Supporting Information

for

Low-Coordinate Sm(II) and Yb(II) Complexes Derived from Sterically-Hindered 1,2-Bis(imino)acenaphthene (Ar^{BIG}-bian)

Daria A. Lukina,[a] Alexandra A. Skatova,[a] Vladimir G. Sokolov,[a] Evgenii V. Baranov,[a] Serhiy Demeshko,[b] Sergey Yu. Ketkov[a] and Igor L. Fedushkin*[a]

[a] *G. A. Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Sciences, Tropinina Str. 49, Nizhny Novgorod 603137, Russian Federation*

[b] *Institut für Anorganische Chemie, Georg-August-Universität Tammannstrasse 4, Göttingen 37077, Germany*

X-ray crystallography. The X-ray data for **2a**, **2b** and **3** were collected at 100(2) K on a Bruker AXS D8 Quest diffractometer (MoKa-radiation, ω- and φ-scan technique, λ = 0.71073 Å). The structures were solved by direct methods using "dual-space" algorithm with SHELXT program [Sheldrick G.M. (2015) Acta Cryst., A71, 3-8] and were refined by full-matrix least squares on F^2 using SHELXTL [Sheldrick G.M. (2003). SHELXTL v. 6.14, Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin, USA]. All hydrogen atoms were placed in calculated positions and were refined in the riding model. SADABS [Sheldrick G.M. (2016). SADABS v.2016/2, Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, Wisconsin, USA] was used to perform area-detector scaling and absorption corrections. Solvent molecules of toluene and DME predominantly located in the common position were found in the crystal of **2a**, **3** and **2b** respectively. The ratios of solvate molecules per Ln complex are 1:1 for **2a**, **3** and 2.5:1 for **2b**. Toluene molecules in **2b** are disordered in both common and special positions. Crystallographic data and structural refinement details are given in Table 1S. CCDC 2022601 (**2a**), 2022602 (**2b**) and 2022603 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

DFT calculations.

Full reference for the Gaussian 09 program package:

Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

Cartesian coordinates of the optimized structure of 2c:

Sm	0.57230002	-1.29289997	-0.12400000
N	0.59820002	1.11240005	-0.42260000
N	-1.66299999	-0.58010000	0.34130001
C	-0.71120000	1.39189994	-0.76050001
C	-1.82560003	0.54710001	-0.42510000
C	-3.06089997	1.21850002	-0.88980001
C	-2.65179992	2.42090011	-1.54610002
C	-1.23179996	2.56069994	-1.50430000
C	-0.67250001	3.68490005	-2.11439991
H	0.41270000	3.86159992	-2.11360002
C	-1.53799999	4.63619995	-2.73990011
H	-1.08440006	5.51889992	-3.21760011
C	-2.92370009	4.49679995	-2.75070000
H	-3.55679989	5.26109982	-3.22849989
C	-3.52920008	3.35540009	-2.12899995
C	-4.92990017	3.06809998	-2.02329993
H	-5.66720009	3.75939989	-2.46099997
C	-5.34840012	1.91980004	-1.35599995
H	-6.42710018	1.71560001	-1.26610005
C	-4.43389988	0.98199999	-0.78160000
H	-4.82840014	0.09240000	-0.26989999
C	1.50790000	2.17560005	-0.26650000
C	1.32480001	3.18300009	0.73809999
C	2.27859998	4.20949984	0.87099999
H	2.11840010	4.98089981	1.64250004
C	3.42199993	4.26789999	0.06110000
C	3.60419989	3.28780007	-0.92150003
H	4.48330021	3.33240008	-1.58529997

C	2.66210008	2.25889993	-1.10889995
C	0.15070000	3.15820003	1.69369996
H	-0.69370002	2.58829999	1.25860000
C	0.42280000	2.61240005	3.09179997
C	1.71940005	2.36059999	3.58500004
H	2.58699989	2.54740000	2.93409991
C	1.91579998	1.87750006	4.89120007
H	2.93910003	1.69009995	5.25339985
C	0.81930000	1.63639998	5.73269987
H	0.97350001	1.25860000	6.75500011
C	-0.47960001	1.88399994	5.25500011
H	-1.35060000	1.69900000	5.90310001
C	-0.67210001	2.36360002	3.95110011
H	-1.69420004	2.55040002	3.58299994
C	2.84439993	1.29439998	-2.25920010
H	1.83519995	0.94379997	-2.57030010
C	3.71190000	0.07350000	-2.00099993
C	3.97460008	-0.39700001	-0.69660002
H	3.59130001	0.17739999	0.16300000
C	4.77629995	-1.53499997	-0.48730001
H	5.00250006	-1.86129999	0.53979999
C	5.31850004	-2.23320007	-1.57679999
H	5.95310020	-3.11730003	-1.41149998
C	5.06269979	-1.77639997	-2.88179994
H	5.49510002	-2.30509996	-3.74569988
C	4.27400017	-0.63470000	-3.08669996
H	4.09800005	-0.27190000	-4.11289978
C	-2.64980006	-1.54349995	0.54610002
C	-2.83360004	-2.03859997	1.87520003
C	-3.83850002	-2.98130012	2.14019990
H	-3.98490000	-3.32999992	3.17589998
C	-4.64839983	-3.48679996	1.10810006
C	-4.37909985	-3.10459995	-0.21660000
H	-4.94000006	-3.56890011	-1.04509997
C	-3.37490010	-2.16810012	-0.51990002
C	-1.84679997	-1.58190000	2.92680001
H	-1.88039994	-0.48080000	3.05710006
C	-0.41970000	-1.97130001	2.56669998
C	0.66610003	-1.09560001	2.80699992
H	0.47690001	-0.10860000	3.25270009

C 1.98689997 -1.46809995 2.47210002
H 2.81139994 -0.76889998 2.67890000
C 2.24810004 -2.73659992 1.89999998
H 3.27729988 -3.03839993 1.65859997
C 1.17820001 -3.61879992 1.65840006
H 1.37119997 -4.61490011 1.23230004
C -0.14530000 -3.23440003 1.97689998
H -0.98110002 -3.92449999 1.78540003
C -2.92810011 -1.93400002 -1.94949996
H -3.12870002 -0.89670002 -2.28620005
C -1.44710004 -2.22530007 -2.15739989
C -0.62879997 -1.34500003 -2.90510011
H -1.06589997 -0.41990000 -3.31040001
C 0.73760003 -1.63789999 -3.12919998
H 1.35200000 -0.95620000 -3.73460007
C 1.31180000 -2.81080008 -2.59850001
H 2.37579989 -3.03160000 -2.77390003
C 0.50809997 -3.69499993 -1.84700000
H 0.94080001 -4.62330008 -1.44430006
C -0.85850000 -3.40280008 -1.62890005
H -1.48769999 -4.09889984 -1.05280006
H -3.51320004 -2.60030007 -2.61989999
H -5.44630003 -4.21150017 1.32819998
H -2.10739994 -2.04099989 3.90549994
H -0.22810000 4.19799995 1.81019998
H 4.15509987 5.07900000 0.18619999
H 3.26830006 1.83620000 -3.13100004

Cartesian coordinates of the optimized structure of decamethylsamarocene Cp^*_2Sm:

C 2.39050007 -1.21280003 0.20039999
C 2.08990002 -0.34650001 1.30680001
C 2.19580007 1.01010001 0.84670001
C 2.56329989 0.98110002 -0.54079998
C 2.68409991 -0.39240000 -0.94050002
C 2.47160006 -2.71580005 0.25900000
H 3.47420001 -3.06859994 0.59240001
H 2.29139996 -3.18790007 -0.72990000
H 1.73870003 -3.15170002 0.97079998
C 1.85309994 -0.78270000 2.72799993
H 2.80809999 -0.90069997 3.28959990

H 1.33280003 -1.76170003 2.78889990
H 1.24119997 -0.05170000 3.29450011
C 2.05640006 2.24250007 1.70140004
H 3.01149988 2.50600004 2.21029997
H 1.29960001 2.11770010 2.50410008
H 1.76250005 3.13479996 1.11010003
C 2.84960008 2.17750001 -1.40999997
H 3.93300009 2.43589997 -1.42439997
H 2.31960011 3.08839989 -1.06120002
H 2.56180000 2.01340008 -2.47110009
C 3.11700010 -0.87769997 -2.29909992
H 4.22580004 -0.92830002 -2.39359999
H 2.77150011 -0.21170001 -3.11929989
H 2.74239993 -1.89890003 -2.52239990
C -2.61179996 -0.88889998 -0.61250001
C -2.24539995 -1.04630005 0.76660001
C -2.06850004 0.26220000 1.33169997
C -2.32470012 1.22780001 0.29830000
C -2.66280007 0.51630002 -0.90170002
C -2.96199989 -1.99899995 -1.56850004
H -4.04670000 -2.25060010 -1.53989995
H -2.42249990 -2.94250011 -1.33920002
H -2.73659992 -1.73730004 -2.62450004
C -2.15939999 -2.34990001 1.51650000
H -3.13400006 -2.63170004 1.97630000
H -1.42219996 -2.30990005 2.34540009
H -1.87070000 -3.19790006 0.86030000
C -1.81900001 0.57819998 2.78200006
H -2.77010012 0.74830002 3.33690000
H -1.21190000 1.49820006 2.91589999
H -1.28960001 -0.24270000 3.30649996
C -2.33660007 2.72300005 0.48269999
H -3.30349994 3.08430004 0.90149999
H -2.19079995 3.26640010 -0.47409999
H -1.54750001 3.07100010 1.18309999
C -3.07890010 1.12930000 -2.21300006
H -4.18529987 1.22689998 -2.29780006
H -2.75850010 0.52389997 -3.08839989
H -2.66790009 2.15140009 -2.35139990
Sm 0.00050000 -0.02920000 -0.46050000

Table 1S. Crystal Data and Structure Refinement Details for Compounds **2a**, **2b** and **3**.

	2a	**2b**	**3**
Formula	$C_{85}H_{68}N_2Sm$	$C_{82}H_{70}N_2O_2Sm$	$C_{99.50}H_{90}N_2O_2Yb$
Formula weight	1267.76	1265.75	1518.77
Temperature/K	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	triclinic
Space group	*P2₁*	*P2₁/c*	*P-1*
a/Å *b*/Å *c*/Å α/deg β/deg γ/deg	13.0258(7) 18.9888(11) 13.8042(8) 90 113.2396(17) 90	13.7407(11) 18.7955(17) 24.607(2) 90 104.497(3) 90	12.9233(4) 14.4027(5) 22.7605(7) 87.887(1) 74.114(1) 67.067(1)
V/Å^3	3137.4(3)	6152.8(9)	3740.9(2)
Z	2	4	2
density/g/sm^3	1.342	1.366	1.348
μ/mm^{-1}	0.985	1.007	1.305
F(000)	1308	2616	1574
Crystal size /mm	0.41 × 0.10 × 0.06	0.34 × 0.14 × 0.06	0.35 × 0.29 × 0.27
θ-range/deg	2.15 – 25.03	2.21 – 27.49	2.32 – 28.00
Index ranges	–15 ≤ h ≤ 15 –22 ≤ k ≤ 22 –16 ≤ l ≤ 16	–17 ≤ h ≤ 17 –24 ≤ k ≤ 24 –31 ≤ l ≤ 31	–17 ≤ h ≤ 17 –19 ≤ k ≤ 19 –30 ≤ l ≤ 30
Reflections collected	32264	75305	39323
Independent reflections	10867 [R_{int} = 0.0795]	14093 [R_{int} = 0.1032]	17959 [R_{int} = 0.0214]
Goodness-of-fit on F^2	1.022	1.030	1.047
R_1/wR_2 (I>2σ(I))	0.0527 / 0.0885	0.0544 / 0.0858	0.0255 / 0.0595
R_1/wR_2 (all parameters)	0.0752 / 0.0984	0.0938 / 0.0952	0.0301 / 0.0608
Largest diff peak/hole [e Å^{-3}]	1.916 / –1.070	1.818 / –1.469	0.868 / –0.705

Table 2S. Averaged calculated electron densities ρ(**r**), potential and kinetic energy densities V(**r**) and G(**r**), and their ratio $|V(\mathbf{r})|/G(\mathbf{r})$ at the Sm-C bonding critical points of complex **2c** and $(Cp^*)_2Sm$

Complex	ρ(BCP)	V(**r**)	G(**r**)	$\lvert V(\mathbf{r})\rvert/G(\mathbf{r})$
2c	0.0200 [a]	-0.0149 [a]	0.0158 [a]	0.94 [a]
	0.0187 [b]	-0.0136 [b]	0.0146 [b]	0.94 [b]
Cp^*_2Sm	0.0325	-0.0279	0.0268	1.04

[a] – Ring A; [b] – ring B.

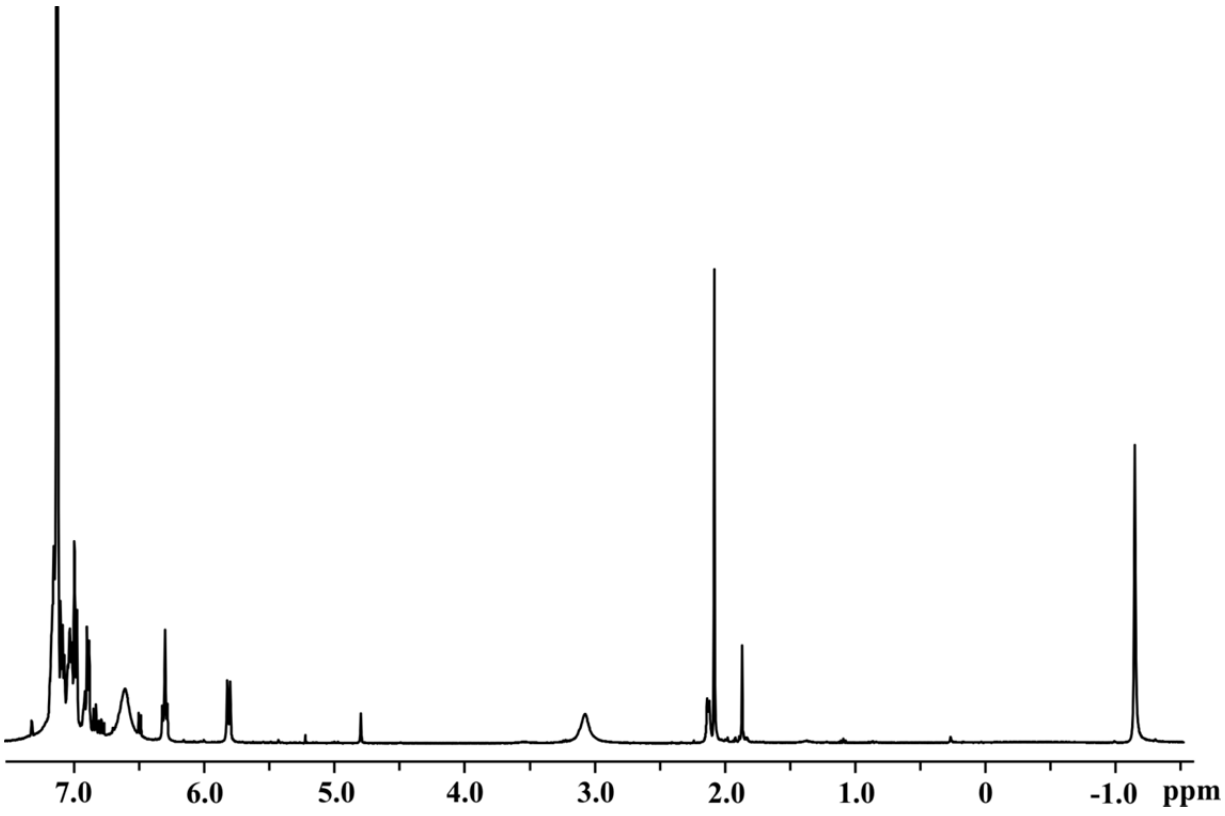

Figure 1S. ^{1}H NMR spectrum of compound **2a** (400 MHz, 295 K, C_6D_6).

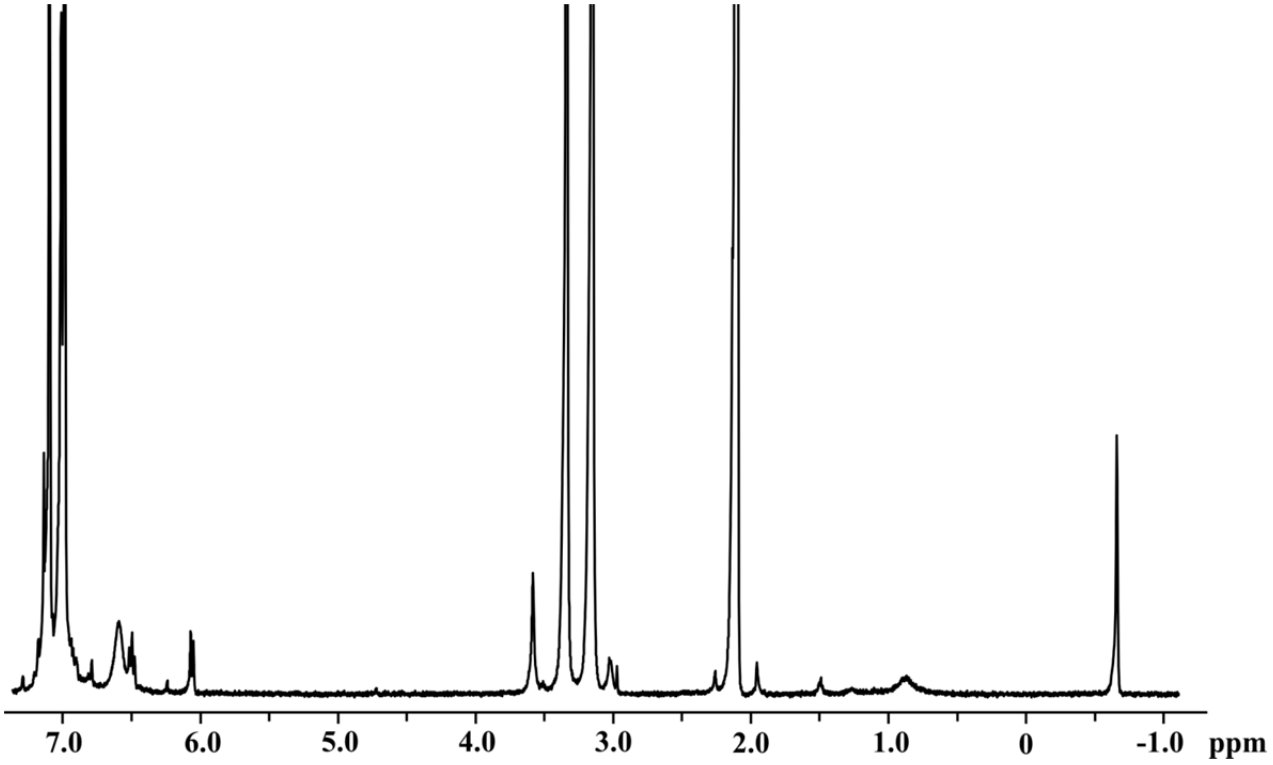

Figure 2S. ^{1}H NMR spectrum of compound **2b** (400 MHz, 333 K, toluene-d_8).

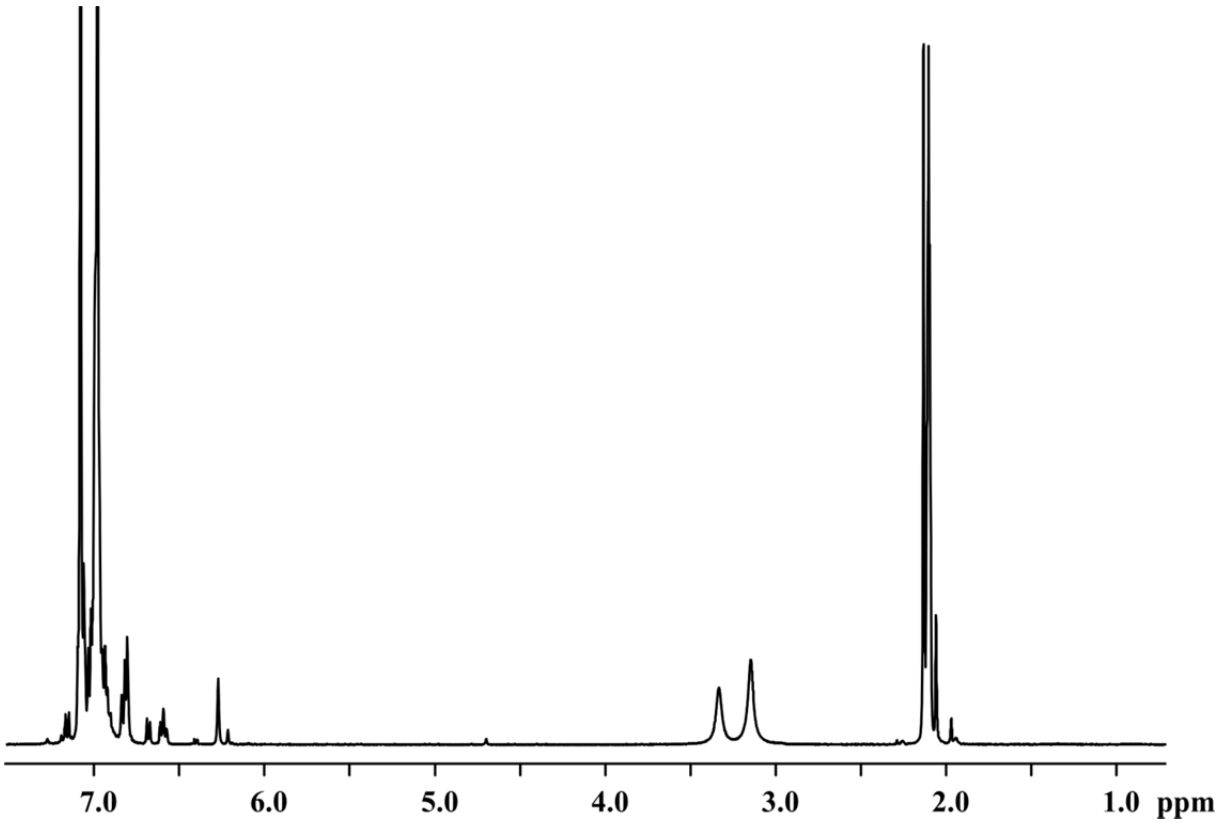

Figure 3S. ^{1}H NMR spectra of compound **3** (400 MHz, 363 K, toluene-d_8).

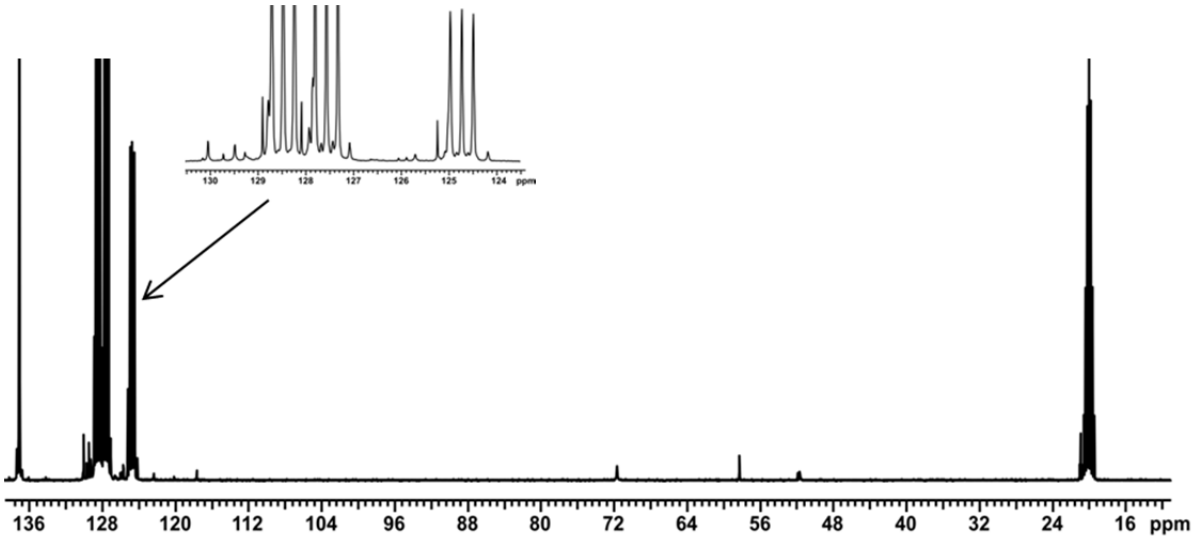

Figure 4S. ^{13}C NMR spectra of compound **3** (100.6 MHz, 297 K, toluene-d_8).

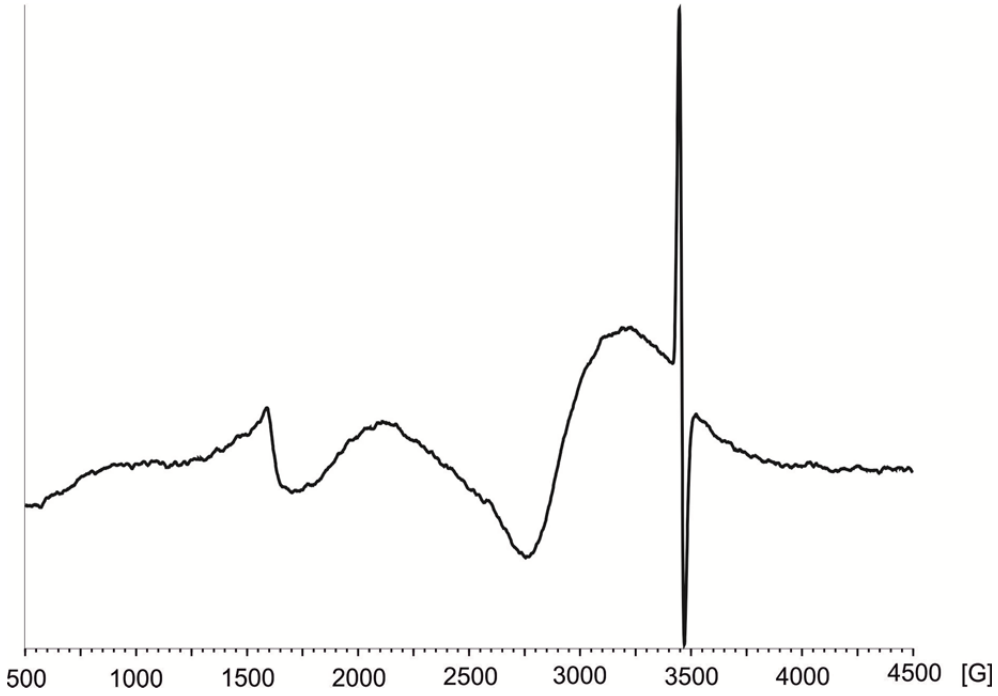

Figure 5S. ESR spectrum of polycrystalline sample of compound **3** at 120 K.

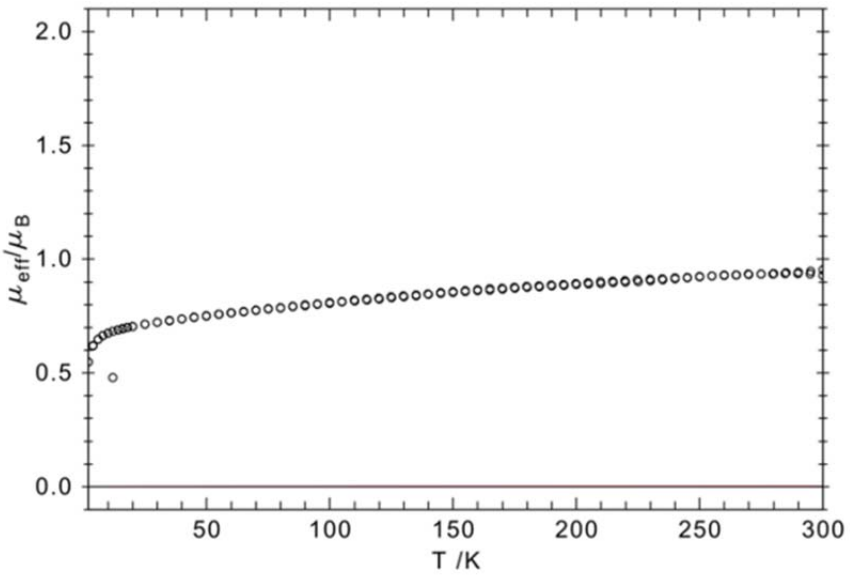

Figure 6S. Plot of μ_{eff} vs. T for a crystalline sample of **3** (300–2 K).

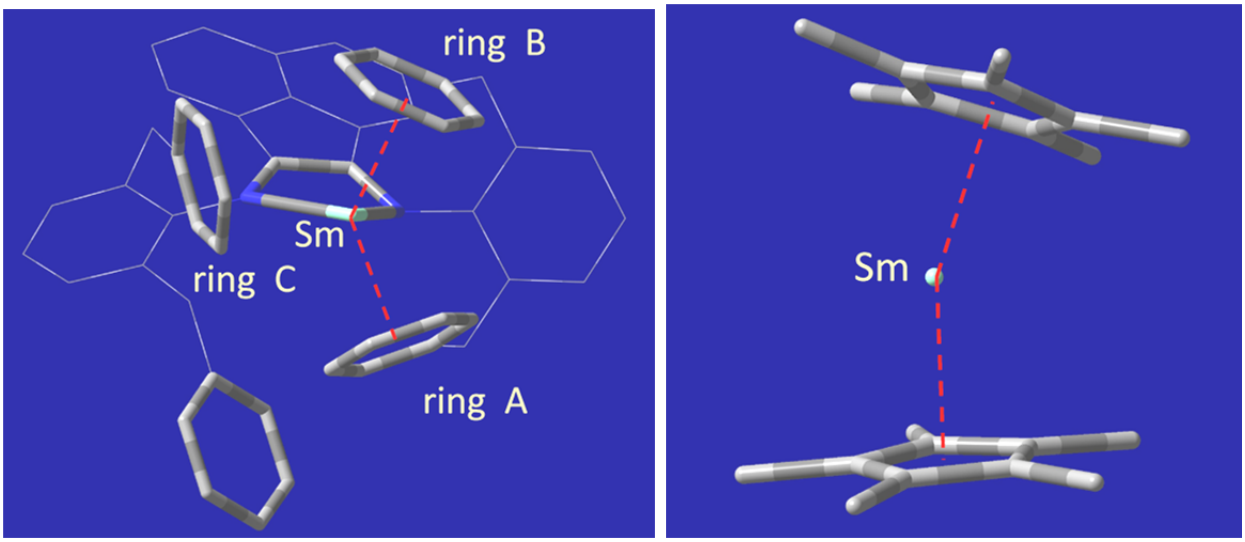

Figure 7S. The optimized geometries of complex **2c** (left) and $(Cp^*)_2Sm$ (right). Hydrogen atoms are omitted.

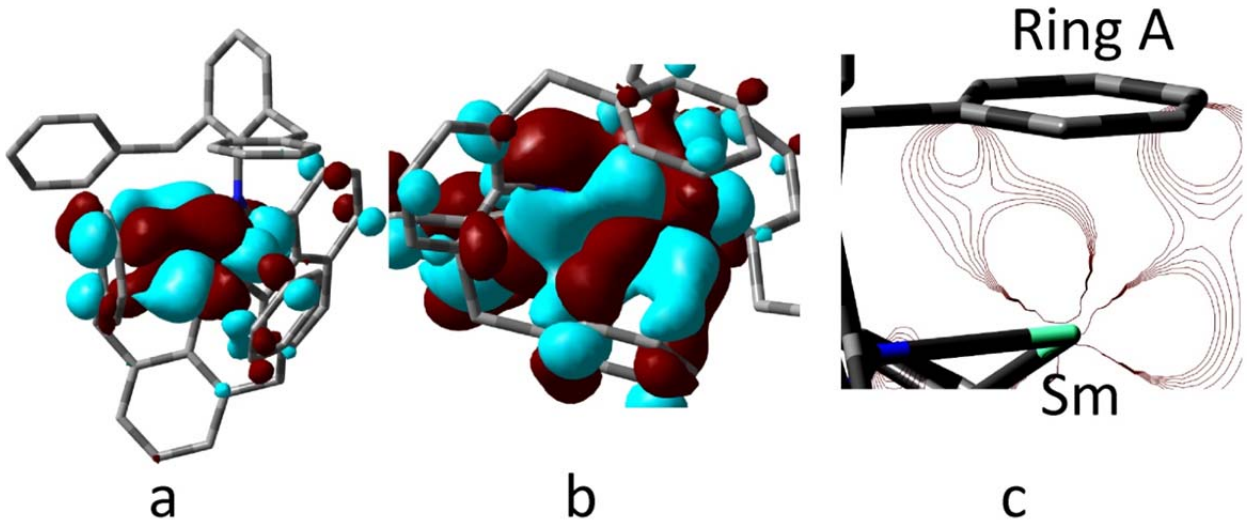

Figure 8S. HOMO (a) and HOMO-1 (b) isosurfaces (isovalue ±0.01) in complex **2c** and the contour map of the HOMO positive part (0.01-0.02, step 0.002) in the SmCC plane showing the Sm-(ring A) orbital overlap (c).