Supplementary Material (ESI) for Chemical Communications

Supporting Information

Tin–Lanthanoid Donor–Acceptor Bonds

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General Methods

All manipulations were carried out using Schlenk line techniques under an atmosphere of dry nitrogen. [Ln(η^5-C_5H_5)$_3$)] (Ln = La, Yb) were prepared and purified by sublimation as described in the literature.[1] [La(η^5-C_5H_5)$_3$(thf)] was recrystallised from THF. THF was refluxed over sodium. Toluene was taken from a MBRAUN solvent purification system. NMR spectroscopic grade d_8-THF was dried over molecular sieve and stored under nitrogen prior to use. NMR spectra were recorded on a BRUKER DRX 400 spectrometer. Chemical shifts reported in ppm (δ) are relative to the proton chemical shift of tetramethylsilane (TMS) for ^{1}H, ^{13}C, ^{7}Li and ^{119}Sn NMR. The ^{139}La NMR chemical shifts are relative to the lanthanum chemical shift of $LaCl_3$ (0.1M in D_2O) with 4,4-dimethyl-4-silapenta-1-sulfonic acid (DSS) as internal reference standard.

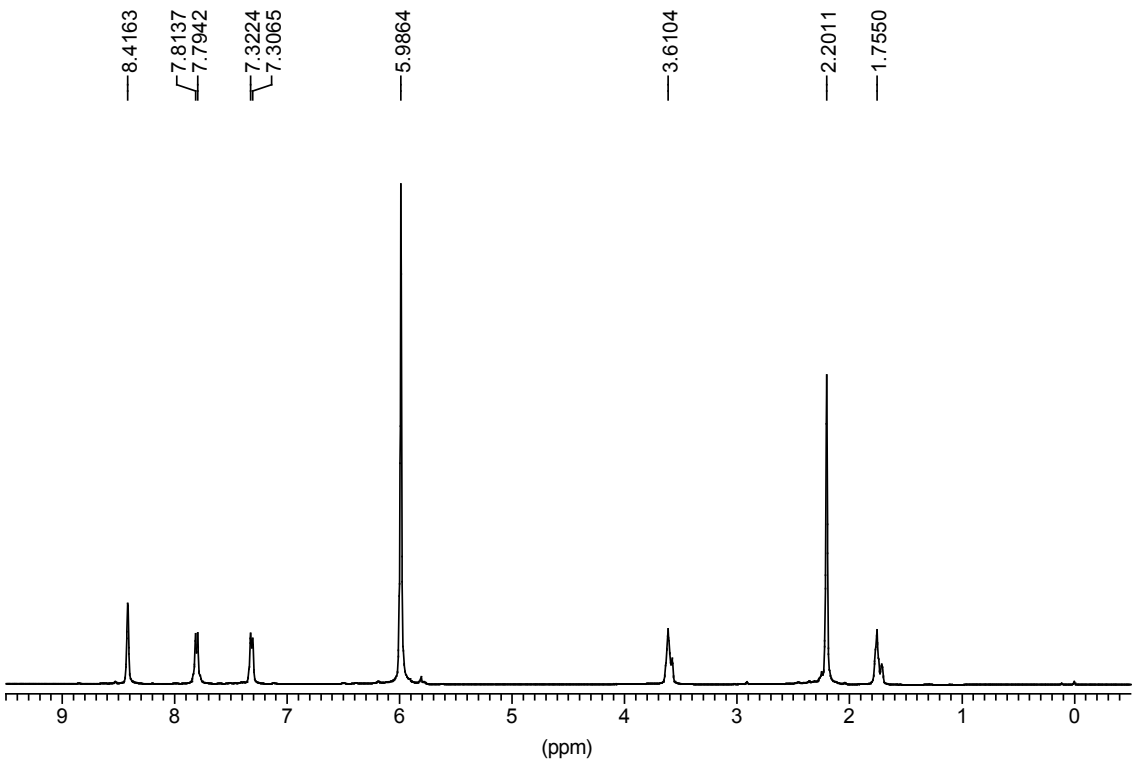


Fig. S1: ^{1}H NMR spectrum of [(thf)Li(2-C_5H_3N-5-Me)$_3$Sn–La(Cp)$_3$] (**2**) in d_8-THF at 298K.

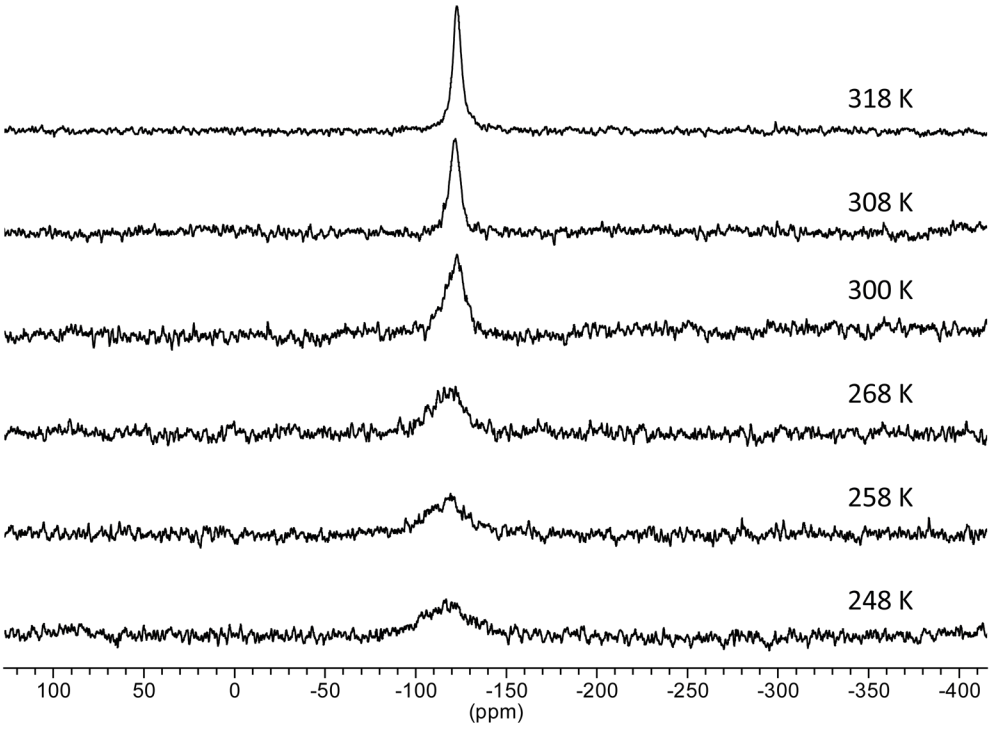


Fig. S2: Variable temperature ^{119}Sn NMR spectra of [(thf)Li(2-C_5H_3N-5-Me)$_3$Sn–La(Cp)$_3$] (**2**) in d_8-THF.

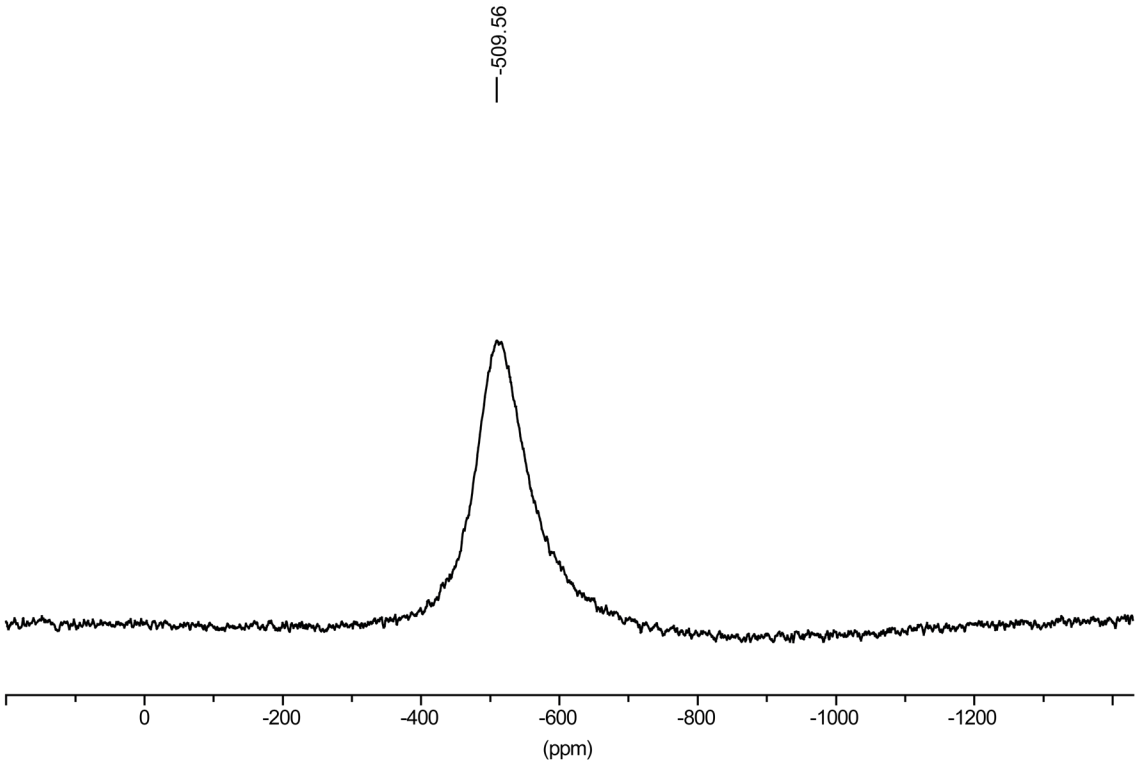
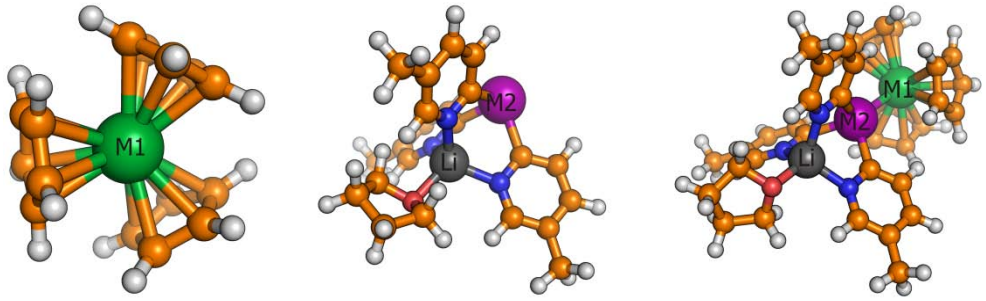


Fig. S3: ^{139}La NMR spectrum of [(thf)Li(2-C_5H_3N-5-Me)$_3$Sn–La(Cp)$_3$] (**2**) in d_8-THF at 298K.

Computational Details

Structure optimisation was performed with the TURBOMOLE-suite[2] program package. The DFT calculations employed the BP86-D[3-5] density functional, allowing the use of the resolution of identity approximation.[6-8] The TZVP[9] basis set was applied for structure optimisation and the convergence criterion of the iteration cycle was increased to 10^{-8} Hartree. All calculations were free of spin contamination. The program SNF[10] was applied for frequency calculation. The NBO[11] analysis was carried out using a NBO 5.0 augmented Gaussian03 Revision D01[12] employing the BP86[3,4] functional with the SDD[13] basis set.



I **II** **2/3**

Fig. S4: Investigated compounds $\{Ln(Cp)_3\}$ (**I**), $\{(thf)LiSn(2\text{-}C_5H_3N\text{-}5\text{-}Me)_3\}$ (**II**) and $\{[(thf)Li(2\text{-}C_5H_3N\text{-}5\text{-}Me)_3Sn–Ln(Cp)_3]\}$ (Ln = La (**2**), Yb (**3**)).

Table-S1: Coordinates of calculated structure for **2**.
SCF-energy for def-TZVP/BP86-D(RI): -1717.5956130460 Hartree

atom	x	y	z
La	-0.851818	7.752029	7.083780
Sn	1.524810	7.520585	4.907813
O	5.147735	6.941063	1.216608
N	4.513696	8.263664	4.177162
N	2.119360	8.121024	1.850598
N	3.184661	5.336928	3.278086
C	3.584452	8.399656	5.156820
C	3.906663	9.119173	6.324432
C	5.167117	9.695906	6.473688
C	6.118892	9.559369	5.451093
C	5.727103	8.827152	4.326142
C	7.490191	10.174399	5.547812
C	1.195029	8.316282	2.824812
C	0.006636	9.011984	2.527136
C	-0.225809	9.493773	1.239778
C	0.734515	9.286624	0.237202
C	1.890061	8.593497	0.610858
C	0.539909	9.781527	-1.171742
C	2.217400	5.486530	4.220015
C	1.611513	4.343723	4.781455
C	1.995598	3.065462	4.382605
C	2.998223	2.917871	3.411660

C	3.549684	4.095859	2.901328
C	3.462487	1.566720	2.936517
C	6.239587	6.179106	1.781374
C	6.786441	5.374533	0.604733
C	5.498809	4.988662	-0.156712
C	4.501300	6.113057	0.207535
C	-2.506209	7.023875	4.819407
C	-3.375495	7.003683	5.938630
C	-3.009843	5.896889	6.760371
C	-1.921492	5.228764	6.136860
C	-1.604693	5.926162	4.940579
C	-1.747212	10.231258	5.880603
C	-0.335765	10.379701	5.941738
C	0.035563	10.494225	7.313251
C	-1.143864	10.417137	8.094904
C	-2.249173	10.245761	7.209725
C	0.988798	7.800012	9.317746
C	-0.223636	7.261797	9.829120
C	-0.393511	5.958588	9.274976
C	0.698926	5.703770	8.410726
C	1.557074	6.842775	8.436992
Li	3.755283	7.218398	2.626458
H	3.153701	9.219710	7.109969
H	5.419327	10.256264	7.378572
H	6.426967	8.691343	3.494291
H	8.101142	9.917864	4.669553
H	8.019863	9.825867	6.448840
H	7.426087	11.272805	5.608796
H	-0.727984	9.166548	3.321403
H	-1.148827	10.032139	1.005472
H	2.677457	8.410362	-0.128541
H	1.398101	9.513615	-1.805938
H	0.427117	10.877343	-1.195170
H	-0.367570	9.348061	-1.621807
H	0.827897	4.479636	5.531334
H	1.523252	2.179961	4.817645
H	4.334016	4.032146	2.140003
H	4.253351	1.665739	2.177808
H	2.631771	0.995238	2.492393
H	3.862681	0.969110	3.771138
H	5.861326	5.524379	2.586912
H	6.950054	6.899074	2.208211
H	7.426219	6.016065	-0.018141
H	7.369191	4.499596	0.924286
H	5.122994	4.014306	0.185663
H	5.663994	4.921577	-1.240175
H	4.268217	6.772373	-0.639948
H	3.561554	5.715102	0.624991
H	-2.532572	7.735909	3.996876
H	-4.189901	7.700174	6.129448
H	-3.509906	5.588059	7.677220

H	-1.424965	4.335030	6.509682
H	-0.854405	5.633279	4.208957
H	-2.343600	10.131613	4.976038
H	0.336151	10.457583	5.089144
H	1.046599	10.635664	7.689575
H	-1.199077	10.491133	9.179683
H	-3.297275	10.186141	7.498643
H	1.407146	8.773949	9.563640
H	-0.878145	7.737355	10.558066
H	-1.216172	5.277676	9.484422
H	0.871035	4.791414	7.843305
H	2.511128	6.934307	7.920276

Table-S2: Coordinates of calculated structure for **3**.
SCF-energy for def-TZVP/BP86-D(RI): -2845.8840419200 Hartree

atom	x	y	z
Yb	-0.796506	7.608188	6.990199
Sn	1.473301	7.394148	4.905956
O	5.118503	6.895823	1.213441
N	4.456786	8.207887	4.149271
N	2.103219	8.031434	1.847783
N	3.205508	5.253664	3.253786
C	3.527868	8.316511	5.133347
C	3.837387	9.050558	6.296086
C	5.079056	9.668998	6.435350
C	6.027179	9.561952	5.405683
C	5.651916	8.811885	4.287040
C	7.377296	10.224706	5.489410
C	1.167429	8.210259	2.815036
C	-0.010778	8.922201	2.512058
C	-0.219530	9.437998	1.234021
C	0.754868	9.248722	0.241647
C	1.897542	8.535461	0.616371
C	0.588836	9.786871	-1.155198
C	2.229369	5.380640	4.190892
C	1.655438	4.219594	4.749896
C	2.078203	2.951662	4.357396
C	3.089466	2.830392	3.391652
C	3.608084	4.023014	2.881012
C	3.592587	1.491978	2.919110
C	6.244215	6.166836	1.753290
C	6.803912	5.394983	0.560082
C	5.520285	4.975506	-0.189888
C	4.494575	6.067886	0.190953
C	-2.382877	6.993973	4.849984
C	-3.235667	7.094500	5.988466
C	-2.932651	6.024657	6.862294
C	-1.899612	5.247057	6.255721
C	-1.561885	5.850455	5.014800
C	-1.756522	9.918638	5.944155

C	-0.348377	10.109566	5.933676
C	0.091939	10.170979	7.279019
C	-1.047273	10.025727	8.123938
C	-2.187559	9.857516	7.303056
C	0.806746	7.715866	9.164189
C	-0.442640	7.181274	9.595189
C	-0.568692	5.884746	9.040658
C	0.587630	5.623425	8.249177
C	1.437852	6.753626	8.328636
Li	3.723648	7.135024	2.624611
H	3.085972	9.129658	7.085740
H	5.319301	10.240217	7.336883
H	6.349827	8.696367	3.450122
H	7.985794	9.994890	4.602067
H	7.930310	9.889790	6.381650
H	7.275880	11.319858	5.558152
H	-0.756115	9.065625	3.298060
H	-1.134021	9.990464	0.998491
H	2.695773	8.363676	-0.114291
H	1.447519	9.515292	-1.787213
H	0.504126	10.885529	-1.149027
H	-0.324037	9.389733	-1.627417
H	0.866004	4.335122	5.497034
H	1.630624	2.053869	4.793888
H	4.397758	3.980440	2.123123
H	4.415918	1.612225	2.198972
H	2.790667	0.917569	2.427789
H	3.960932	0.885663	3.761908
H	5.901872	5.489707	2.556128
H	6.934407	6.906797	2.179500
H	7.415008	6.064195	-0.062694
H	7.418628	4.535526	0.861908
H	5.176448	3.989560	0.153194
H	5.674609	4.917760	-1.275539
H	4.245878	6.733617	-0.647118
H	3.564886	5.639817	0.600737
H	-2.375474	7.663083	3.992907
H	-3.988915	7.861062	6.152607
H	-3.424700	5.807421	7.807983
H	-1.462686	4.340271	6.666596
H	-0.840499	5.470631	4.294800
H	-2.398980	9.847963	5.070088
H	0.271834	10.236976	5.049374
H	1.118299	10.317035	7.607578
H	-1.039087	10.040848	9.211073
H	-3.214157	9.744141	7.644112
H	1.211360	8.686795	9.438429
H	-1.151215	7.666359	10.262873
H	-1.403135	5.204077	9.190473
H	0.790806	4.710614	7.694365
H	2.419039	6.851939	7.868728

Table-S3: selected computed (BP86-D) and experimental (XRD)[a] structural parameters of complex **2** and **3**.

complex	parameter	BP86-D	XRD
2	La–Sn	3.23	3.3175
	La–Cg	2.619 – 2.624	2.586 – 2.587
	C_{ipso}–Sn–C_{ipso}	94.7, 95.6, 96.0	93.0, 95.4, 98.8
	La–Sn–C_{ipso}	119.3, 119.7, 124.8	117.0, 120.1, 126.2
	Cg–La–Cg	119.1 – 119.8	117.5 – 118.2
	Cg–La–Sn	93.7, 95.0, 95.2	95.1, 98.1, 102.1
3	Yb–Sn	3.09	3.0740
	Yb–Cg	2.420 – 2.424	2.422 – 2.428
	C_{ipso}–Sn–C_{ipso}	93.9, 94.2, 95.2	93.3, 96.9, 97.2
	Yb–Sn–C_{ipso}	119.9, 121.3, 124.8	119.6, 120.7, 122.8
	Cg–Yb–Cg	118.3 – 118.4	116.5 – 118.7
	Cg–Yb–Sn	96.6, 97.4, 98.4	97.2, 98.3, 100.0

[a] XRD = data from single-crystal X-ray diffraction experiments. Cg = centroid of each of the Cp rings.

Table-S4: Dissociation energy ΔE (**2**/**3** → **I** + **II**) and free reaction enthalpy ΔG of the dissociation in kJ mol^{-1}, natural partial charge q^{NPA} and bond order BO_{M1M2} as well as the calculated Wiberg bond order BO_W.[14]

complex	M1	M2	ΔE	ΔG	q_{M1}^{NPA}	q_{M2}^{NPA}	BO_{M1M2}	BO_W
	La	Sn			2.307	0.783		
	Yb	Sn			2.053	0.783		
2	La	Sn	121.1	57.9	2.218	0.851	0.38	0.37
3	Yb	Sn	96.6	49.2	2.007	0.887	0.46	0.30

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