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Article

Homoleptic Heavy Alkaline Earth and Europium Triazenides

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The σ-bond metathesis reaction between $PhSiH_3$ and the heteroleptic metal pentafluorophenyl compounds $[Dmp(Tph)N_3MC_6F_5(thf)_n]$ (Dmp = 2,6-$Mes_2C_6H_3$ with Mes = 2,4,6-$Me_3C_6H_2$; Tph = 2-$TripC_6H_4$ with Trip = 2,4,6-$^iPr_3C_6H_2$; n = 1, 2; M = Sr, Ba, Eu) supported by sterically crowded, biphenyl- and terphenyl-substituented triazenido ligands afforded the first homoleptic stontium, barium, and europium triazenides $[M\{N_3Dmp(Tph)\}_2]$ {M = Sr (**2**), Ba (**4**), Eu (**5**)}. Crystallization of **2** from an *n*-heptane/1,2-dimethoxyethane mixture gave the complex $[Sr\{N_3Dmp(Tph)\}_2(dme)]$ (**3**). All new compounds have been characterized by ^1H and ^{13}C NMR spectroscopy (not **5**), elemental analysis, IR spectroscopy (**5** only), and X-ray crystallography. In the solid-state structures, the first coordination sphere of the metal cations consists of four nitrogen atoms of the two bidentate triazenide ligands. Additional metal-η^n-π-arene-interactions of different hapticity n (n = 3−6) are observed to the flanking arms of the terphenyl substituents.

Introduction

The design and development of alternative ligand systems capable of stabilizing monomeric metal complexes while provoking novel reactivity remains one of the most intensely studied areas of organometallic chemistry.[1] Exploration of this field is driven by the potential use of these complexes in catalysis and organic synthesis. Examples of monoanionic chelating N-donor ligands that have received much attention include the β-diketiminate[2] and the amidinate[3] ligand systems. Much less attention has been given to the closely related triazenides.[4] We recently succeeded in the preparation of derivatives of aryl-substituted, sterically crowded triazenido ligands, that are bulky enough to prevent undesirable ligand redistribution reactions.[5−10] These ligands were used to stabilize the first examples of structurally characterized aryl compounds of the heavier alkaline earth metals Ca, Sr, and Ba[5] and unsolvated pentafluorophenyl organyls of the divalent lanthanides Yb and Eu.[6] We have also examined the unusual "inverse" aggregation behavior of alkali metal triazenides in their solid-state structures that can be traced back to a different degree of metal$\cdots\pi$-arene interactions to pending aromatic substituents.[7] A series of homologous potassium and thallium complexes crystallizes in isomorphous cells and consists of the first examples of isostructural molecular species reported for these elements.[9]

As we have reported earlier, heteroleptic metal pentafluorophenyl triazenides are accessible in tetrahydrofuran as solvent by a convenient one-pot transmetalation/deprotonation reaction[11] from the triazene $HN_3(Dmp)Tph$ (Dmp = 2,6-$Mes_2C_6H_3$ with Mes = 2,4,6-$Me_3C_6H_2$; Tph = 2-$TripC_6H_4$ with Trip = 2,4,6-$^iPr_3C_6H_2$), bis(pentafluorophenyl)mercury, and the corresponding alkaline-earth[5] or rare earth metal.[6] After crystallization from *n*-heptane, either the THF-free

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compounds $[M(C_6F_5)\{N_3(Dmp)Tph\}]$ (M = Sr, Ba, Yb, Eu) or the solvate $[M(C_6F_5)\{N_3(Dmp)Tph\}(thf)]$ (M = Ca) were obtained. We have now examined the propensity of these compounds to act as precursors for molecular alkaline-earth and rare earth metal fluorides $[MF\{N_3(Dmp)Tph\}(thf)_x]$ or homoleptic triazenides $[M\{N_3(Dmp)Tph\}_2]$.

It was previously shown by Walsh et al.[12] that solvated magnesium and calcium bis(triazenido) complexes of the composition $[M(N_3Tol_2)_2(Solv)_2]$ (M = Mg, Solv = thf; M = Ca, Solv = dme) could be prepared by salt metathesis or protonolysis reactions. Using the bulkier bis-(2,6-di-iso-propylphenyl)triazenide ligand $[N_3Dip_2]^-$ (with Dip = 2,6-di-*i*-propylphenyl), Hill et al. have demonstrated recently that heteroleptic calcium and strontium triazenides such as the complexes $[Ca(N_3Dip_2)\{N(SiMe_3)_2\}(thf)_2]$, $[CaI(N_3Dip_2)(thf)_2]_2$, and $[Sr(N_3Dip_2)\{N(SiMe_3)_2\}(thf)_2]$ are accessible.[10b] However, the autors noted the kinetic lability of these species in solution with respect to ligand scrambling reactions. From these mixtures the strontium complex $[Sr(N_3Dip_2)_2(thf)_2]$ was isolated while the homologous calcium compound $[Ca(N_3Dip_2)_2(thf)]$ was prepared independently. Attempts to sythesize a similar barium complex afforded the potassium barate $[K(thf)_3Ba(N_3Dip_2)\{N(SiMe_3)_2\}_2(thf)]$ that showed an unusual coordination mode involving both terminal and internal nitrogen atoms of the $[N_3Dip_2]^-$ ligand in the solid state structure.

Experimental Section

General Procedures. All manipulations were performed by using standard Schlenk techniques under an inert atmosphere of purified argon and solvents freshly distilled from Na wire or $LiAlH_4$. The triazene $Dmp(Tph)N_3H$ (**1**) was synthesized as previously described.[5] NMR spectra were recorded on Bruker AC250 or AM400 instruments and referenced to solvent resonances. IR spectra (Nujol mull, CsBr plates) have been obtained in the range 4000−200 cm^{-1} with a Perkin-Elmer paragon 1000 PC spectrometer. Mass spectra were recorded with a Varian MAT711 or Finnegan MAT95 instrument.

$[SrN_3(Dmp)Tph\}_2]$ (2) and $2\cdot(C_6H_6)_{1.5}$. Bis(pentafluorophenyl)mercury (0.802 g, 1.5 mmol) was added at ambient temperature to a stirred mixture of strontium pieces (2.1 g, 24 mmol) and **1** (0.953 g, 1.5 mmol) in THF (50 mL). After stirring overnight a color change from yellow to deep green was observed. The solvent was removed under reduced pressure, the green residue was treated with *n*-heptane, and solid byproducts were separated by centrifugation. Phenylsilane (0.15 mL, 1.5 mmol) was added to the resulting yellow solution and stirring was continued for 17 h at 70 °C. Again, solid byproducts were separated by centrifugation and the volume of the obtained yellow solution was reduced to incipient crystallization under reduced pressure. Storage in a −20 °C freezer overnight afforded **2** as bright yellow microcrystalline material. Yield: 0.42 g (0.309 mmol, 41% {ligand based}). Crystals of the solvate $\mathbf{2}\cdot(C_6H_6)_{1.5}$ that were used for X-ray diffraction experiments and elemental analysis were obtained by crystallization from an *n*-heptane/benzene mixture.

^1H NMR (400.1 MHz, $[D_8]$toluene): δ 0.89, 1.15, 1.17 (3 × d, $^3J_{HH}$ = 6.7 Hz, 3 × 12H, *o*+*p*-CH(C*H*$_3$)$_2$), 2.16 (s, 24H, *o*-CH$_3$), 2.12 (s, 12H, *p*-CH$_3$), 2.69 (sep, $^3J_{HH}$ = 6.7 Hz, 4H, *o*-C*H*(CH$_3$)$_2$), 2.92 (sep, $^3J_{HH}$ = 6.7 Hz, 2H, *p*-C*H*(CH$_3$)$_2$), 6.72 (s, 8H, *m*-Mes), 6.53−7.23 (m, 14H, various Aryl-H), 7.14 (s, 4H, *m*-Trip). ^{13}C NMR (62.9 MHz, $[D_8]$toluene): δ 20.9 (*p*-*C*H$_3$), 21.1 (*o*-*C*H$_3$), 23.0, 23.7, 24.7 (*o*+*p*-CH(*C*H$_3$)$_2$), 30.5 (*o*-*C*H(CH$_3$)$_2$), 33.1 (*p*-*C*H(CH$_3$)$_2$), 121.6, 122.2, 125.4, 125.5, 126.1, 128.2, 129.0, 129.3 (aromatic CH), 128.5, 130.9, 134.9, 135.8, 136.0, 137.2, 139.3, 147.7, 148.0, 149.3 (aromatic C). Anal calcd for $C_{99}H_{113}N_6Sr$: C, 79.63; H, 7.72; N, 6.19. Found: C, 79.20; H, 7.95; N 5.88.

$[Sr\{N_3(Dmp)Tph\}_2(dme)]\cdot(C_7H_{16})$ ($3\cdot(C_7H_{16})$). The compound was synthesized by crystallization of 0.30 g (0.22 mmol) of **2** from a mixture of 5 mL *n*-heptane and two drops 1,2-dimethoxyethane at −20 °C. Yield: 0.19 g (0.12 mmol, 55%). The crystals used for characterization contained one molecule of heptane per formular unit.

^1H NMR (250.1 MHz, $[D_{10}]$DME): δ 0.77, 0.94, 1.22 (3 × d, $^3J_{HH}$ = 6.95 Hz, 3× 12H, *o*+*p*-CH(C*H*$_3$)$_2$), 0.88 (m, 6H, heptane), 1.28 (m, 10H, heptane), 1.91 (s, 24H, *o*-CH$_3$), 2.18 (s, 12H, *p*-CH$_3$), 2.55 (sep, $^3J_{HH}$ = 6.8 Hz, 4H, *o*-C*H*(CH$_3$)$_2$), 2.83 (sep, $^3J_{HH}$ = 6.9 Hz, 2H, *p*-C*H*(CH$_3$)$_2$), 3.22 (m, 4H, OCH$_2$), 3.40 (m, 6H, OCH$_3$), 6.75 (s, 8H, *m*-Mes), 6.77−7.10 (m, 7H, various Aryl-H), 6.96 (s, 4H, *m*-Trip). ^{13}C NMR (100.6 MHz, $[D_{10}]$DME): δ 20.9 (*p*-*C*H$_3$), 21.0 (*o*-*C*H$_3$), 23.9, 24.2, 24.5 (*o*+*p*-CH(*C*H$_3$)$_2$), 31.0 (*o*-*C*H(CH$_3$)$_2$), 35.0 (*p*-*C*H(CH$_3$)$_2$), 57.8 (OCH$_3$), 71.7 (OCH$_2$), 114.2, 121.9, 122.5, 124.8, 126.1, 127.3, 127.7, 129.9 (aromatic CH), 128.2, 130.2, 134.1, 135.1, 136.1, 136.4, 137.8, 138.5, 148.0, 148.9 (aromatic C), 14.3, 23.4, 29.3, 32.6 (*n*-heptane); Anal calcd for $C_{101}H_{130}SrN_6$: C, 78.38; H, 8.47; N, 5.43. Found: C, 77.99; H, 8.32; N 5.52.

$[BaN_3(Dmp)Tph\}_2]$ (4). The synthesis was accomplished in a manner similar to the preparation of **2** with an excess of barium pieces, triazene **1** (0.953 g, 1.5 mmol), and phenylsilane (0.15 mL, 1.5 mmol). Yield: 0.12 g (0.085 mmol, 11%) as a bright yellow powder; ^1H NMR (400.1 MHz, $[D_6]$benzene): δ 0.63, 0.78, 1.14 (3 × d, $^3J_{HH}$ = 6.9 Hz, 3 × 12H, *o*+*p*-CH(C*H*$_3$)$_2$), 2.04 (s, 24H, *o*-CH$_3$), 2.17 (s, 12H, *p*-CH$_3$), 2.57 (sep, $^3J_{HH}$ = 7.0 Hz, 4H, *o*-C*H*(CH$_3$)$_2$), 2.89 (sep, $^3J_{HH}$ = 7.0 Hz, 2H, *p*-C*H*(CH$_3$)$_2$), 6.77 (s, 8H, *m*-Mes), 6.46−7.28 (m, 14H, various Aryl-H), 7.24 (s, 4H, *m*-Trip). ^{13}C NMR (62.9 MHz, $[D_6]$benzene): δ 20.8 (*p*-*C*H$_3$), 21.0 (*o*-*C*H$_3$), 23.1, 24.2, 24.2 (*o*+*p*-CH(*C*H$_3$)$_2$), 30.5 (*o*-*C*H(CH$_3$)$_2$), 33.8 (*p*-*C*H(CH$_3$)$_2$), 116.9, 122.0, 122.0, 123.1, 127.7, 128.6, 129.1, 129.4 (aromatic CH), 128.8, 131.5, 136.6, 137.4, 142.0, 142.4, 148.0, 150.3, 150.6, 152.1 (aromatic C); Anal calcd for $C_{90}H_{104}BaN_6$: C, 76.82; H, 7.45; N, 5.97. Found: C, 76.90; H, 7.40; N 5.87.

$[EuN_3(Dmp)Tph\}_2]\cdot(C_7H_{16})$ ($5\cdot(C_7H_{16})$). The synthesis was accomplished in a manner similar to the preparation of **2** with an excess of europium pieces, triazene **1** (0.95 g, 1.5 mmol), and phenylsilane (0.15 mL, 1.5 mmol). Storage of the obtained *n*-heptane solution at −20 °C for several days afforded $\mathbf{5}\cdot(C_7H_{16})$ as orange crystals. Yield: 0.58 g (0.38 mmol, 51%); mp: 190−195 °C (dec.); IR (Nujol): 1605 m, 1580 w, 1504sh, 1405 m 1283 ms br, 1192 s, 1178 s, 1128 m, 1097 w, 1057 w, 1067 w, 1052 mw, 1033 w br, 1002 m, 934 w, 877 ms, 866 ms, 847 s, 803 m, 787 m, 780 ms, 766 vs, 759 s, 754 s, 743 vs, 718 ms, 678 m, 651 ms, 646 ms, 626 w, 555 w, 540 w, 522 m, 514 m, 500 w, 458 m, 430 w, 411 w; Anal. Calcd for $C_{97}H_{120}EuN_6$: C, 76.55; H, 7.95; N, 5.52. Found: C, 75.68; H, 7.94; N 5.51.

X-ray Crystallography. X-ray-quality crystals were obtained as described in the Experimental section. Crystals were removed from Schlenk tubes and immediately covered with a layer of viscous hydrocarbon oil (Paratone N, Exxon). A suitable crystal was selected, attached to a glass fiber, and instantly placed in a low-temperature N_2-stream.[13a] All data were collected at 173 K using a Siemens P4 diffractometer. Crystal data are given in Table 1. Calculations were performed with the SHELXTL PC 5.03[13b] and SHELXL-97[13c] program system installed on a local PC. The structures were solved by direct methods and refined on

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Table 1. Selected Crystallographic Data for Compounds

	$\mathbf{2}\cdot(C_6H_6)_{1.5}$	$\mathbf{3}\cdot(C_7H_{16})$	**4**	$\mathbf{5}\cdot(C_7H_{16})$
formula	$C_{99}H_{113}N_6Sr$	$C_{101}H_{130}N_6O_2Sr$	$C_{90}H_{104}BaN_6$	$C_{97}H_{120}N_6Eu$
molecular mass	1474.57	1547.73 [1447.53]^e	1407.14	1521.95 [1421.75]^e
color, habit	yellow, prism	yellow, prism	yellow, prism	orange, prism
cryst size (mm)	0.75 × 0.50 × 0.45	0.35 × 0.20 × 0.15	0.30 × 0.15 × 0.10	0.50 × 0.35 × 0.35
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/c$	$Pccn$	$C2/c$	$P2_1/c$
a (Å)	14.450(4)	15.1920(19)	26.840(4)	14.348(3)
b (Å)	23.779(4)	21.588(2)	16.452(2)	24.251(4)
c (Å)	24.628(5)	26.639(4)	19.209(3)	24.394(3)
α (deg)	90	90	90	90
β (deg)	95.356(18)	90	113.820(11)	96.046(12)
γ (deg)	90	90	90	90
V (Å^3)	8425(3)	8736.7(19)	7759.6(19)	8441(2)
Z	4	4	4	4
d_{calc} (g/cm^3)	1.163	1.177 [1.101]^e	1.204	1.198 [1.119]^e
μ (mm^{-1})	0.690	0.670 [0.665]^e	0.560	0.792 [0.787]^e
2θ range (deg)	4−50	5−48	4−48	3−52
collected data	15903	6945	6179	17238
unique data/R_{int}	14832/0.032	6828/0.043	6037/0.056	16557/0.039
data with $I > 2\sigma(I)$ (N_o)	7812	2672	3231	11251
no. of parameters (N_p)	979	478	474	903
no. of restraints	0	2	6	0
$R1$ ($I > 2\sigma(I)$)^b	0.055	0.061	0.048	0.035
$wR2$ (all data)^c	0.127	0.158	0.087	0.083
GOF ^{d}	0.838	0.734	0.663	0.849
resd dens (e/Å^3)	−0.62/0.47	−0.50/0.49	−0.83/0.44	−0.50/0.75

^{a}All data were collected at 173 K, using Mo Kα (λ = 0.71073 Å) radiation. $^b R1 = \sum(||F_o|-|F_c||)/\sum(|F_o|)$. $^c wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. ^{d}GOF $= \{\sum[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$. ^{e}Values in brackets refer to the refinement that omits contributions from the solvent (see the Experimental Section).

F_o^2 by full-matrix least-squares refinement. Absorption corrections were applied by using semiempirical ψ-scans, and anisotropic thermal parameters were included for all non-hydrogen atoms. In **3**, the methyl carbon atoms of a disordered isopropyl group were refined with split positions and side occupation factors of 0.54 (C442) and 0.46 (C444). The corresponding C441−C442 and C441−C444 distances were restrained with DFIX commands. In **4**, the methyl carbon atoms of a disordered isopropyl group were refined with split positions and side occupation factors of 0.50 for C462/C464 and C463/C465. The corresponding C461−C46*n* (n = 2−5) were restrained with SADI commands. Additional *n*-heptane molecules were located in accessible cavities of the structures of **3** and **5**. Since they were heavily disordered their contribution was eliminated from the reflection data, using the BYPASS method[13d] as implemented in the SQUEEZE routine of the PLATON98[13e] package. Final R values are listed in Table 1. Important bond parameters are given in Figures 1−3 and in Table 2. Further details are provided in the Supporting Information. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-751109 {$\mathbf{2}\cdot(C_6H_6)_{1.5}$}, -751110 {$\mathbf{3}\cdot(C_7H_{16})$}, -751111 (**4**), and -751112 {$\mathbf{5}\cdot(C_7H_{16})$}. Copies of the data can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax +(44)-1223-336-033; e-mail deposit@ccdc.cam.ac.uk).

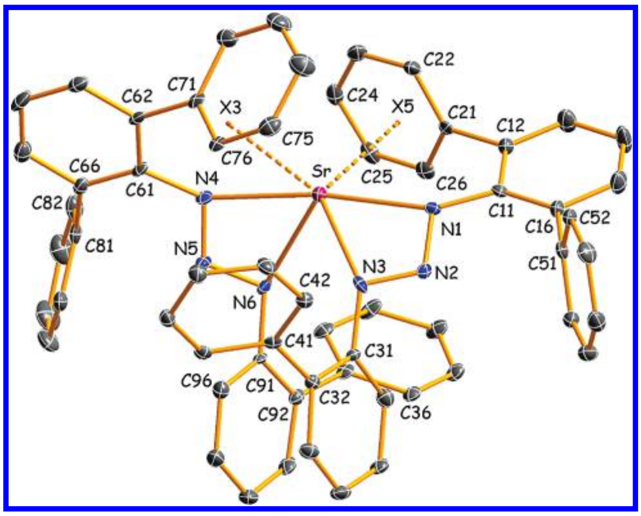

Figure 1. Molecular structure of **2** with thermal ellipsoids set to 30% probability. Hydrogen atoms, methyl and *iso*-propyl groups have been omitted for clarity. Selected bond lengths (Å), angles (deg), and dihedral angles (deg) are listed in Table 2.

Results and Discussion

Syntheses. The synthesis of soluble compounds with bonds between fluorine atoms and the heavier alkaline-earth metals calcium, strontium, or barium is hampered by unwanted ligand-redistribution reactions that yield the thermodynamically stable metal difluorides (Scheme 1).

We initially attempted to synthesize heteroleptic triazenido alkaline earth fluorides by thermal activation of the pentafluorophenyl precursors in high boiling solvents such as *n*-heptane or xylene. A plausible decomposition pathway involves intramolecular elimination of tetrafluoro benzyne and fluoride transfer to the metal. In the case of the decomposition of the calcium derivative [Ca(C_6F_5){N_3(Dmp)Tph}(thf)] formation of a soluble species with Ca−F bond was indicated by the appearance of a singulett in the ^{19}F NMR at $\delta = -72.3$ ppm. Although, isolation of a well-defined product proved difficult, we finally succeeded in obtaining a molecular calcium fluoride with the composition [CaF{N_3(Dmp)Tph}(thf)] by using phenylsilane as a hydride transfer reagent.[14] Most

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(14) These results will be subject of a forthcoming paper: Lee, H. S.; Niemeyer, M. unpublished results.

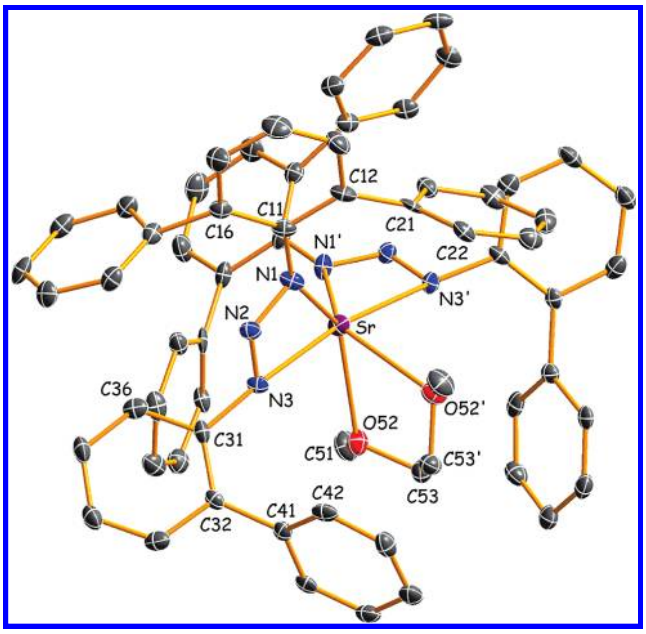


Figure 2. Molecular structure of **3** with thermal ellipsoids set to 30% probability. Hydrogen and carbon atoms of *iso*-propyl and methyl groups have been omitted for clarity. Selected bond lengths (Å), angles (deg), and dihedral angles (deg): Sr−N1 = 2.713(4), Sr−N3 = 2.730(4), Sr−N2 = 3.169(5), Sr−O52 = 2.559(4), N1−N2 = 1.310(5), N2−N3 = 1.315(6), N1−C11 = 1.419(6), N3−C31 = 1.478(6), N1−Sr−O52 = 134.12(13), N3−Sr−N3′ = 171.73(18), N1−Sr−N1′ = 128.03(19), N1−Sr−N3 = 48.11(13), N1−Sr−N3′ = 136.96(13), N1−Sr−O52′ = 92.21(13), N3−Sr−O52 = 88.38(12), N3−Sr−O52′ = 84.68(12), O52−Sr−O52′ = 66.06(17), N1−N2−N3 = 115.4(4), N2···Sr···N2′ = 152.0 (symmetry operation: 1.5 − *x*, 0.5 − *y*, *z*).

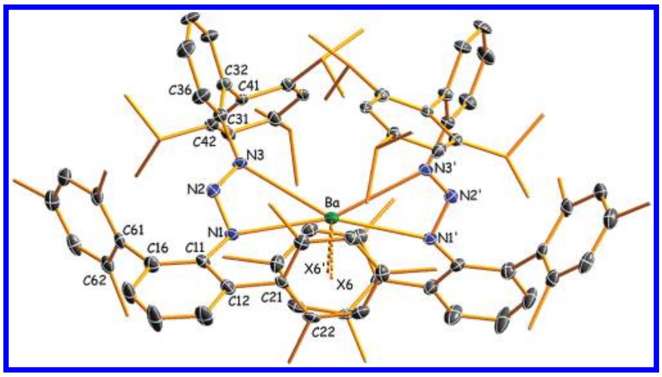


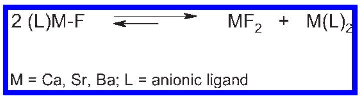
Figure 3. Molecular structure of **4** with thermal ellipsoids set to 30% probability. Hydrogen have been omitted and methyl or *iso*-propyl carbon atoms are shown as lines for clarity. Selected bond lengths (Å), angles (deg), and dihedral angles (deg): Ba−N1 = 2.860(4), Ba−N3 = 2.992(4), Ba···C21 = 3.369(5), Ba···C22 = 3.423(5), Ba···C23 = 3.424(5), Ba···C24 = 3.394(5), Ba···C25 = 3.312(5), Ba···C26 = 3.325(5), Ba···X6 = 3.074, N1−N2 = 1.333(5), N2−N3 = 1.331(5), N1−C11 = 1.430(6), N3−C31 = 1.448(6), N1−N2−N3 = 112.8(4), N1−Ba−N3 = 44.49(11), N2···Ba···N2′ = 156.7, X6···Ba···X6′ = 118.7 (symmetry operation: −*x*, *y*, 2.5 − *z*).

Table 2. Selected Bond Distances (Å), Angles (deg), and Dihedral Angles (deg) for Compounds **2** and **5**.[a,b]

	M = Sr (**2**)	M = Eu (**5**)
M−N1	2.578(3)	2.581(2)
M−N3	2.677(3)	2.676(2)
M−N4	2.571(3)	2.571(2)
M−N6	2.650(3) {2.619}	2.659(2) {2.622}
M···N2	3.043(3)	3.028(2)
M···N5	3.028(3) {3.036}	3.020(2) {3.024}
N1−N2	1.327(4)	1.314(3)
N2−N3	1.324(4)	1.321(3)
N4−N5	1.328(4)	1.317(3)
N5−N6	1.335(4) {1.329}	1.320(3) {1.318}
N1−C11	1.431(5)	1.425(3)
N3−C31	1.453(4)	1.440(3)
M···C21	3.051(4)	3.025(3)
M···C22	3.261(4)	3.250(3)
M···C23	3.347(4)	3.339(3)
M···C24	3.311(4)	3.298(3)
M···C25	3.126(4)	3.086(3)
M···C26	3.011(4)	2.946(3)
M···C71	3.241(4)	3.218(3)
M···C72	3.737(4)	3.720(3)
M···C73	3.920(5)	3.918(4)
M···C74	3.717(5)	3.699(4)
M···C75	3.229(4)	3.201(3)
M···C76	2.980(4)	2.947(3)
η^n/η^m	η^5/η^3	η^5/η^3
M···X5	2.839	2.803
M···X3	2.974	2.944
X5···M···X3	120.6	121.5
N2···M···N5	122.2	122.4
N1−M−N3	49.24(9)	49.03(7)
N4−M−N6	50.03(9)	49.61(7)
N1−N2−N3	111.5(3)	111.9(2)
N4−N5−N6	112.0(3)	112.7(2)
N2−N1−C11−C16	−40.9(5)	−41.9(4)
N2−N3−C31−C36	−45.9(4)	−45.6(3)
N5−N4−C61−C66	−38.4(5)	−40.2(4)
N5−N6−C91−C96	−44.9(4)	−44.5(3)

[a] Average values are given in braces. [b] Centroids of the (C21, C22, C24 → C26) (X5) and (C71, C75, C76) (X3) rings.

Scheme 1. Ligand Scrambling



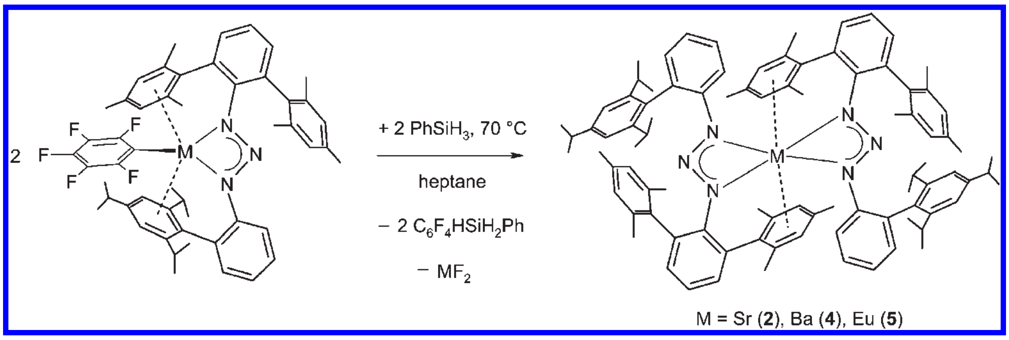
$$2\ (\mathrm{L})\mathrm{M{-}F} \rightleftharpoons \mathrm{MF_2} + \mathrm{M(L)_2}$$

M = Ca, Sr, Ba; L = anionic ligand

probably σ-bond metathesis between the Si−H and Ca−C_6F_5 functionalities first leads to the formation of a heteroleptic calcium hydride species. In a second step, the eliminated $PhSiH_2C_6F_5$ gives rise to a fluoride−hydride exchange. In the present report, we have extented this reaction to the heavier alkaline-earth metals strontium and barium (Scheme 2). Monitoring the reaction between [Sr(C_6F_5){N_3(Dmp)Tph}] and $PhSiH_3$ in hot *n*-heptane by ^{19}F NMR failed to produce any characteristic signal for a Sr−F species. However, workup of the reaction mixture yielded a pale yellow crystalline compound in moderate yield. The analytical and spectroscopic data were in accordance with the formation of a homoleptic strontium triazenide [Sr{N_3(Dmp)Tph}$_2$] (**2**), and this was confirmed by a crystal structure determination. In similar reactions, the barium and europium triazenides [M{N_3(Dmp)Tph}$_2$] {M = Ba (**4**), Eu (**5**)} were obtained in 11 and 51% yield, respectively. Obviously, ligand scrambling as shown in Scheme 1 leads to the formation of homoleptic triazenido complexes. However, the relatively low yields indicate the presence of other products arising from different reaction paths. This is supported by further experiments that will be discussed in detail elsewhere.[14]

A remarkable property of compounds **2**, **4**, and **5** is their low tendency to coordinate additional σ-donor solvent molecules. Attempts to prepare tetrahydrofuran adducts by crystallization from heptane/THF mixtures were unsuccessful, giving the unreacted starting materials only. However, using dimethoxyethane as a stronger chelating

Scheme 2. Synthesis of Compounds **2**, **4**, and **5**



ligand, it is possible to isolate adducts as was proven for the complex [Sr{N$_3$(Dmp)Tph}$_2$(dme)] (**3**)}.

Structural Studies. All new compounds were examined by X-ray crystallography, and their molecular structures and important bond parameters are shown in Figures 1−3 and Table 2.

Yellow crystals of [Sr{N$_3$(Dmp)Tph}$_2$] (**2**) and orange crystals of [Eu{N$_3$(Dmp)Tph}$_2$] (**5**), suitable for X-ray crystallographic studies, were grown from a saturated *n*-heptane/benzene mixture or *n*-heptane solution at ambient temperature and −20 °C, respectively. Considering the small difference in the ionic radii of the M^{2+} cations (Sr, 1.18 Å; Eu, 1.17 Å; for coordination number 6),[15] it is not too surprising that both complexes crystallize in isomorphous cells in the monoclinic space group $P2_1/c$. They differ by the type of solvent, which is packed in cavities of the structure. There are no significant interactions between the metal centers and the cocrystallized benzene or heptane molecule, however. Figure 1 shows a representation of the Sr complex; important bond parameters are provided in Table 2.

The monomeric complexes crystallize without imposed symmetry, and the metal atoms show an apparent coordination number of four. The metal−nitrogen distances to the κ^2-*N*,*N*-chelated triazenide ligands are in the range 2.571(3)−2.677(3) Å (avg 2.619 Å) for **2** and 2.571(2)−2.676(2) Å (avg 2.622 Å) for **5** and notably larger than those in the pentafluorophenyl precursor (Sr^{2+}: 2.562 Å. Eu^{2+}: 2.548 Å) and some related homoleptic β-diketiminates (Sr^{2+}: 2.510,[16a] 2.487, and 2.495 Å[16b]), and guanidinates (Sr^{2+}: 2.538 and 2.566 Å for the terminal Sr−N distances in two dimeric complexes.[17] Eu^{2+}: 2.540 Å[18]) reflecting differences in coordination numbers and donor character of the ligands. With a range of 1.324(4)−1.335(4) Å for **2** and 1.314(3)−1.321(3) Å for **5**, the N−N distances within the triazenido ligand cores are consistent with delocalized bonding.

An interesting feature in the solid-state structures of **2** and **5** is the presence of additional metal···π-arene contacts to the flanking aryl groups that provide steric and electronic saturation of the metal cations. In each compound, the metal ion interacts with the Mes rings of the terphenyl substituents in a η^5/η^3 fashion with M···C distances in the range 3.011(4)−3.311(4) Å (**2**) [**5**: 2.946(3)−3.298(3) Å] for (C21, C22, C24 → C26) and 2.980(4)−3.241(4) Å (**2**) [**5**: 2.947(3)−3.218(3) Å] for (C71, C75, C76). It should be noted that the assignment of the hapticity of the metal···π-arene interactions in the compounds discussed in this paper is based on the evaluation of the shortest metal··· centroid separation. Alternatively, the smallest angle between the M···centroid vector and the normal of the arene plane may be used to determine the best description. Considering these additional metal···π-arene interactions, a distorted tetrahedral coordination by two triazenide ligands and two arene rings may be assumed for the metal centers in **2** and **5**. It is reflected by the angles N2···M···N5 (**2**: 122.2°. **5**: 122.4°), X5−M−X3 (**2**: 120.6°. **5**: 121.5°), and N2/N5···M−X5/X3 (**2**: 91.0−111.5°. **5**: 91.4−110.5°), where X5 and X3 define the centroids of the coordinated arene rings and the bidentate triazenido ligand occupies only one coordination site. The large displacement of the metal atoms from the NNN planes (N1N2N3: 1.291 Å [**2**], 1.352 Å [**5**]. N4N5N6: 1.217 Å [**2**], 1.241 Å [**5**]) deserves a comment. Notably, these two planes are not orientated perpendicular to each other as one might expect but rather show a roughly coplanar arrangement with an interplanar angle of 26.9° (**2**) [**5**: 24.4°] in order to maximize metal··· π-arene bonding and to minimize interligand repulsion.

The molecular structure and important bond parameters of the pale yellow complex [Sr{N$_3$(Dmp)Tph}$_2$(dme)] (**3**) are shown in Figure 2. A 2-fold axis runs through the strontium atom and the backbone of the coordinated DME molecule. The Sr atom has a very distorted octahedral coordination, in which the terminal nitrogen atoms of two triazenide ligands (N1, N3/N1′, N3′) and the oxygen atoms (O52, O52′) of the DME molecule occupy a cis position. The presence of two small-bite ligands with acute N1−Sr−N3 and O52−Sr−O52′ angles of 48.11(13)° or 66.06(17)° and the angles between the trans donor atoms of 134.12(13)° (N1−Sr−O52) and 171.73(18)° (N3−Sr−N3′) reveal a severe distortion from the ideal octahedral environment. The average Sr−N bond length of 2.722(4) Å and the Sr−O52 distance of 2.559(4) Å that are much longer than the corresponding values of 2.600(2) and 2.467(2) Å in Hill's [Sr(N$_3$Dip$_2$)$_2$(thf)$_2$] complex[10b] indicate steric crowding. Further signs of steric crowding are the elongated N3−C31 bond of 1.478(6) Å (cf. 1.453(4) Å [**2**], 1.448(6) Å [**4**], 1.440(3) Å [**5**]) and the widened NNN angle of 115.4(4)° (cf. 111.8(3)° [**2**], 112.8(4)° [**4**], 112.3(2)° [**5**]). A comparison with **2** shows a different alignment of the two NNN planes which are now with 85.6° almost perpendicular to each other.

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Moreover, with 0.617 Å, the displacement of the strontium atom from the NNN plane is smaller for **3** than in the unsolvated complex **2**. Finally, it is notable that the presence of the additional DME ligand prevents any close metal$\cdots\pi$-arene interactions with the shortest Sr$\cdots$C contact to C26 being 3.72 Å. In addition, the angle between the triazenide ligands is widened as indicated by the N2$\cdots$Sr$\cdots$N2′ angle of 152°.

Homoleptic solvent free Ba triazenide **4** crystallizes as yellow prisms in the space group *C*2/*c*. Figure 3 shows the molecular structure of the strictly monomeric complex in which the metal atom is located on a 2-fold axis. The first coordination sphere of the barium cation comprises of four nitrogen atoms of the two κ^2-chelated triazenide ligands. Additional metal$\cdots\eta^6$-π-arene interactions are observed to two Mes rings of the terphenyl substituents. This gives rise to a distorted pseudotrigonal bipyramidal coordination of the metal (with one empty equatorial site) as reflected in part by the angles X6−Ba−X6′ (118.7) and N2$\cdots$Ba$\cdots$N2′ (156.7), where X6 and X6′ define the centroids of the coordinated arene rings and the bidentate triazenido ligand occupies only one coordination site. Notably, the latter is approximately 35° larger than the corresponding N$\cdots$M$\cdots$N angles in the previously discussed compounds **2** and **5**. The average Ba−N distance of 2.926 Å to the slightly asymmetric bound triazenide ligand is considerably longer than that in the pentafluorophenyl precursor (2.726 Å). This big change is somehow surprising since the difference in coordination numbers is only one and both compounds contain similar secondary metal$\cdots$arene interactions. A comparison with Hill's potassium barate [K(thf)$_3$-Ba(N$_3$Dip$_2$){N(SiMe$_3$)$_2$}$_2$(thf)] (CN$_{\mathrm{Ba}}$ = 5; 2.805(7) Å for the terminal Ba−NNN distance)[10b] further indicates that the relatively long Ba−N bonds in **4** are due to steric crowding by the two bulky triazenide ligands. The shorter Ba−N distances in two bis-diketiminates (2.71[16a] and 2.65 Å[16b]) and one bis-phosphiniminate (2.75 Å[19]), the only other monomeric barium complexes with bidentate N-donorligands available for comparison, reflect the better donor ability of these ligands.

Conclusion

Our primary goal, the synthesis of soluble alkaline-earth fluorides that are supported by sterically crowded triazenido ligands, has not been achieved because of unwanted ligand redistribution reactions. Instead, the first homoleptic strontium, barium, and europium triazenides have been isolated. These compounds are rare examples of unsolvated monomeric complexes with those elements.

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Supporting Information Available: X-ray data (CIF) for **2**$\cdot$(C$_6$H$_6$)$_{1.5}$, **3**$\cdot$(C$_7$H$_{16}$), **4**, and **5**$\cdot$(C$_7$H$_{16}$). This material is available free of charge via the Internet at http://pubs.acs.org.

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