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Dearomatization and Functionalization of Terpyridine by Lutetium(III) Alkyl Complexes

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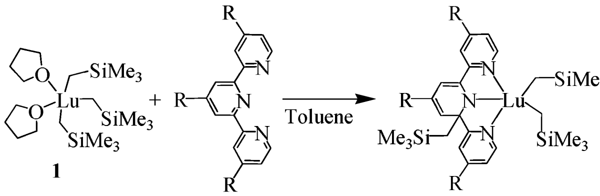
Although transition-metal complexes employing a terminal Schrock-type alkylidene functionality are ubiquitous, analogous lanthanide complexes remain scarce.[1] In 1979, Schumann alluded to the formation of lanthanide complexes supported by terminal alkylidene linkages, ostensibly obtained by $SiMe_4$ elimination from $[Li(Et_2O)_4][Lu(CH_2SiMe_3)_4]$ and $Er(CH_2SiMe_3)_3(THF)_2$. However, no definitive structural data for these proposed alkylidene complexes have ever been reported.[2] Among our efforts to stabilize f-element complexes containing multiply bonded functional groups, we first sought to form a robust lanthanide tris(alkyl) complex.

The popular tridentate ancillary ligand, 2,2′:6′,2″-terpyridine (tpy), has been shown to support transition metal, lanthanide, and actinide centers in a variety of oxidation states.[3] However, reaction of a toluene solution of $Lu(CH_2SiMe_3)_3(THF)_2$ (**1**)[4] with 1 equiv of tpy or 4,4′,4″-tri-*tert*-butyl-2,2′:6′,2″-terpyridine (${}^tBu_3$tpy) unexpectedly results in a 1,3-migration of one of the three alkyl groups to an ortho position in the central pyridine ring to give complexes **3a**−**b** in nearly quantitative yield (eq 1).[5]



(1)

R = H (**2a**), ^{t}Bu (**2b**) R = H (**3a**), ^{t}Bu (**3b**)

A consequence of the alkyl migration is loss of aromaticity and transformation of the neutral pyridine into an anionic amide ligand. While there have been reports of pyridine and pyridine-based ligands undergoing further reactivity upon coordination to a metal center,[6] to the best of our knowledge these are the first examples of dearomatization and ortho (2′ or 6′ position) functionalization of terpyridine ligands. This observation clearly demonstrates that the terpyridine ligand framework is not as innocent as previously thought.

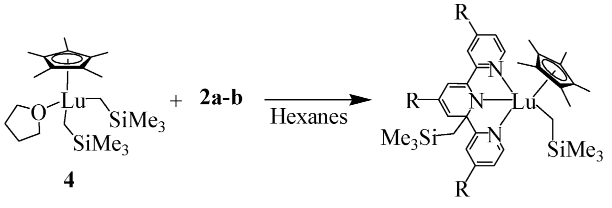
The ^{1}H NMR spectra of **3a** and **3b** display three distinct resonances for the methyl groups of the $-CH_2SiMe_3$ ligands. Additionally, largely separated diastereotopic doublets, corresponding to the methylene group on the migrated alkyl ligand, are observed at δ 2.09 and 0.99 ppm (**3a**) and δ 2.31 and 1.18 ppm (**3b**). The ${}^{13}C\{H\}$ NMR spectra revealed diagnostic upfield resonances, substantially shifted from the aromatic region, at δ 68.43 (**3a**) and 69.50 ppm (**3b**), attributed to the newly formed quaternary carbons.

Single-crystal X-ray diffraction confirmed that a 1,3-alkyl migration had occurred to form complex **3b** (Figure 1). The anionic amide moiety is evidenced by the short Lu(1)−N(2) bond distance of 2.217(7) Å, which compares well with those found in other structurally characterized lutetium amide complexes.[7] The dative interactions Lu(1)−N(1) (2.360(7) Å) and Lu(1)−N(3) (2.355(6) Å) are considerably shorter than those reported for the handful of structurally characterized monomeric neutral lutetium(III) complexes containing a terpyridine ligand[8] and is clearly attributable the anionic charge on the adjacent center ring of the functionalized terpyridine ligand.

The coordination geometry of the lutetium center is best described as distorted trigonal bipyramidal with the equatorial plane being defined by the two metal-bound alkyl groups and the amide nitrogen. Inspection of the bond distances within the central ring of this newly formed monoanionic ligand illustrates deviations in bond length and planarity consistent with loss of aromaticity. For example, the bond distances for N(2)−C(14) (1.444(10) Å) and C(14)−C(15) (1.466(12) Å) are consistent with single bonds to the newly formed quaternary carbon atom.[9]

The next four contiguous bonds in the ring have bond distances of 1.376(10) Å (C(15)−C(16)), 1.415(11) Å (C(16)−C(17)), 1.387(12) Å (C(17)−C(18)), and 1.389(9) Å (C(18)−N(2)) and show a pattern of alternating single and double bonds.[9] The C(18)−N(2) bond is shorter than expected for a single bond but is in agreement with the analogous bond distance observed in the only other structurally characterized dearomatized polypyridyl complex, $(C_5Me_5)Cr(\eta^3\text{-}C_{14}H_{18}N_2Si)$.[10] The Lu(1)−C(1) and Lu(1)−C(5) distances of 2.337(8) Å and 2.346(9) Å, respectively, are within the range typically observed for $Lu-CH_2SiMe_3$ bonds.[7a,11]

This 1,3-alkyl migration appears to be quite general. As shown in eq 2, treatment of a hexanes solution of the lutetium bis(alkyl) complex $(C_5Me_5)Lu(CH_2SiMe_3)_2(THF)$ (**4**)[7b] with 1 equiv of tpy or ${}^tBu_3$tpy affords complexes **5a**−**b** in essentially quantitative yield.[5]



(2)

R = H (**5a**), ^{t}Bu (**5b**)

As with **3a**−**b**, the alkyl migrations were evidenced by upfield resonances in the ${}^{13}C\{H\}$ NMR spectra of these complexes, corresponding to the newly formed quaternary carbons (δ 67.67 ppm (**5a**) and 68.81 ppm (**5b**)) on the dearomatized tpy ligand. Additionally, the diastereotopic methylene protons of the migrated

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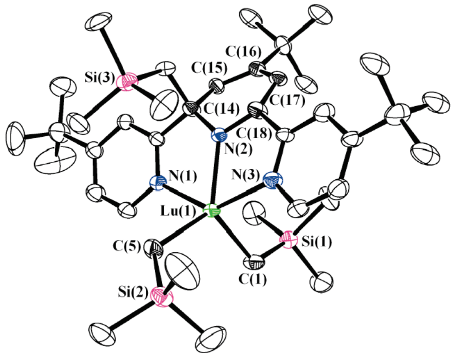

Figure 1. Molecular structure of complex **3b** with thermal ellipsoids at the 33% probability level.

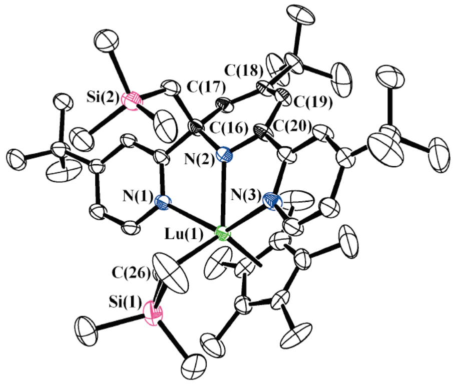

Figure 2. Molecular structure of complex **5b** with thermal ellipsoids at the 33% probability level.

alkyl group display diagnostic doublets at δ 2.03 and 0.93 ppm (**5a**) and δ 2.17 and 1.23 ppm (**5b**).

Complex **5b** was also examined by X-ray crystallography (Figure 2), from which pertinent metrical parameters include the Lu(1)−N(2) distance of 2.253(4) Å, the Lu(1)−N(1) distance of 2.387(4) Å, the Lu(1)−N(3) distance of 2.381(4) Å, and the Lu(1)−C(26) distance of 2.379(5) Å, all of which are comparable to those presented by complex **3b**.

Motivated by these findings, we performed density functional theory (DFT) calculations to gain a better understanding of our results.[5] We investigated the relative energies of the observed product **5a** as well as the target bis(alkyl) complex $(C_5Me_5)(tpy)Lu(CH_2SiMe_3)_2$ (**6**). In accord with the experimental observations, complex **5a** is calculated to be more stable than **6** by 23.5 kcal/mol. Geometries were optimized without symmetry constraints using an effective core potential for Lu.[13] The calculated bond lengths for the Lu−N interactions (2.270, 2.440, and 2.424 Å) in **5a** are in accord with those determined for complex **5b** by X-ray crystallography, especially in the predicted shortening (0.16 Å calculated; 0.13 Å experimental) of the "Lu−N(2)" bond relative to the other two Lu−N interactions. By comparison, the bis(alkyl) complex **6** has nearly equal Lu−N bond lengths (2.397, 2.406, and 2.402 Å). We also note in **6** the calculated Lu−C bond distance (2.431 Å) opposite the tpy ligand is shorter than the Lu−C bond (2.585 Å) trans to the C_5Me_5 ligand.

Similarly, complex **3a** is calculated to be 14.4 kcal/mol more stable than the target tris(alkyl) complex $(tpy)Lu(CH_2SiMe_3)_3$ (**7**). Calculated bond lengths for the Lu−N interactions (2.262, 2.399, and 2.400 Å) in **3a** agree with those determined for complex **3b** by X-ray crystallography. Again, nearly identical Lu−N bond distances (2.405, 2.406, and 2.413 Å) are calculated for **7**. The calculated Lu−C bond lengths (2.350, 2.368 Å) for **3a** are shorter compared to those in **7** (2.401, 2.456, and 2.485 Å).

Finally, the relative stabilities of the alkylidene complexes $(C_5Me_5)(tpy)Lu[{=}C(H)SiMe_3]$ (**8**) and the comparable $(tpy)(CH_2SiMe_3)Lu[{=}C(H)SiMe_3]$ (**9**) resulting from the elimination of $SiMe_4$ from **6** and **7**, respectively, were also calculated. It is interesting that the elimination reaction from **6** to form the alkylidene complex **8** is exothermic by 2.7 kcal/mol, while the corresponding elimination reaction from **7** to give **9** is endothermic by 9.6 kcal/mol. This indicates that the formation of a lutetium alkylidene functional group is energetically viable from a thermodynamic standpoint. These pursuits are currently under investigation in our laboratory.

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Supporting Information Available: Full experimental and spectroscopic details for all compounds and crystallographic data for complexes **3b** and **5b** (PDF, CIF); details of DFT calculations and coordinates of optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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