DOI: 10.1002/anie.201307422

Rare-Earth Complexes

Homometallic Rare-Earth Metal Phosphinidene Clusters: Synthesis and Reactivity**

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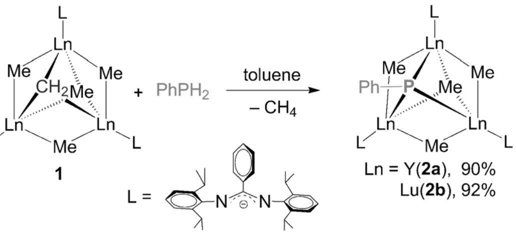
***Abstract:** Two new trinuclear μ_3-bridged rare-earth metal phosphinidene complexes, $[\{L(Ln)(\mu\text{-Me})\}_3(\mu_3\text{-Me})(\mu_3\text{-PPh})]$ ($L = [PhC(NC_6H_4iPr_2\text{-}2,6)_2]^-$, Ln = Y (**2a**), Lu (**2b**)), were synthesized through methane elimination of the corresponding carbene precursors with phenylphosphine. Heating a toluene solution of **2** at 120°C leads to an unprecedented ortho C–H bond activation of the PhP ligand to form the bridged phosphinidene/phenyl complexes. Reactions of **2** with ketones, thione, or isothiocyanate show clear phospha-Wittig chemistry, giving the corresponding organic phosphinidenation products and oxide (sulfide) complexes. Reaction of **2** with CS_2 leads to the formation of novel trinuclear rare-earth metal thione dianion clusters, for which a possible pathway was determined by DFT calculation.*

Metal phosphinidene complexes have received increasing attention, not only because of their rich chemistry, but also their potential utility as intermediates or catalysts in the preparation of phosphorus compounds, organometallic derivatives, and new materials.[1–3] It has been shown that variation of the metals bonded to the phosphinidene ligands could lead to specific changes in structure and catalytic activity, as well as chemical and physical properties.[4]

Various kinds of transition metal phosphinidene complexes with different coordinating modes and reactivities have been documented.[1–6] However, only a few phosphinidene complexes of rare-earth metals, the largest subgroup in the periodic table, have been known so far, owing both to the mismatch in the orbital energy of the electropositive rare-earth metals and the electronegative phosphinidene ligand, and the difficulty in stabilizing low-coordination lanthanide systems having terminal metal–ligand multiply bonded scaffolds.[7–9] Recently, Kiplinger and Chen reported binuclear μ_2-bridged phosphinidene complexes of rare-earth metals $[\{L(Ln)(\mu_2\text{-PAr})(thf)_x\}_2]$ (Ln = Sc, Nd, Lu; $x = 0, 1, 3$; L = $[N(2\text{-P}i\text{Pr}_2\text{-5-MeC}_6H_3)_2]$, C_5Me_5, β-diimino, I; Ar = 2,4,6-$Me_3C_6H_2$, 2,6-$i\text{Pr}_2C_6H_3$).[7] Very recently, two rare-earth metal phosphinidene complexes stabilized through alkali metal halides, $[(pnp)Sc(\mu\text{-PC}_6H_3Mes_2\text{-}2,6)(\mu\text{-Br})Li(dme)]$ (pnp = $N(2\text{-P}i\text{Pr}_2)_2\text{-4-MeC}_6H_3)_2$, Mes = 2,4,6-$Me_3C_6H_2$)[8] and $[IY(\mu_6\text{-P})\{Y(thf)(\mu_3\text{-PC}_6H_3i\text{Pr}_2\text{-}2,6)\}_4(\mu\text{-I})_4K(toluene)]$,[9] were disclosed. Reactivity studies on these mono- or dinuclear rare-earth metal phosphinidene complexes showed their great potential to serve as a source of phosphorus for constructing phosphorus-containing higher organic molecules.[7,8] Therefore, development of a diverse variety of phosphinidene complexes of rare-earth metals and new methods for their construction would be highly desirable.

The polynuclear frameworks show a strong influence on the reactivities of methylidene[10] and imido[11] rare-earth-metal complexes. For example, trinuclear rare earth methyl/methylidenes react easily with various primary amines to generate the corresponding imido complexes,[11c] however, $[(bipm)YI(thf)_2]$ (bipm = $C(PPh_2NSiMe_3)_2$) and $[(pnp)Sc(\mu_3\text{-CH}_2)(\mu_2\text{-Me})_2\{Al(Me)_2\}_2]$, react with 2,6-$i\text{Pr}_2C_6H_3NH_2$ to form only the anilides.[10b,f] Thus, with the aim of establishing how the multimetallic cooperative effect imparts to the phosphinidene methyl complexes an enhanced reactivity analogous to that already observed in the case of methylidene and imido ligands, we decided to extend our study to phosphinidene analogues. Herein, we report the synthesis of the first trinuclear rare-earth metal phosphinidene complexes featuring methyl and amidinate ligands, and their unique reactivity patterns.

The homometallic trinuclear phosphinidene complexes $[\{L(Ln)(\mu_2\text{-Me})\}_3(\mu_3\text{-Me})(\mu_3\text{-PPh})]$ (L = $[PhC(NC_6H_4i\text{Pr}_2\text{-}2,6)_2]^-$; Ln = Y(**2a**), Lu(**2b**)) were synthesized in high yield by a methane elimination reaction of $[\{L(Ln)(\mu_2\text{-Me})\}_3(\mu_3\text{-Me})(\mu_3\text{-CH}_2)]$[10e] with 1 equiv of $PhPH_2$ (Scheme 1). However, attempts to synthesize the corresponding scandium complex by this method were unsuccessful even with prolonged heating at 80°C, wherein most of starting materials was recovered.



Scheme 1. Synthesis of phosphinidene complexes **2**.

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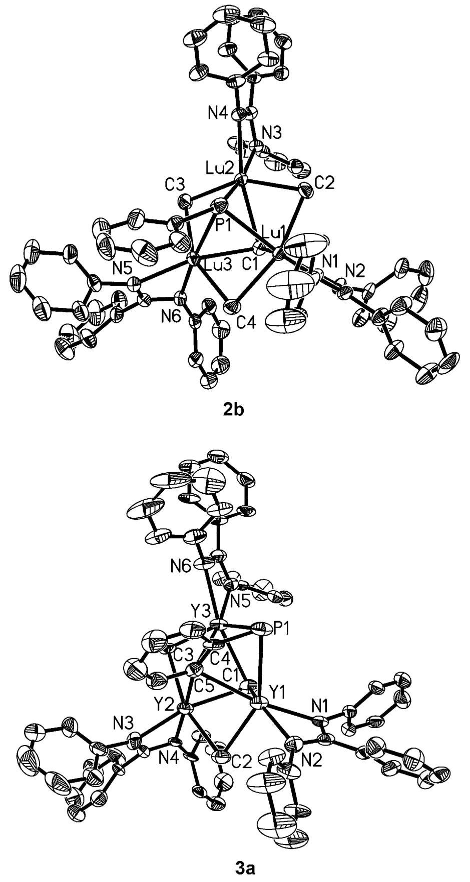
[**] This work was supported by the NSFC, 973 Program (2012CB821604), the Ministry of Education of China. The authors also thank the Network and Information Center of Dalian University of Technology for computational resources.

Supporting information, including full synthetic, spectroscopic, and structural and computational details, for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201307422.

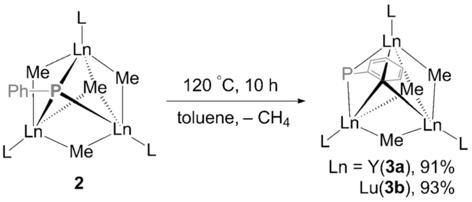


2b

3a

Figure 1. ORTEP structures of **2b** and **3a**. Thermal ellipsoids set at 30% probability. Isopropyl groups of benzamidinate ligands and hydrogen atoms are omitted for clarity.

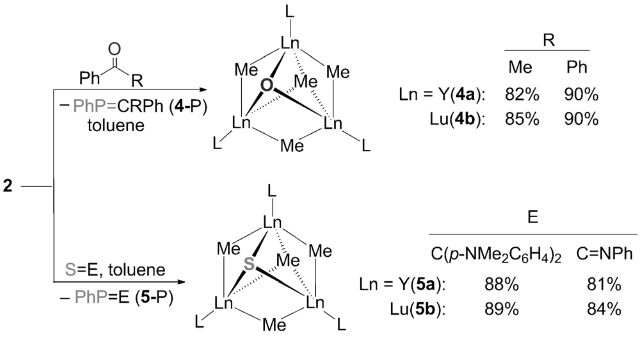
The ^{31}P NMR spectrum of complex **2a** shows a quartet of peaks at $\delta = 138.79$ ppm, thus indicating a μ_3-P coordination mode, which was further confirmed by the X-ray crystal diffraction analysis of **2** (Figure 1; see also the Supporting Information, Figures S31 and S32).[15] Characteristically, compounds **2** have two distinctive Ln–P distances. In **2a**, the Y1–P1 (2.714 Å) and Y2–P1 (2.732 Å) bond lengths are comparable to the values found in [{L(Ln)(μ-PAr)}$_2$]-type complexes,[7] whereas the Y3–P1 (2.943 Å) bond length falls in the range of the Ln^{3+}←:P donating bond lengths for neutral phosphorus ligands when the difference in metal radii is taken into consideration.[12] Similarly, the longest Lu–P bond in **2b** is 0.241 Å longer than the other two Lu–P bonds (avg. of 2.661 Å). Furthermore, the P–C bond displays a bent angle (59.1° for **2a**, 49.3° for **2b**) to the Ln$_3$ plane, which is different from the observation in analogous transition-metal complexes, where P–C bonds are approximately perpendicular to the metal-based plane.[6]



Scheme 2. Formation of complexes **3**.

Complexes **2** are stable at room temperature. But unusual phosphinidene deprotonated products **3** were generated in high yields (91% for **3a**, 93% for **3b**; Scheme 2), when a toluene solution of **2** was heated at 120 °C for 2 days. The liberated CH$_4$ was monitored by ^{1}H NMR spectroscopy of the in situ reaction, which clearly showed a sharp signal of methane at 0.16 ppm. A triplet resonance at $\delta = 262.48$ ppm ($J_{\mathrm{YP}} = 25.9$ Hz) in the ^{31}P NMR spectrum of **3a** was observed, which indicates the existence of a μ_2-P bridge. Crystal structures of **3** (Figure 1; see also Figures S33 and S34)[15] reveal that the phosphorus atom coordinates to two metal atoms, whereas the *ortho* carbon atom of the phenyl ring is bonded to three metals. The average Lu–P(μ_2) distance of 2.646 Å is slightly longer than the observed value in [{(pnp)Lu(μ-PC$_6$H$_2$Me$_3$-2,4,6)}$_2$].[7a] The average Ln–C(μ_3-C$_6$H$_4$P) distance (2.565 Å (**3a**), 2.530 Å (**3b**)) is shorter than the average Ln–C1(μ_3-Me) distance (2.682 Å (**3a**), 2.618 Å (**3b**)), but is much longer than the average Ln–C(μ_2-CH$_2$) distance (2.401 Å (**1a**), 2.376 Å (**1b**)) in [L{(Ln)(μ_2-Me)}$_3$(μ_3-Me)(μ_3-CH$_2$)].[10e] The phenyl ring on P1 is nearly perpendicular to the Ln$_3$ plane, displaying a dihedral angle of 84.3° (**3a**) or 82.4° (**3b**).

In contrast to imido analogues, in which the imido group is inert to many unsaturated substrates such as ketones and thioketones,[11c] complexes **2** show high reactivity toward these substrates (Scheme 3). The reactions of **2** with acetophenone and benzophenone gave the corresponding lanthanide oxo complexes **4** in 82–90% yields. The structures of **4** were determined by X-ray single-crystal diffraction analysis (Figure S35).[15] The resulting bulky phosphaalkene PhP=CPh$_2$ (**4**-P2) was confirmed by ^{31}P NMR spectroscopy (in C$_6$D$_6$: s, $\delta = 233.2$ ppm; Figure S15) and GC-MS.[13] Attempts to isolate [PhP=CMePh] (**4**-P1) have been unsuccessful owing to its instability. **2** reacted with (p-Me$_2$NC$_6$H$_4$)$_2$C=S, generating μ_3-sulfide complexes **5** (Figures S36 and S37) and (p-Me$_2$NC$_6$H$_4$)$_2$C=PPh (**5**-P1; ^{31}P NMR: s, $\delta = 201.3$ ppm; Figures S18–20). Complexes **5** can also be obtained from the reaction of **2** with phenylisothiocyanate. However, the newly formed PhP=C=NPh (**5**-P2) is not stable under the conditions

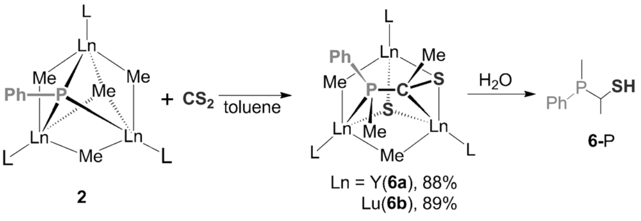


Scheme 3. Reactions of **2** with substrates containing C=X (X = O, S) bonds.

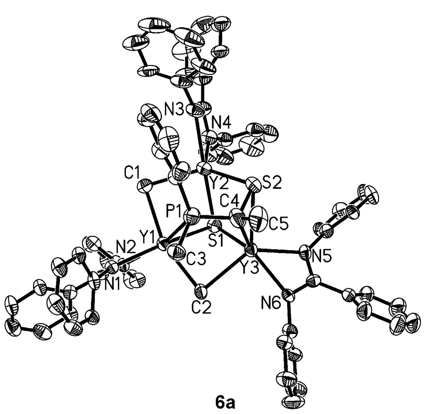
involved, and immediately transforms to a complicated mixture that may result from symmetrical and unsymmetrical dimerization.[14] These results indicate that **2** can act as a source of the phosphinidene moiety, which may be exchanged for an oxo or a sulfido group.

The treatment of **2** with one equivalent of CS_2 in toluene led to the occurrence of an unprecedented reaction, giving unusual thione-dianion-ligated rare-earth sulfide complexes **6** (Scheme 4). This reaction differs from that of the μ_2-phosphinidene Sc complex $[\{LSc(\mu\text{-}PAr)\}_2]$ wherein only CS_2 insertion into the Sc−P bond occurs to give a stable $[\{LSc(\mu\text{-}S_2CPAr)\}_2]$ species.[7d]

In the structures of **6**, the P atom is bonded to three carbon atoms, the Ln–P distances of 3.098 Å (**6a**) and 2.992 Å (**6b**) are slightly longer than the typical Ln–P donating bond length (Figure 2).[12,15] In the ^{31}P NMR spectrum of complex **6a**, only a singlet signal was observed at $\delta = 9.5$ ppm in C_6D_6, which indicates that the weak interaction between the P and Ln metal center no longer exists in solution. Hydrolysis of **6** afforded 1-(methylphenylphosphino)-ethanethiol (**6**-P), which was observed by GC-MS analysis (Figure S26).



Scheme 4. Reaction of **2** with CS_2.



6a

Figure 2. ORTEP structures of **6a**. Thermal ellipsoids set at 30% probability. Isopropyl groups of benzamidinate ligands and hydrogen atoms are omitted for clarity.

Compounds **6** represent rare examples of thione dianion complexes. This one-pot sequence of transformations leading to the formations of two C−P bonds and one C−C bond, provides a straightforward method for the three-component synthesis of phosphinothiols. To elucidate the formation mechanism of **6**, the reaction was further investigated by theoretical calculations (Figures S40–42 and Tables S14–17). As shown in Figure 3, the reaction starts with the insertion of CS_2 into the Ln−P bond of **2a** via the transition state $\mathbf{TS_{AB}}$, with an energy barrier of 16.1 kcal mol^{-1} to give intermediate **B**. **B** subsequently undergoes changes in the coordination of a S atom from μ_1- in **B** to μ_2- in **C**, and of the P atom from μ_2- in **B** to μ_1- in **C**. The cleavage of the C−S bond of the more stable **C** occurs easily via the transition state $\mathbf{TS_{CD}}$, with only a 0.6 kcal mol^{-1} energy barrier, leading to the phosphathioketene species [PhP=C=S] and intermediate **5a** with a μ_3-S atom. The computed ^{31}P NMR chemical shifts of PhP=C=S (−36.6 ppm; Table S18; at the MP2/6-311++G(3df,3pd) level of theory), is close to the observed signal at −29.4 ppm (d, $J_{YP} = 38.3$ Hz; Figure S30), when a mixture of **2b** and CS_2 in toluene was assayed by ^{31}P NMR spectroscopy at −30 °C. The newly formed [PhP=C=S] then attacks the μ_3-

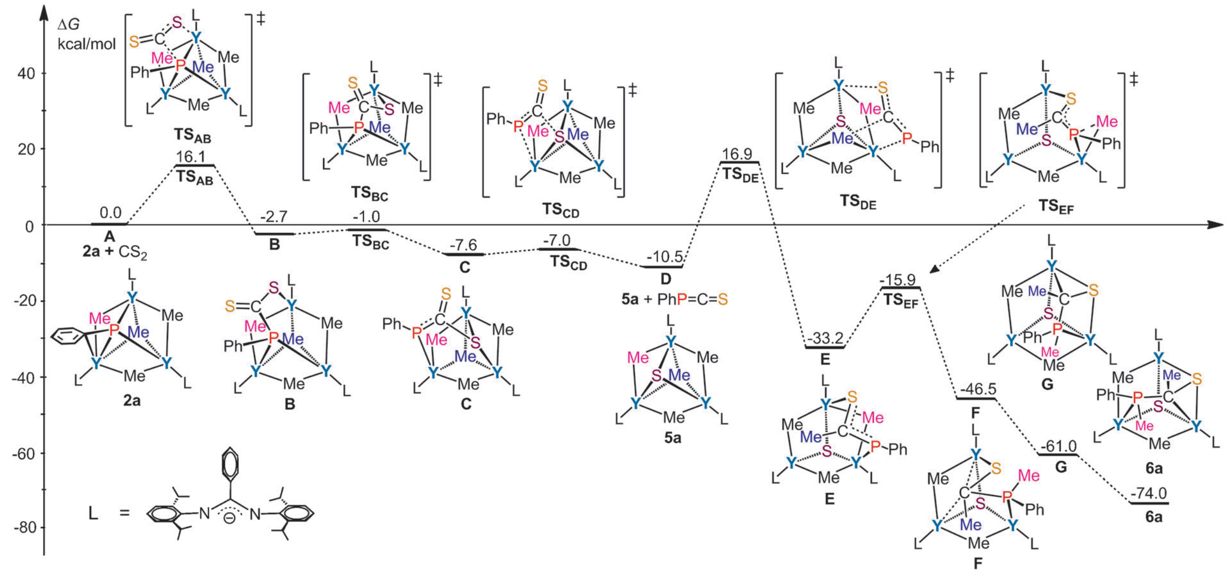


Figure 3. Computed energy profile (Gibbs free energies in kcal mol^{-1}) for the formation of **6a** by the reaction of **2a** with CS_2 at the M06 L/SDD&6-31G**//ONIOM(TPSSTPSS/LanL2DZ&6-31G*:HF/LanL2 MB) level of theory.

Me of **5a**, in which the μ_3-Me is on the opposite side of μ_3-S, to form intermediate **E** (Figure 3). This process has a free energy barrier of 27.4 $\text{kcal}\,\text{mol}^{-1}$, which should be the rate-determining step. Then, the **E** undergoes an intramolecular group transfer (μ_2-CH_3 transferred to the P atom) via $\mathbf{TS_{EF}}$, leading to the formation of a P–CH_3 bond in **F**. This transfer process was feasible because of its exergonic nature and moderate energy barrier of 17.3 $\text{kcal}\,\text{mol}^{-1}$. Complex **F** subsequently isomerized to **G** and then to the energetically more stable complex **6a**. The whole reaction of **2a** with CS_2 to form **6a** is exergonic by 74.0 $\text{kcal}\,\text{mol}^{-1}$. To date, this work is the only joint experimental/theoretical study that deals with a trinuclear rare-earth metal phosphinidene complex.

In summary, two trinuclear μ_3-bridged rare-earth metal phosphinidene complexes have been synthesized and their reactivity described. For the first time, an unusual reaction toward CS_2 and the formation of μ_3-phenyl-μ_2-phosphinidene bridged complex through an unusual C–H bond activation process have been demonstrated; for the former, a possible reaction mechanism was elucidated by DFT calculations. These μ_3-P bridged complexes display phospha-Wittig chemistry, and act as a source of the phosphinidene moiety, which may be exchanged for an oxo, or a sulfido group. These reactions provide new routes to organophosphorus derivatives, as well as the corresponding organolanthanide oxides and sulfides.

Received: August 23, 2013
Revised: October 15, 2013

Keywords: C–H activation · CS_2 activation · density functional calculations · phosphinidenes · rare earths

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[1] a) A. Marinetti, F. Mathey, J. Fischer, A. Mitschler, *J. Am. Chem. Soc.* **1982**, *104*, 4484–4485; b) A. Marinetti, F. Mathey, J. Fischer, A. Mitschler, *J. Chem. Soc. Chem. Commun.* **1982**, 667–668; c) A. H. Cowley, A. R. Barron, *Acc. Chem. Res.* **1988**, *21*, 81–87; d) K. Lammertsma, *Top. Curr. Chem.* **2003**, *229*, 95–119.

[2] For recent reviews, see: a) D. W. Stephan, *Angew. Chem.* **2000**, *112*, 322–338; *Angew. Chem. Int. Ed.* **2000**, *39*, 314–329; b) S. Shah, J. D. Protasiewicz, *Coord. Chem. Rev.* **2000**, *210*, 181–201; c) F. Mathey, N. H. Tran Huy, A. Marinetti, *Helv. Chim. Acta* **2001**, *84*, 2938–2957; d) K. Lammertsma, M. J. M. Vlaar, *Eur. J. Org. Chem.* **2002**, 1127–1138; e) R. Streubel, *Coord. Chem. Rev.* **2002**, *227*, 175–192; f) L. Weber, *Eur. J. Inorg. Chem.* **2007**, 4095–4117; g) L. Kollár, G. Keglevich, *Chem. Rev.* **2010**, *110*, 4257–4302; h) H. Aktaş, J. C. Slootweg, K. Lammertsma, *Angew. Chem.* **2010**, *122*, 2148–2159; *Angew. Chem. Int. Ed.* **2010**, *49*, 2102–2113.

[3] M. E. García, V. Riera, M. A. Ruiz, D. Sáez, J. Vaissermann, J. C. Jeffery, *J. Am. Chem. Soc.* **2002**, *124*, 14304–14305.

[4] a) P. B. Hitchcock, M. F. Lappert, W. P. Leung, *J. Chem. Soc. Chem. Commun.* **1987**, 1282–1283; b) R. Bohra, P. B. Hitchcock, M. F. Lappert, W. P. Leung, *Polyhedron* **1989**, *8*, 1884; c) D. S. J. Arney, R. C. Schnabel, B. L. Scott, C. J. Burns, *J. Am. Chem. Soc.* **1996**, *118*, 6780–6781.

[5] For recent work on binuclear phosphinidene complexes, see: a) T. W. Graham, K. A. Udachin, A. J. Carty, *Chem. Commun.* **2006**, 2699–2701; b) M. Scheer, D. Himmel, C. Kuntz, S. Zhan, E. Leiner, *Chem. Eur. J.* **2008**, *14*, 9020–9029; c) M. Stubenhofer, C. Kuntz, C. Balász, M. Zabel, M. Scheer, *Chem. Commun.* **2009**, 1745–1747; d) M. Scheer, C. Kuntz, M. Stubenhofer, M. Zabel, A. Y. Timoshkin, *Angew. Chem.* **2010**, *122*, 192–196; *Angew. Chem. Int. Ed.* **2010**, *49*, 188–192.

[6] For μ_3-bridged transition metal phosphinidene complexes, see: a) P. S. Elmes, P. Leverett, B. O. West, *J. Chem. Soc. Chem. Commun.* **1971**, 747b–748; b) D. Fenske, R. Basoglu, J. Hachgenei, F. Rogel, *Angew. Chem.* **1984**, *96*, 160–162; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 160–162; c) K. Knoll, G. Huttner, M. Wasiucionek, L. Zsolnai, *Angew. Chem.* **1984**, *96*, 708–709; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 739–740; d) K. Knoll, O. Orama, G. Huttner, *Angew. Chem.* **1984**, *96*, 989; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 976–977; e) H. H. Ohst, J. K. Kochi, *J. Am. Chem. Soc.* **1986**, *108*, 2897–2908.

[7] a) J. D. Masuda, K. C. Jantunen, O. V. Ozerov, K. J. T. Noonan, D. P. Gates, B. L. Scott, J. L. Kiplinger, *J. Am. Chem. Soc.* **2008**, *130*, 2408–2409; b) P. Cui, Y. Chen, X. Xu, J. Sun, *Chem. Commun.* **2008**, 5547–5549; c) P. Cui, Y. Chen, M. V. Borzov, *Dalton Trans.* **2010**, *39*, 6886–6890; d) Y. Lv, C. E. Kefalidis, J. Zhou, L. Maron, X. Leng, Y. Chen, *J. Am. Chem. Soc.* **2013**, *135*, 14784–14796.

[8] B. F. Wicker, J. Scott, J. G. Andino, X. Gao, H. Park, M. Pink, D. J. Mindiola, *J. Am. Chem. Soc.* **2010**, *132*, 3691–3693.

[9] Y. Lv, X. Xu, Y. Chen, X. Leng, M. V. Borzov, *Angew. Chem.* **2011**, *123*, 11423–11425; *Angew. Chem. Int. Ed.* **2011**, *50*, 11227–11229.

[10] a) H. M. Dietrich, K. W. Törnroos, R. Anwander, *J. Am. Chem. Soc.* **2006**, *128*, 9298–9299; b) J. Scott, H. Fan, B. F. Wicker, A. R. Fout, M. H. Baik, D. J. Mindiola, *J. Am. Chem. Soc.* **2008**, *130*, 14438–14439; c) R. Litlabø, M. Zimmermann, K. Saliu, J. Takats, K. W. Törnroos, R. Anwander, *Angew. Chem.* **2008**, *120*, 9702–9706; *Angew. Chem. Int. Ed.* **2008**, *47*, 9560–9564; d) M. Zimmermann, J. Takats, G. Kiel, K. W. Törnroos, R. Anwander, *Chem. Commun.* **2008**, 612–614; e) J. Hong, L. Zhang, X. Yu, M. Li, Z. Zhang, P. Zheng, M. Nishiura, Z. Hou, X. Zhou, *Chem. Eur. J.* **2011**, *17*, 2130–2137; f) D. P. Mills, W. Lewis, A. J. Blake, S. T. Liddle, *Organometallics* **2013**, *32*, 1239–1250.

[11] a) D. Cui, O. Tardif, Z. Hou, *J. Am. Chem. Soc.* **2004**, *126*, 1312–1313; b) D. Cui, M. Nishiura, Z. Hou, *Angew. Chem.* **2005**, *117*, 981–984; *Angew. Chem. Int. Ed.* **2005**, *44*, 959–962; c) J. Hong, L. Zhang, K. Wang, Y. Zhang, L. Weng, X. Zhou, *Chem. Eur. J.* **2013**, *19*, 7865–7873.

[12] a) M. D. Fryzuk, J. B. Love, S. J. Rettig, *J. Am. Chem. Soc.* **1997**, *119*, 9071–9072; b) M. D. Fryzuk, L. Jafarpour, F. M. Kerton, J. B. Love, B. O. Patrick, S. J. Rettig, *Organometallics* **2001**, *20*, 1387–1396; c) W. Miao, S. Li, D. Cui, B. Huang, *J. Organomet. Chem.* **2007**, *692*, 3823–3834; for Lutetium complexes, see: d) H. Schumann, E. Palamidis, G. Schmid, R. Boese, *Angew. Chem.* **1986**, *98*, 726–727; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 718–719; e) O. Tardif, M. Nishiura, Z. Hou, *Tetrahedron* **2003**, *59*, 10525–10539.

[13] G. Becker, W. Uhl, H.-J. Wessely, *Z. Anorg. Allg. Chem.* **1981**, *479*, 41–56.

[14] a) C. Wentrup, H. Briehl, G. Becker, G. Uhl, H. J. Wessely, A. Maquestiau, R. Flammang, *J. Am. Chem. Soc.* **1983**, *105*, 7194–7195; b) X. G. Zhou, L. B. Zhang, R. F. Cai, Q. J. Wu, L. H. Weng, Z. E. Huang, *J. Organomet. Chem.* **2000**, *604*, 260–266; c) J. Escudié, H. Ranaivonjatovo, L. Rigon, *Chem. Rev.* **2000**, *100*, 3639–3696.

[15] CCDC 926452 (**2a**), 926450 (**2b**), 926453 (**3a**), 926455 (**3b**), 973095 (**4a**), 779072 (**4b**), 973096 (**5a**), 845818 (**5b**), 926454 (**6a**), and 926451 (**6b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.