In conclusion, intersections and hairpins are rather typical defects in the regular packing or ordering of the brushes in monolayers. This documents the essential differences in the adsorption behavior of linear flexible macromolecules and stiff brushes;[15–17] the latter are more likely to form trains rather than loops on the surface. A more perfect order—that is, straightening and disentangling of the brushes—may be enforced by charging the vinylpyridine units chemically. Therefore, such polyelectrolyte brushes may constitute a unique system for preparing striped patterns whose periodicity is defined on a sub 10 nm scale.

Experimental Section

The PVP macromonomer with a methacrylate end group was prepared by anionic polymerization as shown in Scheme 1. Tetrahydrofuran was dried over $LiAlH_4$, degassed by three freeze-thaw cycles on a vacuum line, and then distilled directly into the reaction vessel. 2-Vinylpyridine (2-VP) was dried over calcium hydride for 24 h, degassed, and distilled under reduced pressure. 2-VP (20–25 g) was dissolved in THF (≈ 500 mL), and the polymerization started at about −90 °C by *sec*-BuLi. The solution was dark red. After completion of the polymerization the "living" anions were terminated with excess ethylene oxide. Subsequently, the chains with terminal hydroxy groups were esterified with excess methacryloyl chloride at room temperature for 12 h. The resulting macromonomer was purified three times by precipitation of a solution of 2-propanol with petroleum ether (40–60 °C) and then freeze-dried in benzene.

For the free radical polymerization AIBN (20 mg; purified by recrystallization from methanol), was dissolved in 20 mL of acetone or pyridine and carefully degassed. The macromonomer (5 g) was then dissolved in a solution of the initiator (2.5 mL) for 12 h to yield an extremely viscous solution, which was kept at 60 °C in a thermostate bath for one week. During polymerization a phase separation occured into a polymacromonomer rich gel phase and a liquid phase; towards the end of the reaction only the gel phase was present. Addition of more acetone or pyridine resulted in a homogeneous solution, from which the polymer was precipitated with petroleum ether. The maximum yield of polymer was on the order of 70%. The unchanged macromonomer was fractionated off by precipitation with 2-propanol/petroleum ether (1/2).

The atomic force micrographs were recorded at ambient conditions with a Nanoscope III instrument (Digital Instruments, St. Barbara, USA) operating in the tapping mode [6] at a resonance frequency of about 300 kHz. The Si probes had a spring constant of about 50 $N\,m^{-1}$. In this mode a cantilever with a sharp tip is oscillated by a piezo driver near its resonance frequency. As the tip taps the surface both the amplitude and the phase of the oscillation change, which allows recording of images with a topographic or viscoelastic contrast [7–9].

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The First Structurally Authenticated σ-Bonded Organosamarium(II) Derivative and Its Reaction with Benzophenone

William Clegg, Colin Eaborn, Keith Izod,*
Paul O'Shaughnessy, and J. David Smith

Until recently the organometallic chemistry of the three lanthanide elements stable in the +2 oxidation state (Sm, Eu, Yb) was confined to compounds containing cyclopentadienyl-type ligands.[1] Despite much progress in the synthesis of σ-alkyl derivatives of ytterbium(II) and europium(II),[1b] such as the dialkyl compounds $Yb\{C(SiMe_3)_3\}_2$ and $Eu\{C(SiMe_3)_3\}_2$,[2,3] the isolation of a σ-bonded organosamarium(II) complex has remained an elusive goal. We now describe the synthesis and molecular structure of **1**, which contains Sm–C σ bonds, and report its reaction with benzophenone to give the ketyl radical anion complex **2**. Compound **1** was obtained in high yield from the reaction of $[SmI_2(thf)_2]$ with two equivalents of $K\{C(SiMe_3)_2(SiMe_2OMe)\}$ in THF and isolated as air-sensitive, deep green-black crystals.

$[Sm\{C(SiMe_3)_2(SiMe_2OMe)\}_2(thf)]$ **1**

$[Sm\{C(SiMe_3)_2(SiMe_2OMe)\}_2(OCPh_2)]$ **2**

An X-ray diffraction study[4] of **1** revealed that the samarium atom lies in a distorted square pyramidal environment with each alkyl ligand bound through both its carbanion center and the oxygen atom of its methoxy substituent to give a four-membered chelate ring. The coordination sphere of samarium is completed by a molecule of THF at the apex of the pyramid (Figure 1). The Sm–C1 and Sm–C2 distances of 2.787(5) and 2.845(5) Å, respectively, are the first Sm^{II}–C σ bonds lengths to be measured. These values are about 0.3–0.5 Å larger than those found for the Sm^{III}–C(sp^3) bonds in $Sm\{CH(SiMe_3)_2\}_3$ (2.33(2) Å)[5] and for the terminal alkyl group in $[(thf)Li(\mu\text{-}CH_2SiMe_3)(\mu\text{-}OAr)Sm(CH_2SiMe_3)(\mu\text{-}OAr)_2Li(thf)]$ (2.451(10) Å; Ar = 2,6-*i*PrC_6H_3).[6] A smaller difference of about 0.19 Å between the Sm^{II}–C and the Sm^{III}–C σ bonds would be expected from consideration of the reported ionic radii for Sm^{II} and Sm^{III}.[7] The Sm–O1, Sm–O2, and Sm–O(thf) distances in **1** are similar to several previously determined Sm^{II}–O(thf) distances.[8,9]

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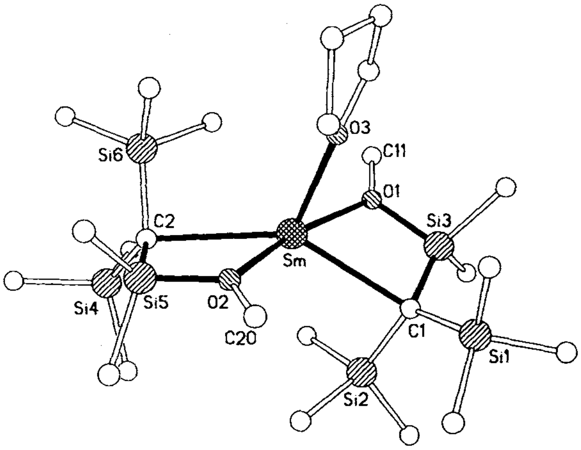

Figure. 1. Molecular structure of **1**. Selected bond lengths [Å] and angles [°]: Sm – C1 2.787(5), Sm – C2 2.845(5), Sm – O1 2.570(3), Sm – O2 2.520(3), Sm – O3 2.545(4); C1-Sm-O1 62.11(12), C1-Sm-C2 144.67(12), C1-Sm-O3 101.06(13), O3-Sm-O1 90.40(13), C2-Sm-O3 110.43(13), O2-Sm-O3 84.55(12).

Samarium diiodide is widely used as a reagent in organic synthesis and is believed to give organosamarium intermediates in Barbier-type SmI_2-mediated additions of alkyl halides to ketones.[10,11] We were interested to see whether ketones would undergo a Grignard-type reaction with **1** or give a ketyl radical anion complex similar to the recently described $[Sm^{III}(OC_6H_3\text{-}2,6\text{-}t\text{Bu-}4\text{-Me})_2(OC_{13}H_8)(thf)_2]$ (**3**), isolated as an intermediate in the pinacol coupling of fluorenone.[12]

Reaction of **1** with one equivalent of benzophenone in light petroleum resulted in an immediate color change from dark green to deep purple. Crystallization of the resulting compound **2** from methylcyclohexane gave dark purple crystals, which exhibited broad peaks in their ^1H NMR spectrum that could be assigned to the alkyl ligands, but no signals for the benzophenone.

An X-ray crystallographic study revealed that **2** has a very similar molecular structure to **1**,[13] but with a molecule of benzophenone bound through its oxygen atom in place of the THF (Figure 2). The essentially isostructural nature and identical coordination numbers of **1** and **2** allow the bond lengths and angles within the two molecules to be compared directly and provide a method for determining whether the benzophenone is bound as a neutral ketone or as a ketyl radical anion. The Sm – C1 and Sm – C2 distances in **2** are 2.625(5) and 2.631(5) Å, respectively, approximately 0.19 Å shorter than the corresponding bond lengths in **1** (consistent with a change in oxidation state from Sm^{II} to Sm^{III}).[7] Similarly, the Sm – O1 and Sm – O2 distances of 2.367(3) and 2.387(3) Å in **2** are approximately 0.17 Å shorter than the corresponding distances in **1**. This strongly indicates that **2** is a Sm^{III} complex of a ketyl radical anion. In support of this, bond lengths and angles within the benzophenone fragment are very similar to those found for fluorenone in **3**.[12] The absence of signals due to benzophenone in the ^1H NMR spectrum of **2** is also consistent with its being bound as a delocalized ketyl radical anion.

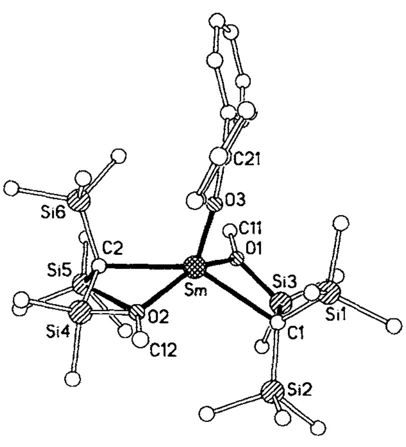

Figure. 2. Molecular structure of **2**. Selected bond lengths [Å] and angles [°]: Sm – C1 2.625(5), Sm – C2 2.631(5), Sm – O1 2.367(3), Sm – O2 2.387(3), Sm – O3 2.093(3), C21 – O3 1.346(6); C1-Sm-O1 66.10(13), C1-Sm-C2 142.33(15), C1-Sm-O3 105.81(14), O3-Sm-O1 107.93(13), C2-Sm-O3 111.67(14), O2-Sm-O3 99.12(12).

In contrast to the behavior observed for **3**, we observed no change upon dissolution of **2** in noncoordinating solvents such as light petroleum or methylcyclohexane. This may be because the sterically demanding alkyl ligands in **2** impede further reaction.

Experimental Section

1: A solution of $[K\{C(SiMe_3)_2(SiMe_2OMe)\}]$ (0.99 g, 3.45 mmol) in THF (30 mL) was added to a solution of $[SmI_2(thf)_2]$ (0.97 g, 1.77 mmol) in THF (20 mL). The mixture was stirred at room temperature for three days, the solvent then removed under reduced pressure, and the residue extracted with methylcyclohexane (40 mL). The extract was filtered and the filtrate concentrated to 10 mL, then kept at – 30 °C for 12 h to give dark green crystals of **1**. Yield 0.90 g (71 %), m.p. 120 °C (decomp); elemental analysis calcd. for $C_{24}H_{62}O_3Si_6Sm$: C 40.14, H 8.71;. found C 39.23, H 8.81; ^1H NMR (500 MHz, C_6D_6, 25 °C): $\delta = -9.22$ (s, 6 H; $SiMe_3$), – 7.06 (s, 3 H; MeO), 4.28 (s, 18 H; $SiMe_3$), 6.94 (s, br, 2 H; THF), 19.29 (s, br, 2 H, THF); EIMS (70 eV): *m*/*z* (%): 648 (18) $[M^+ - THF]$, 249 (20) $[C(SiMe_3)_2(SiMe_2OMe)$ (R)], 233 (100) [RH – Me], 217 (30) [RH – MeO], 73 (90) $[Me_3Si]$.

2: A solution of benzophenone (0.01 g, 0.2 mmol) in light petroleum (b.p. 40 – 60 °C, 5 mL) was added to a solution of **1** (0.15 g, 0.21 mmol) in the same solvent (15 mL). The mixture was stirred for 1 h and the solvent then removed under vacuum. The residue was crystallized from cold (– 30 °C) methylcyclohexane (2 mL) to give deep purple crystals of **2**. Yield 0.08 g (69 %), m.p. 105 °C (decomp); ^1H NMR (500 MHz, C_6D_6, 25 °C): $\delta = -1.81$ (s, 3 H; OMe), – 0.12 (s, br, 18 H; $SiMe_3$), 3.25 (s, br, 6 H; $SiMe_2$).

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[4] Crystal data for $C_{24}H_{62}O_3Si_6Sm$ **1**: $M_r = 717.6$, crystal dimensions $0.28 \times 0.16 \times 0.12\ mm^3$, monoclinic, $P2_1$, $a = 9.4931(9)$, $b = 16.5417(16)$, $c = 12.3227(12)$ Å, $\beta = 106.773(3)°$, $V = 1852.7(3)$ Å^3, $Z = 2$, $\rho_{calcd.} = 1.286\ g\,cm^{-3}$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\mu = 1.80\ mm^{-1}$, $T = 160$ K. 11830 data (6524 unique, $R_{int} = 0.0267$, $2\theta < 56.8°$) were collected on a Siemens SMART CCD area detector diffractometer using 0.3° steps in ω and were corrected semiempirically for absorption (transmission 0.621 – 0.789). The structure was solved by heavy-atom methods and refined on F^2 values for all data (G. M. Sheldrick, SHELXTL-manual, Siemens Analytical X-ray Instruments Inc., Madison, USA, **1994**) to give $R_w = \{\Sigma[w(F_o^2 - F_c^2)]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.0707$, conventional R value $R = 0.0312$ for F values of 5928 reflections with $F_o^2 > 2\sigma(F_o^2)$, $S = 1.007$ for 336 parameters. All non-H atoms were refined anisotropically, H atoms were constrained with a riding model. Twofold disorder was resolved for one CH_2 group of the THF molecule. The residual electron density extremes were +0.93/ – 0.67 e Å^{-3} [13b].

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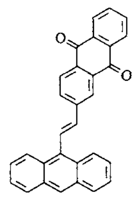
[13] a) Crystal data for $C_{33}H_{64}O_3Si_6Sm$ **2**: $M_r = 827.7$, crystal dimensions $0.20 \times 0.10 \times 0.08$ mm^3, monoclinic, $P2_1/c$, $a = 14.8555(2)$, $b = 12.5108(2)$, $c = 23.9352(3)$ Å, $\beta = 105.960(2)°$, $V = 4276.99(10)$ Å^3, $Z = 4$, $\rho_{calcd.} = 1.285$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 1.57$ mm^{-1}. 25355 data (9695 unique, $R_{int} = 0.0826$, $2\theta < 56.7°$), transmission 0.584–0.890. Methods were as for **1**. $R_w = 0.0951$, $R = 0.0551$ (5710 F values), $S = 0.984$ for 403 parameters, residual electron density extremes $+1.02/-1.56$ e Å^{-3}. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-100466. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ (fax: Int. code + (1223)336-033; e-mail: deposit@chemcrys.cam.ac.uk).

Stuctural Reorganization of Anthracene-Bridged Stilbenoids by Oxidation and Reduction[**]

Andreas Knorr and Jörg Daub[*]

Compounds with conjugated extended π-electron systems are most promising for generating new optoelectronic materials and models for energy and electron transfer as well as for mimicking charge separation. Furthermore, there are additional conceivable applications in display and optical storage devices, electrochromic materials, and systems for optoelectronic switching.[1] Simple stilbenoid pyrenes and anthracenes were recently studied due to their electrochemically generated luminescence (ECL) and application in organic light-emitting diodes (OLEDs).[2] Here we report the oxidation and reduction properties of anthracene systems **5** and **6**, which are composed of electron transfer active stilbenoid subunits that are covalently linked through the 9,10-positions of anthracene. The investigations by cyclic voltammetry and spectroelectrochemical combination techniques were supplemented by semiempirical quantum mechanical calculations.

Derivatives **1**, **4**, and **5** was synthesized by a Wittig reaction of [2-(anthraquinone)methyl]triphenylphosphonium bromide with anthracene-9-carbaldehyde (formation of **1**) or from [3-(10-methyl-10*H*-phenothiazinyl)methyl]triphenylphosphonium bromide with 10-methyl-9-anthracenecarbaldehyde (formation of **4**) or anthracene-9,10-dicarbaldehyde (formation of **5**). Compound **2** was obtained by the reaction of 5,10-dihydro-5,10-dimethyl-2-phenazincarbaldehyde with (9-anthrylmethyl)triphenylphosphonium bromide, and **6** was synthesized by a random 1:1 Wittig reaction of anthracene-9,10-dicarbaldehyde with [11-(dibenzo[*a*,*c*]phenazinyl)methyl]triphenylphosphonium bromide followed by treatment of the formed monoaldehyde with [3-(10-methyl-10*H*-phenothiazinyl)methyl]triphenylphosphonium bromide. Compound **3** was obtained by the reaction of 10-methyl-9-anthracenecarbaldehyde with [11-(dibenzo[*a*,*c*]phenazinyl)methyl]triphenylphosphonium bromide. All reactions, except for the synthesis of **1** (in EtOH/NEt$_3$), were carried out in THF under an N_2 atmosphere with *n*BuLi as base,[3] and led exclusively to (*E*)-stilbenes; the analogous (*Z*)-stilbenes could never be detected.[4]



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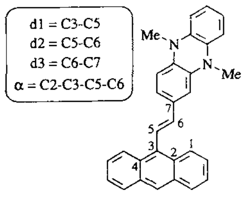

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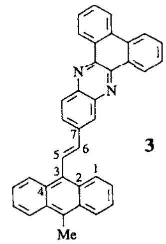

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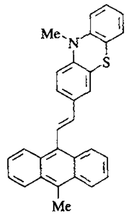

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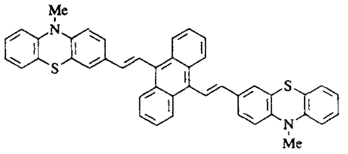

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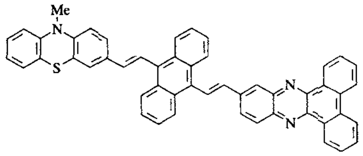

6

Investigations of **1**–**6** by cyclic voltammetry show reversible oxidations and/or reductions. With the exception of the two-electron wave for the oxidation of **5**, all redox reactions involve the transfer of one electron. The electrochemical processes take place at significantly lower potential than for the corresponding basis compounds (Table 1), which indicates an interaction between the functional groups and the anthracene unit. Even the comparison of the oxidations of **4** and **5** as well as of the second reduction steps of **3** and **6** demonstrates the effect of this interaction (Table 1).

Spectroelectrochemistry confirms the findings of cyclic voltammetry and provides insight into the absorption characteristics of the radical ions and respective dications and dianions. Compounds **1**–**6** show a significant red shift of the lowest energy absorption bands when compared with the corresponding absorption bands for radical ions of the basis compounds (Table 1). Doubly charged species such as dianions $\mathbf{1}^{2-}$, $\mathbf{3}^{2-}$, and $\mathbf{6}^{2-}$ or dications $\mathbf{2}^{2+}$ and $\mathbf{5}^{2+}$ exhibit strong absorptions in the near-infrared region, which is in agreement with the presence of a highly delocalized quinoid species (Table 1 as well as Figures 1 and 2).

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