C–H activation motivated by *N*,*N′*-diisopropylcarbodiimide within a lutetium complex stabilized by an amino–phosphine ligand†‡

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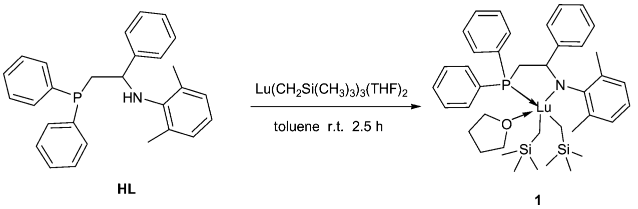
A lutetium bis(alkyl) complex stabilized by a flexible amino–phosphine ligand LLu($CH_2Si(CH_3)_3)_2$(THF) (L = (2,6-C_6H_3-$(CH_3)_2$)NCH(C_6H_5)$CH_2P(C_6H_5)_2$) was prepared which upon insertion of *N*,*N′*-diisopropylcarbodiimide led to C–H activation *via* metalation of the ligand aryl methyl followed by reduction of the C=N double bond.

Rare earth metal alkyl complexes have shown an upsurge in research interest for their rich and unique chemistry, such as hydrogenolysis,[1] amination,[2] alkynide,[2a,3] carbon dioxide fixation,[4] and catalysis of the polymerization of olefins[5] and polar monomers,[6] among which those supported by phosphide ligands are less common but have received considerable attention recently.[7] The impetus for phosphorus chelating complexes centrers around their potential for catalytic activity toward non-polar monomers[8] and new stoichiometric chemistry *via* the introduction of “large” and “soft” phosporus donors. Our group has focused on amino–phosphine ligands and successfully isolated several Group 3 metal bis(alkyl) complexes, $L^rLu(CH_2Si(CH_3)_3)_2$(THF) (L^r = (2,6-$C_6H_3(CH_3)_2$)$NCH_2C_6H_4P(C_6H_5)_2$), where L^r is a rigid bidentate amino–phosphine ligand. These complexes are highly active initiators for the ring-opening polymerization of lactide.[2b] Herein we report a lutetium bis(alkyl) complex attached by a flexible amino–phosphine ligand LLu($CH_2Si(CH_3)_3)_2$(THF) (L = (2,6-$C_6H_3(CH_3)_2$)NCH(C_6H_5)$CH_2P(C_6H_5)_2$) and its unique reactivity with carbodiimide and C–H activation within this complex. Although C–H activation *via* metalation of ligand aryl substituents[2b,7e,9] or motivated upon CO insertion[10] has been reported, we present for the first time, as far as we aware, C–H activation *via* metalation of aryl methyl motivated by insertion of carbodiimide; in addition, the newly formed metal–carbon bond is extremely active, enough to reduce the C=N double bond of carbodiimide. This is proved further to depend significantly on the ligand framework.



Scheme 1

Treatment of a toluene solution of Lu($CH_2Si(CH_3)_3)_3(THF)_2$ with HL for 2.5 h at room temperature afforded complex **1** in 65% yield (Scheme 1). The ^{1}H NMR spectrum shows a singlet at −0.24 ppm assigned to the methylene protons of two metal alkyls which are equivalent owing to their fluxional nature within the NMR timescale. The solid-state structure of **1** was characterized by X-ray analysis to be a monomer, adopting trigonal-bipyramidal geometry around the metal center (Fig. 1).§ Atoms N(1), C(29), C(33) and Lu(1) are equatorial with Lu(1) lying 0.2491 Å above the plane. While atoms P(1) and O(1) locate at the axial positions. The two alkyl species arrange in *cis*-positions. The Lu–C bond lengths (av. 2.331 Å) and C(29)–Lu(1)–C(33) bond angle (114.9(2)°) are comparable to the corresponding values in the literature.[7c,8a,11] Complex **1** represents the first example of rare earth metal bis(alkyl)s stabilized by this flexible amino–phosphine

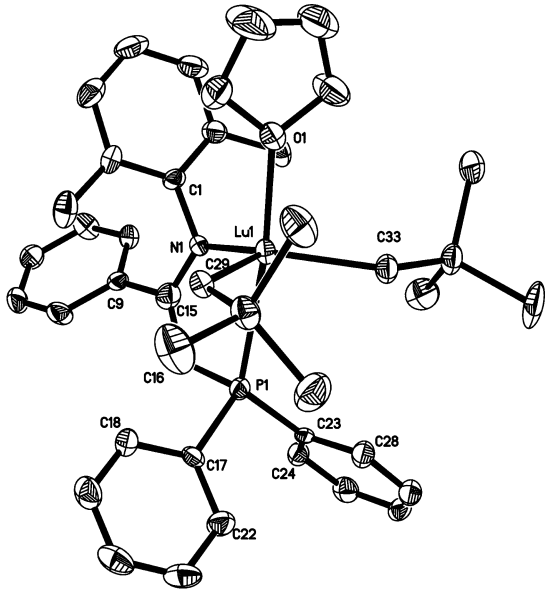


Fig. 1 Molecular structure of **1** (hydrogen atoms omitted for clarity; thermal ellipsoids drawn to 50% probability level). Selected bond distances (Å) and angles (°): Lu(1)–N(1) 2.244(5), Lu(1)–O(1) 2.269(4), Lu(1)–C(29) 2.327(6), Lu(1)–C(33) 2.355(6), Lu(1)–P(1) 2.9161(17); N(1)–Lu(1)–O(1) 102.84(17), N(1)–Lu(1)–C(29) 112.2(2), O(1)–Lu(1)–C(29) 91.7(2), N(1)–Lu(1)–C(33) 129.4(2), O(1)–Lu(1)–C(33) 93.4(2), C(29)–Lu(1)–C(33) 114.9(2), N(1)–Lu(1)–P(1) 70.48(12), O(1)–Lu(1)–P(1) 172.60(12), C(29)–Lu(1)–P(1) 88.12(16), C(33)–Lu(1)–P(1) 93.42(17).

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‡ Electronic supplementary information (ESI) available: Experimental section, ^{1}H NMR, ^{13}C NMR ^{1}H–^{1}H COSY and ^{1}H–^{13}C HMQC and their assignment of complexes **2** and **4**. See DOI: 10.1039/b710039f

ligand although their transition-metal counterparts[12] have been extensively reported and have their unique chemistry studied.

Addition of an equimolar amount of *N*,*N*′-diisopropylcarbodiimide (DIPCDI) to a hexane suspension of **1** started the reaction immediately, and the precipitate disappeared gradually. Concentration of the reaction solution under reduced pressure followed by cooling at −30 °C for several days, gave light yellow crystals of complex **2** (40%). The ^{1}H NMR spectrum of **2**‡ is clean but complicated. The resonances of the metal alkyl species $LuCH_2Si(CH_3)_3$ at upfield region −0.24 ppm disappear; meanwhile, a downfield singlet at 1.34 ppm shows up, which could be assigned to the methylene protons $CH_2Si(CH_3)_3$ of the amidinate moiety;[13] one aryl methyl of the ligand fragment gives a singlet at 2.45 ppm similar to that in **1**, whereas, the two discrete AB spins at 2.03 and 2.17 ppm ($J_{\text{H,H}} = 12$ Hz) are assignable to the diastereotopic methylene protons derived from another aryl methyl of the ligand fragment with the loss of one proton.

The molecular structure of **2** was eventually determined by X-ray diffraction analysis to be a heteroleptic monomer (Fig. 2).§ The Lu ion is coordinated by a monoanionic amidinate ligand and a dianionic P,N,N tridentate moiety. The molecular core adopts distorted square-bipyramidal geometry with P(1) and N(4) locating at the apexes and the N(1), N(2), N(3) and O(1) atoms defining the base. The bond distances Lu(1)–N averaging 2.275 Å are within the reasonsble range for a Lu–N single bond.[2a,11,14] The C(29)–N(2) bond length (1.348(11) Å) is close to C(29)–N(3) (1.339(11) Å). Both are between the values for C–N single bond and C=N double bond. This indicates that the π-electrons delocalize within N–C–N of the amidinate unit, consistent with an η^2 coordination mode.[15] In contrast, a 1.372(11) Å bond length assigns C(44)–N(4) to be a single bond, meanwhile a bond length of 1.301(12) Å for C(44)–N(5) suggests a double bond nature.[16]

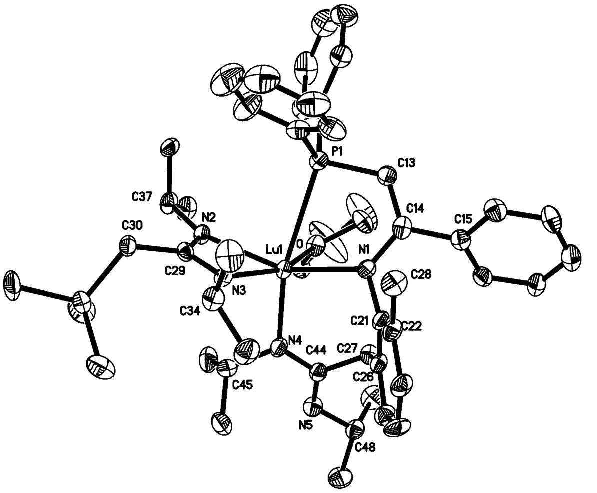
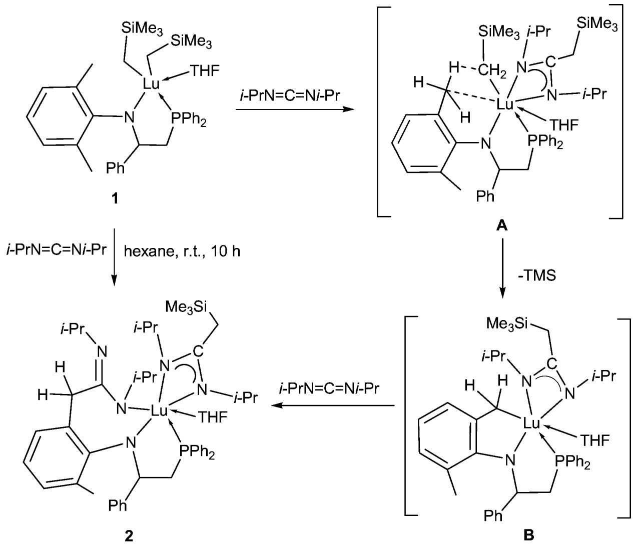


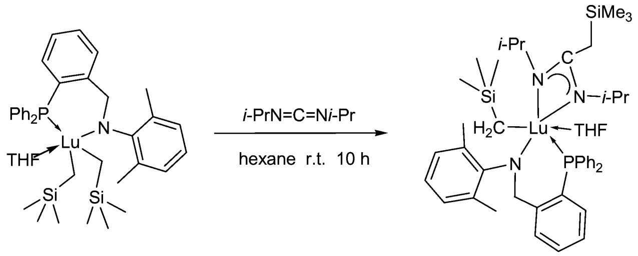
Fig. 2 Molecular structure of **2** (hydrogen atoms omitted for clarity; thermal ellipsoids drawn to 50% probability level). Selected bond distances (Å) and angles (°): Lu(1)–N(4) 2.222(8), Lu(1)–N(3) 2.246(7), Lu(1)–N(1) 2.304(7), Lu(1)–N(2) 2.329(7), Lu(1)–O 2.3816, Lu(1)–P(1) 3.033(3); C(44)–N(4) 1.372(11); C(44)–N(5) 1.301(12); N(4)–Lu(1)–N(3) 99.8(3), N(4)–Lu(1)–N(1) 102.6(3), N(3)–Lu(1)–N(1) 108.1(3), N(4)–Lu(1)–N(2) 105.7(3), N(3)–Lu(1)–N(2) 58.8(3), N(1)–Lu(1)–N(2) 150.4(3), N(4)–Lu(1)–O 86.0(3), N(3)–Lu(1)–O 157.3(2), N(1)–Lu(1)–O 91.7(2), N(2)–Lu(1)–O 98.6(2), N(4)–Lu(1)–P(1) 165.8(2), N(3)–Lu(1)–P(1) 92.9(2), N(1)–Lu(1)–P(1) 66.92(18), N(2)–Lu(1)–P(1) 86.41(19), O–Lu(1)–P(1) 84.81(17).

Thus, the synthetic pathway can be depicted as shown in Scheme 2. Nucleophilic attack of metal alkyl to the carbon atom of DIPCDI results in an insertion intermediate **A** of a mono(alkyl) bearing amidinato moiety. C–H activation *via* metalation of the aryl methyl group of the amino–phosphine moiety by the metal alkyl species in **A** leads to elimination of tetramethylsilane and formation of a Lu–C linkage, generating a heteroleptic intermediate **B** bearing mixed amidinato/dianionic P,N,C fragments. Insertion of DIPCDI into the newly formed Lu–C bond of **B** results in reduction of the C=N double bond to form a dianionic P,N,N tridentate chelate accompanied by cleavage of Lu–C and formation of Lu–N bonds, to afford **2**. This is different from the formation of C–H activation products reported previously that are disproportionation derivatives formed during isolation of the corresponding bis(alkyl)s.[2b,7c,9c] In our case, the bis(alkyl) complex is stable, and C–H activation takes place only upon insertion of DIPCDI.



Scheme 2

To confirm that formation of **2** is *via* a mixed alkyl/amidinate intermediate **A**, we tried to isolate it but failed. Monitoring the reaction by NMR techniques still can not provide information for the transient existence of **A**. We have reported previously a P,N-bidentate ligand stabilized lutetium bis(alkyl) complex **3**[2b] that was employed to react with DIPCDI, anticipated to afford a stable analogue of **A** because it bears a more rigid phosphine–amido moiety. The reaction between **3** and 1 equiv. of DIPCDI took place smoothly at room temperature over night. Fortunately, the mono-DIPCDI insertion product, lutetium mixed alkyl/amidinate complex **4**, was isolated from the above mixture cooled at −30 °C for several days (Scheme 3). Although there is no X-ray crystallographic proof, the ^{1}H NMR spectrum is clear enough to confirm the molecular structure of **4**‡ in solution. The two singlets at upfield region −0.34 ppm and downfield region 1.96 ppm are assignable to the metal alkyl species $LuCH_2Si(CH_3)_3$[2b] and $CH_2Si(CH_3)_3$ of the newly formed amidinate, respectively. Correspondingly, the silylmethyl protons



3 **4**

Scheme 3

exhibit two singlets at 0.19 and 0.39 ppm compared to one singlet in **3**. The typical resonance for the isopropyl methine of DIPCDI is found at 3.57 ppm. The integrated intensities of the related resonances indicate firmly one alkyl moiety and one amidinate ligand in **4**. Thus, we have demonstrated indirectly that the lutetium bis(alkyl) complex **1** bearing a flexible P,N bidentate ligand reacts with carbodiimide to form an unstable mixed alkyl/amidinato intermediate **A** in analogy to **4**, which facilitates C–H activation of the *ortho* methyl proton of the phosphine–amido ligand *via* metalation with release of alkane. This is significantly attributed to the different flexibility of the ligand backbone of complex **1** from **3**.

In summary, we have prepared and characterized a new lutetium bis(alkyl) complex stabilized by a flexible amino–phosphine ligand, which exhibits novel reactivity: C–H activation of the ligand promoted by *N*,*N*′-diisopropylcarbodiimide. We also demonstrated that backbone-flexibility of ligand plays a significant role in this process. The polymerization catalytic activity of these complexes toward some monomers is in process.

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Notes and references

§ Crystal data for **1**·(C_6H_6): $C_{46}H_{63}NOSi_2PLu$, M = 908.09, monoclinic, $C2/c$, a = 41.074(3) Å, b = 11.8955(10) Å, c = 19.6868(16) Å, β = 107.9790(10)°, V = 9149.2(13) Å^3, Z = 8, D_c = 3.218 g cm^{-3}, μ = 17.617 cm^{-1}, no. of reflections collected = 23425, no. of unique reflections = 8379, R_{int} = 0.0719, GOF = 1.003, R = 0.0521, R_w = 0.0965, R (all data) = 0.0883, R_w (all data) = 0.1078. For **2**: $C_{50}H_{71}N_5OSiPLu$, M = 992.15, triclinic, $P\bar{1}$, a = 11.4181(11) Å, b = 12.6687(12) Å, c = 19.722(2) Å, α = 106.954(2)°, β = 102.899(2)°, γ = 91.243(2)°, V = 2648.5(4) Å^3, Z = 2, D_c = 3.300 g cm^{-3}, μ = 18.067 cm^{-1}, no. of reflections collected = 14262, no. of unique reflections = 9546, R_{int} = 0.0409, GOF = 1.059, R = 0.0655, R_w = 0.1726, R (all data) = 0.0864, R_w (all data) = 0.1884.

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