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Supplementary Information

Samarocene Oxide: From an Undesired Decomposition Product to a New Reagent

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Experimental Section

General Considerations

All manipulations of air-sensitive materials were performed with the 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. Elemental analyses were carried out with an Elementar vario Micro Cube. Hydrocarbon solvents were predried by using an MBraun solvent purification system (SPS-800) and degassed, dried and stored in vacuo over $LiAlH_4$. Tetrahydrofuran was distilled under nitrogen from potassium benzophenoneketyl before storage over $LiAlH_4$. IR spectra were obtained on a Bruker Tensor 37 FTIR spectrometer equipped with a room temperature DLaTGS detector and a diamond ATR (attenuated total reflection) unit; for the mid infrared region a KBr beamsplitter was used. $[Cp^*_2Sm(thf)_2]$,[1] and $[Cp^*_2Sm\text{-}O\text{-}SmCp^*_2]$[2] were prepared according to literature procedures with $[Cp^*_2Sm(thf)_2]$ and 1,2-epoxybutane.

Synthesis

NOTE: All yields are based on single crystalline material.

Synthesis of [Cp*$_2$Sm-(μ–CO$_2$S)-SmCp*$_2$] (**2**)

The atmosphere in a flask containing [Cp*$_2$Sm-O-SmCp*$_2$] (250 mg, 0.29 mmol) in THF (20 mL) was changed to COS. The reaction mixture turned orange immediately. The resulting solution was stirred overnight at room temperature. Then THF was removed by evaporation in vacuum, the residue was triturated with *n*-pentane (25 mL) and filtered into a two-section ampule and flame sealed to grow crystals by slow evaporation. Yield: 18 % (53 mg). ^{1}H NMR (C_6D_6, 300 MHz) [ppm]: δ = -0.69 (br, 4H, THF), -0.46 (br, 4H, THF), 1.24 (s, 30H, Cp*), 1.67 (s, 30H, Cp*). IR (cm^{-1}): ν = 2965 (s), 2907 (vs), 2856 (vs), 2723 (w), 1666 (w), 1635 (m), 1439 (s), 1379 (s), 1359 (s), 1247 (m), 1083 (m), 1057 (m), 1016 (m), 955 (m), 921 (m), 837 (m), 620 (w). NIR ν, cm^{-1}: 6108(m), 6224(m), 6382(m), 6419(m), 6734(w), 6779(w), 6877(m), 7212(s), 7401(m), 7735(w), 7796(m), 8092(s), 8215(w), 9151(w), 9262(w). Anal. calcd. (%) for [$C_{49}H_{78}SO_3Sm_2$] (993.82): C 54.61, H 6.92, S 3.24; found C 53.12, H 7.59, S 3.77.

Synthesis of [Cp*$_2$Sm-(μ–COS$_2$)-SmCp*$_2$] (**3**)

[Cp*$_2$Sm-O-SmCp*$_2$] (250 mg, 0.29 mmol) were dissolved in 20 mL of THF yielding a yellow solution and then CS_2 (18 µl, 0.29 mmol) added with a syringe. The reaction mixture was stirred at room temperature for 16 h. The solvent was removed in vacuo and resulting yellow solid was triturated with ca. 15 mL *n*-pentane, filtered into a two-section ampule and flame sealed to grow crystals by slow evaporation. Yield: 25% (74 mg). ^{1}H NMR (C_6D_6, 300 MHz) [ppm]: δ = -0.85 (br, 4H, THF), -0.79 (br, 4H, THF), 1.24 (s, 30H, Cp*), 1.65 (s, 30H, Cp*). IR (cm^{-1}): ν = 2966 (s), 2906 (vs), 2855 (vs), 2723 (w), 1687 (w), 1635 (w), 1439 (s), 1379 (s), 1354 (vs), 1206 (w), 1173 (w), 1084 (m), 1014 (m), 955 (w), 917 (s), 835 (w), 620 (m). NIR ν, cm^{-1}: 6245(s), 6357(m), 6702(m), 7106(w), 7172(m), 7298(s), 7383(m), 7760(w), 7953(m), 8136(m), 8644(w), 8702(w), 8786(w), 8915(w), 9167(m), 9269(w). Anal. calcd. (%) for [$C_{45}H_{68}S_2O_2Sm_2$] (1005.90): C 53.73, H 6.81, S 6.38; found C 53.50, H 6.71, S 6.32. The obtained data are in agreement with the literature.[3]

Synthesis of [Cp*$_2$Sm-(μ–SO_3)-SmCp*$_2$] (**4**)

SO_2 (0.3 mmol) was condensed onto a solution of [Cp*$_2$Sm-O-SmCp*$_2$] (250 mg, 0.29 mmol) in THF (20 mL) at -50 °C upon stirring. The colour of the reaction mixture changed immediately to orange. The resulting solution was stirred for 1 h at -50 °C and then allowed to stand overnight while slowly warming up to room temperature. Then THF was removed by evaporation in vacuum, the residue was triturated with *n*-pentane (15 mL) and filtered, filtered into a two-section ampule and flame sealed to grow crystals by slow evaporation. Yield: 29% (84 mg). ^{1}H NMR (C_6D_6, 300 MHz) [ppm]: δ = -1.28 (br, 4H, THF), -1.12 (br, 4H, THF), 1.24 (s, 60H, Cp*). IR (cm^{-1}): ν = 2966 (s), 2912 (vs), 2857 (vs), 2729 (w), 1689 (m), 1567 (w), 1440 (s), 1378 (s), 1204 (w), 1084 (m), 924 (s), 620 (m). NIR ν, cm^{-1}: 5838(s), 6118(w), 6154(w), 6236(m), 6390(m), 7107(m), 7153(m), 7171(m), 7235(m), 7300(s), 7311(s), 7335(s), 7514(m), 7718(w), 7802(m), 8042(s), 8152(m), 8312(w), 8731(m), 8811(w), 8866(m), 8962(s), 9231(s). Anal. calcd. (%) for [$C_{44}H_{68}SO_4Sm_2$] (993.82): C 53.18, H 6.84, S 3.23; found C 52.97, H 6.69, S 3.35.

Synthesis of [Cp*$_2$Sm(py)-(μ–SO_4)-Sm(py)Cp*$_2$] (**5**)

[Cp*$_2$Sm-O-SmCp*$_2$] (150 mg, 0.17 mmol) and SO_3(Py) (27 mg, 0.17 mmol) were dissolved in 10 mL of pyridine yielding a yellow solution. The reaction mixture was stirred at room temperature for 16 h. The solvent was removed in vacuo and resulting yellow solid was triturated with ca. 15 mL *n*-pentane, filtered into a two-section ampule and flame sealed to grow crystals by slow evaporation. Yield: 33% (44 mg). ^{1}H NMR (C_6D_6, 300 MHz) [ppm]: δ = 1.39 (s, 60H, Cp*), 4.03 (br, 4H, py), 5.59 (br, 4H, py), 6.04 (br, 2H, py). IR (cm^{-1}): ν = 3046 (w), 2984 (m), 2892 (s), 2854 (s), 2725 (w), 1599 (m), 1571 (w), 1490 (w), 1441 (s), 1379 (w), 1223 (w), 1147 (vs), 1089 (vs), 1037 (m), 1004(w), 928 (w), 755 (w), 705 (m), 665 (m), 621 (m), 598 (m). Anal. calcd. (%) for [$C_{50}H_{70}N_2O_4SSm2$] (1095.90): C 54.80, H 6.44, N 2.56, S 2.93; found C 53.80, H 5.99, N 2.15, S 3.17.

Synthesis of [$Cp^*{}_2Sm(MeCN)$-(μ–$ReO_4)_2$-(MeCN)$SmCp^*{}_2$] (**6**)

[$Cp^*{}_2Sm$-O-$SmCp^*{}_2$] (100 mg, 0.12 mmol) and Re_2O_7 (58 mg, 0.12 mmol) were dissolved in 10 mL of acetonitrile yielding a dark greenish suspension. After 16 h of stirring at room temperature the reaction mixture was filtered into a two-section ampule and flame sealed to grow crystals by slow evaporation. Yield: 39% (67 mg). ^{1}H NMR (C_6D_6, 300 MHz) [ppm]: δ = 0.49 (s, 6H, MeCN), 1.03 (s, 60H, Cp*). IR (cm^{-1}): ν = 2960 (s), 2910 (vs), 2857 (s), 1651 (w), 1624 (w), 1439 (m), 1377 (m), 1120 (w), 1062 (m), 1030 (w), 977 (m), 939 (s), 904 (vs), 757 (w), 691 (m), 625 (m). %. Although single crystals were used elemental analysis gave reproducibly low carbon values.

Synthesis of [$Cp^*{}_2Sm$-(μ–$PhCO_2)_2$-$SmCp^*{}_2$] (**7**)

[$Cp^*{}_2Sm$-O-$SmCp^*{}_2$] (100 mg, 0.12 mmol) and $C_{14}H_{10}O_4$ (28 mg, 0.12 mmol) were dissolved in 10 mL of THF yielding a orange solution. After 16 h of stirring at room temperature the solvent was removed in vacuo and resulting orange solid was triturated with ca. 15 mL toluene, filtered into a two-section ampule and flame sealed to grow crystals by slow evaporation. Yield: 46% (60 mg). ^{1}H NMR (C_6D_6, 300 MHz) [ppm]: δ = -0.24 (d, $^3J_{HH}$ = 7.3 Hz, 4H, *o*-C_6H_5), 1.66 (s, 60H, Cp*), 4.85 (t, $^3J_{HH}$ = 7.3 Hz, 4H, *m*-C_6H_5), 5.57 (t, $^3J_{HH}$ = 7.3 Hz, 2H, *p*-C_6H_5). IR (cm^{-1}): ν = 2973 (m), 2928 (m), 2864 (m), 1702 (w), 1598 (s), 1539 (s), 1402 (vs), 1176 (w), 1146 (w), 1069 (m), 1025 (m), 935 (w), 850 (w), 717 (s), 677 (m), 552 (w). The obtained data are in agreement with the literature.[3]

IR measurements

Figure S1. IR-spectrum of **2**.

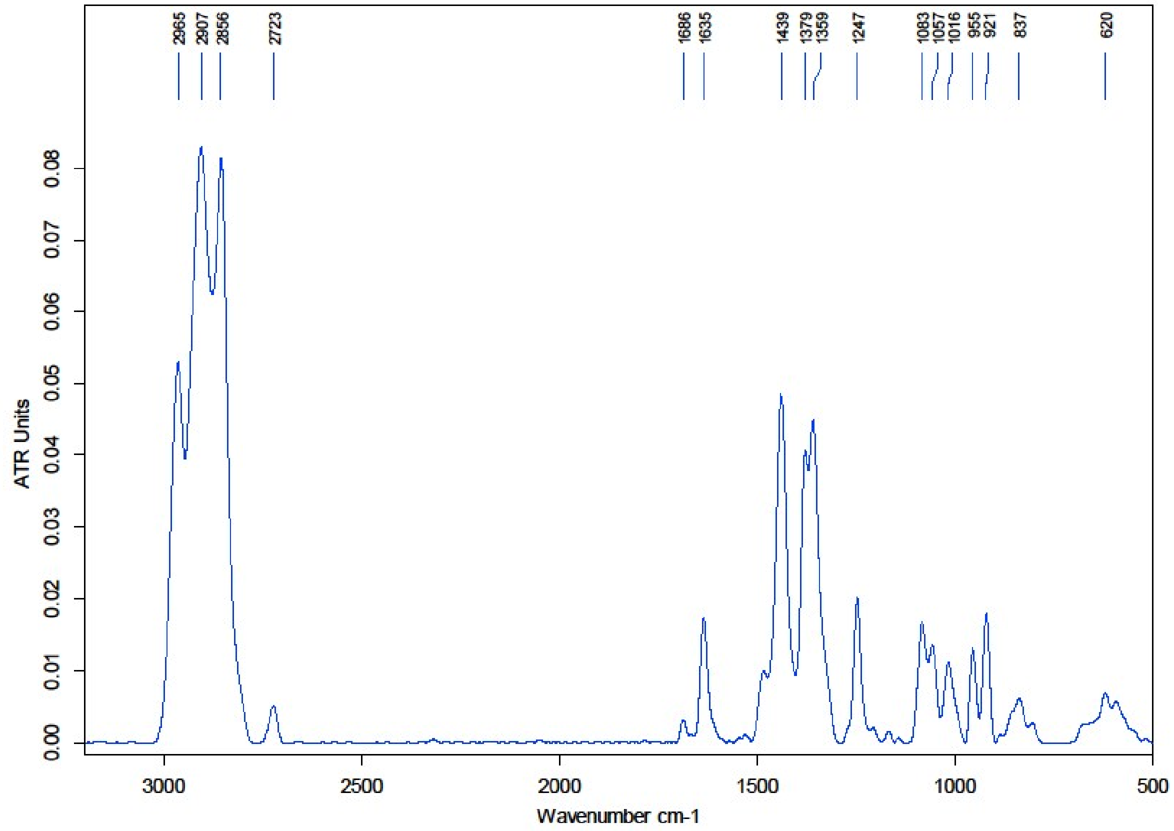


Figure S2. IR-spectrum of **3**.

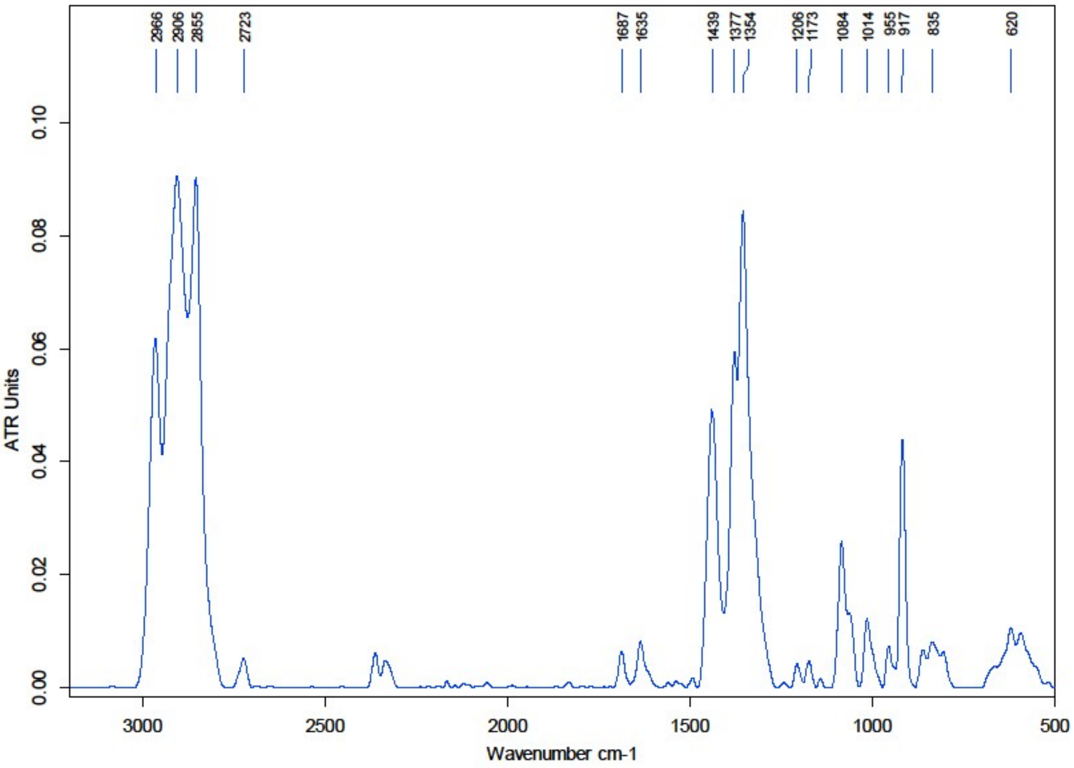


Figure S3. IR-spectrum of **4**.

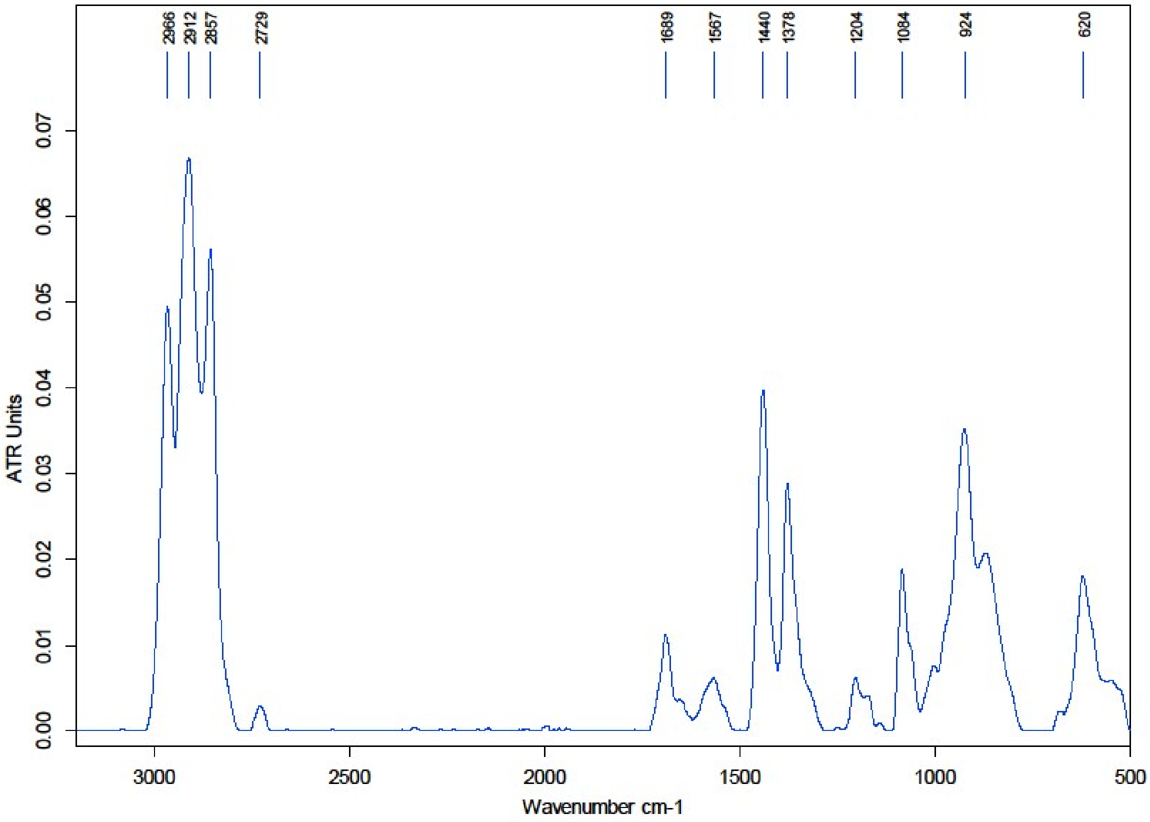


Figure S4. IR-spectrum of **5**.

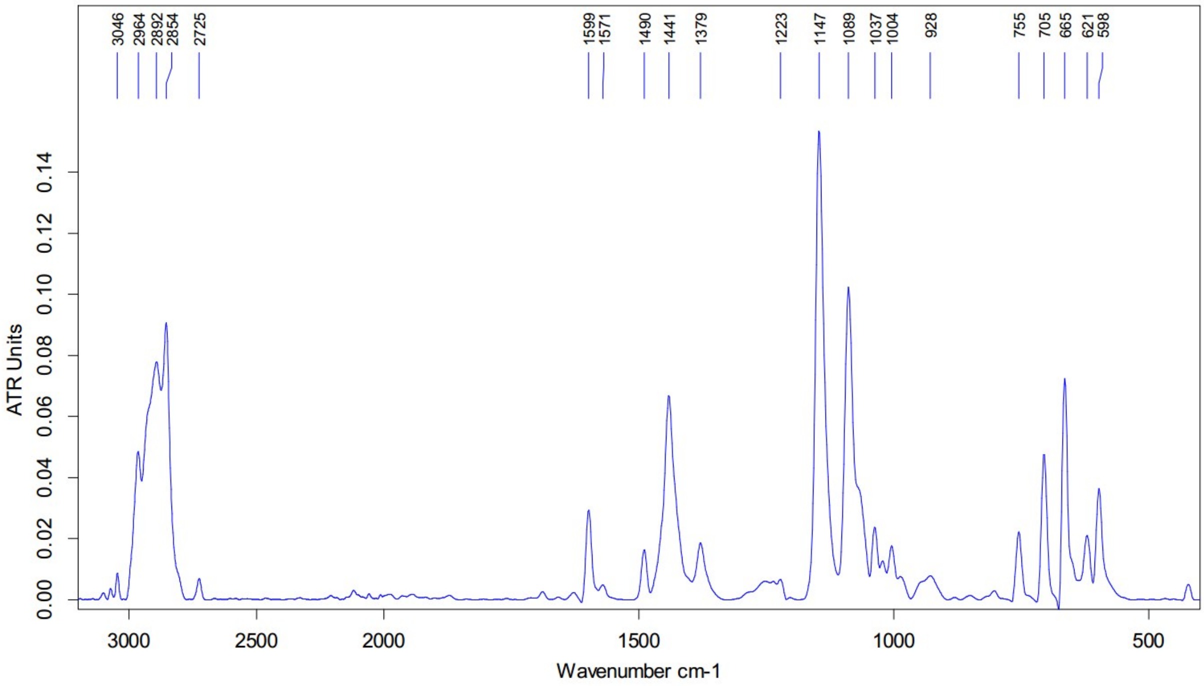


Figure S5. IR-spectrum of **6**.

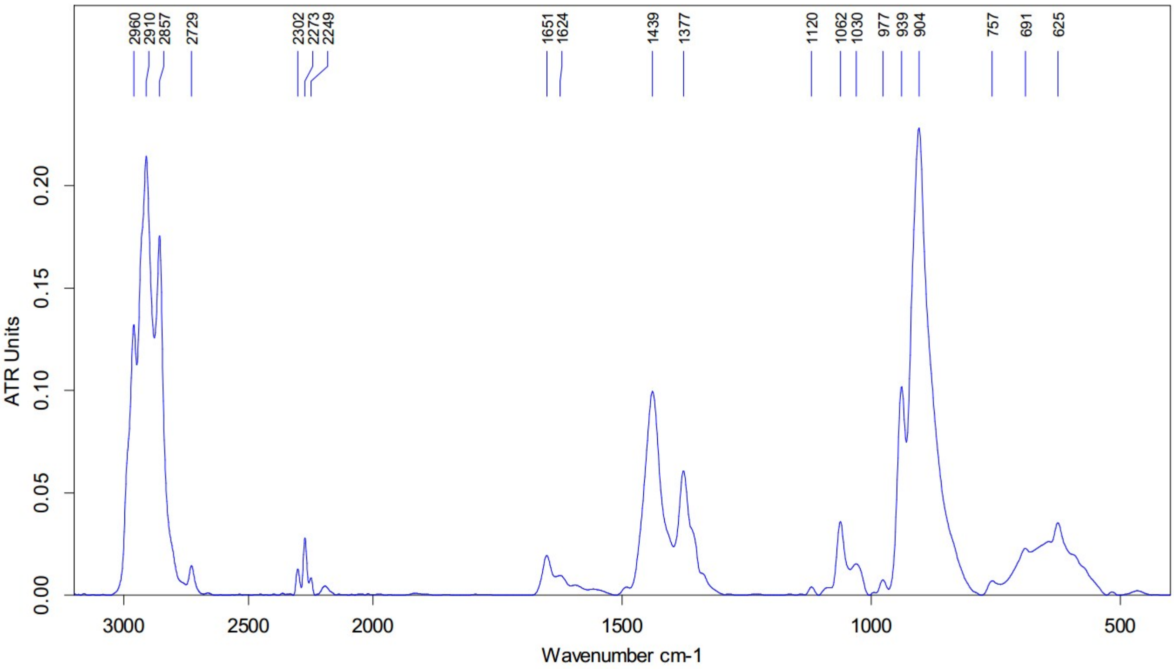
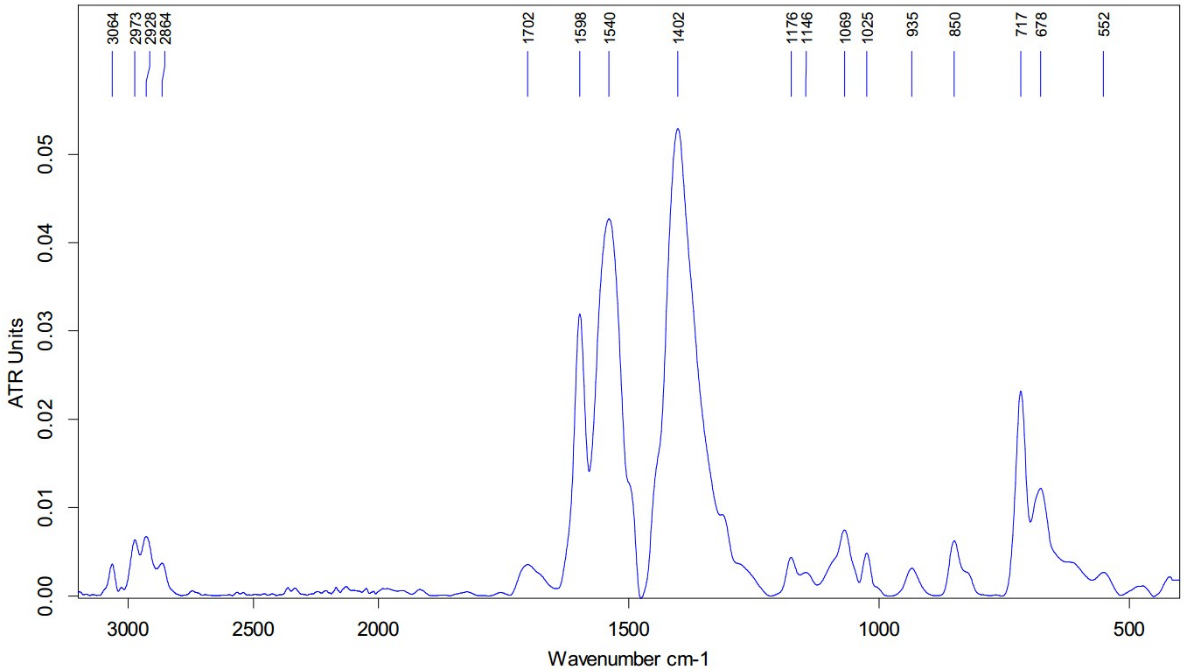


Figure S6. IR-spectrum of **7**.



X-ray Crystallographic Studies of 1-5. 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 or STOE StadiVari diffractometer.

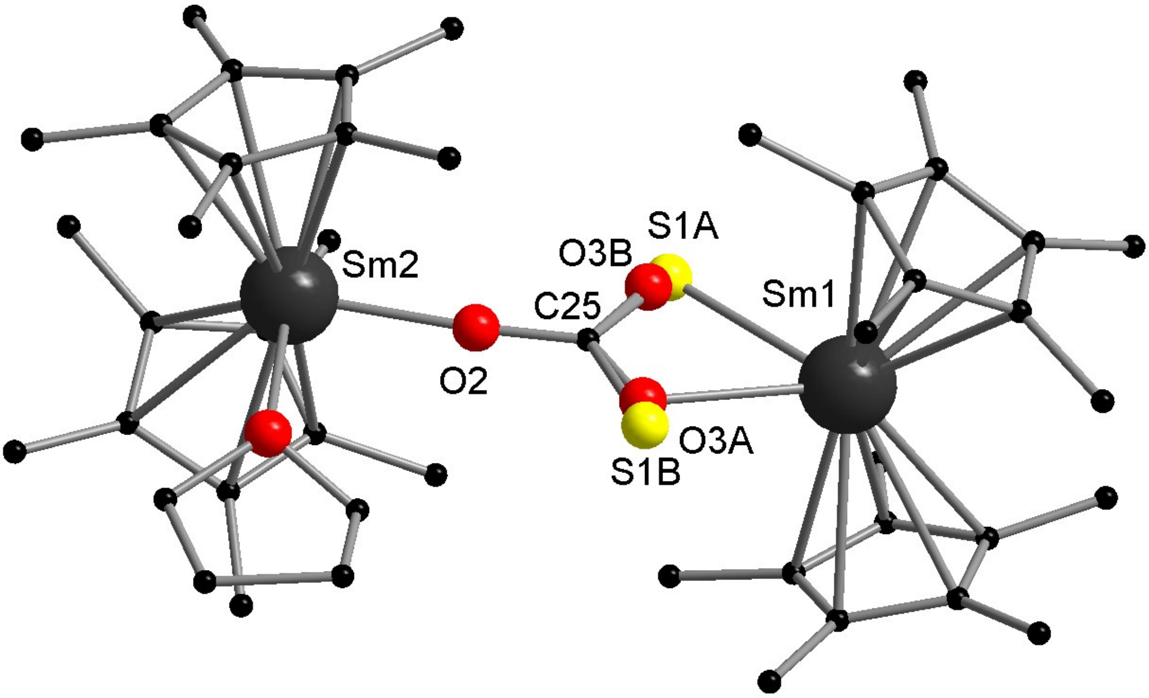
All structures were solved using SHELXS[4]. The remaining non-hydrogen atoms were located from difference in Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function $(F_o\text{-}F_c)^2$, where the weight is defined as $4F_0^2/2(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes using the program SHELXL-2013.[4] Carbon-bound hydrogen atom positions were calculated. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, bond lengths and angles have been deposited as supporting information.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. 1441607-1441610, 1441612, 1456456. 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).

Table S1: Crystal data and structure refinement for **2-7.**

Compound	**2**	**3**	**4**	**5**	**6**	**7**
Chemical formula	$C_{45}H_{68}O_3SSm_2$	$C_{45}H_{68}O_2S_2Sm_2$	$C_{44}H_{68}O_4SSm_2$	$C_{50}H_{70}N_2O_4SSm_2$	$C_{44}H_{66}N_2O_8Re_2Sm_2\bullet2(C_2H_3N)$	$C_{54}H_{70}O_4Sm_2\bullet2(C_7H_8)$
Formula Mass	989.75	1005.81	993.74	1095.84	1424.08	1268.06
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	triclinic
Space group	*P*2$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$	*Pbca*	*P*-1
a/Å	10.7989(9)	18.588(4)	17.824(4)	16.952(3)	16.207(3)	10.561(2)
b/Å	23.324(2)	23.602(5)	16.299(3)	13.879(3)	14.000(3)	10.700(2)
c/Å	18.592(2)	21.654(4)	16.056(3)	20.819(4)	21.465(4)	15.035(3)
α/°						110.25(3)
β/°	106.381(7)	107.26(3)	108.56(3)	90.81(3)		97.77(3)
γ/°						98.73(3)
Unit cell volume/Å^3	4492.8(7)	9072(3)	4421.9(17)	4897.7(17)	4870.5(17)	1542.9(6)
Temperature/K	150	195(2)	195(2)	210(2)	205(2)	200(2)
No. of formula units per unit cell, *Z*	4	8	4	4	4	1
Radiation type	MoKα	MoKα	MoKα	Mo Kα	Mo Kα	Mo Kα
Absorption coefficient, μ/mm^{-1}	2.670	2.689	2.715	2.47	7.375	1.929
No. of reflections measured	34784	39419	18573	21566	34712	26833
No. of independent reflections	8859	17571	8591	9533	4809	6049
R_{int}	0.0845	0.0608	0.0924	0.0640	0.0444	0.0605
Final R_1 values ($I > 2\sigma(I)$)	0.0528	0.0334	0.0471	0.0472	0.0265	0.0325
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1436	0.0573	0.0809	0.0745	0.0481	0.0793
Final R_1 values (all data)	0.0707	0.1015	0.1092	0.0989	0.0436	0.0411
Final $wR(F^2)$ values (all data)	0.1579	0.0639	0.0914	0.0823	0.0509	0.0812
Goodness of fit on F^2	1.041	0.704	0.731	0.840	0.927	0.985

Figure S8. Solid-state structure of **2**, showing the full disorder of the central CO_2S-core.



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