Communications

Buckling under Strain: Relief of Steric Pressure Occurs Differently for Samarium(III) Porphyrinogen Complexes of the π-Bound Auxiliary Ligands Cyclopentadienyl and Cyclooctatetraenediyl

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Summary: An η^2-bound cyclooctatetraenediyl lanthanide complex of an η^5:η^1:η^5:η^1-bound modified porphyrinogen has been prepared, owing to the limited coordination site space at the Sm^{III} center. In contrast, when the auxiliary ligand is the smaller cyclopentadienyl ligand, η^5 binding is achieved through distortion of the macrocycle, leading to a reduction in its hapticity to η^5:η^1:η^1:η^1 binding.

The most adhered to strategy in inorganic chemistry for stabilizing reactive functionalities, achieving reaction selectivities, and accessing novel structural motifs is the use of hindered "nonparticipative ligands" to afford protection and/or force unusual/desired behavior. Little control over the binding modes for the cyclooctatetraenediyl ligand (COT^{2-}) has been achieved in f-element chemistry, where η^8 interactions dominate. The only structurally authenticated exceptions are [(COT)$_3$Nd$_2$(THF)$_2$] (**1**)[1] and [(COT)$_3$U$_2$(C$_5$Me$_5$)$_2$] (**2**),[2] featuring μ,η^8:η^3 and μ,η^3:η^3 binding due to coordination sphere saturation rather than strategic ligand design. Complexes featuring even heavily

substituted COT^{2-} ligands, e.g., [{(1,3,6-(Me$_3$Si)$_3$C$_8$H$_5$)}$_2$Ce] (**3**), or Lewis base tethered COT^{2-} ligands have all featured η^8 binding.[3]

1   **2**   **3** (R = SiMe$_3$)
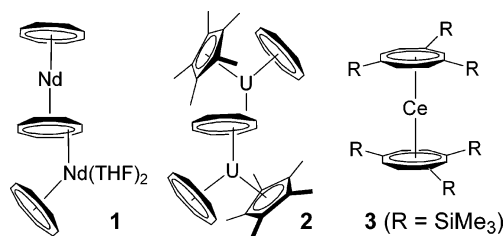
Evans reported the reaction of [(C$_5$Me$_5$)$_2$Sm^{II}] and COT, which serendipitously yielded [(C$_5$Me$_5$)Sm^{III}(COT)] and the first synthesis of the very sterically congested [(C$_5$Me$_5$)$_3$Sm^{III}] (**4**) (Scheme 1).[4] The intended product of this reaction was the bimetallic species [(C$_5$Me$_5$)$_2$Sm^{III}(μ,η^n:η^n-COT)Sm^{III}(C$_5$Me$_5$)$_2$], which was being targeted as a candidate in which a nonplanar COT^{2-} was plausible owing to the anticipated steric congestion of the Sm center accommodating an η^8-bound COT^{2-} ligand.
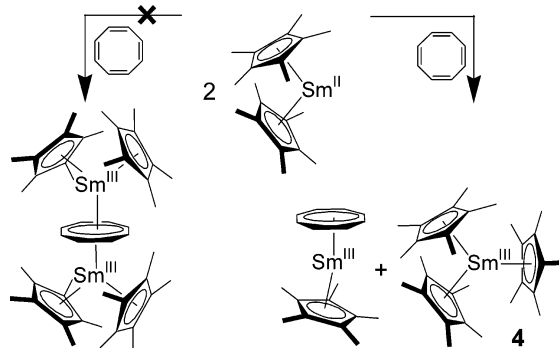
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(4) Evans, W. J.; Foster, S. E. *J. Am. Chem. Soc.* **1991**, *113*, 7423.

Scheme 1. Attempted Synthesis of a Potentially Nonplanar
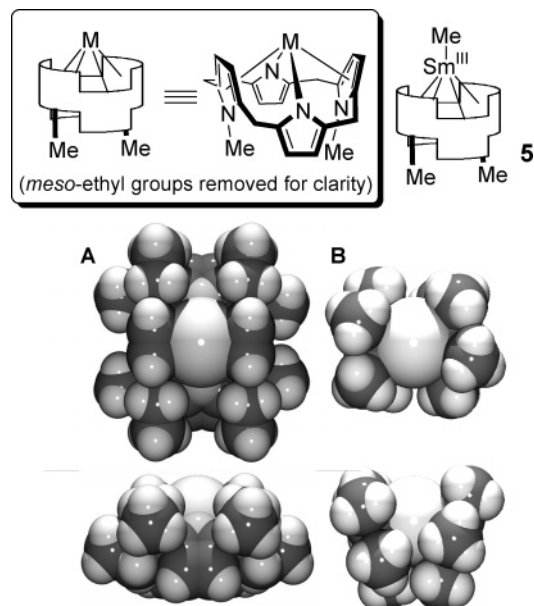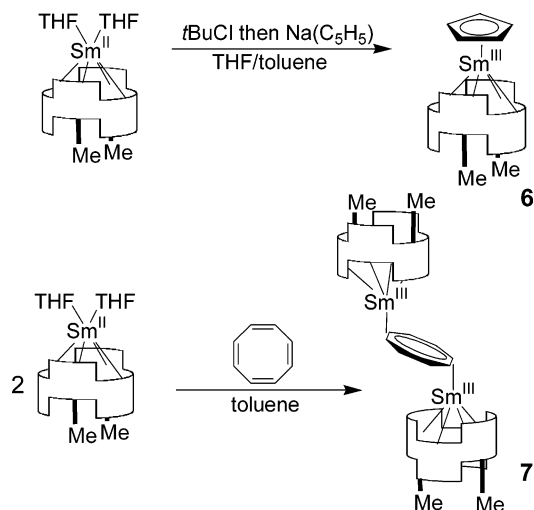**$\mu,\eta^n:\eta^n$-COT^{2-} Complex[4]**

Figure 1. Methyl Sm^{III} porphyrinogen **5** and space-filling depictions of the coordination sphere control of the macrocycle in **5** (A) versus its closest known decamethylsamarocene analogue (the Sm center featuring a single Sm—Me interaction in [{(C$_5$Me$_5$)$_2$SmMe}$_3$] (B).[8]

The very sterically crowded [(C$_5$Me$_5$)$_3$Sm^{III}] is a high-energy species itself, undergoing alkyl-like reactivity (as though one (C$_5$Me$_5$)$^-$ were η^1-bound) and a new class of ligand-based reduction chemistry.[5] One wonders what the reactivity of the intended bimetallic complex would be if it is less stable still![6]

In a previous report we presented a rare, unsolvated, terminal Sm^{III} methyl complex, **5**, which was unreactive toward ethene and C—H activations of common solvents.[7] This is due, we believe, at least partly to the coordination sphere control offered by the *trans-N,N′*-dimethyl-substituted porphyrinogen (Figure 1).

Binding of auxiliary ligands and Lewis bases, dimerization, and small molecule activation for **5** are limited by the *meso*-alkyl substituents and the 3,4-positions of the η^5-bound *N*-methylpyrrolyl units of the macrocycle. The latter structural feature is significant: it demonstrates that the slight metallocene bending angle of 168.9° governed by macrocyclic conformational restrictions and transannular interactions between the *N*-methyl substituents[9] represents an alternative in bulky ligand design to the much-studied peralkylated metallocenes (e.g., 137.0° for the Sm center of [{(C$_5$Me$_5$)$_2$SmMe}$_3$], featuring a single Sm—Me interaction[8]). The result is a narrow, relatively short binding groove available for auxiliary ligands when the metal is bound within the cavity of this macrocycle via $\eta^5:\eta^1:\eta^5:\eta^1$ interactions. This limitation is expected to be most influential when the auxiliary ligand has an oblate shape, such as a cyclic π-bound system. Importantly, disproportionation events in reactions analogous to that shown in Scheme 1 are inherently prevented for this system through the macrocycle effect.

We report here the synthesis and solid-state structures[10] of two very sterically crowded *trans-N,N′*-dimethyl-substituted porphyrinogen complexes featuring the π-bound aromatic auxiliary ligands (C$_5$H$_5$)$^-$ and COT^{2-}, **6** and **7** (46 and 82% yields, respectively) (Scheme 2). **6** decomposes in solution over

Scheme 2. Syntheses of the Sm^{III} Cyclopentadienyl and Cyclooctatetraenediyl Modified Porphyrinogen Complexes 6 and 7

several hours at room temperature to an unknown pale yellow solid and requires low-temperature isolation in order to maximize yields.

The structure of **6** features a unique $\eta^5:\eta^1:\eta^1:\eta^1$ macrocyclic binding mode in response to accommodating the η^5-bound

(5) For reviews, see: (a) Evans, W. J.; Davis, B. L. *Chem. Rev.* **2002**, *102*, 2119. (b) Evans, W. J. *J. Organomet. Chem.* **2002**, *647*, 2. (c) Evans, W. J. *Coord. Chem. Rev.* **2000**, *206−207*, 263.

(6) The stability of [(C$_5$Me$_5$)Sm^{III}(COT)] is an alternative reason for the outcome of Scheme 1, particularly as [(C$_5$Me$_5$)$_3$Sm^{II}] reacts with a further 1 equiv of COT to give [(C$_5$Me$_5$)Sm^{III}(COT)]. See also the related reactions conducted in the presence of coordinated THF: Recknagel, A.; Noltemeyer, M.; Edelmann, F. T. *J. Organomet. Chem.* **1991**, *410*, 53.

(7) Wang, J.; Gardiner, M. G.; Skelton, B. W.; White, A. H. *Organometallics* **2005**, *24*, 815.

(8) Evans, W. J.; Perotti, J. M.; Ziller, J. W. *J. Am. Chem. Soc.* **2005**, *127*, 3894.

(9) The former appears most influential, as tetraanionic, unmodified porphyrinogens reported by others also feature similar metallocene bending angles; for example, see: Dubé, T.; Gambarotta, S.; Yap, G. *Organometallics* **2000**, *19*, 121.

(10) Crystal data for **6**: C$_{43}$H$_{59}$N$_4$Sm·^{1}/$_4$C$_6$H$_{14}$, M_r = 803.83, 0.35 × 0.25 × 0.20 mm^3, orthorhombic, *Pbcn*, a = 16.794(3) Å, b = 30.921(5) Å, c = 15.991(3) Å, V = 8304(3) Å^3, Z = 8, ρ_{calcd} = 1.286 Mg m^{-3}, μ = 1.448 mm^{-1}, $2\theta_{max}$ = 56.66°, 58 100 reflections collected, 10 152 independent reflections (R_{int} = 0.059), R = 0.037 for 6934 ($I > 2\sigma(I)$) data and R_w = 0.091 (all data), s = 1.052, residual electron density −0.58/+0.71 e Å^{-3}. Crystal data for **7**: C$_{84}$H$_{116}$N$_8$Sm$_2$·2C$_7$H$_8$, M_r = 1722.82, 0.26 × 0.13 × 0.07 mm^3, monoclinic, *C2/c*, a = 19.8414(3) Å, b = 13.6819(2) Å, c = 31.6735(5) Å, β = 99.861(1)°, V = 8471.3(2) Å^3, Z = 4, ρ_{calcd} = 1.351 Mg m^{-3}, μ = 1.424 mm^{-1}, $2\theta_{max}$ = 69.98°, 71 858 reflections collected, 18 250 independent reflections (R_{int} = 0.032), R = 0.027 for 15 044 ($I > 2\sigma(I)$) data and R_w = 0.060 (all data), s = 1.026, residual electron density −0.89/+0.96 e Å^{-3}. Data for **6** and **7** were recorded at 150(2) K, with Mo Kα (0.710 73 Å) radiation.
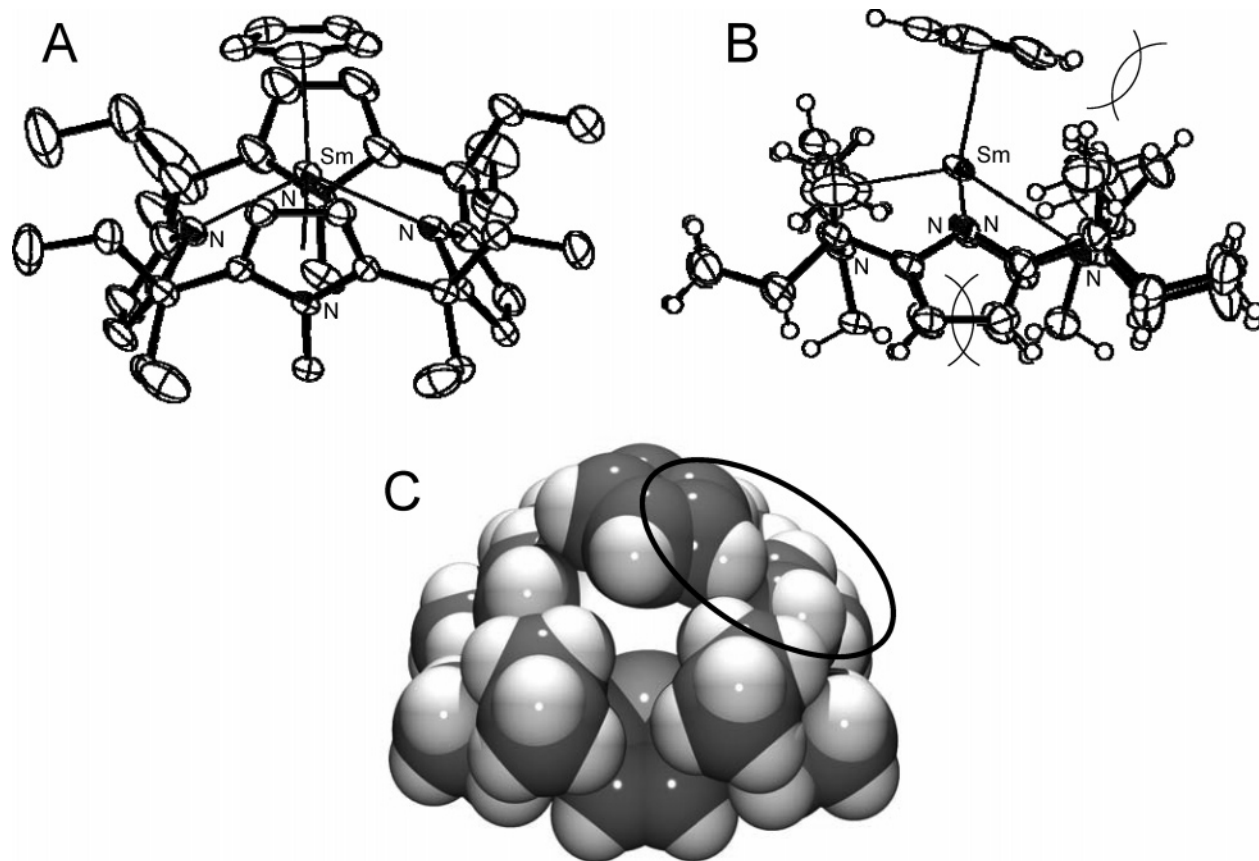
Figure 2. X-ray crystal structure representations of **6**: (A) general view with 50% probability ellipsoids (all hydrogens omitted for clarity); (B) side view highlighting the *N*-Me displacement and the areas of greatest steric restrictions with 50% probability ellipsoids; (C) space-filling representation highlighting the distortion of the macrocycle required to accommodate the η^5-bound $(C_5H_5)^-$ ligand.

auxiliary ligand (Sm—C distances typical at 2.719(3)−2.756-(3) Å) (Figure 2).[11,12] This is achieved by splaying back of a *N*-methylpyrrolyl unit from the Sm (heterocycle plane lies at 48.8(2)° relative to the plane of the meso carbons; cf. the other *N*-methylpyrrolyl plane lies at 75.7(1)°). In consequence, transannular interactions between the *N*-methyl groups lead to a 0.674(6) Å displacement of the *N*-methyl group of the η^1-bound *N*-methylpyrrolyl unit from the heterocycle (the N—C vector is 27.4(2)° from the pyrrolyl plane). In contrast to the case for **6**, minor steric deformations are noted for [(C$_5$Me$_5$)$_2$-Sm(C$_5$H$_5$)],[13] with three η^5-bound ligands featuring typical Sm—C distances (2.733(8)−2.809(8) and 2.724(10)−2.768(9) Å for the $(C_5Me_5)^-$ and $(C_5H_5)^-$ ligands, respectively). [(C$_5$Me$_5$)$_3$Sm], however, features severe steric distortions involving lengthened Sm—C distances (up to ∼0.14 Å) and large Me displacements from the ligand planes (up to 0.52 Å).[4,14] These comparisons reaffirm the conjecture that the featured macrocycle is, at least in this context, more sterically demanding than the {(C$_5$Me$_5$)$_2$}$^{2-}$ ligand set. The energy of a 0.67 Å *N*-Me displacement from the pyrrolyl plane of *N*-methylpyrrole was calculated at a modest 11.5 kJ mol^{-1}, which is greater than that

required for a 0.52 Å methyl displacement in $(C_5Me_5)^-$ (9.6 kJ mol^{-1}).[15] [(C$_5$Me$_5$)$_3$Sm] features a number of methyl displacements, but an additive effect is still unlikely to account for its high reactivity. Thus, we also attribute the high reactivity of [(C$_5$Me$_5$)$_3$Sm] to elongated Sm—C distances, reaffirming the suggestion that large methyl displacements in these systems are an indicator of steric congestion rather than the primary energetic cause for high reactivity.[14] In this regard, the greatly increased Sm—C distances associated with the reduction in hapticity to η^1 for an *N*-methylpyrrolyl unit in **6** due to steric strain may also lead to high reactivity.

In contrast, the structure of the centrosymmetric bimetallic reduced cyclooctatetraenediyl complex **7** features the typical η^5:η^1:η^5:η^1 macrocyclic binding mode (Figure 3). As a result, the preferred η^8 binding mode of COT^{2-} has been reduced to lower hapticity, bridging the Sm centers in a μ,η^2:η^2 fashion.

(11) η^5:η^1:η^1:η^1 binding for a tetraanionic, unmodified porphyrinogen has been noted in response to a π-bound ligand, but in that case *N*-Me substitution is lacking: Korobkov, I.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem., Int. Ed.* **2003**, *42*, 814.

(12) η^1-*N* binding of a *N*-methylpyrrolyl moiety has been noted in a Cr(II) chelate complex recently by displacement of the methyl group from the plane of the heterocycle, though the reason for and energetics of the feature were not discussed: Crewdson, P.; Gambarotta, S.; Djoman, M.-C.; Korobkov, I.; Duchateau, R. *Organometallics* **2005**, *24*, 5214.

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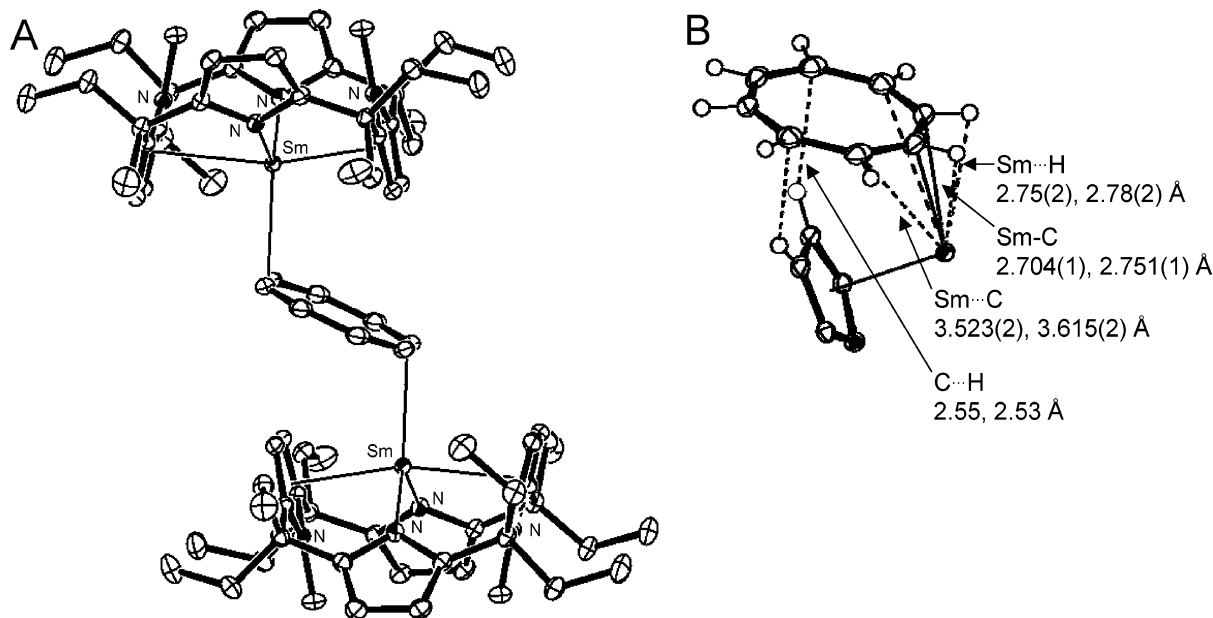
Figure 3. X-ray crystal structure representations of **7** with 50% probability ellipsoids: (A) general view of the whole molecule (all hydrogens omitted for clarity); (B) detail of the COT^{2-} binding mode (Sm/macrocycle interactions on one face of the COT^{2-} shown only).

The COT^{2-} ligand is planar (to within 0.014(1) Å), and the Sm centers bind to opposite ends of the ring (i.e., 1,2:5,6). The closest Sm−C distances to the COT^{2-} ligand are 2.704(1) and 2.751(1) Å, and the next nearest are 3.523(2) and 3.615(2) Å. These distances compare with the Sm−C distances to the η^8-bound COT^{2-} ligands of 2.565(4)−2.615(4) Å and 2.80(3)−2.86(3) Å in the Sm^{III} complexes [(C$_5$Me$_5$)Sm(COT)] and [{(Me$_3$Si)$_2$N}$_2$Sm(COT)Sm{N(SiMe$_3$)$_2$}$_2$], respectively, where an influence of the terminal or bridging nature of the COT^{2-} ligand is clearly evident.[16,17] The latter complex represents the only other crystallographically characterized Sm^{III} complex featuring a bridging COT^{2-} ligand. All other bridging COT^{2-} examples are for Sm^{II}: for example, [(C$_5$Me$_5$)Sm(COT)Sm-(C$_5$Me$_5$)], where the Sm−C distances are 2.798(14)−2.857(12) Å.[18] The Nd−C distances for the η^3-bound COT^{2-} ligand in [(COT)$_3$Nd$_2$(THF)$_2$] are 2.69(2)−3.02(2) Å,[1] with the distance to the central carbon center of the η^3-bound unit being closest to that observed for the more conventional η^8-bridging COT^{2-} interactions in that complex: 2.63(3)−2.74(3) Å. As a consequence of the large ring slippage for **7**, there are close contacts between the Sm centers and protons of the COT^{2-} attached to the Sm-bound carbons (Sm···H = 2.75(2), 2.78(2) Å, isotropically refined H positions), and also between the COT^{2-} and hydrogens in the 3,4-positions of *N*-methylpyrrolyl units (C···H 2.53, 2.55 Å, calculated H positions).

The structures of **6** and **7** demonstrate that the macrocycle can adapt its metal binding characteristics to a certain extent to allow binding of a minimally sized oblate auxiliary ligand. However, either the splaying back of both *N*-methylpyrrolyl

units is insufficient to allow η^8 binding of COT^{2-} or such distortion is energetically too expensive (through macrocyclic strain, the additional *N*-methyl displacement or a further η^5 reduction in hapticity). As disproportionation events are prevented in this case, the novel observed binding mode for COT^{2-} is the outcome, owing to a sheer lack of alternatives.

The ^{1}H NMR spectrum of **6** at room temperature (d_8-toluene) displays a single cyclopentadienyl resonance and C_{2v} macrocyclic symmetry, indicating a fluxional process that interconverts η^5- and η^1-bound *N*-methylpyrrolyl units found in the solid state. Variable-temperature studies (+20 to −60 °C) revealed no changes except for Curie−Weiss behavior. The low solubility of **7** prevented NMR characterization.

Overall, the macrocyclic ligand studied here has demonstrated its capability of influencing the coordination behavior of COT^{2-} to a greater extent than has been demonstrated in f-element chemistry to date by any other ligand system, and both mechanisms of steric stress relief in **6** and **7** are indicators of high-energy species. We are pursuing the reactivity of these complexes, particularly in relation to the behavior of sterically hindered f-element complexes of the type [(C$_5$R$_5$)$_3$M(L)$_n$].[14]

Supporting Information Available: Text giving details of the experimental preparations, tables giving XYZ coordinates for DFT optimized structures, figures giving fully labeled ORTEP drawings of **6** and **7**, and CIF files giving crystallographic data for **6** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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