Activation and Dehydrogenative Silylation of the C–H Bonds of Phosphine-coordinated Ruthenium in Lu/Ru Heteromultimetallic Hydride Complexes

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(Received December 28, 2007; CL-071451; E-mail: houz@riken.jp)

The reaction of half-sandwich lutetium dialkyl complex $Cp^*Lu(CH_2SiMe_3)_2(THF)$ ($Cp^* = C_5Me_5$) with ruthenium–trihydrido–phosphine complexes $Cp^*Ru(PR_3)H_3$ ($R_3 = Ph_3$, Ph_2Me, $PhMe_2$, and Me_3) at 50 °C afforded the corresponding Lu/Ru heterobimetallic dihydride complexes, which was accompanied by selective C–H bond activation of the phosphine ligand. The reaction of such a resulting phosphinomethyl-bridged Lu/Ru complex with $PhSiH_3$ led to selective dehydrogenative silylation at the "CH_2" unit.

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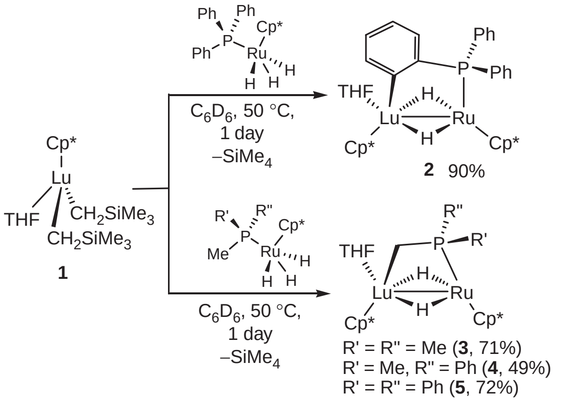
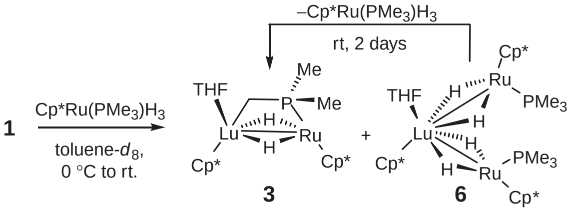
d–f Heterobimetallic hydride complexes consisting of a lanthanide (f-block) metal and a late d-block transition metal are of much interest because of the synergistic effects that may result from the two substantially different metal centers. Despite continuous interest in this area, well-defined d–f heterometallic hydride complexes are still limited, and most of them are constructed by use of the bis(cyclopentadienyl)-ligated lanthanide precursors. The reaction chemistry of d–f heterometallic hydride complexes has so far remained almost unexplored.[1] Therefore, the synthesis and reactivity examination of d–f heterometallic hydride complexes with new structures remain an important research subject.

We have recently found that mono(cyclopentadienyl)-ligated rare-earth (group 3 and lanthanide metal) dialkyl[2] or dihydride[3] complexes can show unique reactivities that differ from those of the bis(cyclopentadienyl)-ligated analogues in olefin polymerization catalysis and other reactions with unsaturated organic substrates. During these studies, we became interested in the use of such half-sandwich rare–earth complexes as building blocks for the synthesis of rare-earth and d-block heteromultimetallic complexes. We report here the synthesis, structural characterization, and C–H bond activation reactions of Lu/Ru heterobimetallic hydride complexes. These complexes represent the first examples of d–f heteromultimetallic complexes that are constructed by a half-sandwich lanthanide unit.



Scheme 1.



Scheme 2.

The reaction of the half-sandwich lutetium dialkyl complex $Cp^*Lu(CH_2SiMe_3)_2(THF)$ ($Cp^* = C_5Me_5$) (**1**)[4] with 1 equiv. of the PPh_3-coordinated ruthenium trihydrido complex $Cp^*Ru(PPh_3)H_3$[5] in C_6D_6 afforded the Lu/Ru heterobimetallic dihydrido complex $Cp^*Lu(THF)(\mu\text{-}H)_2(\mu\text{-}\eta^1{:}\eta^1\text{-}C_6H_4PPh_2)RuCp^*$ (**2**) in 90% isolated yield with liberation of tetramethylsilane (Scheme 1). This reaction proceeded formally via "deprotonation" of the ruthenium hydride by the alkyl groups of **1** followed by activation of a phenyl ortho-C–H bond of the Ru-bound-PPh_3 ligand at the Lu metal center. The reaction of **1** with the PMe_3-coodinatied Ru hydrido complex $Cp^*Ru(PMe_3)H_3$[5] gave analogously the methyl C–H bond activation product $Cp^*Lu(THF)(\mu\text{-}H)_2(\mu\text{-}\eta^1{:}\eta^1\text{-}CH_2PMe_2)RuCp^*$ (**3**). When the mixed methyl/phenyl phosphine complexes $Cp^*Ru(PMe_2Ph)H_3$ and $Cp^*Ru(PMePh_2)H_3$ were used to react with **1**, the C–H bond activation took place selectively only at the methyl group to give $Cp^*Lu(THF)(\mu\text{-}H)_2(\mu\text{-}\eta^1{:}\eta^1\text{-}CH_2P(Me)Ph)RuCp^*$ (**4**)[6] and $Cp^*Lu(THF)(\mu\text{-}H)_2(\mu\text{-}\eta^1{:}\eta^1\text{-}CH_2PPh_2)RuCp^*$ (**5**), respectively. This is in sharp contrast with what was observed previously in the homoleptic Rh[7] or Ru[8] complexes, in which the metallation of a phenyl group or both a phenyl and a methyl group took place in the mixed methyl/phenyl phosphine ligands.

^1H NMR monitoring of the reaction of **1** with 1 equiv. of $Cp^*Ru(PMe_3)H_3$ in toluene-d_8 at 0 °C showed the formation of an intermediate assignable to $Cp^*Lu(THF)[(\mu\text{-}H)_2(PMe_3)RuCp^*]_2$ (**6**) together with a small amount of **3** and the unreacted **1** (Scheme 2). When the reaction mixture was warmed to room temperature, complex **3** increased gradually with decrease of **6** and **1**, and the reaction was completed in about 2 days. These results suggest that the Lu/Ru heterobimetallic complex **3** could be formed first by the reaction of the dialkyl Lu complex **1** with two molecules of $Cp^*Ru(PMe_3)H_3$ to give the trimetallic complex **6**, followed by C–H bond activation of a methyl group in PMe_3 at the Lu center and simultaneous release of one molecule of $Cp^*Ru(PMe_3)H_3$ (Scheme 2).

Complexes **2**–**5** were fully characterized by NMR (^1H, ^{13}C,

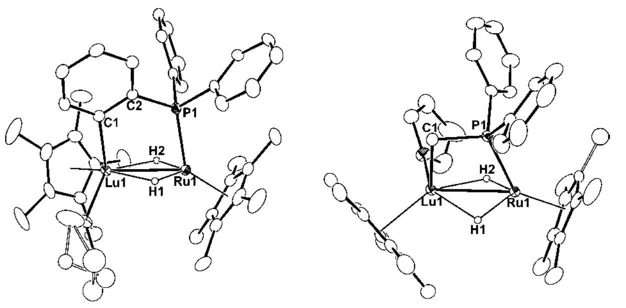
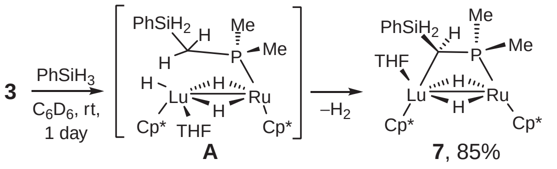


Figure 1. ORTEP drawings of **2** (left) and **5** (right) with 30% thermal ellipsoids. Selected bond lengths (Å) and angles (°) for **2**: Lu1–Ru1, 2.8797(4); Lu1–C1, 2.364(4); Ru1–P1, 2.2735(9); Ru1–H$_{av.}$, 1.60(4); Lu1–H$_{av.}$, 2.15(4); Lu1–Ru1–P1, 82.11(2); Ru1–Lu1–C1, 92.80(9); Ru1–P1–C2, 120.10(11); P1–C2–C1, 116.6(3); Lu1–C1–C2, 118.5(2). **5**: Lu1–Ru1, 2.8517(4); Ru1–P1, 2.2931(10); Lu1–C1, 2.333(4); P1–C1, 1.806(4); Ru1–H$_{av.}$, 1.65(3); Lu1–H$_{av.}$, 2.12(3); C1–Lu1–Ru1, 82.26(9); P1–Ru1–Lu1, 69.54(3); C1–P1–Ru1, 113.21(13); P1–C1–Lu1 90.77(15).



Scheme 3.

and ^{31}P), X-ray, and micro elemental analyses.[9] The X-ray structures of **2** and **5** are shown in Figure 1. The Lu and Ru atoms in **2** are bridged by two hydrido ligands and one ortho-phosphinophenyl unit (Figure 1, left). The bond distance of the Lu1–Ru1 bond (2.8797(4) Å) in **2** is much shorter than that of the only previously reported Lu–Ru bond in (THF)$(C_5H_5)_2$-$LuRu(CO)_2(C_5H_5)$ (2.995(2) Å).[1f] The Lu1–Ru1 bond distance (2.8517(4) Å) in **5** is further shorter probably because of its phosphinomethyl bridge (Figure 1, right). The bond distances of the Lu1–H bonds (av. 2.15(4) Å) and the Ru1–H bonds (av. 1.60(4) Å) in **2** are comparable with those in **5** (2.12(3) and 1.65(3) Å), respectively.

The reaction of **3** with $PhSiH_3$ at room temperature led to dehydrogenative silylation at the methylene unit to give **7** (Scheme 3).[10] This reaction could proceed via the intermediate **A**.[11] However, formation of such an intermediate (or any other) was not observed even at low temperatures, suggesting that the dehydrogenation of the methylene C–H bond could be very fast.

In summary, we have demonstrated for the first time that a half-sandwich lanthanide dialkyl complex such as **1** can serve as a useful building block for the synthesis of d–f heteromultimetallic complexes. The easy formation of complexes **2**–**5** and **7** demonstrated that C–H bond activation could take place facilely in a d–f heteromultimetallic hydride complex. Further studies on the synthesis and reactivity of d–f heteromultimetallic hydride complexes with other metal combinations are in progress.

This work was supported by Grant-in-Aid for Scientific Research on Priority Areas (No. 18065020, "Chemistry of Concerto Catalysis") from Ministry of Education, Culture, Sports, Science and Technology, Japan.

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9 See Supporting Information for details, which is available electronically on the CSJ-Journal web site, http://www.csj.jp/journals/chem-lett/. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC-675087–675091. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

10 For examples of silylation of a C(sp^3)–H bond, see: a) F. Kakiuchi, K. Tsuchiya, M. Matsumoto, E. Mizushima, N. Chatani, *J. Am. Chem. Soc.* **2004**, *126*, 12792. b) A. D. Sadow, T. D. Tilley, *J. Am. Chem. Soc.* **2005**, *127*, 643.

11 The reaction of a lanthanide alkyl unit Ln–R with $PhSiH_3$ to give Ln–H and $RSiH_2Ph$ has been well documented. For examples: See: a) A. Z. Voskoboynikov, I. N. Parshina, A. K. Shestakova, K. P. Butin, I. P. Beletskaya, L. G. Kuz'mina, J. A. K. Howard, *Organometallics* **1997**, *16*, 4041. b) S. Arndt, P. Voth, T. P. Spaniol, J. Okuda, *Organometallics* **2000**, *19*, 4690. c) I. Castillo, T. D. Tilley, *Organometallics* **2001**, *20*, 5598. d) O. Tardif, M. Nishiura, Z. Hou, *Organometallics* **2003**, *22*, 1171.