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Stabilization of Unsolvated Europium and Ytterbium Pentafluorophenyls by π-Bonding Encapsulation through a Sterically Crowded Triazenido Ligand

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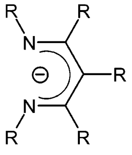
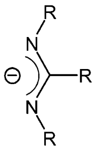
The one-pot transmetalation/deprotonation reaction of the bulky triazene Dmp(Tph)N_3H with bis(pentafluorophenyl)mercury and europium or ytterbium affords the structurally characterized unsolvated metal(II) pentafluorophenyl triazenides [Dmp(Tph)$N_3MC_6F_5$] (M = Eu, Yb; Dmp = 2,6-$Mes_2C_6H_3$ with Mes = 2,4,6-$Me_3C_6H_2$; Tph = 2-TripC_6H_4 with Trip = 2,4,6-$^i Pr_3C_6H_2$) or, depending on the molar ratio, the solvated complex [Dmp(Tph)-$N_3YbC_6F_5$(THF)].

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. Exploration of this field is driven by the potential use of these compounds in catalysis and organic synthesis.[1] Examples of monoanionic chelating N-donor ligands that have received much recent attention include the β-diketiminate (**I**)[2] and the amidinate (**II**)[3] ligand systems. Much less attention has been given to the closely related triazenides (**III**).[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. In comparison to the isoelectronic amidinates and the related β-diketiminates, triazenides are weaker donors and should induce greater electrophilicity at a bonded metal atom.[5]

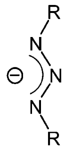
We recently succeeded in the preparation of aryl-substituted sterically crowded triazenes, which were used to stabilize the first examples of structurally characterized aryl compounds of the heavier alkaline-earth metals Ca, Sr, and Ba.[6] As a continuation of this work, we report the synthesis of heteroleptic pentafluorophenylmetal(II) triazenides of the rare-earth metals Eu and Yb. These compounds are accessible via a convenient one-pot transmetalation/deprotonation reaction in tetrahydrofuran (THF) as the solvent from the triazene Dmp(Tph)N_3H (**1**) (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-$^i Pr_3C_6H_2$), bis(pentafluorophenyl)mercury,[7] and the corresponding metal (Scheme 1).



I



II



III

After crystallization from *n*-heptane/toluene mixtures, either the deep orange, THF-free [Eu(C_6F_5)(N_3Dmp(Tph))] (**2**) or the deep red solvate [Yb(C_6F_5)(N_3Dmp(Tph))(THF)] (**4**) is isolated in good yield. Remarkably, solvate-free purple [Yb(C_6F_5)(N_3Dmp(Tph)] (**3**)[8] is accessible only in the presence of a second equivalent of the triazene **1**. A possible explanation involves the formation of a loose adduct between **4** and **1** in solution, which enables displacement of coordinated THF under reduced pressure. Upon crystallization, the adduct may dissociate in its components, and the less soluble compound **3** is isolated. It is notable 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 the formation of the homoleptic complexes.[9]

Solutions of **2**−**4** in aromatic or aliphatic solvents show considerable thermal stability and can be stored at ambient temperature for months with only minor decomposition. This behavior may be contrasted with that of other europium or ytterbium pentafluorophenyls that are much more thermally labile.[10] The IR spectra show three (**4**) or four (**2** and **3**) strong ν_{as} absorptions in the range 1231−1295 cm^{-1}, which

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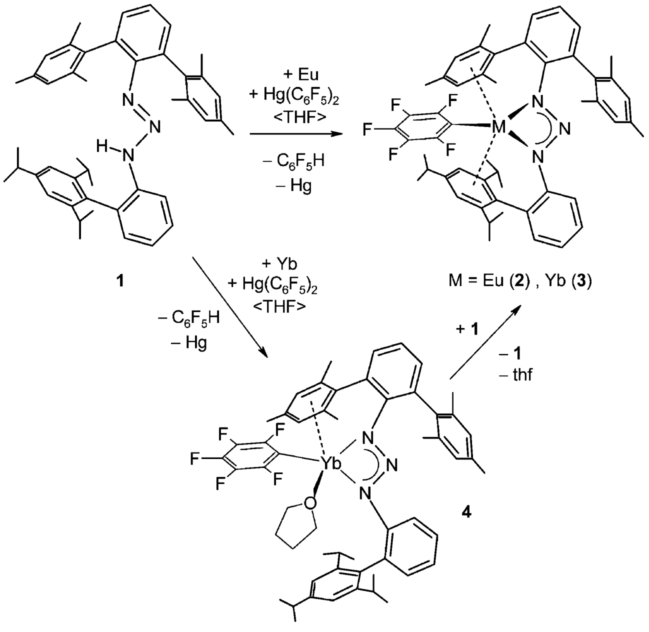
10.1021/ic0514602 CCC: $30.25

Scheme 1. Synthesis of **2**−**4**



are indicative of the triazenides acting as chelating ligands.[4a] Additional bands at 686 cm^{-1} (**2**), 687 cm^{-1} (**3**), or 683 cm^{-1} (**4**) may be assigned to δ_{as} N_3 vibrations. Characteristic absorptions of the C_6F_5 groups are observed at 1072/923 cm^{-1} (**2**), 1071/929 cm^{-1} (**3**), and 1072/923 cm^{-1} (**4**), respectively. For **4**, the presence of coordinated THF is indicated by prominent bands at 1020 and 874 cm^{-1}.

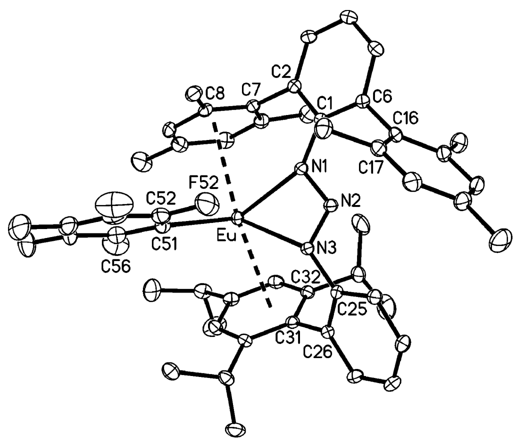


Figure 1. Molecular structure of **2** with thermal ellipsoids set to 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for **2** and **3** (in brackets): M−N1, 2.5510(17) {2.445(4)}; M−N3, 2.5448(17) {2.444(4)}; M−C51, 2.643(2) {2.527(6)}; M···C7, 3.127(2) {3.047(5)}; M···C8, 3.088(2) {3.003(5)}; M···C9, 3.134(2) {3.062(5)}; M···C10, 3.233(2) {3.160(6)}; M···C11, 3.246(2) {3.189(6)}; M···C12, 3.232(2) {3.160(6)}; M···C31, 3.255(2) {3.237(5)}; M···C32, 3.153(2) {3.070(5)}; M···C33, 3.179(2) {3.136(5)}; M···C34, 3.344(2) {3.421(6)}; M···C35, 3.415(2) {3.535(6)}; M···C36, 3.395(2) {3.476(5)}; M···F56, 3.426(2) {3.489(4)}; N1−N2, 1.312(2) {1.327(6)}; N2−N3, 1.313(2) {1.299(6)}; M−C51−C52, 128.64(18) {125.4(4)}; M−C51−C56, 117.12(18) {121.5(5)}.

Compounds **2** and **3** were examined by X-ray crystallography.[11] The molecular structure of the Eu derivative and important structural parameters for both complexes are shown in Figure 1. Despite the relatively large ionic radii of the M^{2+} cations (Yb, 1.02 Å; Eu, 1.17 Å; for coordination number 6),[12] the size of the η^2-bonded triazenide ligands enforces the formation of strictly monomeric compounds in which the metal atoms possess apparent low coordination numbers of 3. With a range of 1.299−1.327 Å, the N−N distances within the triazenido ligand cores are consistent with delocalized bonding. The coordination of the triazenide ligand is rather symmetrical with very little variation of the Eu−N [average 2.5510(17) Å] and Yb−N [average 2.445(4) Å] bond lengths. The latter distances are slightly shorter than those of the amidinate $[\{PhC(NSiMe_3)_2\}_2Yb(THF)_2]$ (2.473 Å),[13] which contains a 6-coordinate metal atom.

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(8) All manipulations were carried out under strictly anaerobic and anhydrous conditions using argon as an inert atmosphere. Synthetic, spectroscopic, and analytical data for **2** and **4** are given in the Supporting Information. $[Yb(C_6F_5)(N_3DmpTph)]$ (**3**): Bis(pentafluorophenyl)mercury (0.535 g, 1.00 mmol) was added at ambient temperature to a stirred mixture of Yb chips (0.34 g, 1.96 mmol) and **1** (1.27 g, 2.00 mmol) in THF (40 mL). Stirring was continued for 12 h, whereupon the solvent was removed under reduced pressure. The foamy residue was treated with a mixture of 30 mL of *n*-heptane and 10 mL of toluene, and solid materials were separated by centrifugation. The volume of the resulting maroon solution was reduced to incipient crystallization under reduced pressure. Storage at ambient temperature overnight afforded **3** as a deep red crystalline material. Yield: 0.60 g (0.62 mmol, 62%). Mp: crystals change to blue-green between 80 and 85 °C and decompose to a black foam at 165 °C. ^1H NMR (250.1 MHz, benzene-d_6): δ 0.58, 0.77, 1.22 (ddd, $^3J_{HH} = 6.7$ Hz, 3 × 6H, *o*- + *p*-$CH(CH_3)_2$), 2.06 (s, 12H, *o*-CH_3), 2.21 (s, 6H, *p*-CH_3), 2.52 (sep, $^3J_{HH} = 6.7$ Hz, 2H, *o*-$CH(CH_3)_2$), 3.04 (sep, $^3J_{HH} = 6.7$ Hz, 1H, *p*-$CH(CH_3)_2$), 6.70−7.27 (m, 7H, various aryl-H), 6.79 (s, 4H, *m*-Mes), 7.15 (s, 2H, *m*-Trip). ^{13}C NMR (62.9 MHz, toluene-d_8): δ 20.9 (*o*-CH_3), 21.1 (*p*-CH_3), 22.7, 23.4, 25.2 (*o*- + *p*-$CH(CH_3)_2$), 30.7 (*o*-$CH(CH_3)_2$), 33.0 (*p*-$CH(CH_3)_2$), 116.5, 121.2, 122.2, 123.3, 128.9, 129.1, 129.2, 129.3 (aromatic CH), 129.3, 131.4, 136.0, 136.8, 139.3, 141.5, 145.6, 148.8, 149.0, 149.7 (aromatic C); signals for the C_6F_5 group could not be detected or assigned because of signal overlap and their weak appearance. ^{19}F NMR (235.4 MHz, benzene-d_6): δ −160.5 (m, 2F, *m*-C_6F_5), −158.5 (t, $^3J_{FF} = 18.3$ Hz, 1F, *p*-C_6F_5), −110.7 (m, 2F, *o*-C_6F_5). ^{171}Yb NMR (70.1 MHz, benzene-d_6): no signal was detected. IR (Nujol): $\tilde{\nu}$ 1624 w, 1593 m, 1533 w, 1485 sh, 1420 s, 1397 m, 1366 s, 1294 ms, 1280 ms, 1262 s, 1244 s, 1230 sh, 1208 ms, 1180 m, 1101 w, 1071 ms, 1027 vs, 1003 sh, 929 vs, 880 m, 861 m, 849 ms, 801 w, 792 w, 767 sh, 760 sh, 754 vs, 738 ms, 687 m, 658 m, 587 w, 575 w, 510 w, 471 w, 427 w, 410 w, 394 m. Anal. Calcd for $C_{51}H_{52}YbF_5N_3$: C, 62.82; H, 5.38; N, 4.31. Found: C, 62.21; H, 5.43; N 4.39.

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(11) Shock-frozen crystals in Paratone N, diffractometer Siemens P3, $T = 173$ K, SHELXL-97 refinement with all data on F^2. Crystal data for **2**: deep orange block, 0.70 × 0.65 × 0.55 mm, $C_{51}H_{52}EuF_5N_3$, $M = 953.92$, triclinic, space group $P\bar{1}$, $a = 9.043(2)$ Å, $b = 11.166(3)$ Å, $c = 23.368(4)$ Å, $\alpha = 96.206(16)°$, $\beta = 93.326(17)°$, $\gamma = 106.806(19)°$, $V = 2235.6(9)$ Å^3, $Z = 2$, $\rho_{calc} = 1.417$ g cm^{-1}, μ(Mo Kα) = 1.461 mm^{-1}, $2\Theta_{max} = 55°$, 10 905 ($R_{int} = 0.020$) collected and 10 256 unique reflections, 594 parameters, absorption correction by Ψ scans, R1 = 0.025 for 9558 reflections with $I > 2\sigma(I)$, wR2 = 0.068 (all data), GOF = 1.376. Crystal data for **3**: purple plate, 0.30 × 0.25 × 0.08 mm, $C_{51}H_{52}F_5N_3Yb$, $M = 975.00$, triclinic, space group $P\bar{1}$, $a = 9.0770(18)$ Å, $b = 11.114(2)$ Å, $c = 23.416(5)$ Å, $\alpha = 96.91(3)°$, $\beta = 93.71(3)°$, $\gamma = 106.93(3)°$, $V = 2231.0(8)$ Å^3, $Z = 2$, $\rho_{calc} = 1.451$ g cm^{-1}, μ(Mo Kα) = 2.155 mm^{-1}, $2\Theta_{max} = 54°$, 10167 ($R_{int} = 0.042$) collected and 9552 unique reflections, 599 parameters, absorption correction by Ψ scans, R1 = 0.051 for 7365 reflections with $I > 2\sigma(I)$, wR2 = 0.103 (all data), GOF = 1.136. 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-268133 (**2**) and -268132 (**3**). Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax +(44)-1223-336-033; e-mail deposit@ccdc.cam.ac.uk).

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The pentafluorophenyls **2** and **3** appear to be the first examples of well-characterized unsolvated aryl compounds of the lanthanides in the oxidation state 2+.[14] The Yb−C and Eu−C distances of 2.527(6) and 2.643(2) Å are comparable or slightly longer to those in the metal(II) aryls [M(Dpp)$_2$(THF)$_2$] {Dpp = 2,6-Ph$_2$C$_6$H$_3$; M = Yb [2.520(3) Å], Eu [2.615(4) Å]} and [Yb(Dpp)I(THF)$_3$] (2.520 Å).[15] Considerably longer bonds have been observed in the metal(II) pentafluorophenyls [M(C$_6$F$_5$)$_2$(THF)$_n$] {M = Yb, $n = 4$ [2.649(3) Å], Eu, $n = 5$ [2.822(2) Å]}, [Yb(C$_5$Me$_5$)(C$_6$F$_5$)(THF)$_3$] (2.597(5) Å), and [M(C$_6$F$_5$)(THF)$_n$][BPh$_4$] {M = Yb, $n = 5$ [2.59(1) Å], Eu, $n = 6$ [2.735(2) Å]}.[10] The deviations of the metal atoms from least-squares planes defined by the carbon atoms of the bonded C$_6$F$_5$ ligands (Yb, 0.262 Å; Eu, 0.268 Å) or the nitrogen atoms of the triazenide group (Yb, 0.374 Å; Eu, 0.533 Å) also merit comment.

Perhaps the most striking features in the solid-state structures of **2** and **3** are the additional metal−π-arene interactions[16] with the pending arms of the biphenyl and terphenyl groups in the triazenide ligands. Apparently, these arene rings compete with THF to bind the M^{II} cations and allow the isolation of solvate-free derivatives.[17,18] In both compounds, the metal ion interacts with one mesityl (Mes) ring of the terphenyl group in a η^5 fashion,[19] with M···C distances in the ranges 3.088(2)−3.233(2) Å (**2**) and 3.003(5)−3.160(6) Å (**3**). In addition, there are metal···π-arene interactions to the triisopropylphenyl (Trip) ring of the biphenyl substituent, which are best described as being η^4 for the smaller metal Yb and η^5 in the case of the Eu derivative. The M···C distances considered to be bonding are in the ranges 3.153(2)−3.395(2) Å (**2**) and 3.070(5)−3.421(6) Å (**3**). The resulting rather distorted pseudotetrahedral coordination of the metal cations is reflected by the angles N2···M−C51 (Yb, 104.5°; Eu, 102.5°) and X1−M−X2 (Yb, 131.2°; Eu, 139.5°), where X1 and X2 define the centroids of the coordinated arene rings and the bidentate triazenido ligand occupies only one coordination site.

Although we could not obtain X-ray-quality crystals of the THF solvate **4**, it is probable that this compound is isostructural to its calcium analogue [Ca(C$_6$F$_5$)(N$_3$Dmp(Tph))(THF)][6] because the ionic radii of Yb^{2+} (1.02 Å) and Ca^{2+} (1.00 Å) are very similar. Here the Ca atom is coordinated to a η^2-bonded triazenide ligand, the *ipso* C atom of the C$_6$F$_5$ group, and the O atom of a THF molecule. There is only one additonal η^5-π contact to the pending arm of a Mes group.

To clarify if the metal···arene interactions in **2** and **3** also persist in solution, variable-temperature NMR experiments were performed for the diamagnetic compound **3**. At 298 K, the ^{1}H NMR spectra in toluene-d_8 show only one set of signals for the Mes substituents. This is consistent with a fast exchange of the C7 → C12 and C16 → C21 arene rings on the NMR time scale. Upon cooling, decoalescence of the *o*-CH$_3$ and *m*-CH groups is detected at 226 K with a corresponding energy barrier of 47.1 kJ mol^{-1}. 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 [Yb(S-2,6-Trip$_2$C$_6$H$_3$)$_2$].[17] Additional low-temperature ^{19}F NMR experiments for **3** show decoalescence of the *o*- and *m*-C$_6$F$_5$ fluorine atoms to two sets of signals, respectively, below 222 K with a corresponding ΔG_{T_c} value of 42.9 kJ mol^{-1}. It should be noted that there are no exceptional short M···F contacts in the solid-state structures of **2** and **3** [M···F56 = 3.426(2)/3.489(4) Å], which might be responsible for the restricted rotation around the M−C51 bond in solution.[20] Therefore, it is more plausible that the inequivalence of the *o*- and *m*-C$_6$F$_5$ fluorine atoms at low temperatures is due to the additional metal π contacts. Further evidence for a frozen conformation in solution, similar to the solid-state structure, is provided by the decoalescence of the *o*-^{i}Pr groups ($\Delta G_{216\,\mathrm{K}} = 44.8$ kJ mol^{-1}) in the Tph substituent.

A comparison of compounds **2** and **3** with other lanthanide pentafluorophenyls, in particular Eu(C$_6$F$_5$)$_2$(THF)$_5$[10b] and the dimer (Cp*$_2$SmC$_6$F$_5$)$_2$,[21] allows one to estimate the steric properties of the N$_3$Dmp(Tph) ligand. Apparently, one triazenide seems to offer more steric protection than two Cp* groups and is able to substitute one C$_6$F$_5$ ligand and five THF molecules.

In summary, we have prepared and characterized, with the help of a very bulky aryl-substituted triazenide ligand, the first structurally characterized unsolvated metal(II) aryls of the rare-earth metals Eu and Yb. In the solid-state and in solution, kinetic stabilization through steric and electronic saturation of the metal centers is achieved by additional π-arene interactions to the pendent aryl substituents. As a result, decomposition pathways involving *o*-fluoride elimination are effectively blocked.

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Supporting Information Available: Details on the preparation and characterization of **2**−**4** and X-ray data (CIF) for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) This unusual behavior is in contrast to the preparation of other unsolvated lanthanide(II) compounds, e.g., LnCp*$_2$ or Ln(OAr)$_2$, from solvated complexes, which normally requires repeated sublimation at elevated temperatures.

(19) The assignment of the hapticity of the metal−π-arene interactions in compounds **2** and **3** is based on the evaluation of the M−C distances and the angle between the M−centroid vector and the normal of the arene plane (see Figure S3 of the Supporting Information).

(20) No decoalescence of the C$_6$F$_5$ signals down to 223 K was observed for the compound Cp′$_2$CeC$_6$F$_5$ (Cp′ = 1,3,4-^{t}Bu$_3$C$_5$H$_2$), which shows a very strong Ce···F interaction of 2.682 Å in the solid state: Maron, L.; Werkema, E. L.; Perrin, L.; Eisenstein, O.; Andersen, R. A. *J. Am. Chem. Soc.* **2005**, *127*, 279.

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