View Article Online / Journal Homepage / Table of Contents for this issue

Single, double and triple deprotonation of a β-diketimine bearing pendant pyridyl group and the corresponding rare-earth metal complexes†

Xin Xu,[a,b] Yaofeng Chen,*[b] Gang Zou*[a] and Jie Sun[b]

Received 22nd December 2009, Accepted 16th February 2010
First published as an Advance Article on the web 16th March 2010
DOI: 10.1039/b926898g

A new β-diketimine bearing the pendant pyridyl group, CH$_3$C(2,6-(^{i}Pr)$_2$C$_6$H$_3$NH)CHC(CH$_3$)(NCH$_2$–C$_5$NH$_4$) (**L1**), was synthesized. The reaction of **L1** with one equivalent of Sc(CH$_2$SiMe$_3$)$_3$(THF)$_2$ at room temperature gave a singly deprotonated product (**L1–H**)Sc(CH$_2$SiMe$_3$)$_2$ (**1**). Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ under the same conditions led to the unexpected dimer [(**L1–H$_3$**)Y(THF)]$_2$ (**2**), in which the ligand precursor **L1** was triply deprotonated. The reaction of **L1** with Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ at −35 °C provided a mixture of singly deprotonated product (**L1–H**)Y(CH$_2$SiMe$_3$)$_2$ (**3**) and doubly deprotonated product (**L1–H$_2$**)Y(CH$_2$SiMe$_3$)(THF)$_2$ (**4**). The reactions of **L1** with Ln[N(SiMe$_3$)$_2$]$_3$ gave only singly deprotonated products (**L1–H**)Ln[N(SiMe$_3$)$_2$]$_2$ (**5**: Ln = Y; **6**: Ln = La). The complexes **1**, **2** and **4–6** have been characterized by single-crystal X-ray diffraction.

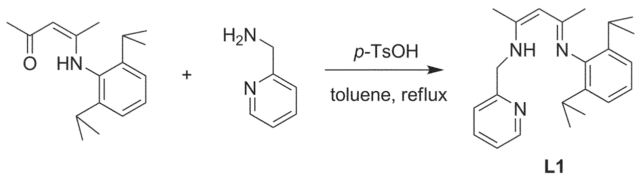
Introduction

Due to their rich and diverse coordinating properties and reactivities, organometallic complexes of rare-earth metals have received great attention.[1-3] The most widely investigated organometallic complexes of rare-earth metals are those bearing Cp-type ligands. Recently, there is a tendency to explore "non-Cp" rare-earth metal complexes.[4] In this context, ligands with nitrogen donor atoms have received a growing attention, as they form strong Ln–N bonds with the hard Ln^{3+} ions and are expected to stabilize the highly electrophilic rare-earth metal complexes. One promising ancillary ligand set of nitrogen containing ligands is the family of β-diketiminato ligands. Numerous β-diketiminato rare-earth metal complexes have been reported.[5]

We recently designed a new type of tridentate monoanionic β-diketiminato ligand with a pendant amino group and prepared several corresponding rare-earth metal dialkyl complexes.[6] As an extension of our research, we prepared a new β-diketimine derivative CH$_3$C(2,6-(^{i}Pr)$_2$C$_6$H$_3$NH)CHC(CH$_3$)(NCH$_2$–C$_5$NH$_4$) (**L1**), which bears a pendant pyridyl group. From reactions of **L1** with LnR$_3$(THF)$_n$ (Ln = Sc, Y, La; R = –CH$_2$SiMe$_3$, –N(SiMe$_3$)$_2$; n = 0, 2), we found that this ligand precursor can be singly-, doubly-, or triply deprotonated depending on the metal ion (Ln^{3+}), the R group and the reaction conditions.

Results and discussion

2-((2,6-Diisopropylphenyl)imido)-2-penten-4-one was prepared by condensation of acetylacetone with 2,6-diisopropylaniline. This product was subsequently treated with 2-(aminomethyl)pyridine in toluene in the presence of a catalytic amount of *p*-toluenesulfonic acid, to provide the desired ligand precursor **L1** in 61% yield (Scheme 1). It was characterized by NMR (^{1}H, ^{13}C) and mass spectroscopy and by elemental analysis. Notably, in ^{1}H NMR spectroscopy of **L1** at 25 °C, the –C*H*$_2$– unit of pendant arm displayed a doublet at 4.32 ppm with a *J* value of 6.3 Hz due to the coupling with –N*H*–, indicating a slow exchange rate of –N*H*–. This doublet became a singlet when the temperature rose to 80 °C.



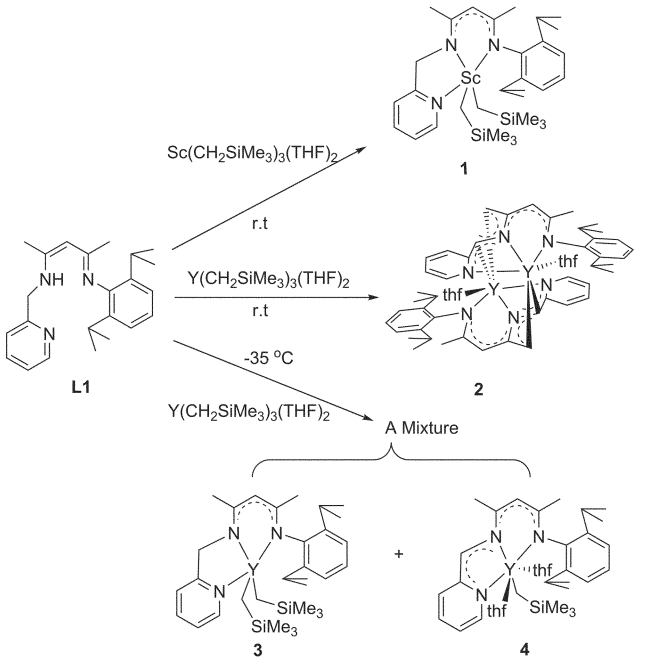
Scheme 1 Synthesis of the ligand precursor **L1**.

The reaction of **L1** with one equivalent of Sc(CH$_2$SiMe$_3$)$_3$(THF)$_2$ in hexane at room temperature for one day gave a Sc(III) dialkyl complex Sc(**L1–H**)(CH$_2$SiMe$_3$)$_2$ (**1**) in 71% yield (Scheme 2). During the reaction, the ligand precursor **L1** was singly deprotonated, and the resulting ligand **L1–H** acts as the monoanionic ligand in the metal complex **1**. On the other hand, the reaction of **L1** with one equivalent of Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ under same conditions provided an unexpected Y(III) dimer [Y(**L1–H$_3$**)(THF)]$_2$ (**2**) in 94% yield (Scheme 2), where **L1** was triply deprotonated to give an unusual trianionic ligand (**L1–H$_3$**). The red complex **2** is readily soluble in THF, but nearly insoluble in benzene, toluene, and hexane. Although the deprotonation of

---

[a] *Laboratory of Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, 130 Meilong Road, Shanghai, 200237, China. E-mail: zougang@ecust.edu.cn*
[b] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai, 200032, China; Fax: 86-21-64166128. E-mail: yaofchen@mail.sioc.ac.cn*

† CCDC reference numbers 744083–744085 and 759490–759491. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b926898g



Scheme 2 Reactions of **L1** with Ln(CH_2SiMe_3)$_3$(THF)$_2$ (Ln = Sc, Y).

the methyl group of the monoanionic β-diketiminato ligand[7] and the deprotonation of the methyl group attached to the pyridyl ring[8] have been documented, such triple deprotonation of a ligand precursor to a trianionic ligand as in our case is interesting. It has been commonly accepted that the alkyl complexes of larger rare-earth metal ions are less stable than those of the smaller,[9] and it's also known that the complexes are generally more stable at low temperature. Thus, the reaction of **L1** with Y(CH_2SiMe_3)$_3$(THF)$_2$ was carried out in hexane at −35 °C, and a dark green product precipitated from the reaction solution. From this experiment, several single crystals were collected and characterized by X-ray diffraction, which showed them to belong to **4**, a Y(III) monoalkyl complex Y(**L1–H$_2$**)(CH_2SiMe_3)(THF)$_2$ (**4**) containing the dianionic ligand (**L1–H$_2$**), in which the methylene group on the pendant arm was deprotonated. The product was then dissolved in C_6D_6 for NMR analysis. The C_6D_6 solution was clear at the beginning, but a red precipitate **2** formed in two minutes. The ^{1}H NMR spectrum clearly showed the existence of **3**, a Y(III) dialkyl complex Y(**L1–H**)(CH_2SiMe_3)$_2$ containing the monoanionic ligand (**L1–H**). This showed that the singly deprotonated product and the doubly deprotonated product could be achieved at low temperature. Surprisingly, no signals for **4** were observed, but a strong signal of $SiMe_4$ was observed, and in consistency with the formation of $SiMe_4$, the signals for **2** were observed in the ^{1}H NMR spectrum. These observations suggest that **4** is unstable in solution at room temperature and quickly transforms into **2** with a release of $SiMe_4$. It was also observed that the intensity of the ^{1}H NMR signals of **3** gradually decreased while that due to $SiMe_4$ increased with time, and the amount of the red precipitate **2** increased with time. **3** had nearly completely changed into **2** after 24 h. To gain further information on the formation of **4**, ^{1}H NMR spectral monitoring of the reaction of **L1** with Y(CH_2SiMe_3)$_3$(THF)$_2$ at room temperature in C_6D_6 was also performed. The spectra indicated the nearly quantitative formation of the dialkyl complex **3** within ten minutes along with a release of $SiMe_4$. Then the intensity of the signals belonging to **3** gradually decreased while that of $SiMe_4$ increased with time, and a red precipitate **2** formed. After 24 h, the signals of **3** had disappeared. No signals belonging to **4** were observed during the process. These results were consistent with the former observation and suggested that **3** was produced first through a single deprotonation of **L1**, and the doubly deprotonated product **4** was very instable and immediately converted to the triply deprotonated product at room temperature.

Single crystals of **1**, **4** and **2** were characterized by X-ray diffraction, and the molecular structures are shown in Fig. 1, 2 and 3, respectively. **1** is a solvent-free, five-coordinate monomer. The monoanionic ligand **L1–H** serves as one tridentate ligand and the five-coordinate center is completed by a pair of –CH_2SiMe_3 substituents. The geometry at the metal ion is best described as distorted square pyramidal, the metal ion sits out of the N1-N2-N3-C26 plane 0.68 Å, and one of the –CH_2SiMe_3 substituents takes the apical position. The C–N and C–C bond lengths of the

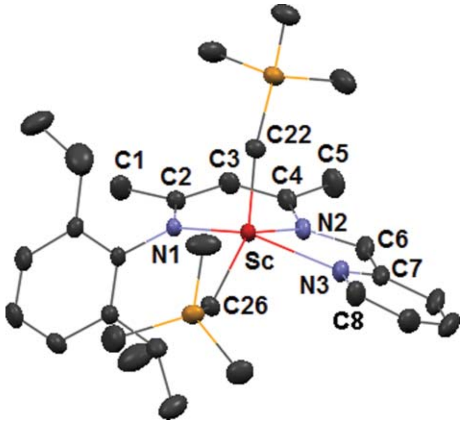


Fig. 1 Molecular structure of complex **1**. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Sc–N1 2.198(2), Sc–N2 2.198(2), Sc–N3 2.308(2), Sc–C22 2.197(3), Sc–C26 2.254(2), C1–C2 1.504(4), C2–C3 1.396(4), C3–C4 1.381(4), C4–C5 1.519(4), C2–N1 1.326(3), C4–N2 1.326(3), N2–C6 1.461(3), C6–C7 1.478(4), C7–N3 1.333(3), C8–N3 1.344(4), ∠N2–C6–C7 113.1(2).

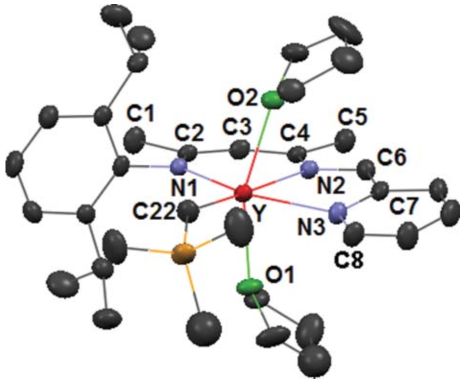


Fig. 2 Molecular structure of complex **4**. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Y–N1 2.310(4), Y–N2 2.423(4), Y–N3 2.346(4), Y–C22 2.406(5), Y–O1 2.363(4), Y–O2 2.400(4), C1–C2 1.533(7), C2–C3 1.353(7), C3–C4 1.433(7), C4–C5 1.506(7), C2–N1 1.372(6), C4–N2 1.324(6), N2–C6 1.393(6), C6–C7 1.373(7), C7–N3 1.390(6), C8–N3 1.344(7), ∠N2–C6–C7 120.9(5).

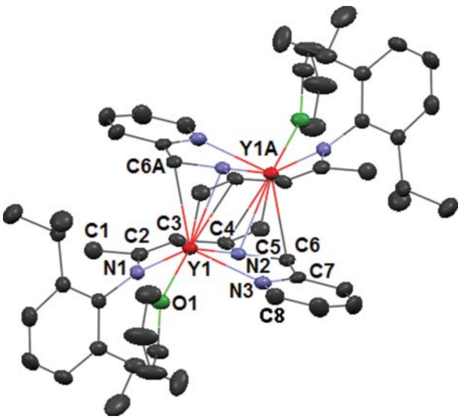


Fig. 3 Molecular structure of complex **2**. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Y1–N1 2.298(3), Y1–N2 2.336(3), Y1–N3 2.394(4), Y1–O1 2.425(3), Y1–C4A 2.688(4), Y1–C5A 2.698(4), Y1–C6A 2.540(4), Y1–N2A 2.488(3), Y1–Y1A 3.6939(9), C1–C2 1.525(6), C2–C3 1.331(6), C3–C4 1.428(6), C4–C5 1.402(6), C2–N1 1.397(6), C4–N2 1.360(5), N2–C6 1.435(5), C6–C7 1.397(6), C7–N3 1.383(6), C8–N3 1.352(6), ∠N2–C6–C7 116.1(4). The 'A' denoted atoms are at symmetrically equivalent positions (1 – x, 2 – y, 1 – z).

β-diketiminato backbone are intermediate between those of typical single and double bonds, and the N1, C2, C3, C4 and N2 atoms are coplanar, indicating a delocalized electronic structure. The β-diketiminato backbone coordinates to the metal ion in bidentate σ, σ'-bonded fashion; the Sc–N1 and Sc–N2 bond lengths are both 2.198(2) Å, while the distances from the metal ion to the carbon atoms C2, C3 and C4 are too long for effective interaction (> 3.13 Å). The pyridyl group coordinates to the metal ion with a Sc–N3 bond length of 2.308(2) Å, which is longer than the Sc–N(imine) bond length (2.198(2) Å), implying the pendant arm acts as a neutral donor while the backbone is an anionic donor.

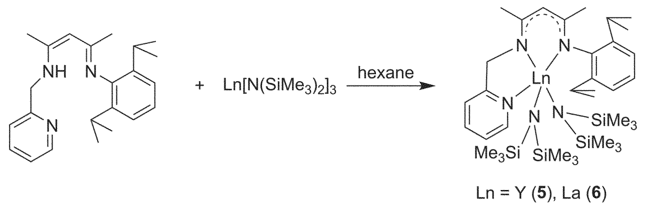
4 is a six-coordinate monomer, in which the metal ion is coordinated by one dianionic ligand **L1–H$_2$**, one –CH$_2$SiMe$_3$ substituent, and two THF molecules. The geometry at the metal ion is distorted octahedral, the metal ion lies in the N1-N2-N3-C22 plane, and two THF molecules occupy the axial positions. Both THF molecules are bent towards the β-diketiminato backbone to avoid steric repulsion with the bulky 2,6-(^{i}Pr)$_2$-C$_6$H$_3$ substituent. In contrast to the two equal metal–N(imine) bonds in **1**, one Y–N(imine) bond in **4** (Y–N2 = 2.423(4) Å) is significantly longer than the other (Y–N1 = 2.310(4) Å). Similarly, the C(imine)–N(imine) bonds and C3–C(imine) bonds in **4** are unequal, 1.372(6) Å *vs.* 1.324(6) Å and 1.353(7) Å *vs.* 1.433(7) Å, while **1** has equal C(imine)–N(imine) bonds and similar C3–C(imine) bonds. A distinguished structural difference between **L1–H$_2$** and **L1–H** lies in the pendant arm. The N2–C6 and C6–C7 bond lengths in **4** (1.393(6) and 1.373(7) Å) are significantly shorter than those in **1** (1.461(3) and 1.478(4) Å) and are intermediate between those of typical single and double bonds, furthermore the ∠N2–C6–C7 in **4** (120.9(5)°) is larger than that in **1** (113.1(2)°). The N3–C7 bond length in **4** (1.390(6) Å) is longer than that in **1** (1.333(3) Å), while the N3–C8 bond lengths in these two complexes are same (1.344(7) Å in **4** and 1.344(4) Å in **1**). The N2, C6, C7 and N3 atoms in **4** are coplanar, and the plane is nearly planar with the pyridine plane. These structural data demonstrate the electronic delocalized structure of NCH–C$_5$NH$_4$(pyridyl). The distance from the metal ion to the nitrogen atom on the pyridyl group in **4** is 2.346(4) Å, which is close to the average Y–N(imine) distance (2.36 Å) in the same complex.

2 exists as a centrosymmetric dimer, and each metal ion is coordinated by one trianionic ligand **L1–H$_3$**, one THF molecule, and the C5-C4-N2-C6 unit of another **L1–H$_3$**, which acts as a bridge. The geometry at the metal ions can be described as distorted square pyramidal when the C5-C4-N2-C6 unit is regarded as occupying a single polyhedral vertex. The metal ion sits out of the N1-N2-N3-O1 plane by 0.92 Å, and the C5-C4-N2-C6 unit takes the apical position. As observed in **4**, the backbone of **L1–H$_3$** coordinates to the metal ion with two unequal Y–N(imine) bonds (2.298(3) and 2.336(3) Å). The Y–N3 bond length in **2**, 2.394(4) (Å), is slightly longer than that in **4**, 2.346(4) Å. The distances from the metal ion to C5, C4, N2 and C6 atoms of the other **L1–H$_3$** are 2.698(4), 2.688(4), 2.488(3) and 2.540(4) Å, respectively, the average Y–C distance (2.64 Å) is close to that in [(C$_5$H$_5$)$_2$YCl]$_2$ (2.60 Å).[10] The Y–Y separation (3.69 Å) indicates that there is no bonding interaction between the two metal ions. **L1–H$_3$** shows some similar character to **L1–H$_2$**, for example, the C6–C7 bond length (1.397(6) Å) is intermediate between those of typical single and double bonds and the N3–C7 bond length (1.383(6) Å) is longer than that in **1**. However, differences between **L1–H$_3$** and **L1–H$_2$** are also significant. The C4–C5 bond length (1.402(6) Å) in **2** is much shorter than that in **4** (1.506(7) Å) and is intermediate between those of typical single and double bonds, and the ∠C3–C4–C5 in **2** (119.8(4)°) is larger than that in **4** (115.9(5)°).

In the ^{1}H NMR spectra of complexes **1** and **3**, the signals for Py-H_α (8.89 ppm for both complexes) are shifted downfield in comparison to that of the ligand precursor (8.34 ppm), indicating that the coordination interaction between the metal ion and the pendant pyridyl group is retained in solution.[11] The signals for the –CH_2– unit of the pendant arm in **1** and **3** are singlets, which is in contrast to the ligand precursor and consistent with deprotonation of the ligand precursor. Distinct differences between the trianionic ligand **L1–H$_3$** in **2** and the monoanionic ligand **L1–H** in **3** were observed from the ^{1}H NMR spectra. **L1–H$_3$** has a –CH_2– unit from deprotonation of the methyl group on the backbone, which contains two diastereotopic protons and displays two singlets at 2.37 and 2.58 ppm. $^2J_{HH}$ coupling was not observed for these two protons, which is probably due to a very small coupling constant in contrast to those of the reported Sc and Ca complexes containing similar dianionic ligands.[7b,c] Furthermore, the ^{1}H NMR spectra of **2** showed that **L1–H$_3$** has a –C*H*– unit on the pendant arm.

As **L1** was triply deprotonated during its reaction with Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ at room temperature, it was worth checking if this could also be achieved by employing the yttrium amide Y[N(SiMe$_3$)$_2$]$_3$. The experiment showed that treatment of ligand precursor **L1** with one equivalent of Y[N(SiMe$_3$)$_2$]$_3$ in hexane at room temperature gave the yttrium bis(amide) **5** in 75% yield (Scheme 3), which contains the monoanionic ligand (**L1–H**). Furthermore, the reaction of **L1** with La[N(SiMe$_3$)$_2$]$_3$ at room temperature also gave the singly deprotonated product **6** in 71% yield. Complexes **5** and **6** were both characterized by NMR spectroscopy (^{1}H, ^{13}C) and elemental analyses.

Single crystals of **5** and **6** were grown from hexane solutions at –35 °C and characterized by X-ray diffraction. Their molecular



Scheme 3 Reactions of **L1** with Ln[N(SiMe$_3$)$_2$]$_3$ (Ln = Y, La).

structures are shown in Fig. 4 and 5, respectively. **5** and **6** are both five-coordinate monomers and the metal ions adopt distorted square pyramidal geometry. The monoanionic ligand **L1–H** serves as a tridentate ligand and a pair of –N(SiMe$_3$)$_2$ substituents complete the coordination sphere. Atoms N1, C2, C4 and N2 of the backbone are coplanar, but the central atom C3 is bent out of the above plane. The dihedral angles between the C2-C3-C4 plane and N1-C2-C4-N2 plane in **5** and **6** are 23.2° and 25.0°, respectively, which are significantly larger than that in the dialkyl complex **1** (10.5°). The deviation values of the metal ion from the N1-C2-C4-N2 plane in **5** and **6** (1.53 Å and 1.82 Å) are significantly larger than that in **1** (0.70 Å), if the differences in Ln^{3+} radii are taken into account. In addition, the distances from the metal ion to the carbon atoms on the backbone are rather short (3.04 ~ 3.19 Å in **5** and 3.02 ~ 3.18 Å in **6**) and the difference between these distances is not significant. These structural features indicated a tendency for an η^5 bonding pattern between the metal ion and the β-diketiminato backbone, especially in **6**.[12] Although **5** and **6** contain bulky –N(SiMe$_3$)$_2$ ligands, the metal ions of both complexes are coordinated by the pendant arms (Ln–N3 2.502(3) Å for **5** and 2.682(5) Å for **6**). The ^{1}H NMR spectra of **5** and **6** show some similarities to those of **1** and **3** in that the signals for Py-H_α (9.44 ppm for **5** and 9.36 ppm for **6**) are shifted downfield in comparison to in the ligand precursor and the signals for the –CH_2– unit of the pendant arm are singlets.

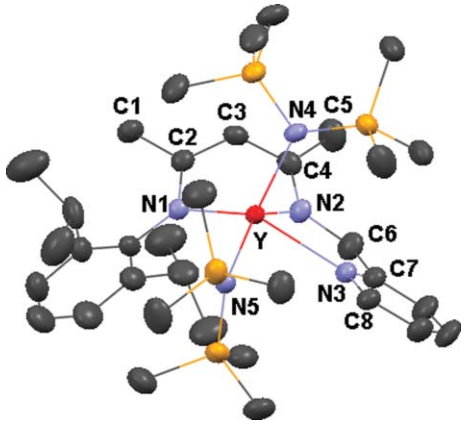


Fig. 4 Molecular structure of complex **5**. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Y–N1 2.375(3), Y–N2 2.308(3), Y–N3 2.502(3), Y–N4 2.297(3), Y–N5 2.288(3), C1–C2 1.503(5), C2–C3 1.392(5), C3–C4 1.406(6), C4–C5 1.505(5), C2–N1 1.338(5), C4–N2 1.305(5), N2–C6 1.463(5), C6–C7 1.484(6), C7–N3 1.346(5), C8–N3 1.347(5), ∠N2–C6–C7 112.0(3).

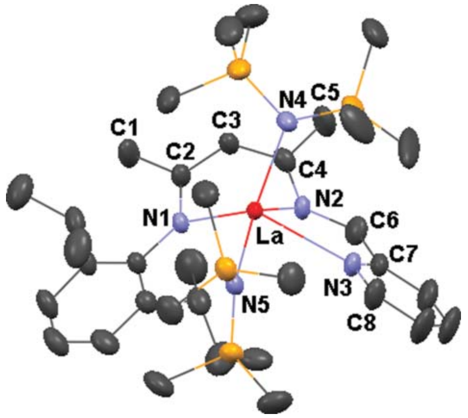


Fig. 5 Molecular structure of complex **6**. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): La–N1 2.553(5), La–N2 2.428(5), La–N3 2.682(5), La–N4 2.441(5), La–N5 2.428(5), C1–C2 1.524(9), C2–C3 1.392(9), C3–C4 1.386(10), C4–C5 1.514(10), C2–N1 1.311(8), C4–N2 1.329(9), N2–C6 1.450(8), C6–C7 1.482(11), C7–N3 1.335(9), C8–N3 1.349(10), ∠N2–C6–C7 110.8(6).

Conclusions

A new β-diketimine derivative CH$_3$C(2,6-(^{i}Pr)$_2$C$_6$H$_3$NH)-CHC(CH$_3$)(NCH$_2$–C$_5$NH$_4$) (**L1**), which bears a pendant pyridyl group, was prepared. This ligand precursor reacted with LnR$_3$(THF)$_n$ (Ln = Sc, Y, La; R = –CH$_2$SiMe$_3$, –N(SiMe$_3$)$_2$; n = 0, 2) to give the singly deprotonated products (**L1–H**)Ln(CH$_2$SiMe$_3$)$_2$ (Ln = Sc, Y) and (**L1–H**)Ln[N(SiMe$_3$)$_2$]$_2$ (Ln = Y, La), the doubly deprotonated product (**L1–H$_2$**)Y(CH$_2$SiMe$_3$)(THF)$_2$, and the triply deprotonated product [(**L1–H$_3$**)Y(THF)]$_2$. How far the deprotonations proceed depends on the reaction temperature, the rare-earth metal ion and the R group. The di-, and trianionic ligands represent new multidentate ligands.

Experimental

General procedures

All operations were carried out under an atmosphere of argon using standard Schlenk techniques or in a nitrogen gas filled glovebox. Toluene and hexane were dried over Na/K alloy. C$_6$D$_6$ and THF-d_8 were purchased from Cambridge Isotopes, dried over Na/K alloy, distilled under vacuum and stored in the glovebox. 2-(Aminomethyl)pyridine was purchased from Acros and used without further purification. 2-(2,6-Diisopropylphenylimido)-2-pentene-4-one,[13] Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (Ln = Sc, Y)[14] and Ln[N(SiMe$_3$)$_2$]$_3$ (Ln = Y, La)[15] were synthesized following the literature procedures. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 or 400 spectrometer, and the chemical shifts were reported in δ (ppm) units with reference to the residual solvent resonance of the deuterated solvents. Elemental analysis was performed by Analytical Laboratory of Shanghai Institute of Organic Chemistry. Melting points of the complexes were determined on a Digital Melting Point Apparatus SWG X-4 in a sealed capillary and are uncorrected.

L1. 2-(2,6-Diisopropylphenylimido)-2-pentene-4-one (5.62 g, 21.6 mmol), 2-(aminomethyl)pyridine (2.61 g, 24.1 mmol), and a catalytic amount of p-toluenesulfonic acid in toluene (30 mL) were combined and heated at reflux overnight. H_2O produced during the reaction was removed as a toluene azeotrope using a water separator. The toluene was removed *in vacuo* after the reaction was completed, and the residue was dissolved in 20 mL of ether. The ether solution was washed with saturated aqueous Na_2CO_3 3 times, and then the volatiles were removed in vacuo. Recrystallization of the crude product from hexane gave **L1** as a pale yellow solid (4.62 g, 61% yield). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ = 11.50 (br, 1H, N*H*), 8.34 (d, $^3J_{HH}$ = 4.2 Hz, 1H, Py-*H*), 7.18–7.02 (m, 5H, Py-*H* and Ar-*H*), 6.52 (m, 1H, Py-*H*), 4.70 (s, 1H, MeC(N)C*H*), 4.32 (d, $^3J_{HH}$ = 6.3 Hz, 2H, NCH_2), 3.14 (sp, $^3J_{HH}$ = 6.9 Hz, 2H, ArC*H*Me$_2$), 1.64 (s, 3H, *Me*C), 1.61 (s, 3H, *Me*C), 1.20 (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCHMe_2), 1.14 ppm (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCHMe_2). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ = 166.8, 160.4, 155.6 (imine-*C* and Py-*C*), 149.6, 147.3, 138.2, 136.3, 123.5, 123.2, 121.7, 120.3 (Ar-*C* and Py-*C*), 94.9 (MeC(N)*C*H), 48.9 (N*C*H$_2$), 28.5 (Ar*C*HMe$_2$), 24.1 (ArCHMe_2), 23.1 (ArCHMe_2), 21.8 (*Me*C), 19.1 ppm (*Me*C). EIMS *m/z* 349 (M$^+$, 60.25), 133 (100). Elemental analysis (%) calcd for $C_{23}H_{31}N_3$: C 79.04, H 8.94, N 12.02; found: C 78.67, H 8.72, N 12.13. m. p. 76–78 °C.

(L1–H)Sc(CH$_2$SiMe$_3$)$_2$ (1). **L1** (70 mg, 0.20 mmol) in 2 mL of hexane was added to Sc(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (90 mg, 0.20 mmol) in 3 mL of hexane at room temperature. The reaction mixture was stirred at room temperature for 24 h and filtered. The filtrate was concentrated to approximately 2 mL and cooled to –35 °C to afford **1** as a pale green crystalline solid (80 mg, 71% yield). Single crystals of **1** suitable for X-ray diffraction were obtained from a toluene solution. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 8.89 (d, $^3J_{HH}$ = 5.6 Hz, 1H, Py-*H*), 7.21 (m, 3H, Ar-*H*), 6.88 (td, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.6 Hz, 1H, Py-*H*), 6.57 (t, $^3J_{HH}$ = 6.8 Hz, 1H, Py-*H*), 6.43 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Py-*H*), 5.05 (s, 1H, MeC(N)C*H*), 4.48 (s, 2H, NCH_2), 3.51 (sp, $^3J_{HH}$ = 6.8 Hz, 2H, ArC*H*Me$_2$), 1.80 (s, 3H, *Me*C), 1.75 (s, 3H, *Me*C), 1.49 (d, $^3J_{HH}$ = 6.8 Hz, 6H, ArCHMe_2), 1.20 (d, $^3J_{HH}$ = 6.8 Hz, 6H, ArCHMe_2), 0.11 (s, 4H, CH_2SiMe$_3$), –0.02 ppm (s, 18H, SiMe_3). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 167.7, 164.9, 161.1 (imine-*C* and Py-*C*), 149.8, 146.8, 142.9, 139.1, 126.4, 124.8, 122.3, 121.8 (Ar-*C* and Py-*C*), 99.4 (MeC(N)*C*H), 57.3 (N*C*H$_2$), 40.4 (br, *C*H$_2$SiMe$_3$), 28.8 (Ar*C*HMe$_2$), 25.5 (ArCHMe_2), 25.2 (ArCHMe_2), 24.9 (*Me*C), 23.6 (*Me*C), 4.2 ppm (SiMe_3). Elemental analysis (%) calcd for $C_{31}H_{52}N_3Si_2Sc$: C 65.56, H 9.23, N 7.40; found: C 64.86, H 8.88, N 7.32. m. p. 125–127 °C.

[(L1–H$_3$)Y(THF)]$_2$ (2). **L1** (70 mg, 0.20 mmol) in 2 mL of hexane was added to Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (100 mg, 0.20 mmol) in 3 mL of hexane at room temperature. The color of reaction mixture immediately changed to dark green. After standing at room temperature for 24 h, a red product precipitated from the solution. The supernatant liquid was removed and **2** was obtained as red crystals (95 mg, 94% yield). **2** is nearly insoluble in toluene and benzene, but soluble in THF. ^{1}H NMR (300 MHz, THF-d_8, 25 °C): δ = 7.46 (d, $^3J_{HH}$ = 5.7 Hz, 2H, Py-*H*), 7.14 (m, 2H, Ar-*H*), 6.96 (m, 4H, Ar-*H*), 6.63 (t, $^3J_{HH}$ = 7.4 Hz, 2H, Py-*H*), 6.30 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Py-*H*), 5.68 (t, $^3J_{HH}$ = 6.0 Hz, 2H, Py-*H*), 4.35 (s, 2H, MeC(N)C*H*), 4.01 (s, 2H, NC*H*), 3.79 (sp, $^3J_{HH}$ = 6.9 Hz, 2H, ArC*H*Me$_2$), 3.60 (m, 8H, THF), 3.17 (sp, $^3J_{HH}$ = 6.8 Hz, 2H, ArC*H*Me$_2$), 2.58 (s, 2H, CH_2), 2.37 (s, 2H, CH_2), 1.76 (m, 8H, THF), 1.53 (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCHMe_2), 1.37 (s, 6H, *Me*C), 1.28 (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCHMe_2), 0.99 (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCHMe_2), 0.98 ppm (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCHMe_2). ^{13}C NMR (75 MHz, THF-d_8, 25 °C): δ = 166.7, 159.1, 152.0, 149.7, 145.9, 145.0, 132.4, 124.1, 123.8, 117.9, 106.5 (imine-*C*, Ar-*C*, and Py-*C*), 101.6 (MeC(N)*C*H), 68.2 (THF), 60.7 (NC*H*), 28.3 (Ar*C*HMe$_2$), 28.1 (Ar*C*HMe$_2$), 26.6 (*C*H$_2$), 26.4 (THF), 25.3 (overlapped with THF-d_8 signals, ArCHMe_2), 25.1 (ArCHMe_2), 24.1 ppm (*Me*C). Elemental analysis (%) calcd for $C_{54}H_{72}N_6O_2Y_2$: C 63.90, H 7.15, N 8.28; found: C 63.59, H 7.55, N 7.83. m. p. >300 °C.

A mixture of (L1–H)Y(CH$_2$SiMe$_3$)$_2$ (3) and (L1–H$_2$)-Y(CH$_2$SiMe$_3$)(THF)$_2$ (4). **L1** (120 mg, 0.34 mmol) in 2 mL of hexane was added to Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (168 mg, 0.34 mmol) in 5 mL of hexane at –35 °C. The color of the reaction mixture gradually changed to green. After standing at –35 °C for 24 h, a dark green product precipitated from the solution. The supernatant liquid was removed, 125 mg dark green crystals were obtained. ^{1}H NMR of **3** (300 MHz, C_6D_6, 25 °C): δ = 8.89 (d, $^3J_{HH}$ = 5.1 Hz, 1H, Py-*H*), 7.17 (m, 3H, Ar-*H*), 6.83 (td, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.6 Hz, 1H, Py-*H*), 6.51 (t, $^3J_{HH}$ = 6.0 Hz, 1H, Py-*H*), 6.38 (d, $^3J_{HH}$ = 8.1 Hz, 1H, Py-*H*), 4.97 (s, 1H, MeC(N)C*H*), 4.47 (s, 2H, NCH_2), 3.37 (sp, $^3J_{HH}$ = 6.8 Hz, 2H, ArC*H*Me$_2$), 1.81 (s, 3H, *Me*C), 1.70 (s, 3H, *Me*C), 1.43 (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCHMe_2), 1.20 (d, $^3J_{HH}$ = 6.9 Hz, 6H, ArCHMe_2), 0.10 (s, 18H, SiMe_3), –0.40 (dd, $^2J_{HH}$ = 10.2 Hz, $^2J_{YH}$ = 2.7 Hz, 2H, CH_2SiMe$_3$), –0.49 (dd, $^2J_{HH}$ = 10.2 Hz, $^2J_{YH}$ = 2.7 Hz, 2H, CH_2SiMe$_3$).

(L1–H)Y[N(SiMe$_3$)$_2$]$_2$ (5). Following the procedure described for **1**, reaction of **L1** (78 mg, 0.22 mmol) with Y[N(SiMe$_3$)$_2$]$_3$ (128 mg, 0.22 mmol) gave **5** as a colorless crystalline solid (125 mg, 75% yield). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 9.44 (d, $^3J_{HH}$ = 5.2 Hz, 1H, Py-*H*), 7.11 (m, 3H, Ar-*H*), 6.91 (td, $^3J_{HH}$ = 7.6 Hz and $^4J_{HH}$ = 1.6 Hz, 1H, Py-*H*), 6.67 (t, $^3J_{HH}$ = 6.4 Hz, 1H, Py-*H*), 6.51 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Py-*H*), 5.08 (s, 1H, MeC(N)C*H*), 4.57 (s, 2H, NCH_2), 3.16 (br, 2H, ArC*H*Me$_2$), 1.88 (s, 3H, *Me*C), 1.75 (s, 3H, *Me*C), 1.39 (d, $^3J_{HH}$ = 6.8 Hz, 6H, ArCHMe_2), 1.10 (d, $^3J_{HH}$ = 6.4 Hz, 6H, ArCHMe_2), 0.21 ppm (s, 36H, SiMe_3). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 166.7, 162.1, 161.7 (imine-*C* and Py-*C*), 152.1, 147.4, 142.8, 138.7, 125.2, 124.1, 121.4, 121.3 (Ar-*C* and Py-*C*), 97.9 (MeC(N)CH), 55.9 (N*C*H$_2$), 27.9 (Ar*C*HMe$_2$), 25.4 (ArCHMe_2), 25.3 (ArCHMe_2), 24.3 (*Me*C), 21.5 (*Me*C), 6.1 ppm (SiMe_3). Elemental analysis (%) calcd for $C_{35}H_{66}N_5Si_4Y$: C 55.45, H 8.77, N 9.24; found: C 55.58, H 8.78, N 9.13. m. p. 165–167 °C.

(L1–H)La[N(SiMe$_3$)$_2$]$_2$ (6). Following the procedure described for **1**, reaction of **L1** (70 mg, 0.20 mmol) with La[N(SiMe$_3$)$_2$]$_3$ (124 mg, 0.20 mmol) gave **6** as a pale red crystalline solid (115 mg, 71% yield). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 9.36 (d, $^3J_{HH}$ = 5.2 Hz, 1H, Py-*H*), 7.10 (m, 3H, Ar-*H*), 6.90 (td, $^3J_{HH}$ = 7.6 Hz and $^4J_{HH}$ = 1.6 Hz, 1H, Py-*H*), 6.66 (t, $^3J_{HH}$ = 6.6 Hz, 1H, Py-*H*), 6.53 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Py-*H*), 5.03 (s, 1H, MeC(N)C*H*), 4.64 (br, 2H, NCH_2), 3.08 (br, 2H, ArC*H*Me$_2$), 1.94 (s, 3H, *Me*C), 1.75 (s, 3H, *Me*C), 1.36 (br, 6H, ArCHMe_2), 1.10 (br, 6H, ArCHMe_2), 0.21 ppm (s, 36H, SiMe_3). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ = 164.6, 162.9, 159.8 (imine-*C* and Py-*C*), 151.3, 146.8, 141.6, 138.6, 125.2, 124.1, 121.7, 121.6 (Ar-*C* and Py-*C*), 93.3 (MeC(N)CH), 57.6 (N*C*H$_2$), 28.4 (Ar*C*HMe$_2$), 25.1 (ArCHMe_2), 24.9 (*Me*C), 24.7 (br, ArCHMe_2), 22.1 (*Me*C),

Table 1 Crystallographic Data and Refinement for Complexes **1**, **2** and **4–6**

	1	**2**	**4**	**5**	**6**
Formula	$C_{31}H_{52}N_3Si_2Sc$	$C_{54}H_{72}N_6O_2Y_2$	$C_{35}H_{56}N_3O_2SiY$	$C_{35}H_{66}N_5Si_4Y$	$C_{35}H_{66}N_5Si_4La$
fw	567.90	1015.00	667.83	758.20	808.20
Color	Colorless	Red	Black	Colorless	Colorless
Cryst.syst	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a/Å	9.6221(12)	10.2136(13)	9.6283(18)	20.1051(19)	10.6794(18)
b/Å	10.3910(12)	11.1187(14)	18.118(3)	12.0332(11)	11.7544(19)
c/Å	18.515(2)	13.3747(17)	21.637(4)	18.0092(18)	18.051(3)
α (°)	77.516(2)	68.788(2)	90	90	85.938(3)
β (°)	81.161(2)	84.920(2)	100.217(4)	93.836(2)	86.272(3)
γ (°)	72.257(2)	65.451(2)	90	90	81.210(3)
V/Å^3	1713.7(4)	1284.5(3)	3714.5(12)	4347.2(7)	2230.4(6)
Z	2	1	4	4	2
D_c/g cm^{-3}	1.101	1.312	1.194	1.158	1.203
F(000)	616	532	1424	1624	848
θ range, (°)	2.19–26.00	1.64–26.00	1.91–25.50	1.97–27.00	1.76–25.50
No. of reflns collected	9448	7104	18865	25104	11582
No. of unique reflns	6612	4972	6889	9469	8145
No. of obsd reflns($I > 2\sigma(I)$)	4520	3457	3109	4561	6860
No.of params	346	294	378	424	424
Goodness of fit	0.945	0.948	0.885	0.937	1.030
Final R, R_w($I > 2\sigma(I)$)	0.0540, 0.1190	0.0483, 0.1041	0.0583, 0.1308	0.0508, 0.1068	0.0654, 0.1587
$\Delta\rho_{max,min}$/e Å^{-3}	0.382, −0.231	0.466, −0.414	0.753, −0.555	0.774, −0.463	3.449, −1.292

5.4 ppm (Si*Me*$_3$). Elemental analysis (%) calcd for $C_{35}H_{66}N_5Si_4La$: C 52.01, H 8.23, N 8.67; found: C 52.63, H 7.98, N 8.38. m. p. 197–199 °C.

X-ray Crystallography

Suitable single crystals of **1**, **2** and **4–6** were sealed in thin-walled glass capillaries, and data collection was performed at 20 °C on a Bruker SMART diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The SMART program package was used to determine the unit-cell parameters. The absorption correction was applied using SADABS. The structures were solved by direct methods and refined on F^2 by full-matrix least squares techniques with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed at calculated positions and were included in the structure calculation without further refinement of the parameters. All calculations were carried out using the SHELXS-97 program. The software used is listed in the references.[16-20] Crystallographic data and refinement are given in Table 1.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant Nos. 20872164 and 20821002), Chinese Academy of Sciences and Shanghai Municipal Committee of Science and Technology (Grant No. 07JC14063).

Notes and references

1 (*a*) H. Schumann, J. A. Meese-Marktscheffel and L. Esser, *Chem. Rev.*, 1995, **95**, 865; (*b*) S. Arndt and J. Okuda, *Chem. Rev.*, 2002, **102**, 1953; (*c*) W. J. Evans and B. L. Davis, *Chem. Rev.*, 2002, **102**, 2119; (*d*) W. J. Evans, *Inorg. Chem.*, 2007, **46**, 3435.

2 (*a*) G. A. Molander and J. A. C. Romero, *Chem. Rev.*, 2002, **102**, 2161; (*b*) S. Hong and T. J. Marks, *Acc. Chem. Res.*, 2004, **37**, 673.

3 (*a*) H. Yasuda, *J. Organomet. Chem.*, 2002, **647**, 128; (*b*) Z. Hou and Y. Wakatsuki, *Coord. Chem. Rev.*, 2002, **231**, 1; (*c*) J. Gromada, J. F. Carpentier and A. Mortreux, *Coord. Chem. Rev.*, 2004, **248**, 397.

4 (*a*) F. T. Edelmann, D. M. M. Freckmann and H. Schumann, *Chem. Rev.*, 2002, **102**, 1851; (*b*) W. E. Piers and D. J. H. Emslie, *Coord. Chem. Rev.*, 2002, **233–234**, 131; (*c*) V. C. Gibson and S. K. Spitzmesser, *Chem. Rev.*, 2003, **103**, 283.

5 L. Bourget-Merle, M. F. Lappert and J. R. Severn, *Chem. Rev.*, 2002, **102**, 3031.

6 X. Xu, X. Y. Xu, Y. F. Chen and J. Sun, *Organometallics*, 2008, **27**, 758.

7 (*a*) Y. Ding, H. Hao, H. W. Roesky, M. Noltemeyer and H.-G. Schmidt, *Organometallics*, 2001, **20**, 4806; (*b*) A. M. Neculai, H. W. Roesky, D. Neculai and J. Magull, *Organometallics*, 2001, **20**, 5501; (*c*) S. Harder, *Angew. Chem., Int. Ed.*, 2003, **42**, 3430; (*d*) F. Basuli, J. C. Huffman and D. J. Mindiola, *Inorg. Chem.*, 2003, **42**, 8003; (*e*) S. Harder, *Angew. Chem., Int. Ed.*, 2004, **43**, 2714; (*f*) P. B. Hitchcock, M. F. Lappert and A. V. Protchenko, *Chem. Commun.*, 2005, 951; (*g*) F. Basuli, J. C. Huffman, B. C. Bailey and D. J. Mindiola, *Organometallics*, 2005, **24**, 3321; (*h*) S. T. Liddle and P. L. Arnold, *Dalton Trans.*, 2007, 3305; (*i*) S. Bambirra, F. Perazzolo, S. J. Boot, T. J. J. Sciarone, A. Meetsma and B. Hessen, *Organometallics*, 2008, **27**, 704; (*j*) A. Jana, C. Schulzke and H. W. Roesky, *J. Am. Chem. Soc.*, 2009, **131**, 4600; (*k*) A. Jana, I. Objartel, H. W. Roesky and D. Stalke, *Inorg. Chem.*, 2009, **48**, 7645.

8 H. Ott, U. Pieper, D. Leusser, U. Flierler, J. Henn and D. Stalke, *Angew. Chem., Int. Ed.*, 2009, **48**, 2978and references therein.

9 (*a*) P. G. Hayes, W. E. Piers, L. W. M. Lee, L. K. Knight, M. Parvez, M. R. J. Elsegood and W. Clegg, *Organometallics*, 2001, **20**, 2533; (*b*) A. L. Kenward, W. E. Piers and M. Parvez, *Organometallics*, 2009, **28**, 3012; (*c*) Z. Hou, Y. Luo and X. Li, *J. Organomet. Chem.*, 2006, **691**, 3114.

10 É. B. Lobkovskii, G. L. Soloveichik, B. M. Bulychev and A. B. Erofeev, *J. Struct. Chem.*, 1984, **25**, 151.

11 S. Li, D. Cui, D. Li and Z. Hou, *Organometallics*, 2009, **28**, 4814.

12 P. B. Hitchcock, M. F. Lappert and S. Tian, *J. Chem. Soc., Dalton Trans.*, 1997, 1945.
13 X. H. He, Y. Z. Yao, X. Luo, J. Zhang, Y. Liu, L. Zhang and Q. Wu, *Organometallics*, 2003, **22**, 4952.
14 M. F. Lappert and R. Pearce, *J. Chem. Soc., Chem. Commun.*, 1973, 126.
15 D. C. Bradley, J. S. Ghotra and F. A. Hart, *J. Chem. Soc., Dalton Trans.*, 1973, 1021.
16 G. M. Sheldrick, *SADABS, An Empirical Absorption Correction Program for Area Detector Data*, University of Goettingen, Germany, 1996.
17 G. M. Sheldrick, *SHELXS-97*, University of Goettingen, Germany, 1997.
18 *SMART Version 5.628*, Bruker Asx Inc.
19 *SAINT + Version 6.22a*, Bruker Axs Inc.
20 *SHELXTL* NT/2000, Version 6.1.