

C–H activation of a 2,2'-bipyridine ligand within (mono)pentamethylcyclopentadienyl lutetium complexes†

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We report the activation of a 2,2'-bipyridine ligand within a class of (mono)cyclopentadienyl lanthanide complexes when reacted with carbon monoxide.

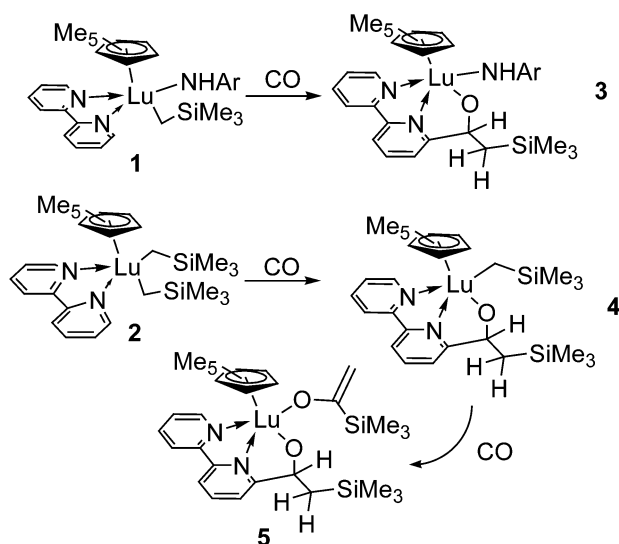
The synthesis and reactivity of lanthanide (Ln) complexes stabilized by two cyclopentadienyl (Cp) ligands have been studied extensively.¹ In contrast, Ln species containing only one Cp ligand are less common but have received considerable attention in the literature of late.² The impetus for mono-cyclopentadienyl complexes centers around the potential for increased coordinative unsaturation and control of the electronic structure about the metal center through ancillary ligands, thereby offering the possibility of enhanced or new reactivity. We recently reported the synthesis and characterization of (mono)pentamethylcyclopentadienyl (Cp*) lutetium complexes supported by 2,2'-bipyridine (bipy), [Cp*Lu(NHAr)(CH₂SiMe₃)(bipy)] (1) and [Cp*Lu(CH₂SiMe₃)₂(bipy)] (2) (Scheme 1, Ar = 2,6-*i*-Pr₂C₆H₃).³ Herein, we present reactions of 1 and 2 with carbon monoxide (CO) which generate [Cp*Lu(NHAr)(OCH(CH₂SiMe₃)–C₁₀H₇N₂)] (3) and [Cp*Lu(OC(SiMe₃)=CH₂)(OCH(CH₂SiMe₃)–(C₁₀H₇N₂))] (5) (Scheme 1). This chemistry can be formally described as insertion of a putative acyl (from carbonylation of an alkyl) into a C–H bond of the bipy ligand. While similar chemistry has been described for two early transition metal systems,^{4,5} our work is the first observation, to our knowledge, of a transformation of this kind within a mono-Cp heteraromatic Ln system.⁶ Of particular note is that our chemistry proceeds at much lower pressures of CO (*ca.* 15 psi).

Treatment of a benzene solution of 1 with CO gas (*ca.* 15 psi) for 1 day at room temperature resulted in the generation of 3.‡ Crystals of 3 were isolated from concentrated benzene solutions by decantation in 39% yield. The solution structure of 3 as determined by NMR spectroscopy is consistent with the depiction in Scheme 1

as well as the solid-state structure (see below). Treatment of a concentrated benzene solution of 2 with CO gas (*ca.* 15 psi) over a 3 day period resulted in the formation of 5.§ When reaction of 2 with CO gas was monitored by ¹H NMR spectroscopy, the bipy activation product 4 was observed§ to accumulate and then be consumed as 5 formed. Red microcrystals of 5 precipitated from the reaction mixture over the 3 day period and were isolated by decantation in 26% yield. Complex 5 has been fully characterized by solution NMR spectroscopy.§ The inequivalent SiMe₃ groups resonate at 0.32 ppm and 0.43 ppm while the alkoxide proton appears at 5.77 ppm in the proton NMR spectrum. The inequivalent olefinic protons resonate at 4.61 ppm and 5.13 ppm (²J_{H–H} = 1.0 Hz) in the ¹H NMR spectrum. Of particular interest in both reactions is the observed formation of only one diastereomer of 3 or 5 with the CH₂SiMe₃ and Cp* functionalities adopting an *anti* relationship as determined by X-ray crystallography and NMR spectroscopy. This is presumably a result of steric interactions between the SiMe₃ and Cp* groups during the reaction.

The structures of 3 and 5 were confirmed by single crystal X-ray crystallography.¶ As shown in Fig. 1, the geometry about the metal in 3 is best described as distorted square pyramidal with the Cp* functionality occupying the apical position. The Lu(1)–N(3) bond length of 2.238(4) Å is within the expected range for a Lu–amide interaction.⁷ The Lu(1)–O(1) bond length is 2.112(3) Å and is consistent with a Lu–O terminal alkoxide interaction.⁸ As shown in Fig. 2, the distorted square pyramidal geometry in 5 is similar to that in 3 as are the related Lu(1)–N(1), N(2), and O(1) distances. An interesting feature in 5 is the enolate ligand. Within the enolate fragment the C(26)–C(27) bond length of 1.32(1) Å is as expected for a C=C bond and there is no evidence of interaction with the metal.⁹

The net reaction of 1 and 2 with CO can be formally viewed as CO insertion into a Lu–C bond, forming an acyl, followed by subsequent acyl “insertion” into a bipy C–H bond. In the case of 2, a second CO insertion followed by SiMe₃ migration¹⁰ generates the final enolate product (5). Two examples where early transition metal species show this type of reactivity when treated with pyridine (py) and CO have been described by Rothwell (for a



Scheme 1

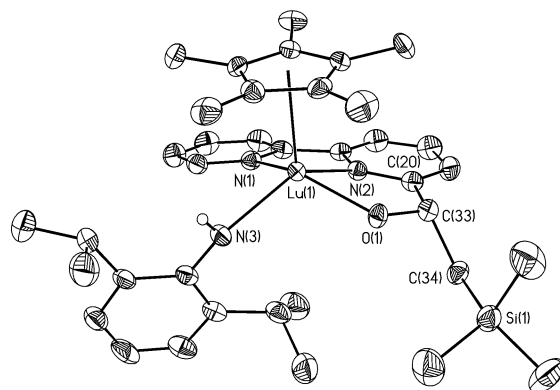


Fig. 1 Thermal ellipsoid plot of 3 (35% probability thermal ellipsoids). Selected bond lengths (Å) and angles (°): Lu(1)–N(1) 2.456(3), Lu(1)–N(2) 2.360(3), Lu(1)–O(1) 2.112(3), O(1)–C(33) 1.397(5), Lu(1)–N(3) 2.238(4), N(1)–Lu(1)–N(2) 65.4(1), N(2)–Lu(1)–O(1) 70.4(1), O(1)–Lu(1)–N(3) 108.8(1), N(3)–Lu(1)–N(1) 86.2(1).

† Electronic supplementary information (ESI) available: experimental details. See <http://www.rsc.org/suppdata/cc/b4/b405039h/>

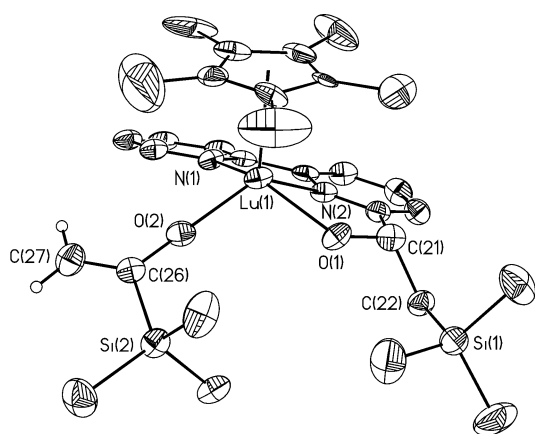
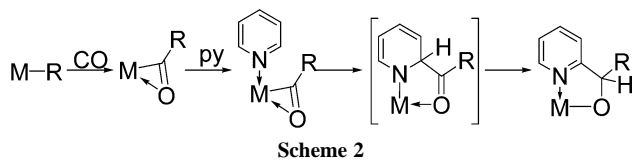


Fig. 2 Thermal ellipsoid plot of **5** (35% probability thermal ellipsoids). Selected bond lengths (Å) and angles (°): Lu(1)–N(1) 2.445(7), Lu(1)–N(2) 2.400(4), Lu(1)–O(1) 2.104(5), Lu(1)–O(2) 2.062(5), O(1)–C(21) 1.39(1), C(27)–C(26) 1.32(1), O(2)–C(26) 1.345(9), C(26)–Si(2) 1.873(8), N(1)–Lu(1)–N(2) 65.9(2), N(2)–Lu(1)–O(1) 68.9(2), O(1)–Lu(1)–O(2) 102.7(2), O(2)–Lu(1)–N(1) 88.6(2).

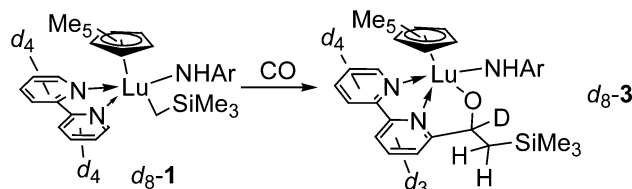
[M(OAr)₂Me₂] system, M = Zr, Hf; Ar = 2,6-*t*-Bu₂C₆H₃, *ca.* 1000 psi CO) and Tilley (for [Cp*Cl₂HfSi(SiMe₃)₃], *ca.* 100 psi CO),^{4,5} Based on their results, including the observation of no kinetic isotope effect when *d*₅-pyridine was used, both authors proposed a mechanism involving the nucleophilic attack of an η²-acyl carbon on the py functionality followed by a facile hydrogen shift (Scheme 2).^{4c,5a} Evans *et al.* reported that treatment of (Cp*)₂Sm(THF)₂ with diphenylacetylene followed by reaction with CO (*ca.* 90 psi) produces a dihydroxyindenoindene containing species.⁶ Evans advanced an alternative mechanism where an acyl acts as an oxycarbene and inserts into the *ortho*-CH bond of an aryl group resulting in product formation. The oxycarbene nature of Ln acyls has also been put forth to explain the conversion of an acyl to an enolate *via* a shift of a trimethylsilyl group.^{10a}

To gain insight into the reactivity of **1** and **2** we have prepared the deuterated bipy analogue of **1** (*d*₈-**1**, Scheme 3).[§] ¹H and ²H NMR analysis of the reaction of *d*₈-**1** with CO confirmed the formation of *d*₈-**3** where the deuterium in the 6 position of bipy was transferred to the alkoxide β-carbon of *d*₈-**3** (Scheme 3). Scrambling of the deuteria into the other ligands is not observed. To determine whether there is any significant isotope effect, we followed the reaction progress of both **1** and *d*₈-**1** with CO in parallel by NMR spectroscopy. We observed the same time profiles for **1** and *d*₈-**1** indicating no measurable kinetic isotope effect.

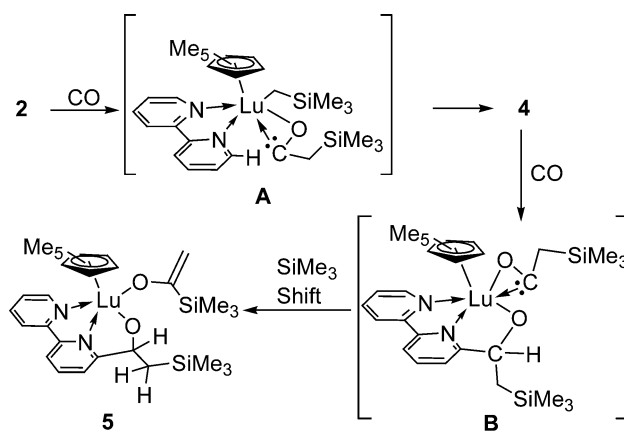
The lack of a kinetic isotope effect when **1** reacts with CO requires that the step involving C–H bond cleavage must follow at least one rate-determining step. Our results are consistent with the mechanism in Scheme 2, however, we believe that our results do not rule out the mechanism advanced by Evans (*i.e.* oxycarbene insertion into a C–H bond; Scheme 4). The observation of complex **4** strongly suggests that the cyclization of a putative acyl is faster than CO insertion into alkyls **2** or **4**. This result suggests that C–H bond cleavage would occur in a step following a rate-determining step; therefore, we cannot favor either mechanism at this time.



Scheme 2



Scheme 3



Scheme 4

In summary, we have observed that mono-Cp Lu complexes react with CO resulting in the C–H activation of a bipy ligand. Our work shows that a bipy ligand can stabilize interesting mono-ring lutetium complexes and can also participate in interesting chemistry.

Notes and references

‡ Currently on assignment at: US Department of Energy, Office of Basic Energy Sciences, Germantown, MD, USA.

§ *Synthesis*: see the ESI for details involving the synthesis of **3** and **5** as well as the ¹H and ¹³C NMR data. The conversion of **1** to **3** was quantitative as determined by NMR spectroscopy. The low yield of **3** was due to difficulty in crystallization. Generation of **5** from **2** was not quantitative as determined by NMR spectroscopy and the other products of this reaction have not yet been identified. Compound *d*₈-**1** was generated using *d*₈-bipy following the procedure for the synthesis of **1**.³ Full structural assignment of **5** by two-dimensional NMR and selected ¹H NMR data for **4** are also included in the ESI.

¶ *Crystal data*: for **3**: C₃₇H₅₂N₃OSiLu, *M* = 757.88, *a* = 11.390(4) Å, *b* = 19.073(6) Å, *c* = 17.675(5) Å, β = 106.877(6)°, *V* = 3674.4(19) Å³, monoclinic, space group *P*2₁/*c*, *Z* = 4, μ(Mo–Kα) = 2.750 mm^{−1}, *T* = 203 K, final *R*1 (*I* > 2σ) = 0.0326, *wR*2 (*I* > 2σ) = 0.0785, GOF (on *F*²) = 1.793. For **5**: C₃₀H₄₅N₂O₂Si₂Lu, *M* = 696.83, *a* = 11.367(2) Å, *b* = 20.140(5) Å, *c* = 14.186(3) Å, β = 98.178(4)°, *V* = 3214.6(12) Å³, monoclinic, space group *P*2₁/*n*, *Z* = 4, μ(Mo–Kα) = 3.173 mm^{−1}, *T* = 203 K, final *R*1 (*I* > 2σ) = 0.0711, *wR*2 (*I* > 2σ) = 0.1155, GOF (on *F*²) = 1.256. CCDC 235857 and 236211. See <http://www.rsc.org/suppdata/cc/b4/b405039h/> for crystallographic data in .cif format.

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