Supporting Information

Rhenium is different: CO Tetramerization Induced by a Divalent Lanthanide Complex in Rhenium Carbonyls.

Ravi Yadav,[a] Thomas Simler,[a] Michael T. Gamer,[a] Ralf Köppe,[a] and Peter W. Roesky*,[a]

[a]*Institute of Inorganic Chemistry, Karlsruhe Institute of Technology, Engesserstr. 15, 76131 Karlsruhe (Germany)*

E-mail: roesky@kit.edu

Contents

I. Experimental section

I.1. General methods

All the manipulations of air- and water-sensitive reactions were performed with rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10^{-3} torr) line or in an argon-filled MBraun glove box. Tetrahydrofuran was distilled under nitrogen from potassium benzophenoneketyl before storage *in vacuo* over $LiAlH_4$. Hydrocarbon solvents were dried by using an MBraun solvent purification system (SPS 800) and degassed and stored *in vacuo* over $LiAlH_4$. Elemental analyses were carried out with an Elementar vario Micro cube. IR spectra were obtained on a Bruker Tensor 37 spectrometer equipped with a room temperature DLaTGS detector and a diamond ATR (attenuated total reflection) unit. $[(DippForm)_2Sm(thf)_2]$[1] and $[(DippForm)_2Yb(thf)_2]$[2] were prepared according to literature procedure. $[(Cp^*)_2Sm(thf)_2]$ was prepared following the reported procedure.[3] $[Re_2(CO)_{10}]$ and $[Mn_2(CO)_{10}]$ were purchased from ABCR and used as received. No reasonable NMR studies were possible for complexes **1**-**5** due to their low solubility in non-polar solvents, possible decomposition in polar solvents and paramagnetic character.

I.2. Synthesis of $[\{(Cp^*)_2Sm^{III}\}_3\{(Cp^*)_2Sm^{III}(thf)\}\{(\mu\text{-}O_4C_4)(\mu\text{-}\eta^2\text{-}CO)_2(\mu\text{-}\eta^1\text{-}CO)(CO)_5Re_2\}]$ (1).

To a mixture of $[(Cp^*)_2Sm(thf)_2]$ (200 mg, 0.353 mmol) and $[Re_2(CO)_{10}]$ (57 mg, 0.088 mmol) was condensed toluene (15 mL) at -78 °C, and the reaction mixture was stirred at room temperature for 48 h. A light-green coloured solid precipitated during the course of reaction. The reaction mixture was filtered through a P4 frit. The filtrate was concentrated to *c.a.* 5 mL and allowed to stand at room temperature. Red coloured crystals were obtained after a few weeks. The mother liquor was decanted off, and the product was dried under vacuum. Yield: 40 mg, (based on crystals), 0.016 mmol, 18%. Anal. Calcd for $C_{96}H_{128}O_{13}Re_2Sm_4$ (2463.92): C, 46.80; H, 5.24. Found: C, 46.68; H, 5.57. IR (ATR) ν (cm^{-1}): 2962 (m), 2907 (m), 2854 (m), 2091 (vw), 2038 (w), 2010 (m), 1978 (vs), 1890 (m), 1858 (s), 1792 (s), 1777 (m), 1733 (s), 1663 (w), 1523 (m), 1437 (m), 1385 (w), 1377 (w), 1280 (w), 1253 (w), 1080 (vw), 1060 (vw), 1020 (w), 956 (w), 864 (vw), 837 (vw), 801 (vw), 784 (vw), 729 (m), 694 (w), 624 (w), 584 (s), 557 (m), 554 (vw), 463 (m), 435 (w) 419 (w).

I.3. Synthesis of [{(DippForm)$_2$Sm^{III}(thf)}$_2${(μ-η^2-CO)$_2$(μ-η^1-CO)$_2$(CO)$_4$Re$_2$}] (2).

To a mixture of [(DippForm)$_2$Sm(thf)$_2$] (205 mg, 0.20 mmol) and [Re$_2$(CO)$_{10}$] (65 mg, 0.10 mmol) was condensed toluene (15 mL) at -78 °C and the resulting solution was stirred at 80 °C for 18 h. The reaction mixture was filtered through a P4 frit into a double ampule, and the latter was flame sealed. Red coloured crystals suitable for X-ray diffraction studies were obtained by slow evaporation of toluene. The crystals were washed with a minimum amount of toluene and dried under vacuum. Yield: 155 mg, (based on crystals), 0.062 mmol, 62%. Anal Calcd for $C_{116}H_{156}N_8O_{10}Re_2Sm_2$ (2495.70): C, 55.83; H, 6.30; N, 4.49. Found: C, 55.94; H, 5.76; N, 4.09. IR (ATR) ν (cm^{-1}): 2960 (vs), 2927 (m), 2866 (m), 2070 (w), 2012 (m), 1973 (s), 1903 (m), 1804 (w), 1664 (vs), 1636 (m), 1588 (m), 1520 (m), 1463 (m), 1438 (m), 1383 (m), 1361 (m), 1332 (m), 1317 (m), 1287 (m), 1271 (m), 1254 (m), 1235 (m), 1182 (m), 1110 (w), 1097 (w), 1057 (w), 1042 (vw), 1002 (w), 934 (w), 822 (w), 799 (w), 768 (m), 753 (m), 729 (m), 694 (m), 673 (w), 591 (m), 563 (w) 536 (w), 506 (vw), 464 (w), 435 (vw).

I.4. Synthesis of [{(Cp*)$_2$Sm^{III}(thf)}{(μ-CO)$_2$(CO)$_3$Mn}]$_\infty$ (3).

Toluene (15 mL) was condensed onto a mixture of [(Cp*)$_2$Sm(thf)$_2$] (200 mg, 0.353 mmol) and [Mn$_2$(CO)$_{10}$] (68 mg, 0.176 mmol) at -78 °C and the reaction mixture was stirred at room temperature for 16 h. A red-coloured solid precipitated during the course of the reaction. All the volatiles were removed *in vacuo*. The residue was dissolved in hot thf (10 mL) and red-colored crystals suitable for X-ray diffraction studies were obtained upon slowly cooling to room temperature. The mother liquor was decanted off and the product was dried under vacuum. Yield: 136 mg, (based on crystals), 0.110 mmol, 62%. Anal. Calcd for $C_{50}H_{60}O_{10}Mn_2Sm_2$ (**3**- thf) (1231.62): C, 48.76; H, 4.91. Found: C, 48.53 ; H 5.18. IR (ATR) ν (cm^{-1}): 2976 (m), 2911 (m), 2856 (m), 2013 (m), 1968 (s), 1940 (s), 1875 (w), 1830 (s), 1770 (vs), 1744 (s, sh), 1489 (vw), 1436 (m), 1388 (w), 1376 (w), 1246 (vw), 1062 (w), 1017 (w), 868 (br), 693 (vs), 684 (vs), 664 (vs), 588 (w), 541 (vw), 501 (w), 458 (w), 428 (vw).

I.5. Synthesis of [{(DippForm)$_2$Sm^{III}(thf)}{Mn(CO)$_5$}] (4).

Toluene (15 mL) was condensed onto a mixture of [(DippForm)$_2$Sm(thf)$_2$] (205 mg, 0.20 mmol) and [Mn$_2$(CO)$_{10}$] (39 mg, 0.10 mmol) at -78 °C and the resulting solution was stirred for 16 h at 60 °C. The reaction mixture was filtered through a P4 frit into a double ampule and the latter was flame sealed.

Yellow crystals were grown by slow evaporation of toluene. The crystals were washed with a minimum amount of toluene and dried under vacuum. Yield: 140 mg, (based on crystals), 0.113 mmol, 56%. Anal. Calcd for $C_{59}H_{78}N_4O_6MnSm*C_7H_8$ (1236.73): C, 64.10; H, 7.01; N,4.53. Found: C, 64.29; H, 6.974; N, 4.50. IR (ATR) ν (cm^{-1}): 3061 (w), 2961 (s), 2927 (m), 2868 (m), 2061 (m), 2037(m), 2022 (m), 2012 (m), 1948 (m, sh), 1909 (s), 1734 (vw), 1665 (vs), 1588 (m), 1516 (w), 1456 (m), 1438 (m), 1383 (m), 1361 (m), 1315 (m), 1272 (s), 1255 (w), 1234 (m), 1190 (s), 1110 (m), 1098 (m), 1055 (w), 1044 (w), 1028 (w), 1004 (w), 985 (m), 945 (m), 933 (w), 831 (w), 800 (s), 770 (m), 755 (vs), 701 (vs), 680 (m), 664 (s), 641 (s), 571 (m), 555 (m), 517 (w), 462 (w), 426 (w), 414 (w).

I.6. Synthesis of [{(DippForm)$_2$Yb^{III}(thf)}{Mn(CO)$_5$}] (5).

Following the procedure described above for **4**, the reaction of [(DippForm)$_2$Yb(thf)$_2$] (209 mg, 0.20 mmol) and [$Mn_2(CO)_{10}$] (39 mg, 0.10 mmol) afforded orange crystals of **5**. Yield: 130 mg, (based on crystals), 0.107 mmol, 53%. Anal. Calcd for $C_{59}H_{78}N_4O_6MnYb$ (1167.29): C, 60.71; H, 6.74; N, 4.80. Found: C, 60.71; H, 6.72, N, 4.85. IR (ATR) ν (cm^{-1}): 2961 (s), 2927 (m), 2865 (m), 2060 (w), 2038 (m), 2012 (m), 1951 (m), 1932 (s), 1906 (vs), 1701 (w), 1666 (vs), 1587 (m), 1521 (s), 1465 (s), 1457 (m), 1439 (s), 1385 (m), 1362 (m), 1332 (w), 1316 (m), 1289 (w), 1268 (s), 1255 (s), 1235 (m), 1193 (w), 1114 (w), 1098 (m), 1055 (w), 1044 (m), 1007 (w), 951 (w), 933 (w), 844 (w), 823 (m), 775 (w), 767 (m), 755 (vs), 724 (vs), 699 (w), 680 (m), 665 (m), 610 (w), 570 (m), 559 (m), 504 (w), 456 (w), 425 (m).

II. IR Spectra:

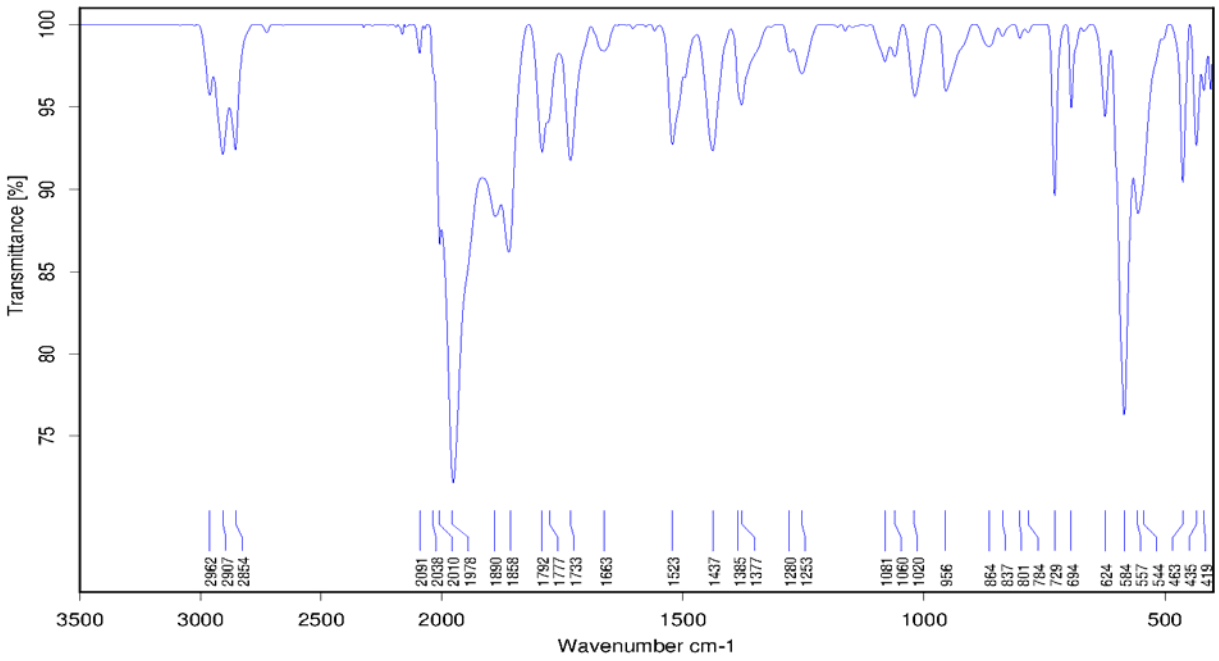

Figure S1: IR spectrum of **1**

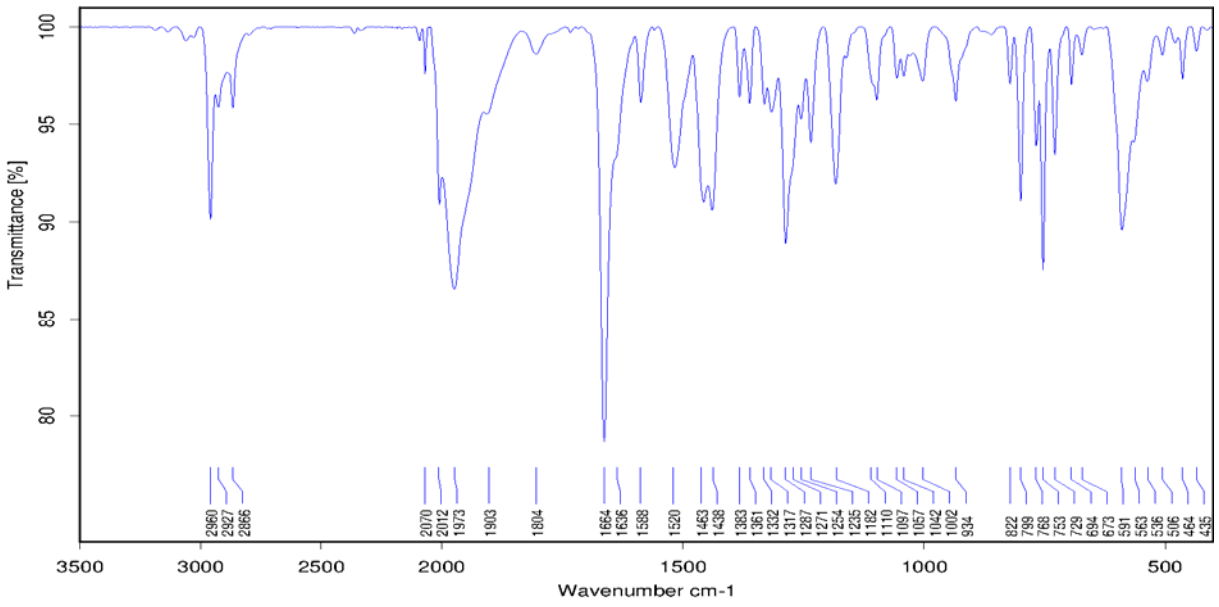

Figure S2: IR spectrum of **2**

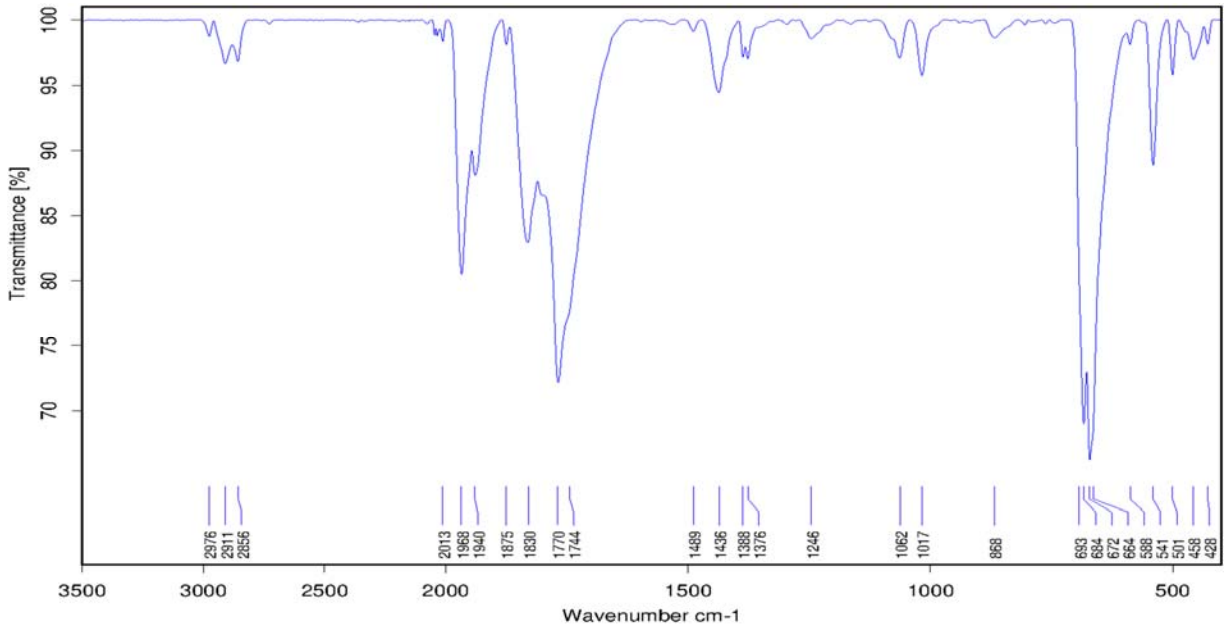

Figure S3: IR spectrum of **3**

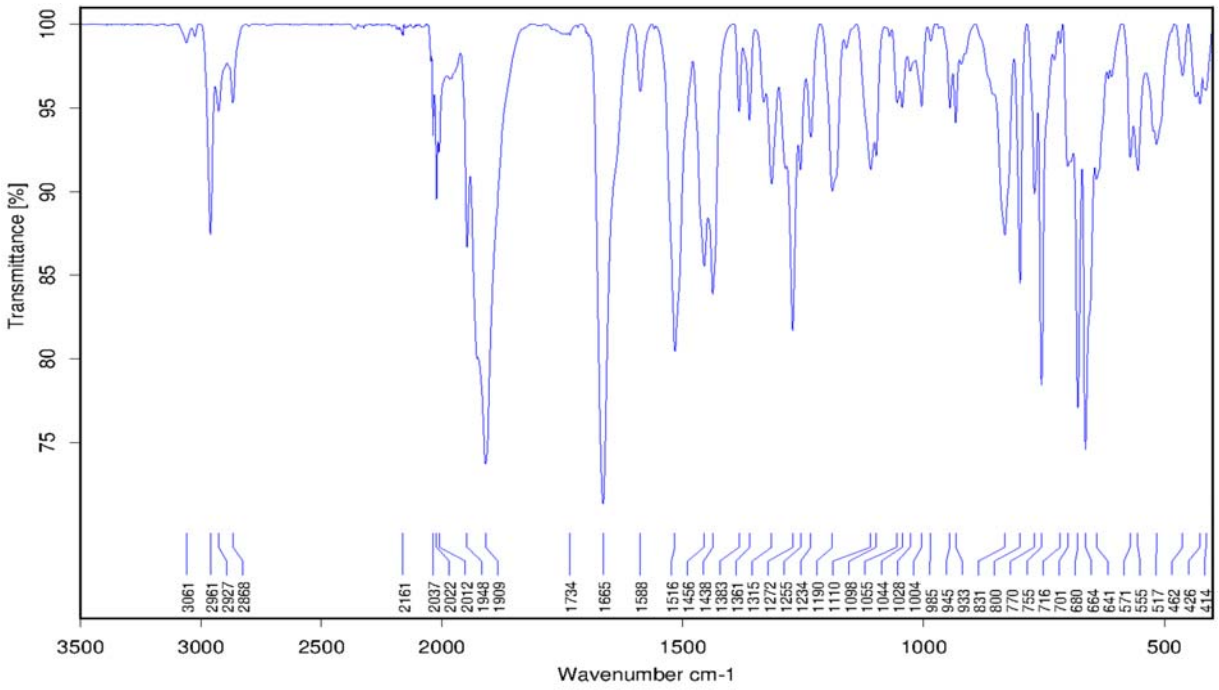

Figure S4: IR spectrum of **4**

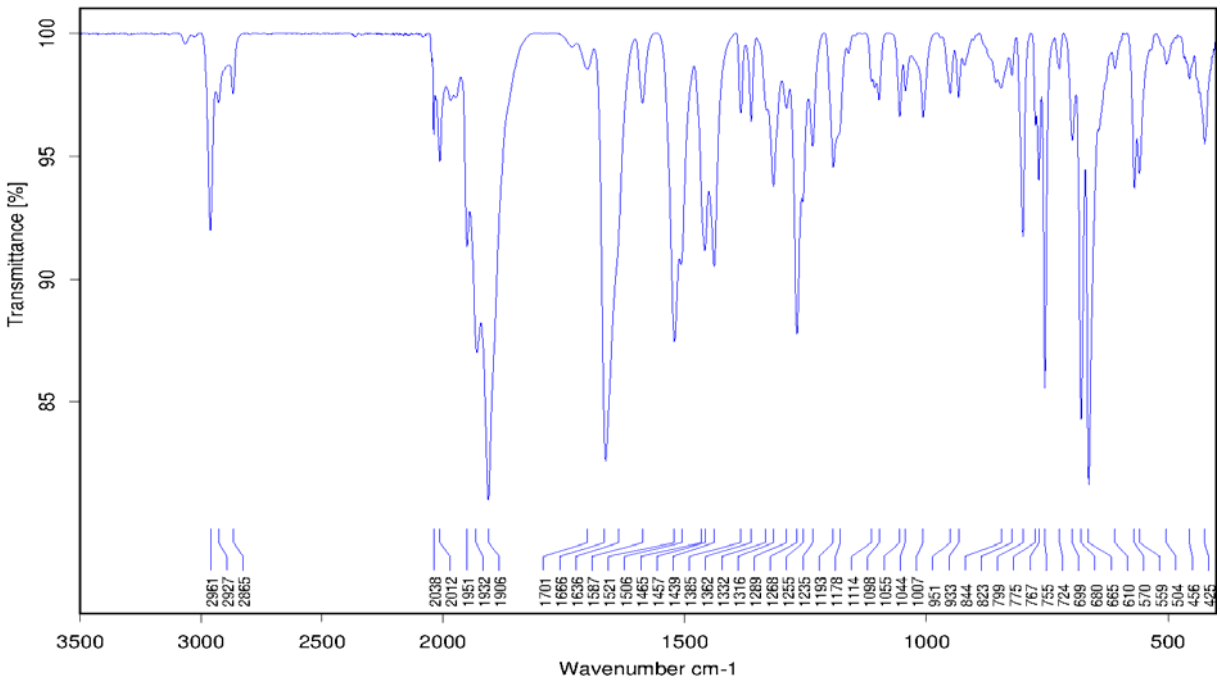

Figure S5: IR spectrum of **5**

III. X-ray crystallography

III.1. General methods

Suitable crystals for the X-ray analysis of all compounds were obtained as described above. A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to the cold stream of a STOE IPDS 2 (150 K) or a STOE StadiVari (100 K) diffractometer. All structures were solved by using the program SHELXS/T[4] and Olex[2].[5] The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F^2 by using the program SHELXL.[4] The H-atoms were introduced into the geometrically calculated positions (SHELXL procedures) unless otherwise stated and refined riding on the corresponding parent atoms. In each case, the locations of the largest peaks in the final difference Fourier map calculations, as well as the magnitude of the residual electron densities, were of no chemical significance. Summary of the crystal data, data collection and refinement for compounds are given in Table S1.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC 1905031-1905035. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+(44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

III.2. Table S1. Crystal data, data collection and refinement for compounds 1, 2, 3, 4, and 5.

Compound	**1* 4 toluene**	**2* 2 toluene**	**2(3* 1.5 thf)**	**4* toluene**	**5* 1.5 toluene**
Formula	$C_{124}H_{160}O_{13}Re_2Sm_4$	$C_{130}H_{172}N_8O_{10}Re_2Sm_2$	$C_{128}H_{176}Mn_4O_{27}Sm_4$	$C_{66}H_{86}MnN_4O_6Sm$	$C_{69.5}H_{90}MnN_4O_6Yb$
$D_{calc.}$/ g cm^{-3}	1.570	1.445	1.505	1.298	1.357
μ/mm^{-1}	3.998	2.957	2.203	1.169	1.706
Formula Weight	2832.31	1339.92	2967.84	1236.67	1305.43
Color	red	red	orange	yellow	orange
Shape	prism	prism	rod	plate	fragment
T/K	150(2)	150	150	150	100
Crystal System	monoclinic	monoclinic	triclinic	triclinic	triclinic
Space Group	$P2_1/n$	$P2_1/n$	P-1	P-1	P-1
a/Å	16.1898(3)	16.7981(4)	12.6229(4)	12.3657(3)	12.1458(6)
b/Å	26.5820(7)	19.3819(5)	12.8766(4)	14.0273(3)	13.5433(7)
c/Å	28.8793(6)	19.0314(6)	20.6420(7)	19.3568(5)	19.7641(10)
α/°			101.808(3)	89.302(2)	90.345(4)
β/°	105.441(2)	96.237(2)	94.242(3)	74.549(2)	96.876(4)
γ/°			90.676(3)	78.249(2)	98.184(4)
V/Å^3	11979.8(5)	6159.5(3)	3273.91(19)	3165.26(14)	3193.9(3)
Z	4	2	1	2	2
Z'	1	1	0.5	1	1
Wavelength/Å	0.71073	0.71073	0.71073	0.71073	0.71073
Radiation type	MoK_α	MoK_α	MoK_α	MoK_α	MoK_α
Θ_{min}/°	1.315	1.504	1.616	1.793	2.431
Θ_{max}/°	25.600	29.544	29.517	29.264	31.064
Measured Refl.	73301	32481	34794	31661	30724
Independent Refl.	22410	17078	18120	16880	15702
Reflections with I > 2(I)	18613	12990	12194	13537	13513
R_{int}	0.0493	0.0382	0.0591	0.0341	0.0250
Largest Peak	3.323	1.769	1.580	0.805	0.891
Deepest Hole	-1.335	-1.533	-1.262	-1.044	-0.571
GooF	1.036	0.965	0.953	0.978	1.024
wR_2 (all data)	0.1234	0.0836	0.1084	0.0840	0.0697
wR_2	0.1133	0.0786	0.0986	0.0802	0.0665
R_1 (all data)	0.0581	0.0512	0.0806	0.0489	0.0400
R_1	0.0456	0.0333	0.0446	0.0342	0.0305

III.3. Crystal structures

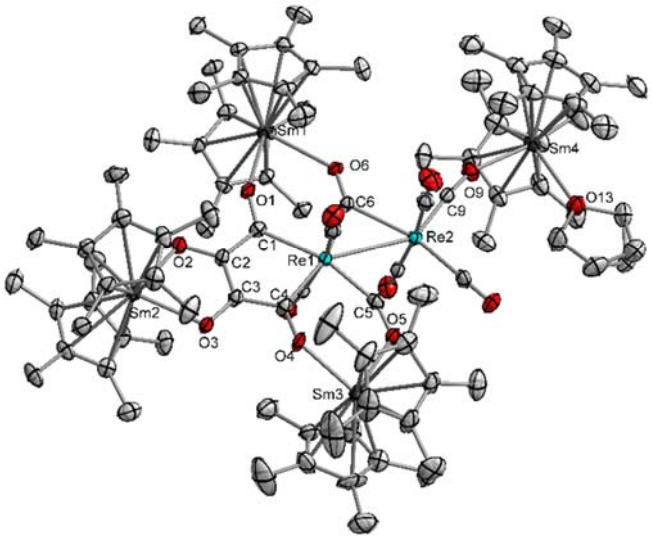

Figure S6: Molecular structure of **1** in the solid state with thermal ellipsoids at the 40% probability. H atoms and non-coordinating solvent molecules are omitted for clarity. Selected bond distances (Å) and angles [°]: Sm1-O1 2.277(4), Sm1-O6 2.396(4), Sm2-O2 2.290(4), Sm2-O3 2.326(4), Sm3-O4 2.278(4), Sm3-O5 2.413(5), Sm4-O9 2.422(5), Sm4-O13 2.421(5), Re1-Re2 2.934(3), Re1-C1 2.188(6), Re1-C4 2.164(7), Re1-C6 2.052(6), Re1-C5 1.972(7), Re2-C5 2.547(6), Re2-C6 2.265(6), Re2-C9 1.878(7), O1-C1 1.257(7), O2-C2 1.314(7), O3-C3 1.294(8), O4-C4 1.261(8), O5-C5 1.192(8), O6-C6 1.209(8), O9-C9 1.179(8), C1-C2 1.445(9), C2-C3 1.406(9), C3-C4 1.460(9); C4-Re1-C1 75.0(2), Re1-C6-Re2 85.5(2), Re1-C5-Re2 79.9(2), C2-C1-Re1 116.1(4), C3-C2-C1 115.9(5), C2-C3-C4 114.8(6), C3-C4-Re1 117.2(4).

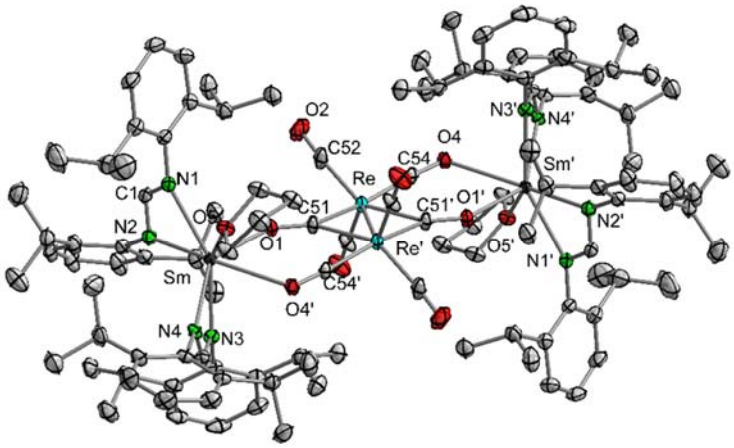

Figure S7: Molecular structure of **2** in the solid state with thermal ellipsoids at the 40% probability. H atoms and non-coordinating solvent molecules are omitted for clarity. Selected bond distances (Å) and angles [°]: Sm-O1 2.365(2), Sm-O4' 2.628(2), Sm-O5 2.429(2), Sm-N1 2.495(3), Sm-N2 2.418(3), Sm-N3 2.454(3), Sm-N4 2.468(3), Re-Re' 2.689(3), Re'-C51 2.206(3), Re-C51 2.049(3), Re-C52 1.939(4), Re-C54 1.910(3), O1-C51 1.240(4), O2-C52 1.145(5), O4-C54 1.168(4); O1-Sm-O4' 67.85(7), N2-Sm-N1 55.48(9), N2-Sm-N3 90.76(9), N2-Sm-N4 114.70(9), N3-Sm-N4 55.67(8), N1-C1-N2 119.6(3), C54-Re-C52 90.43(15), Re-C51-Re' 78.30(11), C54-Re-C51 70.33(12).

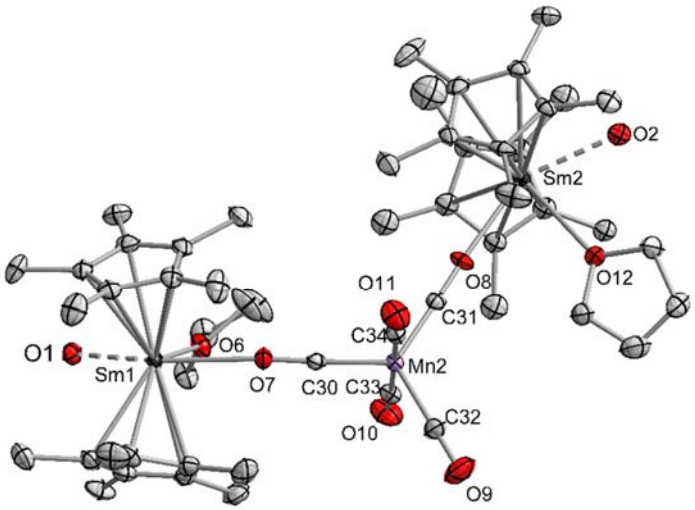

Figure S8: Cut-out of the polymeric structure of **3** in the solid state with thermal ellipsoids at the 40% probability. H atoms and non-coordinating solvent molecules are omitted for clarity. Selected bond distances (Å) and angles [°]: Sm1-O1-2.463(3), Sm1-O6 2.518(3), Sm1-O7 2.449(3), Sm2-O12 2.555(3), Sm2-O8 2.458(3), Sm2-O2 2.474(3), Mn2-C30 1.762(4), Mn2-C31 1.772(4), Mn2-C32 1.831(5), Mn2-C33 1.834(5), Mn2-C34 1.845(5), O7-C30 1.184(5), O8-C31 1.181(5), O9-C32 1.149(6), O10-C33 1.144(6), O11-C34 1.136(6); O1-Sm1-O6 74.34(10), O6-Sm1-C7 91.00(13), C30-Mn2-C31 121.7(2), C30-Mn2-C32 119.2(2), C30-Mn2-C33 89.1(2), C30-Mn2-C34 88.82(19), C31-Mn2-C32 119.1(2), C31-Mn2-C33 91.0(2), C31-Mn2-C34 91.8(2), C32-Mn2-C33 90.9(2), C32-Mn2-C34 88.4(2), C33-Mn2-C34 177.1(2).

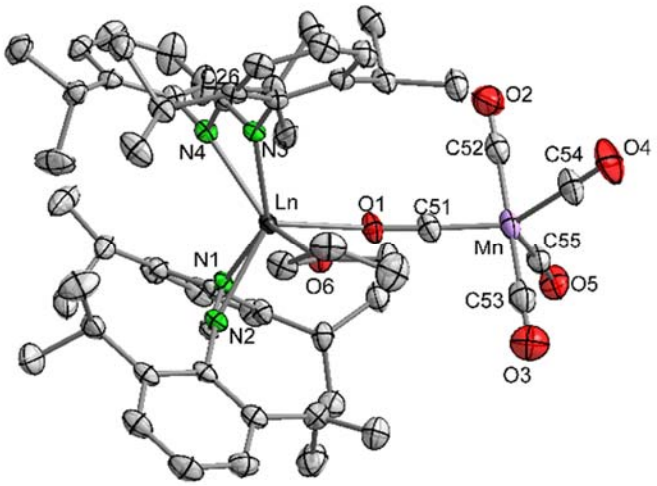

Figure S9: Molecular structure of **4** (Ln = Sm) and **5** (Ln = Yb) in the solid state with thermal ellipsoids at the 40% probability. H atoms and non-coordinating solvent molecules are omitted for clarity. Selected bond distances (Å) and angles [°]: For **4**; Sm-O1 2.325(2), Sm-O6 2.435(2), Sm-N1 2.474(2), Sm-N2 2.344(2), Sm-N3 2.418(2), Sm-N4 2.399(2), Mn-C51 1.739(3), Mn-C52 1.823(4), Mn-C53 1.823(4), Mn-C54 1.826(3), Mn-C55 1.820(3), O1-C51 1.205(3), O2-C52 1.148(4), O3-C53 1.150(4), O4-C54 1.150(4), O5-C55 1.152(3); N2-Sm-N1 56.06(6), N4-Sm-N3 55.78(6), N1-C1-N2 117.6(2), C51-Mn-C52 87.72(13), C51-Mn-C53 91.30(14), C51-Mn-C54 128.16(13), C51-Mn-C55 117.13(13), C52-Mn-C54 87.52(16), C53-Mn-C52 174.95(14), C53-Mn-C54 89.19(16), C55-Mn-C52 93.11(14), C55-Mn-C53 91.74(15), C55-Mn-C54 114.67(13). For **5**; Yb-O1 2.192(2), Yb-O6 2.308(2), Yb-N1 2.280(2), Yb-N2 2.342(2), Yb-N3 2.300(2), Yb-N4 2.348(2), Mn-C51 1.725(3), Mn-C52 1.829(3), Mn-C53 1.835(3), Mn-C54 1.824(3), Mn-C55 1.831(3), O1-C51 1.211(3), O2-C52 1.148(3), O3-C53 1.138(3), O4-C54 1.149(4), O5-C55 1.147(3); N1-Yb-N2 58.85(7), N3-Yb-N4 57.85(7), C1-N1-C2 117.2(2), C51-Mn-C52 89.71(12), C51-Mn-C53 91.58(12), C51-Mn-C54 118.61(13), C51-Mn-C55 120.04(13), C52-Mn-C53 178.53(13), C52-Mn-C55 90.63(12), C54-Mn-C52 90.03(13), C54-Mn-C53 89.96(13), C54-Mn-C55 121.34(13), C55-Mn-C53 88.12(12).

IV. Quantum chemical calculations

IV.1. General methods

The theoretical calculations were performed with the RI-DFT/BP-86 method [6] using def2-TZVP basis sets for all atoms.[7] For Re, as well as for Sm,[8] effective core potentials containing 60 or 51 core electrons, respectively, were chosen. The population analyses based on occupation numbers were performed using 13 modified atoms orbitals (MAOs) on Re, 10 on Sm, 5 each on C and O and 1 MAO on H.[9]

For the quantum chemical calculations the program package TURBOMOLE 7.3[10] was chosen. The wave function analyzer multiwfn 3.6 [11] was taken for the Bader AIM analysis.

IV.2 Countour plots obtained from AIM analysis of complex 1 and 2

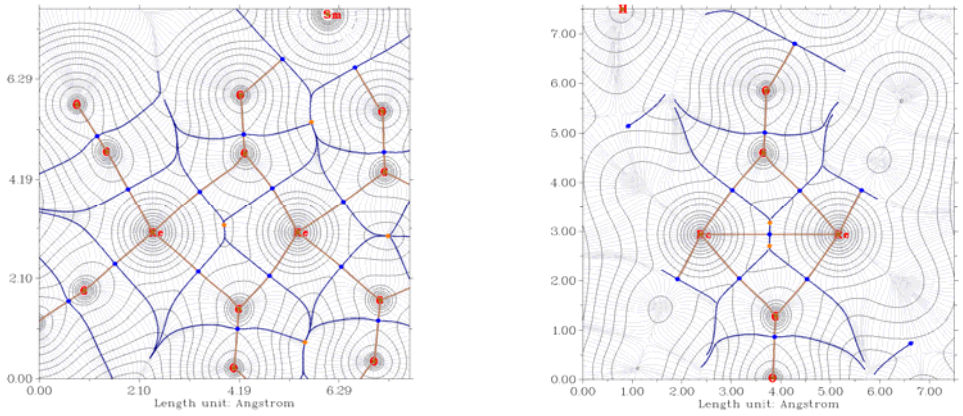

Figure **S10**: Contour plots of the electron densities of a) **1** and b) **2** each in the plane Re-Re-C. The connections of Re and C in each molecule and between Re and Re in **2** are depicted by the bond paths (orange) and the bond critical points (blue). Ring critical points are given in orange. The blue line represents the zero flux surface that defines the sub space of each atom.

V. References

(1) (a) M. L. Cole, P. C. Junk, *Chem. Commun.*, 2005, 2695. (b) C. Schoo, S. Bestgen, M. Schmidt, S.N. Konchenko, M. Scheer, P.W. Roesky, *Chem. Commun.*, 2016, **52**, 13217.

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