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η^2-Acetylene Sm^{II} and Sm^{III} complexes: mirage or reality?

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EXPERIMENTAL SECTION

General consideration. All experiments were performed by using standard Schlenk or glove-box techniques, with rigorous exclusion of traces of moisture and air. After being dried over CaH_2, THF was purified by distillation from sodium/benzophenoneketyl; hexane and toluene were dried by distillation from sodium/triglyme and benzophenone ketyl prior to use. $Sm[N(SiMe_3)_2]_2(THF)_2$ was prepared according to previously published procedure.[S1] 3,6-di-*tert*-butyl-1,8-bis(trimethylsilylethynyl)-9*H*-carbazole (**L^{1}H**)[S2] and 3,6-di-*tert*-butyl-1,8-bis(phenylethynyl)-9*H*-carbazole (**L^{2}H**)[S3] and were prepared according to the published. IR spectra were recorded as Nujol mulls on a Bruker-Vertex 70 spectrophotometer. Raman spectra in the region 80–3500 cm^{-1} for solid complexes sealed in capillaries were registered with using a Horiba Jobin Yvon Larbram 300 spectrometer equipped Olympus BX2 microscope (Olympus M-Plan 50x), cooled CCD detector and excitation 632.8 nm He Ne laser with power on sample 1 mW. The C, H, N elemental analyses were performed in the microanalytical laboratory of the G. A. Razuvaev Institute of Organometallic Chemistry. Samarium metal analysis were carried out by complexometric titration.[S4]

Synthesis of $Sm[3,6\text{-}Bu^t_2\text{-}1,8\text{-}(Me_3SiCC)_2Carb]_2$ (1): Carbazole **L^{1}H** (0.125 g, 0.26 mmol) and $Sm[N(SiMe_3)_2]_2(THF)_2$ (0.082 g, 0.13 mmol) were dissolved in toluene (10 mL). After 12 h at room temperature the formation of dark greenish brown microcrystalline solid of **1** was observed. Toluene was removed in vacuum and the brown solid residue was dried in vacuum for 30 min. Afterwards the reaction product was dissolved in THF/hexane mixture (approx. 1:2, 10 mL). Slow concentration of the resulted solution at ambient temperature resulted in the formation of dark greenish brown cubic crystals of **1**. The mother liquor was decanted, the crystals were washed with hexane (5 mL) and dried in vacuum for 30 min. Complex **1** was isolated in 75% yield (0.110 g, 0.10 mmol). Elemental analysis calculated for $C_{60}H_{80}N_2Si_4Sm$ (1091.99 g·mol^{-1}): C, 65.99; H, 7.38; N, 2.57; Sm, 13.77. Found: C, 70.10; H, 7.57; N, 2.41; Sm 13.94. IR (Nujol, KBr, ν, cm^{-1}): 2100 (s), 1420 (w), 1320 (w), 1265 (s), 1235 (m), 1200 (w), 1180 (w), 1040 (m), 1015 (m), 920 (w), 845 (s), 755 (s), 690 (m), 670 (m), 640 (m).

Synthesis of [3,6-Bu$^t_2$-1,8-(PhCC)$_2$Carb]$_2$SmN(SiMe$_3$)$_2$ (2): Carbazole **L^{2}H** (0.150 g, 0.31 mmol) and Sm[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ (0.095 g, 0.16 mmol) were dissolved in toluene (10 mL). After 12 h at room temperature the formation of orange crystalline solid of **2** was observed. Toluene was decanted, the crystals were washed with hexane (5 mL) and dried in vacuum for 30 min. Complex **2** was isolated in 65% yield (0.127 g, 0.10 mmol). Elemental analysis calculated for $C_{78}H_{82}N_3Si_2Sm$ (1267.99 g·mol^{-1}): C, 73.88; H, 6.52; N, 3.31; Sm, 11.86. Found: C, 73.49; H, 6.30; N, 3.52; Sm, 12.10. IR (Nujol, KBr, ν, cm^{-1}): 2180 (m), 1940 (w), 1755 (m), 1600 (S), 1485 (m), 1400 (m), 1315 (w), 1280 (m), 1255 (s), 1230 (m), 990 (s), 925 (w), 910 (w), 870 (s), 830 (m), 750 (s), 690 (s), 660 (w), 645 (m), 600 (m), 550 (m), 520 (m).

Calculation details. The QTAIM [S5] calculations were performed using MultiWFN program [S6] for X-ray geometry of **1** and **2** at the PBE0 [S7] level of theory using Def2-TZVP and Def2-SVP for light and Sm atoms, respectively.[S8,S9] It should be noted that SCF convergence are successfully achieved only for singlet and doublet multiplicity state for **1** and **2**, correspondingly. The complexes **1** and **2** exhibit a multi reference system, however any attempts to perform calculations at CASSCF level (namely, NEVPT2) with a different set of active spaces were unsuccessful. All calculation were performed using ORCA v. 5 program.[S10] To accelerate the process, the RIJCOSX [S11,S12,S13] approximation was utilized with Def2/J fitting basis set.[S14]

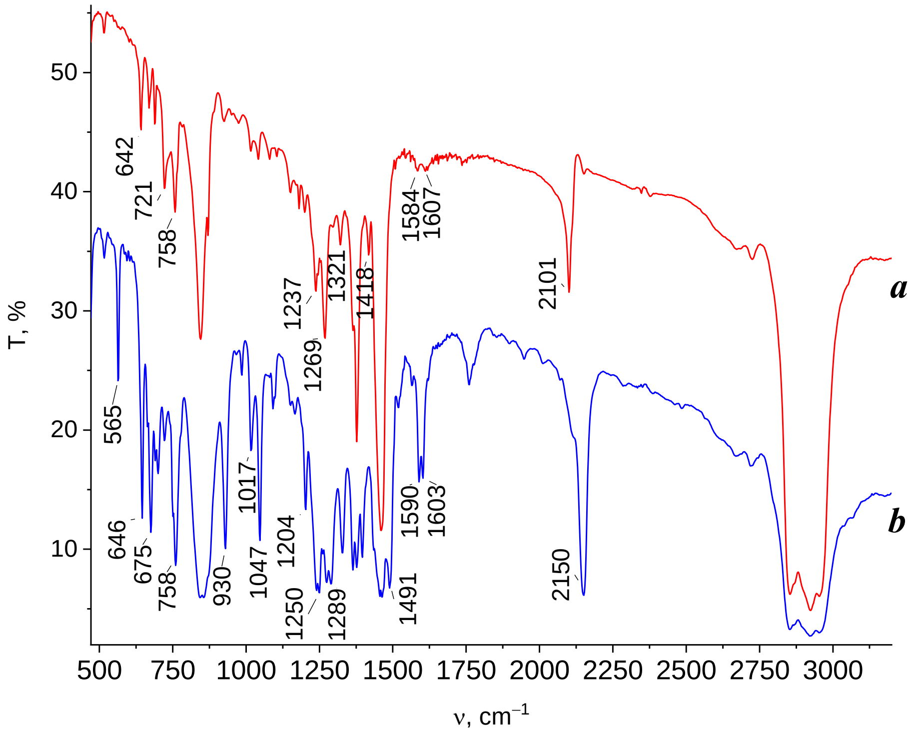


Figure S1. FTIR spectra in nujol for complex **1** (***a***) and the ligand **L^{1}H** (***b***).

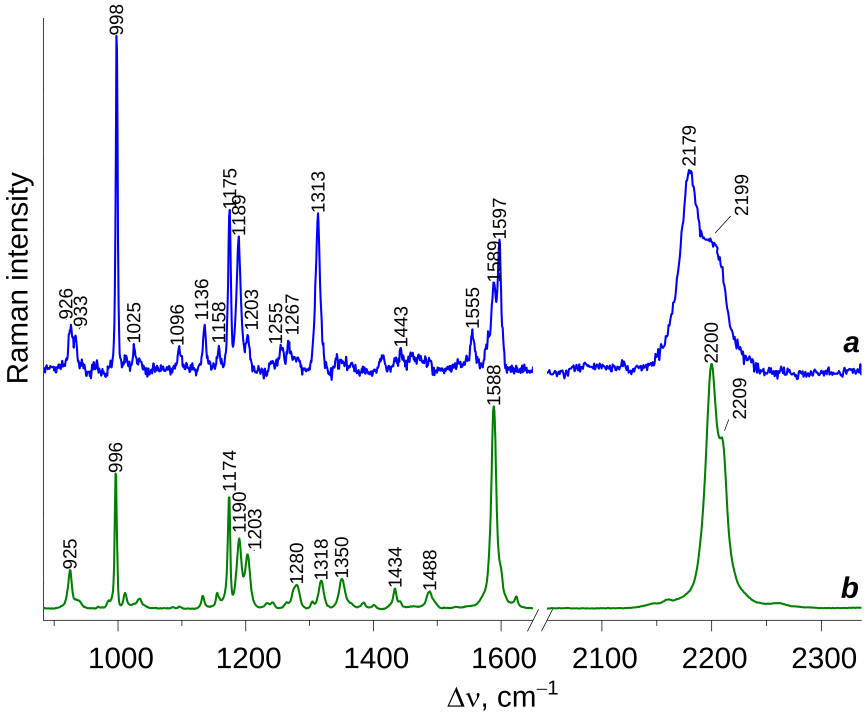
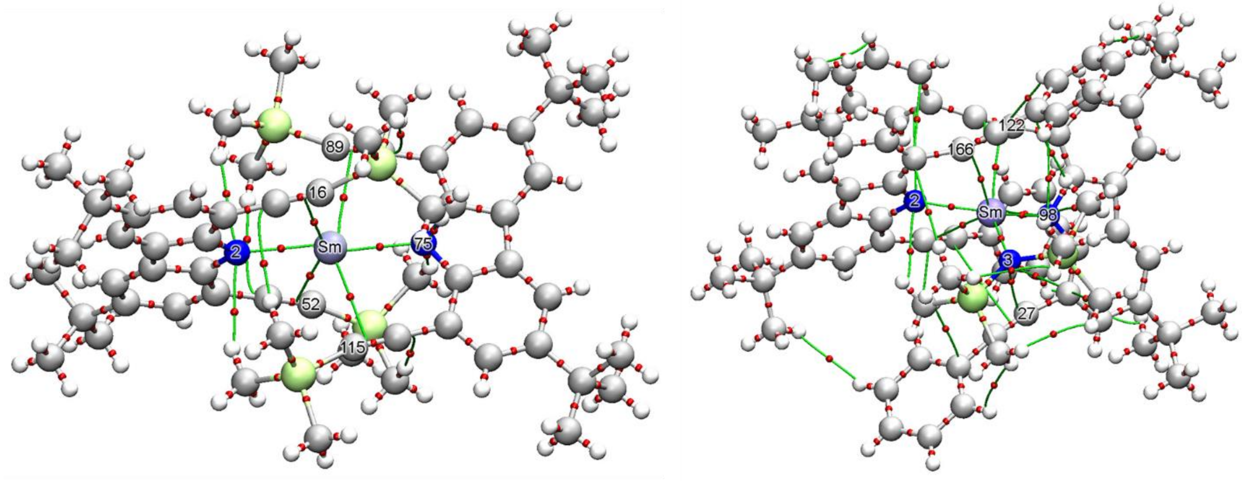


Figure S2. Raman spectra for the complex **2** (***a***) and the ligand **L^{2}H** (***b***).



a ***b***

Figure S3. The QTAIM molecular graphs for complexes **1** (**a**) and **2** (**b**). (Sm – purple, Si – green, C – grey, N – blue, H – white, BCP (3;−1) – red dots, bond paths – green lines).

Table S1. The selected QTAIM parameters for complexes **1** and **2**

BCP	distance, Å	$\rho(r)$, a.u	$\nabla^2\rho(r)$, a.u.	$H(r)$, a.u.	$V(r)$, a.u.	E_{cont}, kcal/mol
1						
Sm−N(75)	2.499	0.05220	0.16335	0.00555	−0.05193	16.3
Sm−N(2)	2.496	0.05228	0.16198	0.00564	−0.05177	16.2
Sm···C(16)	3.086	0.01674	−0.00005	0.00005	−0.01165	3.7
Sm···C(89)	3.084	0.01626	0.04921	0.00026	−0.01178	3.7
Sm···C(115)	3.085	0.01618	0.04819	0.00037	−0.01130	3.6
Sm···C(52)	3.085	0.01677	0.04598	0.00008	−0.01165	3.7
2						
Sm−N(2)	2.390	0.06433	0.19427	0.00797	−0.06450	20.2
Sm−N(3)	2.204	0.09556	0.29016	0.01980	−0.11214	35.2
Sm−N(98)	2.334	0.07068	0.22104	0.00984	−0.07495	23.5
Sm···C(27)	2.947	0.02146	0.05468	0.00068	−0.01503	4.7
Sm···C(122)	3.376	0.00870	0.02559	0.00058	−0.00523	1.6
Sm···C(166)	3.160	0.01223	0.03375	0.00031	−0.00783	2.5

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