Supporting Information

Stitching Together SN_x Units in the Coordination Sphere of Zirconium: Assembly of a Tris(imido)sulfite and a Hydrazidobis(imido)sulfite[†]

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SI.1 – **Experimental section**

All manipulations of air- and moisture-sensitive materials were performed under an inert atmosphere of dry argon using standard Schlenk techniques or by working in a glove box. Solvents were dried over sodium (toluene), potassium (hexanes) or sodium/potassium alloy (pentane, diethyl ether), distilled, and degassed prior to use. Deuterated solvents were dried over potassium (C_6D_6, thf-d_8, toluene-d_8), vacuum distilled and stored in Teflon valve ampoules under argon. Samples for NMR spectroscopy were prepared under argon in 5 mm Wilmad tubes equipped with J. Young Teflon valves. ^{1}H, ^{13}C, ^{29}Si and ^{15}N NMR spectra were recorded on Bruker Avance 400 and 600 NMR spectrometers and were referenced internally, using the residual protio solvent (^{1}H) or solvent (^{13}C) resonances or externally to $SiMe_4$ and $^{15}NH_3$. Elemental analyses were recorded by the analytical service of the Heidelberg Chemistry Department. The dichloro zirconium complex $[Zr(N_2{}^{TBS}N_{py})Cl_2]$ and the hydrazinediido zirconium complex $[Zr(N_2{}^{TBS}N_{py})(NNPh_2)(py)]$ (**3**) were prepared according to published procedures.[1] All other reagents were obtained from commercial sources and used as received unless explicitly stated.

Preparation of $[Zr(N_2{}^{TBS}N_{py})(=N^{DIPP})(py)]$ (1)

To a stirred solution of $[Zr(N_2{}^{TBS}N_{py})Cl_2]$ (1.00 g, 1.8 mmol) in toluene (40 ml) was added a suspension of lithium 2,6-diisopropyl aniline (331 mg, 1.8 mmol) in 5 ml toluene. The reaction mixture was stirred for 2 days at room temperature Then pyridine (150 µl, 1.8 mmol) and a solution of lithium hexamethyldisilazide (303 mg, 1.8 mmol) in 5 ml toluene was added and stirred for two days at 80° C. The reaction mixture was filtered from lithium choride and the volatiles were removed *in vacuo*. The remaining solid was washed with hexane (3 x 5 ml) and dried to yield 800 mg (1.50 mmol, 61 %) of $[Zr(N_2{}^{TBS}N_{py})(=N^{DIPP})(py)]$ (**1**) as a light orange solid. ^{1}H NMR (600.13 MHz, C_6D_6, 296 K)δ = - 0.10, 0.21 (s, 6 H, $Si(CH_3)_2$), 0.79 (s, 18 H, Si-$C(CH_3)_3$), 1.13 (s, 3 H, CH_3), 1.43 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, $CH(CH_3)_2$) 3.49 (d, $^2J_{HH}$ = 12.1 Hz, 2 H, CH*H*), 3.96 (d, $^2J_{HH}$ = 12.1 Hz, 2 H, C*H*H), 4.65 (sep, $^3J_{HH}$ = 6.7 Hz, 2 H, $CH(CH_3)_2$), 6.50, (t, $^3J_{H5H6/H4}$ = 6.6 Hz, 1H, $H5_{py}$), 6.59 (t, $^3J_{mHpH/oH}$ = 6.7 Hz, 2 H, m-H_{py}), 6.81 – 6.90 (m, 2 H, $H3_{py}$, p-H_{py}), 7.00 – 7.08 (m, 2 H, $H4_{py}$, p-H_{DIPP}), 7.35 (d, $^3J_{mHpH}$ = 7.4 Hz, 2 H, m-H_{DIPP}), 9.01 (d, $^3J_{oHmH}$ = 5.1 Hz, 2 H, o-H_{py}), 9.42 (d, $^3J_{H6pyH5py}$ = 5.0 Hz, 1 H, $H6_{py}$);^{13}C {^{1}H} NMR (150.90 MHz, C_6D_6, 296 K)δ = -4.3, -2.4 ($Si(CH_3)_2$), 20.3 (Si-$C(CH_3)_3$), 25.6 (C-CH_3), 26.0 ($CH(CH_3)_2$), 27.3 ($CH(CH_3)_2$), 27.8 (Si-$C(CH_3)_3$), 47.3 (C-CH_3), 64.3 (CH_2), 116.2 (p-C_{DIPP}), 120.5 ($C3_{py}$), 121.0 ($C5_{py}$), 123.3 (m-C_{DIPP}), 124.0 (m-C_{py}), 139.0 ($C4_{py}$), 139.2 (p-C_{py}), 140.0 (o-C_{DIPP}), 151.3 ($C6_{py}$), 152.3 (o-C_{py}), 154.8 (i-C_{DIPP}) 161.0 ($C2_{py}$); ^{29}Si {^{1}H} NMR (79.45 MHz, C_6D_6, 296 K) δ = 0.80 ($Si(CH_3)_3$; ^{15}N NMR (60.82 MHz, C_6D_6, 296 K)δ = 146.0 (*N*-$Si(CH_3)_2{}^t$Bu), 278.9 (N_{py}), 288.8 (L-N_{py}), 323.0 (Zr=*N*); IR (Nujol, NaCl) υ = 1601 m, , 1462 s, 1410 m, 1377 m, 1225 m, 1273 s, 1254 sh, 1085 w, 1061 m, 1010 w, 935 w, 890 s, 867 s, 826 w, 772 w, 700 w, 663 w cm^{-1}; Elemental analysis calcd (%) for : 61.90, H 8.61, N 9.50; found: C 61.67, H 8.69, N 9.63.

Preparation of $[\mathrm{Zr(N_2^{TBS}N^{py})}\kappa^2$-*N,N'*(TMS-N-S(=N-TMS)$\mathrm{N^{DIPP}}$)] (2)

To a stirred solution of $[\mathrm{Zr(N_2^{TBS}N_{py})(=N^{DIPP})(py)}]$ (**1**) (300 mg, 0.45 mmol) in toluene (15 ml) was added a solution of bis(trimethylsilyl)sulfur diimide (96 mg, 0.27 mmol) in 1 ml of toluene. The reaction mixture was stirred overnight at room temperature, filtered and the volatiles were removed. The crude product was washed with hexane (2 x 5 ml) and dried to yield 300 mg (87 %) of $[\mathrm{Zr(N_2^{TBS}N^{py})}\kappa^2$-*N,N'*(TMS-N-S(=N-TMS)$\mathrm{N^{DIPP}}$)] (**2**) as a yellow solid. Single crystals for X-ray diffraction were grown from a saturated toluene solution at room temperature; ^{1}H NMR (600.13 MHz, C_6D_6, 296 K) δ = 0.02, 0.35 (bs, 6 H, $\mathrm{Si(C}\mathit{H}_3)_2$), 0.14, 0.64 (bs, 9 H, $\mathrm{Si(C}\mathit{H}_3)_3$, 0.97 (s, 3 H, $\mathrm{C}\mathit{H}_3$), 1.02 (bs, 18 H, $\mathrm{Si\text{-}C(C}\mathit{H}_3)_3$), 1.59 (d, ^3J = 6.8 Hz, 6 H, $\mathrm{CH(C}\mathit{H}_3)_2$), 3.30 (bs, 2 H, CH*H*), 3.74 – 4.12 (m, 4 H, $\mathrm{C}\mathit{H}\mathrm{(CH_3)}$, C*H*H), 6.10 (t, $^3J_{\mathrm{H5HH4/H6}}$ = 6.7 Hz, 1 H, $\mathit{H5}_{\mathrm{py}}$), 6.71 (d, $^3J_{\mathrm{H3H4}}$ = 8.5 Hz 1 H, $\mathit{H3}_{\mathrm{py}}$), 6.84 (dt, $^3J_{\mathrm{H4HH5/H3}}$ = 7.8 Hz, $^4J_{\mathrm{H4H6}}$ = 1.8 Hz, 1 H, $\mathit{H4}_{\mathrm{py}}$), 7.21 (t, $^3J_{\mathrm{pHmHAr}}$ = 7.6 Hz, 1 H, p-H_{Ar}), 7.28 (t, 2 H, m-H_{Ar}), 8.37 (d, $^3J_{\mathrm{H6pyH5py}}$ = 5.6 Hz, $^4J_{\mathrm{H6pyH4py}}$ = 1.2 Hz, 1 H, $\mathit{H6}_{\mathrm{py}}$);^{13}C {^{1}H} NMR (150.90 MHz, C_6D_6, 296 K)δ = -3.2, -0.4 ($\mathrm{Si(}\mathit{C}\mathrm{H_3)_2}$), 2.9, 3.1 ($\mathrm{Si(}\mathit{C}\mathrm{H_3)_3}$), 19.9 ($\mathrm{Si\text{-}}\mathit{C}\mathrm{(CH_3)_3}$), 25.4 ($\mathrm{C\text{-}}\mathit{C}\mathrm{H_3}$), 26.0 ($\mathrm{CH(}\mathit{C}\mathrm{H_3)_2}$), 28.4 ($\mathrm{CH(C}\mathit{H}_3)_2$, $\mathrm{Si\text{-}C(}\mathit{C}\mathrm{H_3)_3}$), 48.6 ($\mathit{C}\mathrm{\text{-}CH_3}$), 61.4, 63.7 ($\mathit{C}\mathrm{H_2}$), 121.2 ($\mathit{C3}_{\mathrm{py}}$), 121.9 ($\mathit{C5}_{\mathrm{py}}$), 124.5 (m-$\mathit{C}_{\mathrm{Ar}}$), 125.3 (p-$\mathit{C}_{\mathrm{Ar}}$), 140.3 ($\mathit{C4}_{\mathrm{py}}$), 143.4 (i-$\mathit{C}_{\mathrm{Ar}}$), 147.2 ($\mathit{C6}_{\mathrm{py}}$), 148.5 (o-$\mathit{C}_{\mathrm{Ar}}$), 161.2 ($\mathit{C2}_{\mathrm{py}}$);^{29}Si {^{1}H} NMR (79.45 MHz, C_6D_6, 296 K) δ = - 4.66, - 0.64 ($\mathit{Si}\mathrm{(CH_3)_3}$), n.o. ($\mathit{Si}\mathrm{(CH_3)_2{}^tBu}$);^{15}N NMR (60.82 MHz, C_6D_6, 296 K)δ = 121.8 (*N*-TMS), 150.3 ($\mathit{N}\mathrm{\text{-}Si(CH_3)_2{}^tBu}$), 197.4, 197.9 (Zr-*N*TMS, Zr-*N*Ar), 279.4 (L-N_{py});IR (Nujol, NaCl) υ = 1603 w, 1577 w, 1465 s, 1379 m, 1360 sh, 1360 w, 1318 w, 1250 s, 1198 w, 1137 m, 1088 w, 1033 m, 952 s, 890 m, 851 w, 776 s, 716 w, 666 w cm^{-1}; Elemental analysis calcd (%) for $C_{39}H_{76}N_6SSi_4Zr$: C 54.17, H 8.86, N 9.72; found: C 53.87, H 8.76, N 9.58.

Preparation of $[\mathrm{Zr(N_2^{TBS}N^{py})}\kappa^2$-*N,N'*(TMS-N-S(=N-TMS)$\mathrm{NNPh_2}$)] (4)

To a stirred solution of $[\mathrm{Zr(N_2^{TBS}N_{py})(=NNPh_2)(py)}]$ (**3**) (200 mg, 0.27 mmol) in toluene (10 ml) was added a solution of bis(trimethylsilyl)sulfur diimide (62 mg, 0.27 mmol) in 1 ml of toluene. The reaction mixture was stirred overnight at room temperature, filtered and the volatiles were removed. The crude product was recrystallized from toluene and dried to yield 180 mg (77 %) of $[\mathrm{Zr(N_2^{TBS}N^{py})}\kappa^2$-*N,'N*(TMS-N-S(=N-TMS)$\mathrm{NNPh_2}$)] (**4**) as a yellow solid. Single crystals for X-ray diffraction were grown from a saturated toluene solution at room temperature. ^{1}H NMR (600.13 MHz, C_6D_6, 296 K)δ = 0.17 (bs, 12 H, $\mathrm{Si(C}\mathit{H}_3)_2$), 0.37, 0.64 ($\mathrm{Si(C}\mathit{H}_3)_3$), 0.73 (s, 18 H, $\mathrm{Si\text{-}C(C}\mathit{H}_3)_3$), 0.90 (s, 3 H, $\mathrm{C}\mathit{H}_3$), 3.24 (d, $^2J_{\mathrm{HH}}$ = 12.6 Hz, 2 H, CH*H*), 3.85 (d, $^2J_{\mathrm{HH}}$ = 12.6 Hz, 2 H, C*H*H), 6.62 (ddd, $^3J_{\mathrm{H5HH4}}$ = 7.8 Hz, $^3J_{\mathrm{H5H6}}$ = 5.4 Hz, $^4J_{\mathrm{H5H3}}$ = 1.2 Hz, 1 H, $\mathit{H5}_{\mathrm{py}}$), 6.66 (d, $^3J_{\mathrm{H3H4}}$ = 8.0 Hz, 1 H, $\mathit{H3}_{\mathrm{py}}$), 6.78 – 6.89 (m, 3 H, p-H_{Ph}, $\mathit{H4}_{\mathrm{py}}$), 7.20 (t, $^3J_{\mathrm{mHoH/ph}}$ = 7.6 Hz, 4 H, m-H_{Ph}), 7.66, 8.08 (bs, 2 H, o-H_{Ph}), 9.10 (dd, $^3J_{\mathrm{H6pyH5py}}$ = 5.6 Hz, $^4J_{\mathrm{H6pyH4py}}$ = 1.2 Hz, 1 H, $\mathit{H6}_{\mathrm{py}}$); ^{13}C {^{1}H} NMR (150.90 MHz, C_6D_6, 296 K) δ = -2.8 ($\mathrm{Si(}\mathit{C}\mathrm{H_3)_2}$), 2.8, 3.3 ($\mathrm{Si(}\mathit{C}\mathrm{H_3)_3}$), 19.7 ($\mathrm{Si\text{-}}\mathit{C}\mathrm{(CH_3)_3}$), 25.0($\mathrm{C\text{-}}\mathit{C}\mathrm{H_3}$), 28.0 ($\mathrm{Si\text{-}C(}\mathit{C}\mathrm{H_3)_3}$), 47.9 ($\mathit{C}\mathrm{\text{-}CH_3}$), 62.7 ($\mathit{C}\mathrm{H_2}$), 120.5 (p-$\mathit{C}_{\mathrm{Ph}}$), 121.1 ($\mathit{C3}_{\mathrm{py}}$), 122.6 ($\mathit{C5}_{\mathrm{py}}$), 128.7 (m-$\mathit{C}_{\mathrm{Ph}}$), 128.8 (m-$\mathit{C}_{\mathrm{Ph}}$), 140.1 ($\mathit{C4}_{\mathrm{py}}$), 147.4 ($\mathit{C6}_{\mathrm{py}}$), 147.3 (i-$\mathit{C}_{\mathrm{Ph}}$), 160.5 ($\mathit{C2}_{\mathrm{py}}$), n.o (o-$\mathit{C}_{\mathrm{Ph}}$); ^{29}Si {^{1}H} NMR (79.45 MHz, C_6D_6, 296 K) δ = - 4.19, - 4.69 ($\mathit{Si}\mathrm{(CH_3)_3}$), 3.07 ($\mathit{Si}\mathrm{(CH_3)_2{}^tBu}$);^{15}N NMR (60.82 MHz, C_6D_6, 296 K) δ = 125.8 (*N*-TMS), 193.0 (Zr-*N*TMS), 226.1 (Zr-$\mathit{N}\mathrm{NPh_2}$), 279.8 (L-N_{py}), n. o. ($\mathit{N}\mathrm{Ph_2}$), ($\mathit{N}\mathrm{\text{-}Si(CH_3)_2{}^tBu}$); IR (Nujol, NaCl) υ = 2110 m, 1602 m, 1573 s, 1491 s, 1464 s, 1377 m, 1329 w, 1260 m, 1156 m, 1031 s, 936 w, 833 s, 775 w, 743 w, 694 cm^{-1}; Elemental analysis calcd (%) for $C_{39}H_{69}N_7SSi_4Zr$: C 53.74, H 7.98, N 11.25; found: C 53.54, H 7.91, N 11.10.

SI.2 – **Computational Studies**

The molecular structures of the compounds **2** and **4** were optimised using the BP86 functional with a SV(P) basis set as implemented in the TURBOMOLE program package.[K] The molecular structure optimisation of **4** and the bond analyses were performed using the B3PW91 hybrid functional with a Stuttgart-Dresden effective small core potential augmented with an extra p-polarization function for the Zr(SDD) atom and the 6-31g(d) basis set for the rest of the atoms using the GAUSSIAN09 program package.[L,M] The natural population analyses were performed with the NBO 3.0[N] facilities and all the orbital visualizations have been obtained with the GaussView and Molekel programs.[O] All optimised structures are in good agreement with the experimentally determined ones.
As a semi-quantitative measure of the bond order, the Wiberg bond index,[P] was used. BP86 and B3LYP structures gave equal bond indices. The molecular systems were optimised from X-ray diffraction data as input. The stationary points were verified by frequency analysis.

Table 1 Experimentally and theoretically determined bond lengths and angles for **2**, bond lengths in Å and angles in ° at the BP86/SV(P) level of theory.

Bond	X-Ray	BP86	Angle	X-Ray	BP86
S(1) – N(4)	1.727	1.824	N(4) – Zr(1) – N(5)	67.12	70.60
S(1) – N(5)	1.670	1.742	Zr(1) – N(4) – S(1)	98.73	98.30
S(1) – N(6)	1.544	1.571	Zr(1) – N(5) – S(1)	101.54	102.40
Zr(1) – N(4)	2.139	2.174	N(4) – S(1) – N(5)	90.56	88.60
Zr(1) – N(5)	2.117	2.137			
S (1)– N(4)	1.727	1.824			

Table 2 Experimentally and theoretically determined bond lengths and angles for **4**, bond lengths in Å and angles in °: Comparison between BP86/SV(P) and B3PW91/6-31G(d),SDD.

Bond	X-Ray	BP86	B3PW91	Angle	X-Ray	BP86	B3PW91
S(1) – N(5)	1.686	1.744	1.720	N(5) – Zr(1) – N(4)	67.12	68.6	67.74
S(1) – N(4)	1.725	1.837	1.775	Zr(1) – N(5) – S(1)	103.80	104.9	104.75
S(1) – N(6)	1.542	1.577	1.560	N(5) – S(1) – N(4)	88.26	85.9	86.56
N(4) – N(7)	1.409	1.388	1.390	S(1) – N(5) – Zr(1)	100.20	99.5	100.34
Zr(1) – N(5)	2.119	2.138	2.118	N(5) – S(1) – N(6)	108.39	111.5	110.10
Zr(1) – N(4)	2.176	2.196	2.182	S(1) – N(4) – N(7)	109.96	113.8	113.38

SI.2.1 – **Bonding analysis of the compounds 2 and 4.**

Table 3 Wiberg bond indices for the discussed bonds. **4*** denotes the structure optimised using B3PW91/6-31G(d),SDD.

Bond	2	4	4*	ligand fragment
S(1) – N(4)	0.73	0.88	0.89	0.89
S(1) – N(5)	0.87	0.73	0.69	1.01
S(1) – N(6)	1.33	1.31	1.32	1.12
N(4) – N(7)	n.a.	1.08	1.10	1.06

Table 4 Natural population analysis – natural charge on atoms. **4*** denotes the structure optimised using B3PW91/6-31G(d),SDD.

Atom	2	4	4*	ligand fragment
S(1)	1.469	1.469	1.425	1.304
N(4)	-0.837	-0.702	-0.676	-0.765
N(5)	-1.274	-1.296	-1.272	-1.388
N(6)	-1.256	-1.291	-1.272	-1.442
N(7)	n.a.	-0.229	-0.226	-0.250
Zr(1)	0.810	0.780	0.850	n.a.

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