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Stabilization of Aryl–Calcium, –Strontium, and –Barium Compounds by Designed Steric and π-Bonding Encapsulation

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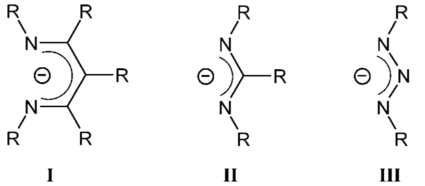
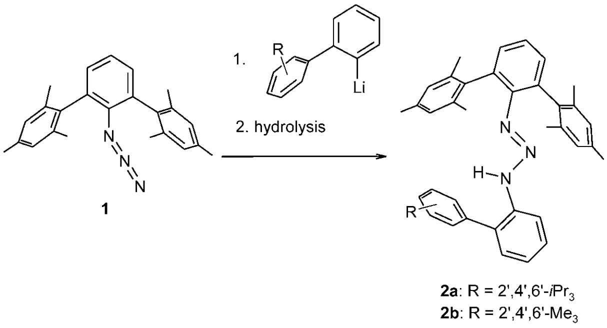
In the last decade a major theme of organometallic chemistry has been the design and development of alternative ligand systems capable of stabilizing monomeric metal complexes while provoking novel reactivity. Exploration of this field is driven by the potential use of these complexes in catalysis and organic synthesis. Examples of monoanionic chelating N-donor ligands that have received much recent attention (Scheme 1) include the β-diketiminate (**I**)[1] and the amidinate (**II**)[2] ligand systems. Much less attention has been given to the closely related triazenides (**III**).[3,4] This may be attributed to the lack of suitable ligands that are sterically crowded enough to prevent undesirable ligand redistribution reactions and allow better control of the electronic and steric properties at the metal center.



Scheme 1. A comparison of some monoanionic chelating N ligands.

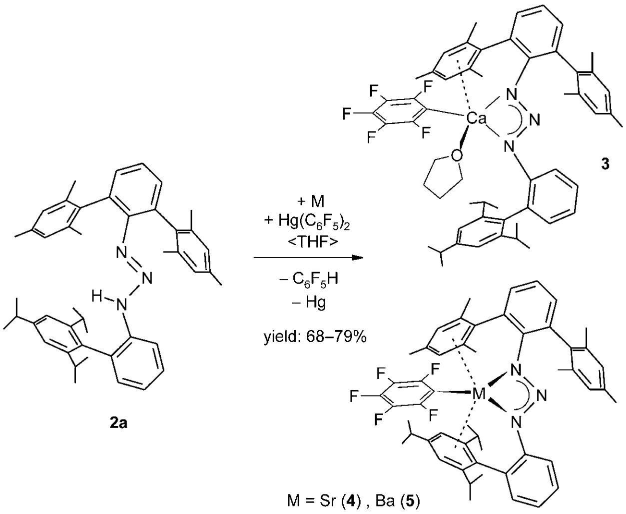
Triazenides are weaker donors than the isoelectronic amidinates and the related β-diketiminates, and should induce greater electrophilicity at a bonded metal atom.[5] This is reflected by the results of an NBO (natural bond orbitals) analysis of the energy-minimized structures[6] of the model anions 1,3-diphenyl-1,3-diketiminate ($\mathbf{I_M}$), 1,3-diphenyl-1,3-diazaallyl ($\mathbf{II_M}$), and 1,3-diphenyltriazenide ($\mathbf{III_M}$) (see Supporting Information), which shows an NPA (natural population analysis) charge for the chelating N atoms of −0.54, −0.60, and −0.38, respectively.

We recently succeeded in the preparation of aryl-substituted, sterically crowded triazenes. Ligands of this type may be synthesized in excellent yields by the reaction of different substituted 2-lithiobiphenyls with the *m*-terphenyl azide **1**, followed by hydrolysis (Scheme 2).



Scheme 2. Synthesis of the triazene ligands **2a** and **2b**.

In a first attempt to test their properties, we have used the obtained triazenes to stabilize pentafluorophenyl compounds of the heavier alkaline-earth metals calcium, strontium, and barium. The heteroleptic pentafluorophenyl triazenides are accessible in tetrahydrofuran as solvent by a convenient one-pot transmetalation/deprotonation[7] reaction from the triazene **2a** (HN_3ArAr'), bis(pentafluorophenyl)mercury, and the corresponding alkaline-earth metal (Scheme 3). After crystallization from *n*-heptane, either the THF-free compounds $[M(C_6F_5)(N_3ArAr')]$ (M = Sr (**4**), Ba (**5**)) or the solvate $[Ca(C_6F_5)(N_3ArAr')(thf)]$ (**3**) were isolated in good yields. It is remarkable that attempts to replace the pentafluorophenyl substituents by a second triazenide ligand have not been successful so far. Apparently, the steric bulk of the latter prevents further substitution or ligand redistribution and therefore formation of the homoleptic complexes.[8]



Scheme 3. Synthesis of **3**–**5**.

Solutions of **4** or **5** in aromatic or aliphatic solvents show considerable thermal stability and can be stored at ambient

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temperature for months with only minor decomposition. This may be contrasted with the behavior of some related pentafluorophenyl compounds of the di- and trivalent rare earth metals, which are thermally much more labile.[9] Compared to **4** and **5**, solutions of the calcium complex **3** are more sensitive and decompose within weeks at room temperature or within two days at 70 °C. We have not been able to isolate a well-defined decomposition product so far. However, NMR spectroscopic evidence, in particular a ^{19}F NMR signal at $\delta = -72.3$ ppm, points to the formation of a molecular fluoride, presumably [CaF(N_3ArAr′)(thf)], as one of the main products.

Compounds **3**–**5** were examined by X-ray crystallography.[10] The molecular structures of the Ca and Ba derivatives are shown in Figures 1 and 2, respectively, while important structural parameters for all complexes are summarized in Table 1. Despite the relatively large ionic radii of the M^{2+} ions (Ca: 1.14 Å; Sr: 1.32 Å; Ba: 1.49 Å for coordination number four[11]) the size of the η^2-bonded triazenide ligands enforces the formation of strictly monomeric complexes in which the metal atoms possess apparent low coordination numbers of three (**4**, **5**) and four (**3**). It should be noted that the deviation of the metal atoms from the N_3 plane increases in the order Sr (0.406 Å), Ba (0.706 Å), Ca (0.850 Å), while the bite angles N1-M-N3 decrease in the order Ca (53.25(18)°), Sr (48.89(17)°), Ba (46.33(10)°).

Table 1: Important structural parameters [Å, °] for the compounds [(ArAr′N_3)M(C_6F_5)] (**3**–**5**) and the DFT-calculated model complex [(2-MesC_6H_4)(2-TripC_6H_4)N_3SrC_6F_5] (**4_M**).

	M = Ca(thf)	M = Sr	**4_M**	M = Ba
N1–N2	1.338(7)	1.314(7)	1.305	1.309(5)
N2–N3	1.325(6)	1.307(8)	1.307	1.306(4)
Coord. no. (M)	4	3	3	3
M–N1	2.371(5)	2.576(6)	2.591	2.740(3)
M–N3	2.496(6)	2.548(5)	2.596	2.711(3)
N1–M–N3	53.3	48.9	48.7	46.3
M/N_3[a]	0.850	0.406	0.038	0.706
M–C	2.499(11)	2.673(7)	2.638	2.808(5)
M/C_6F_5[b]	0.797	0.712	0.246	1.086
M–O	2.308(5)			
C–M–N2	112.2	114.8	127.0	113.1
η^n/η^n[c]	η^5	η^6/η^5	η^6/η^5	η^5/η^5
M···C(Mes)[d]	3.015–3.132	3.165–3.306	3.310–3.400	3.327–3.430
M···C(Trip)[d]		3.078–3.283	3.277–3.470	3.286–3.406
M···F[e]	3.414	3.076	2.881	3.417

[a] Displacement of M from the N_3 plane. [b] Displacement of M from the C_6F_5 plane. [c] Hapticity of the M···π-arene interaction to the Mes and Trip rings. [d] M···C(arene) distances considered to be bonding. [e] Closest M···F contact.

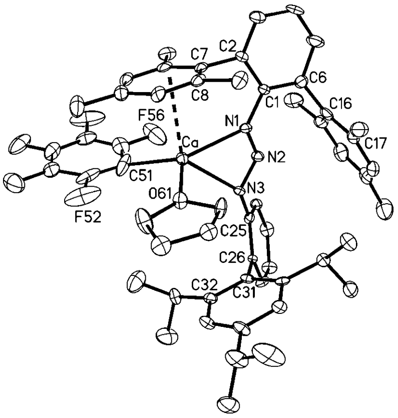

Figure 1. Molecular structure of **3** with thermal ellipsoids set to 30% probability. Hydrogen atoms are omitted for clarity.

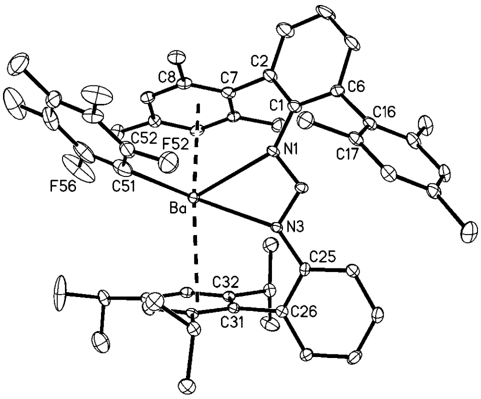

Figure 2. Molecular structure of **5** with thermal ellipsoids set to 50% probability. Hydrogen atoms are omitted for clarity.

The average M–N distances to the triazenide ligands (Ca = 2.434, Sr = 2.562, Ba = 2.726 Å) are comparable to those of the amidinates [{PhC(NSiMe_3)$_2$}$_2$M(thf)$_2$] (M = Ca 2.431 Å,[12a] Sr 2.584 Å[12b]), [{HC(NDip)$_2$}$_2$M(thf)$_n$] (Dip = 2,6-diisopropylphenyl, M = Ca 2.383 Å ($n = 1$), Sr 2.585 Å, Ba 2.728 Å ($n = 2$)),[12d] and [{PhC(NSiMe_3)$_2$}$_2$Ba(dme)(thf)] (2.779 Å),[12c] which contain five- to seven-coordinate metal atoms, and are longer than those of the four-coordinate homoleptic β-diketiminates [(Dip-nacnac)$_2$M] (Dip-nacnac = (Dip)NC(Me)C(H)C(Me)N(Dip)) (M = Ca 2.379 Å, Sr 2.510 Å, Ba 2.712 Å).[13] Taking into account the apparent lower coordination numbers in the triazenides **3**–**5** the longer M–N bond lengths are most likely a result of the decreased donor ability of the triazenide relative to the amidinate and β-diketiminate ligands and/or a consequence of the additional metal–π-arene interactions (see below). Furthermore, the average Ca–N distance of 2.434 Å in the THF solvate **3** is considerably shorter than the corresponding values found in the eight-coordinate triazenide [Ca{N_3(tol)$_2$}$_2$(dme)$_2$] (av 2.524 Å) (tol = 4-Me-phenyl),[8] which is the only derivative of the heavier alkaline-earth metals currently available for comparison.

Well-defined σ-bonded organometallic compounds of the heavier alkaline-earth metals calcium, strontium, and barium are scarce and are currently restricted to some structurally characterized trimethylsilylmethanides or -benzyls, di- and triphenylmethanides, and acetylides.[14] The heteroleptic pentafluorophenyls **3**–**5** therefore are the first structurally authenticated Ar–Ca, Ar–Sr, and Ar–Ba compounds. The observed M–C distances are toward the short end of the range of M–C bonds reported for other organyls. The Ca–C bond (2.499 Å) is comparable to the value in the four-coordinate alkyl [Ca{CH(SiMe_3)$_2$}$_2$(dioxane)$_2$] (2.48 Å)[15] but slightly longer than the distance in the two-coordinate compound

$[\mathrm{Ca\{C(SiMe_3)_3\}_2}]$ (2.46 Å).[16] The Sr−C and Ba−C distances of 2.673(7) and 2.808(5) Å, respectively, seem to be the shortest such bonds reported so far. The deviations of the metal atoms from the least-squares plane defined by the carbon atoms of the bonded C_6F_5 ligands also merit comment. They increase in the order Sr (0.712 Å), Ca (0.797 Å), Ba (1.086 Å). These unusually large displacements are explained by the highly ionic, nondirectional character of the metal–carbon bonds,[6] which is further increased by the electronic influence of the fluoro substituents. As a result, relatively weak intra- or intermolecular forces such as steric repulsion or π-stacking may lead to severe distortions (see Figure S5 in the Supporting Information). It is notable that similar, although even larger, displacements in the range 0.75 to 1.50 Å have been observed for the aryl lanthanides $[\mathrm{Ln(Dpp)_2(thf)_2}]$ (Dpp = 2,6-$\mathrm{Ph_2C_6H_3}$), which also contain highly polar M−C bonds.[17]

Perhaps the most striking features in the solid-state structures of **3**–**5** are the additional metal–π-arene interactions[18] with the pendent arms of the biphenyl and terphenyl groups in the triazenide ligands. These arene rings apparently compete with THF to bind the M^{II} cations, thus allowing the isolation of solvent-free derivatives.[19] The calcium ion in the THF solvate **3** interacts with only one mesityl (Mes) ring in an η^5 fashion,[20] with Ca⋯C distances in the relatively narrow range 3.015(7)–3.132(7) Å. In the solvent-free compounds **4** and **5** the metal ions show η^6- or η^5-π-arene interactions to one Mes group and also to the triisopropylphenyl (Trip) ring of the triazenide ligand. The resulting, rather distorted pseudotetrahedral coordination of the metal cations is reflected in part by the angles N2-M-C51 (Ca: 112.2°; Sr: 114.8°; Ba: 113.1°) and X1-M-X2 (Sr: 129.5°; Ba: 145.0°), where X1 and X2 define the centroids of the coordinated arene rings and the bidentate triazenido ligand occupies only one coordination site. The importance and specificity of the ($\mathrm{N_3ArAr'}$) ligand, and in particular its π-bonding capability, is shown by the failure of a reaction analogous to Scheme 3 between Ca, Sr, or Ba, $\mathrm{Hg(C_6F_5)_2}$, and the bulky *N*,*N'*-bis(2,6-diisopropylphenyl)formamidine.[12d] Only decomposition products were obtained, plausibly derived from an unstable $[\mathrm{ML(C_6F_5)}]$ species.

A relatively short Sr⋯F52−C52(*ortho*) contact of 3.076 Å is observed in the solid-state crystal structure of the Sr derivative **4**, which is accompanied by different Sr−C51−C52/C56 angles (105.7(5)° and 139.6(6)°). In contrast, the other pentafluoroaryl derivatives show considerably longer M⋯F contacts of more than 3.41 Å. To clarify if the metal⋯arene and metal⋯fluorine interactions also persist in solution, variable-temperature NMR experiments were performed for the most soluble compounds **4** and **5**. At 298 K, the ^{1}H NMR spectra in $[\mathrm{D_{14}}]$methylcyclohexane show only one set of signals for the Mes substituents, which, however, splits at lower temperatures. Upon warming, coalescence is detected at 238 K (**4**) and 258 K (**5**), with corresponding energy barriers of 49.0 and 53.1 kJ mol^{-1}, respectively. This observation can be interpreted in terms of a hindered rotation around the N1−C1 bond and therefore the persistence of the metal–π-arene interactions in solution. A similar behavior, with a rotational barrier of 54.3 kJ mol^{-1}, was recently observed and confirmed by quantum-chemical calculations for the unsolvated ytterbium thiophenolate $[\mathrm{Yb(S\text{-}2,6\text{-}Trip_2C_6H_3)_2}]$.[19] In addition, low-temperature ^{19}F NMR experiments for **4** and **5** show coalescence of the signals of the *ortho*-C_6F_5 fluorine atoms at 218 K and 203 K, with corresponding ΔG values of 39.1 and 34.5 kJ mol^{-1}, respectively. Unfortunately, we have not yet been able to determine which intra- or intermolecular processes are responsible for this fluxional behavior. According to preliminary quantum-chemical calculations (see Supporting Information), the binding energy for the Sr⋯F interaction in the model complex $[\mathrm{H_2N_3SrC_6F_5}]$ is estimated to be only 22.1 kJ mol^{-1} at the MP2 level of theory. DFT calculations for the more sophisticated model compound $[\{(1\text{-}\mathrm{MesC_6H_4})(1\text{-}\mathrm{TripC_6H_4})\mathrm{N_3}\}\mathrm{Sr(C_6F_5)}]$ ($\mathbf{4_M}$), in which the noncoordinating Mes group in **4** has been replaced by a hydrogen atom, reveal a shorter Sr⋯F contact (2.881 Å for $\mathbf{4_M}$ versus 3.076 Å for **4**) but weaker π-coordination (av M⋯C 3.363 Å for $\mathbf{4_M}$ versus 3.210 Å for **4**). Since it is known that DFT methods tend to underestimate weak interactions such as π-arene bonding to electropositive metals,[19] it is plausible that in the real systems **3**–**5** these interactions are actually stronger and dominate over any M⋯F coordination. As a result, decomposition pathways involving *ortho*-fluoride elimination are effectively blocked.

In summary, we have designed and prepared very bulky aryl-substituted triazenide ligands that have permitted the synthesis of the first structurally characterized aryl compounds of the heavier alkaline-earth metals Ca, Sr, and Ba. Kinetic stabilization in the solid-state and in solution through steric and electronic saturation of the metal centers is achieved by additional π-arene interactions to the pendent aryl substituents. These novel, sterically crowded triazenides may find use as ancillary ligands in catalysis and we are currently exploring this field.

Experimental Section

All manipulations were carried out under strictly anaerobic and anhydrous conditions under argon. The starting materials 2-iodo-2′,4′,6′-triisopropylbiphenyl,[21] 2,4,6,2″,4″,6″-hexamethyl-1,1′:3′,1″-terphenyl-2′-azide,[22] and bis(pentafluorophenyl)mercury[23] were prepared by known procedures.

$\mathrm{HN_3ArAr'}$ (**2a**): *n*-Butyllithium (44.4 mmol, 2.5 M hexane solution) was added at 0 °C to a solution of 2-iodo-2′,4′,6′-triisopropylbiphenyl (18.1 g, 44.4 mmol) in diethyl ether (250 mL) and stirring was continued for 2 h. The clear solution of the aryl lithium compound thus obtained was then treated with small portions of 2,4,6,2″,4″,6″-hexamethyl-1,1′:3′,1″-terphenyl-2′-azide (15.8 g, 44 mmol). After warming to ambient temperature and stirring for an additional 12 h, the orange solution was quenched with water (400 mL). The aqueous phase was separated and extracted with diethyl ether (3 × 100 mL). The organic phases were combined, repeatedly washed with water, and dried with $\mathrm{Na_2SO_4}$. Filtration followed by solvent removal in vacuo afforded **2a** as a yellow solid. Analytically pure, pale yellow crystals were obtained by recrystallization from hot acetone. Yield: 25.2 g (39.6 mmol, 89 %); m.p. 174–176 °C; ^{1}H NMR (400.1 MHz, $[\mathrm{D_6}]$benzene): $\delta = 0.87, 1.00, 1.13$ ($3\times$d, $^3J_{\mathrm{H,H}} = 6.9$ Hz, 3×6H; *o*+*p*-$\mathrm{CH(C}H_3)_2$), 2.04 (s, 12 H; *o*-$\mathrm{CH_3}$), 2.18 (s, 6 H; *p*-$\mathrm{CH_3}$), 2.54 (sept, $^3J_{\mathrm{H,H}} = 6.9$ Hz, 2 H; *o*-$\mathrm{C}H\mathrm{(CH_3)_2}$), 2.69 (sept, $^3J_{\mathrm{H,H}} = 6.9$ Hz, 1 H; *p*-$\mathrm{C}H\mathrm{(CH_3)_2}$), 6.79 (s, 4 H; *m*-Mes), 6.85–7.14 (m, 7 H; various aryl-H), 7.00 (s, 2 H; *m*-Trip), 8.70 ppm (s, 1 H; NH); ^{13}C NMR (62.9 MHz, $[\mathrm{D_6}]$benzene): $\delta = 20.9$ (*o*-$\mathrm{CH_3}$), 21.1 (*p*-$\mathrm{CH_3}$), 23.8, 24.0, 24.5 (*o*+*p*-$\mathrm{CH(}C\mathrm{H_3)_2}$), 30.7 (*o*-$\mathrm{CH(CH_3)_2}$), 34.5 (*p*-$\mathrm{CH(CH_3)_2}$), 121.4, 122.2, 126.8, 128.3, 129.8, 130.8 (aromatic CH), 113.7, 125.6, 134.8, 135.8, 136.1, 137.3, 139.3, 146.2, 147.5, 149.3 ppm (aromatic C). elemental analysis calcd (%) for $C_{45}H_{53}N_3$: C 84.99, H 8.40, N 6.61; found: C 84.88, H 8.41, N 6.64.

$[Ba(C_6F_5)(N_3ArAr')]$ (**5**): Bis(pentafluorophenyl)mercury (1.07 g, 2.00 mmol) was added at ambient temperature to a stirred mixture of barium ingots (2.5 g, 18.2 mmol) and **2a** (1.27 g, 2.00 mmol) in THF (60 mL). Stirring was continued for 14 h, whereupon the solvent was removed under reduced pressure. The green residue was treated with *n*-heptane, and solid materials were separated by centrifugation. The volume of the resulting deep yellow solution was reduced to incipient crystallization under reduced pressure. Storage in a freezer at −20 °C for several days afforded **5** as a bright yellow, crystalline material. Yield: 1.48 g (1.58 mmol, 79 %); m.p. 144–170 °C (decomp); ^{1}H NMR (250.1 MHz, [D$_6$]benzene): $\delta = 0.63, 0.78, 1.18$ (3 × d, $^3J_{H,H} = 6.8$ Hz, 3 × 6 H; *o*+*p*-CH(C*H*$_3$)$_2$), 2.04 (s, 12 H; *o*-CH$_3$), 2.19 (s, 6 H; *p*-CH$_3$), 2.57 (sept, $^3J_{H,H} = 6.8$ Hz, 2 H; *o*-C*H*(CH$_3$)$_2$), 2.90 (sept, $^3J_{H,H} = 6.8$ Hz, 1 H; *p*-C*H*(CH$_3$)$_2$), 6.46–7.27 (m, 7 H; various aryl-H), 6.78 (s, 4 H; *m*-Mes), 7.04 ppm (s, 2 H; *m*-Trip); ^{13}C NMR (62.9 MHz, [D$_6$]benzene): $\delta = 20.8$ (*o*-CH$_3$), 21.0 0(*p*-CH$_3$), 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, 128.6, 129.0, 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 ppm (aromatic C); signals for the C_6F_5 group could not be detected or assigned completely due to signal overlap and their weak appearance; ^{19}F NMR (235.4 MHz, [D$_6$]benzene): $\delta = -159.0$ (m, 2 F; *m*-C$_6$F$_5$), −154.2 (tt, $^3J_{F,F} = 20.3$, $^4J_{F,F} = 3.3$ Hz, 1 F; *p*-C$_6$F$_5$), −113.2 ppm (m, 2 F; *o*-C$_6$F$_5$); ^{15}N NMR (40.6 MHz, [D$_6$]benzene): $\delta = 109.5$ (s; -N*N*N-), −69.3, −70.4 ppm (s; -*N*N*N*-); elemental analysis calcd (%) for $C_{51}H_{52}BaF_5N_3$: C 65.21, H 5.58, N 4.47; found: C 64.76, H 5.76, N 4.52.

Details of the preparation and characterization of compounds **2b**, **3**, and **4**, and additional spectroscopic data for **2a** and **5** are given in the Supporting Information.

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Keywords: barium · calcium · fluorinated ligands · N ligands · strontium

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[6] The Gaussian 03 package (Revision B.01, Gaussian Inc., Pittsburgh PA, 2003) was used for all energy and frequency calculations. The geometries of the molecules were optimized using either density functional theory (DFT) with the functional B3LYP for the model ligands $\mathbf{I_M}$–$\mathbf{III_M}$ (all with implied C_2 symmetry) and the model complex $\mathbf{4_M}$ or second-order Møller–Plesset perturbation theory (MP2) for two conformers of the model compound $[H_2N_3SrC_6F_5]$ (C_s symmetry). In each case the GDIIS algorithm with the TIGHT convergence criterion was used. A quasi-relativistic 10-valence-electron pseudopotential was employed for the heavy atom Sr (M. Kaupp, P. von R. Schleyer, H. Stoll, H. Preuss, *J. Chem. Phys.* **1991**, *94*, 1360). The corresponding 6s6p5d valence basis was augmented by one set of f-functions. The basis sets for C, H, N, and F were either 6-311+G** ($\mathbf{I_M}$–$\mathbf{III_M}$) or 6-31G* ($\mathbf{4_M}$, $[H_2N_3SrC_6F_5]$). All stationary points were characterized by analytical or numerical frequency analyses. The natural bond orbital analysis employed the Gaussian 03 adaptation of the NBO program (E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold, NBO Version 3.1). For the model complex $\mathbf{4_M}$ the following NPA charges were calculated: +1.728 (Sr), −0.505 (N1), −0.509 (N3), −0.637 (C51).

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