1)-C(1) 2.2693(10), Zn(2)-C(10) 2.6085(8), Zn(2)-C(9) 2.7751(10), Zn(2)-C(8) 2.9298(13), Zn(2)-N(1) 1.9148(9), O(1)-C(7) 1.2317(14), N(1)-C(7) 1.3471(13), C(7)-C(8) 1.5652(16); Cp^*_{centr}-Zn1-Zn2 177.76, C10-Zn2-Zn1 102.56(2), C(7)-N(1)-C(14) 118.76(9), C(7)-N(1)-Zn(2) 119.29(8), C(14)-N(1)-Zn(2) 121.95(6), N(1)-Zn(2)-Zn(1) 153.20(3), O(1)-C(7)-N(1) 126.73(11), O(1)-C(7)-C(8) 119.29(9), N(1)-C(7)-C(8) 113.98(9).

Scheme S3. Drawings of compounds **2** and **3** (left) and homoleptic amidate complexes $Zn(OC(Cp^*)NR)_2$ (right).[2]



R = 2,6-*i*-Pr_2-C_6H_3, *t*-Bu



R' = Et, *i*-Pr

Table S4. C–C bond lengths [Å] of the tethered Cp* group of **2** and **3** as well as of the homoleptic zinc amidate complexes $Zn(OC(Cp^*)N$*i*-$Pr)_2$.[2]

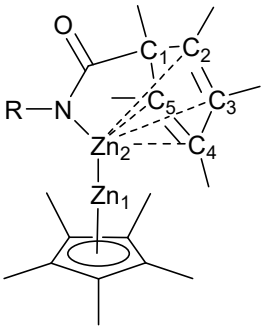
	2	**3**	**Zn(OC(Cp*)N*i*-Pr)$_2$**
C_1–C_2	1.5237(17)	1.5181(11)	1.5087(30) - 1.5189(30)
C_2–C_3	1.3561(17)	1.3548(11)	1.3294(31) - 1.3448(37)
C_3–$C_{3'}$	1.4885(18)	1.4865(17)	1.4552(49) - 1.4700(27)
$C_{3'}$–$C_{2'}$	1.3587(17)	1.3548(11)	1.3294(31) - 1.3448(37)
$C_{2'}$–C_1	1.5188(17)	1.5181(11)	1.5087(30) - 1.5189(30)
C_{NCO}–C_1	1.5569(17)	1.5652(16)	1.5342(33) - 1.5423(27)

V. Computational Details

The geometric parameters of all investigated Zn(I) complexes were fully optimized in the gas phase at the B3LYP[7-10]/Def2-TZVP[11] theoretical level using Gaussian16. Input geometries were taken from crystal structure data. The stationary points were characterized as true minima on the potential energy surface by vibrational analysis (the number of imaginary frequencies (N_{Imag}) was equal to zero) and the structures obtained were used for the subsequent calculations. The natural bond orbital analysis (NBO)[12] was performed at the B3LYP/ Def2-TZVP theoretical level as implemented in Gaussian16.[13-15]

Table S5. Structural parameters and calculated NPA and WBI values for **2'** and **3'** / **3''**.

	2 / **2'** (exp. / calc.[i])	**3** / **3'** / **3''** (exp. / calc.[i] / calc.[ii])
Zn_1-Zn_2	2.296(1) / 2.361	2.303(1) / 2.369 / 2.376
$Cp^*_{centr.}$-Zn_1	1.906 / 1.962	1.919(1) / 1.974 / 1.980
Zn_2-C_1	2.9329(13) / 3.123	2.9298(13) / 3.029 / 2.930
Zn_2-C_2	2.7148(11) /2.579	2.7751(10) / 2.602 / 2.755
Zn_2-C_3	2.5272(13) / 2.754	2.6085(8) / 2.704 / 2.609
Zn_2-C_4	2.5861(12) / 3.318	2.6085(8) / 3.108 / 2.609
Zn_2-C_5	2.7988(13) /3.509	2.7751(10) / 3.265 / 2.755
$Cp^*_{centr.}$-Zn_1-Zn_2	165.9 / 176.8	177.8 / 175.9 / 175.7
NPA Zn_1	0.42	0.50 / 0.53
NPA Zn_2	0.88	0.79 / 0.75
NPA C_1	-0.21	-0.20 / -0.22
NPA C_2	-0.02	-0.01 / +0.06
NPA C_3	-0.02	-0.02 / -0.08
NPA C_4	-0.07	-0.07 / -0.08
NPA C_5	+0.09	+0.08 / +0.06
WBI (Zn_1-Zn_2)	0.89	0.92 / 0.92
WBI (Zn_2-C_1)	0.01	0.01 / 0.01
WBI (Zn_2-C_2)	0.05	0.05 / 0.03
WBI (Zn_2-C_3)	0.04	0.05 / 0.05
WBI (Zn_2-C_4)	0.01	0.01 / 0.05
WBI (Zn_2-C_5)	0.01	0.01 / 0.03



R = 2,6-*i*-Pr_2-C_6H_3 **2**, *t*-Bu **3**

[i] Structure optimization without any restraints; [ii] Structure optimization with fixed Zn-C bond lengths to the tethered Cp* ligand (values from sc-XRD)

Table S6: Cartesian coordinates (x,y,z) for the optimized geometries of Cp*Zn-ZnCp* **1**.

Zn	1.170705	-0.003203	0.001685
Zn	-1.170698	-0.003116	0.000293
C	-3.133457	1.02133	0.661353
C	-3.135272	-0.435289	-1.13514
C	3.133572	1.014805	0.670904
C	3.135279	-0.424365	-1.139558
C	3.136029	-0.324217	1.171175
C	-3.136119	-0.312748	1.17449
C	3.137017	-1.213724	0.052159
C	-3.137161	-1.213058	0.064202
C	3.133159	0.952845	-0.757118
C	-3.13299	0.945609	-0.766034
C	-3.242921	-0.972444	-2.532062
H	-4.289653	-1.086224	-2.835002
H	-2.774277	-1.952865	-2.62857
H	-2.769894	-0.311812	-3.260084
C	3.242476	-0.948003	-2.541619
H	2.769429	-0.280249	-3.263098
H	2.773561	-1.927332	-2.647475
H	4.289104	-1.059114	-2.845903
C	-3.247918	-2.70737	0.143442
H	-2.777832	-3.103466	1.044725
H	-2.778281	-3.196474	-0.711183
H	-4.295349	-3.028254	0.16071
C	3.237521	2.124779	-1.688336
H	4.283531	2.382564	-1.887774
H	2.762095	3.016115	-1.276361
H	2.769408	1.921596	-2.652559
C	-3.244816	-0.698998	2.620353
H	-4.291779	-0.779353	2.933017
H	-2.771668	0.034629	3.274638
H	-2.776976	-1.66405	2.82028
C	3.247548	-2.70876	0.116922
H	4.294924	-3.029973	0.13099
H	2.777751	-3.189498	-0.742351
H	2.777486	-3.113487	1.014377
C	3.244936	-0.72451	2.6132
H	4.291954	-0.808423	2.924768
H	2.776663	-1.691211	2.803936
H	2.772346	0.002985	3.274695
C	-3.238161	2.277382	1.475476
H	-4.284244	2.552738	1.649519
H	-2.763235	3.125055	0.979408
H	-2.769671	2.168206	2.454635
C	-3.237345	2.108413	-1.708628

H	-4.283362	2.363335	-1.911694
H	-2.767987	1.896372	-2.670346
H	-2.763148	3.004073	-1.304723
C	3.23863	2.262914	1.497123
H	2.771175	2.144002	2.475633
H	2.762896	3.115222	1.009836
H	4.28479	2.536941	1.672777

Table S7: Cartesian coordinates (x,y,z) for the optimized geometries of Cp*Zn-Zn(L^1)$_2$Cp*.

Zn	2.403408	0.211968	-0.03541
Zn	0.083568	0.123923	0.789881
N	-1.218239	1.183197	-0.627232
N	-3.627678	3.199064	-3.406039
N	-0.762696	-1.852492	0.16344
N	-2.292506	-5.519869	-1.181411
C	3.943714	0.518113	-1.882396
C	4.244517	1.482943	-0.878289
C	4.678912	0.784602	0.287143
C	4.645905	-0.612041	0.000494
C	4.191235	-0.775	-1.340074
C	3.541523	0.814614	-3.297497
H	2.996108	1.757448	-3.376057
H	2.903109	0.032032	-3.713645
H	4.412368	0.897819	-3.958638
C	4.221932	2.973628	-1.05084
H	5.184768	3.353177	-1.412773
H	4.00944	3.488645	-0.112396
H	3.464897	3.289647	-1.771219
C	5.198055	1.412385	1.547676
H	6.27787	1.594039	1.492401
H	5.025997	0.778322	2.419135
H	4.723185	2.374149	1.74903
C	5.119168	-1.706279	0.912141
H	4.605959	-2.650096	0.71776
H	4.954977	-1.459876	1.962538
H	6.192273	-1.896398	0.792175
C	4.096429	-2.073059	-2.087221
H	3.302154	-2.056154	-2.836948
H	3.89767	-2.913441	-1.418698
H	5.027562	-2.305724	-2.617554
C	-0.32855	0.571061	2.884061
C	-1.564671	-0.149983	3.195257
C	-2.611544	0.749945	3.20532
C	-2.084441	2.073082	2.959385
C	-0.718168	1.979872	2.795321

C	0.952985	0.195048	3.617112
H	1.815541	0.747837	3.240936
H	1.190877	-0.866633	3.517743
H	0.868775	0.409657	4.690981
C	-1.60208	-1.587674	3.621188
H	-1.262168	-1.703877	4.657954
H	-0.953818	-2.220203	3.010446
H	-2.60877	-2.007843	3.571518
C	-4.065838	0.463472	3.444223
H	-4.702607	0.790684	2.612183
H	-4.4415	0.981597	4.333573
H	-4.251588	-0.601279	3.59324
C	-2.934976	3.30792	2.898818
H	-2.343451	4.198184	2.683051
H	-3.455409	3.488026	3.845962
H	-3.714987	3.244986	2.129565
C	0.258214	3.106501	2.632545
H	0.992143	2.9046	1.847009
H	0.828478	3.283877	3.552534
H	-0.238944	4.044398	2.379881
C	-2.488319	1.511372	-0.347513
H	-2.838085	1.242963	0.640596
C	-3.31993	2.172303	-1.226733
H	-4.32547	2.402409	-0.910694
C	-2.843527	2.54489	-2.501955
C	-1.503964	2.19984	-2.782093
H	-1.040724	2.449056	-3.724103
C	-0.756305	1.535229	-1.833384
H	0.274769	1.270575	-2.037642
C	-4.976688	3.601364	-3.04646
H	-5.58965	2.739526	-2.769076
H	-5.444413	4.081703	-3.901745
H	-4.985155	4.30918	-2.210825
C	-3.074039	3.623394	-4.680367
H	-2.261569	4.347214	-4.555131
H	-3.857188	4.092449	-5.269984
H	-2.688495	2.773816	-5.250367
C	-2.058384	-2.165546	0.296157
H	-2.677667	-1.424806	0.786649
C	-2.611764	-3.354046	-0.129486
H	-3.666827	-3.518289	0.02578
C	-1.794758	-4.328885	-0.742259
C	-0.430054	-3.993056	-0.87015
H	0.279628	-4.671386	-1.317779
C	0.019719	-2.771142	-0.416172
H	1.064337	-2.501257	-0.519484

C	-3.694095	-5.844876	-0.980693
H	-3.95665	-5.888036	0.081571
H	-3.900162	-6.817534	-1.41927
H	-4.347678	-5.113271	-1.463937
C	-1.40348	-6.515945	-1.754516
H	-0.884686	-6.129378	-2.636122
H	-1.98746	-7.379123	-2.062306
H	-0.649619	-6.853718	-1.035713

Table S8: Cartesian coordinates (x,y,z) for the optimized geometries of Cp*Zn-ZnL^2.

Zn	-0.760839	0.12144	0.075183
Zn	-3.091223	0.673019	-0.036542
P	2.348685	1.050085	0.431155
P	1.623533	-1.937486	-0.172117
N	0.803771	1.461088	0.089619
N	0.015115	-1.783972	0.037916
C	2.535549	-0.64629	0.498163
H	3.45164	-0.946429	0.987486
C	2.273361	-3.483188	0.55724
C	2.998888	-3.489405	1.749668
H	3.203798	-2.560867	2.263608
C	3.4538	-4.684426	2.295368
H	4.021837	-4.669627	3.216984
C	3.175013	-5.89115	1.666175
H	3.526702	-6.821754	2.093543
C	2.43991	-5.898465	0.48605
H	2.213155	-6.834413	-0.008443
C	1.996009	-4.704226	-0.065088
H	1.440426	-4.725645	-0.992323
C	2.034498	-2.109925	-1.964135
C	3.270698	-2.645926	-2.344326
H	3.94403	-3.038842	-1.593032
C	3.649911	-2.687122	-3.678971
H	4.605044	-3.118374	-3.952337
C	2.806072	-2.178541	-4.661847
H	3.100471	-2.210332	-5.703247
C	1.583219	-1.63165	-4.296565
H	0.918864	-1.233113	-5.052998
C	1.20013	-1.601302	-2.959285
H	0.238421	-1.186114	-2.692157
C	-0.864741	-2.794409	0.559068
C	-1.55832	-3.679775	-0.302788
C	-2.487863	-4.568562	0.235059
H	-3.022889	-5.237879	-0.426069
C	-2.748155	-4.615153	1.593683

H	-3.477774	-5.310475	1.989934
C	-2.05685	-3.765175	2.437635
H	-2.251016	-3.806166	3.502233
C	-1.114597	-2.857905	1.953387
C	-1.348792	-3.673512	-1.808306
H	-0.390525	-3.200379	-1.996326
C	-1.284345	-5.076338	-2.429384
H	-0.571201	-5.718093	-1.908547
H	-0.975818	-5.005817	-3.474841
H	-2.253035	-5.57971	-2.41292
C	-2.417388	-2.828598	-2.517321
H	-3.407847	-3.270565	-2.384834
H	-2.217299	-2.770005	-3.59044
H	-2.451118	-1.814517	-2.118105
C	-0.404911	-1.967215	2.965168
H	0.380293	-1.430233	2.433803
C	0.271159	-2.776192	4.08371
H	-0.463312	-3.264345	4.727706
H	0.871291	-2.117419	4.716619
H	0.925391	-3.54826	3.679803
C	-1.359473	-0.927623	3.575492
H	-1.821527	-0.304213	2.808673
H	-0.826506	-0.273382	4.270581
H	-2.164597	-1.414204	4.130701
C	0.414438	2.783608	-0.325518
C	0.055794	3.767171	0.629231
C	-0.3437	5.029572	0.189839
H	-0.612151	5.78087	0.922217
C	-0.419798	5.341337	-1.155907
H	-0.731897	6.328005	-1.475363
C	-0.109433	4.366591	-2.087953
H	-0.192202	4.600223	-3.141885
C	0.301596	3.090265	-1.706296
C	0.04013	3.503687	2.12802
H	0.418248	2.498695	2.28625
C	0.943915	4.471597	2.905468
H	0.586695	5.501	2.829938
H	1.970651	4.446445	2.539031
H	0.961472	4.206031	3.964583
C	-1.388928	3.538129	2.690163
H	-1.384043	3.293552	3.755464
H	-2.029444	2.819236	2.179235
H	-1.840258	4.526363	2.57807
C	0.558611	2.070759	-2.808431
H	1.009581	1.193737	-2.348582
C	1.533171	2.570361	-3.884653

H	1.112844	3.400881	-4.456109
H	1.751715	1.766343	-4.590932
H	2.474983	2.903082	-3.451646
C	-0.762834	1.63341	-3.463147
H	-1.459953	1.223751	-2.73069
H	-0.581896	0.873878	-4.227732
H	-1.255796	2.479485	-3.947367
C	3.009028	1.578157	2.079377
C	2.349421	1.103524	3.219194
H	1.458612	0.500337	3.10619
C	2.827481	1.381044	4.490631
H	2.297147	1.008562	5.358248
C	3.990843	2.129594	4.650656
H	4.369141	2.342598	5.642652
C	4.66529	2.592747	3.530735
H	5.576902	3.16642	3.642641
C	4.177791	2.32025	2.254243
H	4.727312	2.68244	1.398104
C	3.499006	1.891092	-0.73388
C	3.60243	3.286187	-0.805415
H	2.972189	3.913932	-0.190352
C	4.515426	3.883757	-1.664818
H	4.582638	4.963628	-1.707432
C	5.335276	3.100063	-2.470885
H	6.046373	3.568229	-3.140095
C	5.233356	1.715923	-2.416186
H	5.862838	1.098194	-3.044379
C	4.323168	1.116898	-1.551263
H	4.24951	0.038627	-1.505328
C	-5.209533	0.724679	0.946121
C	-4.919714	2.040011	0.467882
C	-4.810878	1.97774	-0.953565
C	-5.04255	0.627196	-1.354942
C	-5.288955	-0.146722	-0.181135
C	-5.517057	0.349008	2.365967
H	-5.234413	-0.682321	2.582743
H	-6.588175	0.439711	2.580293
H	-4.993999	0.987784	3.079346
C	-4.907005	3.294538	1.289804
H	-4.228249	4.044278	0.881077
H	-4.603253	3.106312	2.3202
H	-5.90345	3.749811	1.328041
C	-4.617708	3.150682	-1.869256
H	-5.573503	3.628284	-2.114064
H	-4.157159	2.856403	-2.813378
H	-3.980555	3.915898	-1.423299

C	-5.141776	0.140826	-2.770977
H	-4.888972	-0.916313	-2.858381
H	-4.476969	0.6912	-3.438893
H	-6.158331	0.260828	-3.162614
C	-5.683923	-1.593506	-0.139357
H	-5.317638	-2.138372	-1.00962
H	-6.773893	-1.708072	-0.123256
H	-5.294114	-2.100006	0.74492

Table S9: Cartesian coordinates (x,y,z) for the optimized geometries of **2'**.

Zn	0.021036	0.373204	0.248857
Zn	-2.28528	-0.093973	0.057352
O	4.104289	0.425698	0.364641
N	1.892238	-0.13175	0.179686
C	2.917431	0.71871	0.421242
C	2.506395	2.201014	0.732407
C	2.277102	2.926981	-0.587677
C	1.019172	3.415709	-0.622043
C	0.33361	3.080248	0.644646
C	1.171203	2.353521	1.435414
C	3.628429	2.873293	1.545164
H	4.574893	2.778037	1.018037
H	3.747013	2.391514	2.516119
H	3.402183	3.929634	1.701446
C	3.35298	3.049809	-1.613979
H	2.974552	3.445527	-2.555724
H	3.829427	2.087443	-1.809111
H	4.147178	3.71975	-1.268654
C	0.358912	4.200433	-1.713071
H	1.023862	4.348387	-2.562228
H	0.047633	5.188747	-1.362169
H	-0.541434	3.698747	-2.079817
C	-1.018672	3.618356	0.992901
H	-1.74819	3.422037	0.20459
H	-0.969849	4.704886	1.116235
H	-1.404021	3.197096	1.919716
C	0.967418	1.957966	2.866758
H	-0.086122	1.957455	3.146627
H	1.481699	2.65232	3.539265
H	1.370362	0.964998	3.076091
C	-4.491573	0.572833	0.083296
C	-4.227593	-0.035127	-1.184032
C	-3.895389	-1.406733	-0.955041
C	-3.952876	-1.646377	0.451966
C	-4.320821	-0.423431	1.094483

C	-4.99816	1.9683	0.301021
H	-4.691311	2.368204	1.268642
H	-6.092863	2.001825	0.274154
H	-4.640782	2.656651	-0.46634
C	-4.40285	0.614303	-2.525309
H	-4.204979	1.686566	-2.488768
H	-5.42662	0.49055	-2.895055
H	-3.738474	0.184662	-3.276189
C	-3.64797	-2.441142	-2.013253
H	-3.204771	-2.007953	-2.910845
H	-4.581148	-2.926975	-2.318453
H	-2.976588	-3.227065	-1.665275
C	-3.776222	-2.97554	1.125209
H	-3.07147	-3.613006	0.589901
H	-4.724687	-3.52086	1.180573
H	-3.408938	-2.869187	2.146805
C	-4.608761	-0.250924	2.556961
H	-3.995505	-0.909253	3.173866
H	-5.65515	-0.481424	2.785168
H	-4.428272	0.772083	2.890382
C	2.203729	-1.481514	-0.202037
C	2.398774	-2.464067	0.790126
C	2.622191	-3.781659	0.39393
H	2.777458	-4.544016	1.147474
C	2.657206	-4.136305	-0.944973
H	2.831404	-5.165841	-1.232706
C	2.4791	-3.161397	-1.912405
H	2.522578	-3.439405	-2.958413
C	2.25789	-1.828476	-1.567097
C	2.409056	-2.126255	2.272931
H	2.128147	-1.07822	2.368062
C	1.384634	-2.946278	3.070648
H	0.376322	-2.822417	2.669905
H	1.375486	-2.630231	4.116771
H	1.61837	-4.012798	3.053345
C	3.820469	-2.271289	2.864235
H	4.161395	-3.308568	2.821746
H	3.830881	-1.960598	3.912355
H	4.533155	-1.656296	2.314407
C	2.120237	-0.793718	-2.674361
H	1.919015	0.167711	-2.202898
C	3.432822	-0.646206	-3.460732
H	4.26299	-0.413609	-2.792638
H	3.349551	0.153993	-4.20062
H	3.68116	-1.56668	-3.994067
C	0.945039	-1.095726	-3.616055

H	1.087233	-2.038923	-4.147819
H	0.843499	-0.306872	-4.365595
H	0.003611	-1.164782	-3.067154

Table S10: Cartesian coordinates (x,y,z) for the optimized geometries of **3'**.

Zn	-1.792733	0.115316	-0.035348
Zn	0.564641	0.315876	-0.164312
O	4.561514	1.027982	-0.014451
N	2.27176	1.252102	-0.078018
C	-3.746347	1.205638	0.605769
C	-3.685647	-0.044942	1.292937
C	-3.732269	-1.088405	0.316271
C	-3.825519	2.559247	1.248289
H	-3.299939	2.58788	2.203814
H	-3.394765	3.336665	0.615699
C	-3.703394	-0.232691	2.781525
H	-3.20829	-1.157223	3.082078
H	-4.728925	-0.279954	3.164061
H	-3.206515	0.587386	3.301791
C	-3.826334	-2.557816	0.605111
H	-3.420142	-3.16114	-0.208235
H	-4.867632	-2.86941	0.742684
H	-3.290552	-2.830912	1.51563
C	3.432504	0.560212	-0.13055
C	3.292252	-0.993288	-0.311844
C	2.900291	-1.641151	1.008523
C	1.773603	-2.366078	0.838144
C	4.634743	-1.563503	-0.810691
H	4.893016	-1.146522	-1.784078
H	4.57411	-2.650205	-0.894407
C	3.715843	-1.458862	2.243928
H	4.715556	-1.88717	2.12343
H	3.254384	-1.930939	3.110381
H	3.86195	-0.399431	2.468475
C	1.040348	-3.194961	1.84629
H	0.998849	-4.245292	1.543031
H	0.005889	-2.859746	1.963753
H	1.515181	-3.153736	2.825118
C	2.332884	2.727978	0.15048
C	0.900079	3.272997	0.165988
H	0.915476	4.354344	0.312824
H	0.38538	3.074738	-0.777853
C	2.982337	3.051645	1.507651
H	4.015046	2.713853	1.536375
H	2.43032	2.567748	2.317092

H	2.962555	4.129644	1.685237
C	2.175196	-1.420726	-1.24279
C	1.328625	-2.24606	-0.570266
H	5.433208	-1.294829	-0.123138
C	2.189383	-1.098805	-2.704252
H	2.95958	-1.675607	-3.226341
H	1.235768	-1.322996	-3.182356
H	2.414543	-0.043847	-2.877176
C	0.190416	-3.041638	-1.125789
H	0.449792	-4.104863	-1.148616
H	-0.70665	-2.946396	-0.51073
H	-0.063468	-2.741402	-2.14112
H	0.311513	2.838886	0.978019
C	3.093448	3.424481	-0.992039
H	4.127414	3.092748	-1.033641
H	2.616161	3.209011	-1.951035
H	3.078475	4.507088	-0.844705
C	-3.828071	0.937576	-0.794328
C	-3.819636	-0.480367	-0.974596
H	-4.864333	2.845729	1.44552
C	-4.014326	1.960145	-1.876499
H	-3.597459	1.627405	-2.828199
H	-5.076094	2.168907	-2.047557
H	-3.539096	2.909603	-1.626052
C	-4.008047	-1.201758	-2.276785
H	-3.531169	-2.183069	-2.272797
H	-5.070081	-1.363441	-2.491799
H	-3.594887	-0.641036	-3.116531

Table S11: Cartesian coordinates (x,y,z) for the optimized geometry of complex **3''**. The Zinc-Cp* distances to the tethered Cp* group were fixed to the η^4 coordination observed in the sc-XRD analysis.

Zn	-1.743309	0.096505	0.000023
Zn	0.631015	0.17357	0.000042
O	4.603278	0.966651	-0.000147
N	2.307158	1.189492	0.000137
C	-3.67482	1.394453	-0.000007
C	-3.706205	0.555972	1.155549
C	-3.759425	-0.802478	0.714635
C	-3.71893	2.89423	-0.000187
H	-3.230397	3.316613	0.879113
H	-3.229481	3.316383	-0.878877
C	-3.795868	1.021395	2.579244
H	-3.346166	0.307451	3.270956
H	-4.838153	1.154567	2.889579
H	-3.29453	1.978893	2.727127
C	-3.932165	-2.00435	1.596289

H	-3.528597	-2.90882	1.138412
H	-4.990828	-2.19744	1.802177
H	-3.438774	-1.877769	2.561273
C	3.467224	0.503092	0.000042
C	3.288178	-1.060606	-0.000003
C	2.467255	-1.536866	1.18478
C	1.379014	-2.212365	0.743161
C	4.672294	-1.733477	-0.000021
H	5.242677	-1.427574	-0.875123
H	4.565725	-2.820048	-0.000043
C	2.908778	-1.297204	2.589756
H	3.820758	-1.858005	2.816321
H	2.151151	-1.593141	3.314327
H	3.142545	-0.241983	2.753028
C	0.365153	-2.959084	1.55266
H	0.467165	-4.037296	1.395615
H	-0.654996	-2.689975	1.271183
H	0.478447	-2.769536	2.618836
C	2.353249	2.680754	0.000078
C	0.914897	3.209762	-0.000175
H	0.920485	4.301268	-0.000122
H	0.366703	2.880498	-0.885999
C	3.057089	3.205504	1.264266
H	4.092203	2.875289	1.300534
H	2.542141	2.8492	2.159727
H	3.038285	4.297912	1.278122
C	2.467268	-1.536751	-1.18484
C	1.379022	-2.212293	-0.743289
H	5.242716	-1.427533	0.875073
C	2.908786	-1.29696	-2.589797
H	3.820811	-1.857669	-2.816399
H	2.151186	-1.592909	-3.31439
H	3.142473	-0.24171	-2.752997
C	0.365159	-2.958935	-1.552857
H	0.467183	-4.037163	-1.395927
H	-0.654987	-2.689862	-1.271339
H	0.478435	-2.769275	-2.619015
H	0.36635	2.880394	0.885454
C	3.057469	3.205364	-1.26397
H	4.092676	2.875382	-1.299758
H	2.542964	2.84869	-2.159534
H	3.038389	4.297767	-1.278112
C	-3.70626	0.555922	-1.155544
C	-3.75948	-0.802509	-0.71459
H	-4.751013	3.261638	-0.00081
C	-3.795987	1.021403	-2.579222

H	-3.347163	0.307029	-3.271051
H	-4.838258	1.1555	-2.889203
H	-3.293846	1.978445	-2.727317
C	-3.932249	-2.004435	-1.596156
H	-3.528309	-2.90881	-1.138413
H	-4.990938	-2.197777	-1.801672
H	-3.439216	-1.87775	-2.561308

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