C–H bond activation of N-heterocyclic carbene IMes by rare-earth metal alkyl complexes

Waldemar Fegler [a], Teruhiko Saito [b], Kazushi Mashima [b], Thomas P. Spaniol [a], Jun Okuda [a,*]

[a] Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, D-52056 Aachen, Germany
[b] Department of Chemistry, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan

ABSTRACT

Excess N-heterocyclic carbene 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) reacted with the tris(trimethylsilylmethyl) rare-earth metal complex $[Ln(CH_2SiMe_3)_3(THF)_2]$ (Ln = Y, Lu) in toluene to give a C_2-symmetric mono(trimethylsilylmethyl) complex with two IMes' ligands $[Ln(CH_2SiMe_3)(IMes')_2]$ (IMes' = IMes deprotonated at the *ortho*-methyl group of the mesityl substituent), formed by C–H bond activation of the mesityl substituents' *ortho*-methyl groups. With one equivalent of IMes in THF, a mono-activated product $[Ln(CH_2SiMe_3)_2(IMes')(THF)_n]$ is selectively formed. The molecular structure of the lutetium compound $[Lu(CH_2SiMe_3)_2(IMes')(THF)]$ in the crystal shows a strongly distorted trigonal bipyramid with a strained chelate ligand IMes'.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Schumann et al. were the first to report that N-heterocyclic carbenes (NHCs) can act as ligands at Lewis acidic rare-earth metal centers to give isolable complexes of the type $[LnR_3(THF)(NHC)]$ and $[LnR_3(NHC)_2]$ (Ln = Er, Lu; NHC = C{N^{i}PrCMe}$_2$) [1]. Subsequently, chelating and functionalized NHCs, including indenyl- and fluorenyl-functionalized NHCs, were introduced in rare-earth metal chemistry [2]. Due to their structural, electronic, and steric diversity [3], NHCs continue to attract attention as spectator ligands for homogeneous catalysts based on organotransition metal complexes [4]. In our effort to identify ancillary ligands for reactive alkyl and, in particular, hydride complexes of the rare-earth metals [5], we have found that sterically demanding NHCs 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) and 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) coordinate at tris(trimethylsilylmethyl) complexes of yttrium and lutetium $[Ln(CH_2SiMe_3)_3(NHC)]$ [6]. In the case of IMes, this NHC undergoes C–H bond activation at the distal mesityl substituent to give a chelate complex of the type $[Ln(CH_2SiMe_3)_2(IMes')(THF)_n]$ (IMes' = IMes deprotonated at the *ortho*-methyl group of the mesityl substituent). We report here that two IMes ligands can be activated to give complexes of the type $[Ln(CH_2SiMe_3)(IMes')_2]$.

2. Results and discussion

### 2.1. $[LuR_2(THF)(IMes')]$ (2-Lu)

Previously we reported that tris(trimethylsilylmethyl)yttrium (1-Y) reacted with IMes in THF at room temperature within 5 min to give $[Y(CH_2SiMe_3)_2(THF)_2(IMes')]$ (2-Y) [6]. Treatment of tris(trimethylsilylmethyl)lutetium (1-Lu) with one equivalent of IMes in THF at room temperature resulted in the C–H bond activation of one of the *ortho*-methyl groups of the mesityl substituent with elimination of tetramethylsilane to give complex 2-Lu (Scheme 1). In contrast to the instantaneous C–H bond activation observed in the reaction of the analogous tris(trimethylsilylmethyl)yttrium 1-Y with IMes [6], a reaction time of 2 h was required for the formation of 2-Lu.

The ^{1}H NMR spectrum of 2-Lu in benzene-d_6 shows five singlets at 2.06, 2.07, 2.13, 2.19, and 2.21 ppm for the mesityl methyl protons and four broad singlets at 6.46, 6.65, 6.80, and 6.83 ppm for the aromatic protons due to the inequivalence resulting from the C–H bond activation. The resonance of the methylene protons of the trimethylsilylmethyl ligands appears as two doublets at −1.13 ppm ($^2J_{HH}$ = 11.4 Hz) and −1.06 ppm ($^2J_{HH}$ = 11.4 Hz), consistent with the
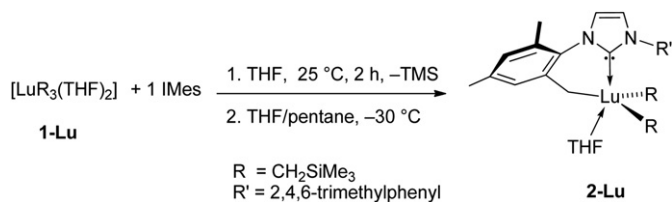
Scheme 1. Formation of complex 2-Lu.

diastereotopicity of the two protons. Accordingly, the resonance of the methylene bridge features two doublets at 1.68 ppm ($^2J_{HH} = 6.3$ Hz) and 1.90 ppm ($^2J_{HH} = 6.3$ Hz). In the ^{13}C NMR spectrum the signal for the methylene group of the bridging mesityl substituent can be found at 51.98 ppm and the signal for the carbene carbon atom appears at 201.26 ppm. No resonance could be observed for the methylene carbon atoms of the trimethylsilylmethyl ligands, which was confirmed by correlation signals missing in an HSQC (heteronuclear single quantum correlation) experiment.

Crystallization of 2-Lu from THF/pentane at −30 °C gave light yellow crystals suitable for X-ray diffraction. A single crystal structure analysis was carried out to determine the molecular structure of 2-Lu in the solid state (Fig. 1). Compound 2-Lu exhibits a distorted trigonal bipyramidal coordination geometry around the lutetium center. In contrast to the analogous yttrium compound [Y(CH$_2$SiMe$_3$)$_2$(IMes')(THF)$_2$] [6], there is only one THF molecule coordinating to the lutetium center. This finding is consistent with the smaller radius of lutetium (0.86 vs. 0.90 Å) [7]. The activation of the methyl group forces the attached mesityl ring to twist by 37° from its perpendicular position to the imidazole plane. The Lu–C$_{alkyl}$ bond lengths of 2.363(3) Å and 2.331(3) Å as well as the Lu–C$_{carbene}$ distance of 2.491(2) Å are comparable to those found in the tris(trimethylsilylmethyl) NHC complex, [LuR$_3$(THF)(C{N^{i}PrCMe}$_2$)], reported by Schumann et al. (Lu–C$_{alkyl}$ 2.364(4)–2.376(3) Å; Lu–C$_{carbene}$ 2.488(3) Å) [1].

2.2. [LnR(IMes')$_2$] (3-Ln; Ln = Y, Lu)

When the reaction of 1-Ln with IMes was performed in non-basic solvents such as toluene or with an excess of IMes, complex 3-Ln could be isolated from the reaction mixture, containing two metalated IMes ligands and only one trimethylsilylmethyl group. For the yttrium compound 3-Y, the C−H bond activation occurred within 10 min reaction time evidenced by a color change from colorless to yellow. In the case of lutetium, longer reaction times of 2 h were needed. This longer reaction time also resulted in partial decomposition. When the work-up was performed after 10 min, only the NHC mono-adduct [LuR$_3$(IMes)] could be isolated [6] (Scheme 2).

The ^{1}H NMR spectra of 3-Y and 3-Lu in benzene-d_6 exhibit similar splitting patterns for the signals, in agreement with C_2-symmetry that is retained in solution at room temperature. The
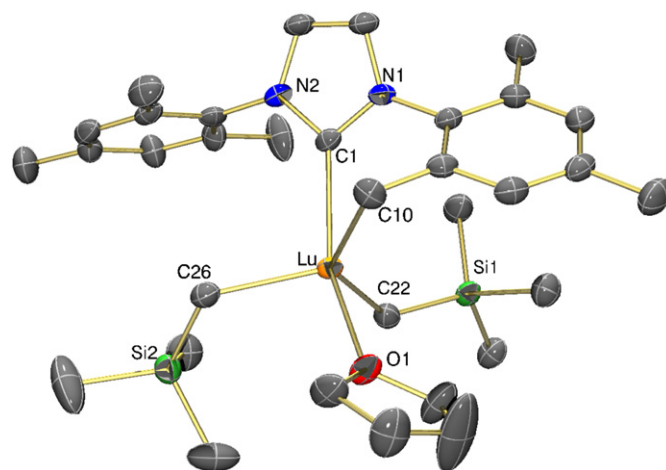

Fig. 1. ORTEP plot of 2-Lu. Thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Lu–C1 2.491(2), Lu–C10 2.416(3), Lu–C22 2.363(3), Lu–C26 2.331(3), Lu–O1 2.3048(18); C1–Lu–C10 72.49(9), C1–Lu–C22 98.73(8), C1–Lu–C26 102.14(9), C1–Lu–O1 156.18(8), C22–Lu–C26 114.56(9), C10–Lu–C22 134.73(10), C10–Lu–C26 110.69(10).

resonance of the methylene protons of the remaining trimethylsilylmethyl ligand in 3-Lu features two doublets at −1.37 and −1.31 ppm with $^2J_{HH} = 10.8$ Hz due to their diastereotopic character. The methylene protons of the bridging mesityl substituent appear at 1.32 and 1.44 ppm ($^2J_{HH} = 6.3$ Hz). In 3-Y, the methylene resonances appear as pairs of doublets of doublets at −1.23 ($^2J_{HH} = 10.8$ Hz, $^2J_{YH} = 2.8$ Hz) and −1.12 ppm ($^2J_{HH} = 10.8$ Hz, $^2J_{YH} = 2.5$ Hz) for the Me$_3$SiCH$_2$ and 1.53 ppm ($^2J_{HH} = 5.0$ Hz, $^2J_{YH} = 2.0$ Hz) and 1.71 ppm ($^2J_{HH} = 5.0$ Hz, $^2J_{YH} = 2.3$ Hz) for the bridging mesityl-methylene due to the additional coupling to yttrium ($I = 1/2$). In the ^{13}C NMR spectrum of 3-Lu all three types of carbon atoms bonded to the metal center can be observed at 37.57 ppm (C$_{alkyl}$), 54.68 (C$_{Mes}$) and 201.51 (C$_{carbene}$). For 3-Y, these carbon resonances appear as doublets at 30.13 ($^1J_{YC} = 37.3$ Hz), 48.94 ($^1J_{YC} = 18.2$ Hz) and 194.69 ($^1J_{YC} = 35.6$ Hz), respectively.

3. Conclusion

Depending on the stoichiometry and the solvent, tris(trimethylsilylmethyl) complexes [Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$] (1-Ln; Ln = Y, Lu) reacted with IMes to give products with one or two activated IMes' ligands. Despite the apparent ring strain of the IMes' ligand, the formation of the chelate structure is thermodynamically favored. As noted previously, the significantly more sluggish C−H bond activation in the lutetium complex vis-à-vis the yttrium complex can be ascribed primarily to the size difference as well as to the difference in electrophilicity of the trivalent rare-earth metal center. Further reaction to give a tris(IMes') complex was so far not detected, probably due to prohibitive steric congestion. Reactivity
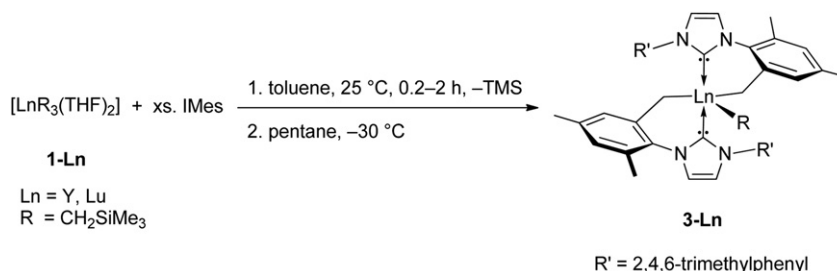
Scheme 2. Formation of complex 3-Ln.

studies, in particular hydrogenolysis with dihydrogen or silanes [5h, 5i] are currently underway.

4. Experimental section

All experiments were carried out under purified argon using standard Schlenk techniques or in a glove box (<1 ppm O_2, <1 ppm H_2O). Toluene, pentane, and THF were purified from the MBraun SPS-800 system prior to use. Deuterated solvents were purchased from Aldrich and purified before use. All other chemicals were commercially available and used after appropriate purification.

Compounds **1-Y** and **1-Lu** were prepared according to literature methods [5b, 8]. IMes was prepared by deprotonation of the corresponding imidazolium chloride which was synthesized by following literature procedures [9]. NMR spectra were recorded on Bruker DRX 400 (^{1}H, 400 MHz; ^{13}C, 101 MHz) and Varian 200 spectrometers in Teflon-valved NMR tubes at 25 °C. ^{1}H and ^{13}C NMR chemical shifts were determined using residual solvent resonances and are reported vs. $SiMe_4$. Assignment of signals was made from ^{1}H–^{13}C HSQC 2D NMR experiments. Coupling constants are given in Hertz.

4.1. Synthesis of [Lu(CH₂SiMe₃)₂(IMes')(THF)] (**2-Lu**)

A solution of compound **1-Lu** (50 mg, 0.083 mmol) and IMes (25 mg, 0.083 mmol) in THF (1 mL) was stirred for 2 h. The light yellow solution was concentrated in vacuo and a few drops of pentane were added. Storage at −30 °C provided light yellow crystals (32 mg, 53%), suitable for X-ray diffraction. ^{1}H NMR (400 MHz, C_6D_6): $\delta = -1.13$ (d, $^2J_{HH} = 11.4$ Hz, 2H, LuCH_2SiMe₃), −1.06 (d, $^2J_{HH} = 11.4$ Hz, 2H, LuCH_2SiMe₃), 0.17 (s, 18H, LuCH₂Si(CH_3)₃), 1.29 (m, 4H, β-CH_2, THF), 1.68 (d, $^2J_{HH} = 6.3$ Hz, 1H, LuCH_2Ph), 1.90 (d, $^2J_{HH} = 6.3$ Hz, 1H, LuCH_2Ph), 2.06 (s, 3H, Mes-CH_3), 2.07 (s, 3H, Mes-CH_3), 2.13 (s, 3H, Mes-CH_3), 2.19 (s, 3H, Mes-CH_3), 2.21 (s, 3H, Mes-CH_3), 3.84 (m, 4H, α-CH_2, THF), 6.11 (d, 1H, $^3J_{HH} = 1.6$ Hz, Im-H), 6.33 (d, 1H, $^3J_{HH} = 1.6$ Hz, Im-H), 6.46 (br s, 1H, Mes-CH), 6.65 (br s, 1H, Mes-CH), 6.80 (br s, 1H, Mes-CH), 6.83 (br s, 1H, Mes-CH); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): $\delta = 4.59$ (LuCH₂Si(CH_3)₃), 17.99 (Mes-CH_3), 18.32 (Mes-CH_3), 19.21 (Mes-CH_3), 21.00 (Mes-CH_3), 21.45 (Mes-CH_3), 25.07 (β-CH_2, THF), 51.98 (LuCH_2Ph), 70.66 (α-CH_2, THF), 120.43 (Mes-CH), 120.53 (Im-C), 121.31 (Im-C), 124.20 (Mes-CH), 128.65 (Mes-C), 129.53 (Mes-CH), 129.60 (Mes-CH), 132.70 (Mes-C), 135.22 (Mes-C), 135.30 (Mes-C), 136.45 (Mes-C), 138.39 (Mes-C), 138.93 (Mes-C), 145.96 (Mes-C), 201.26 (carbene-C) ppm. No signal could be observed for LuCH₂SiMe₃.

4.2. Synthesis of [Y(CH₂SiMe₃)(IMes')₂] (**3-Y**)

A solution of compound **1-Y** (100 mg, 0.195 mmol) and IMes (119 mg, 0.390 mmol) in toluene (3 mL) was stirred for 10 min at room temperature. The resulting yellow solution was concentrated in vacuo and a few drops of pentane were added. Storage at −30 °C gave **3-Y** as a yellow powder (131 mg, 86%). ^{1}H NMR (400 MHz, C_6D_6): $\delta = -1.23$ (dd, $^2J_{HH} = 10.8$ Hz, $^2J_{YH} = 2.8$ Hz, 1H, YCH_2SiMe₃), −1.12 (dd, $^2J_{HH} = 10.8$ Hz, $^2J_{YH} = 2.5$ Hz, 1H, YCH_2SiMe₃), 0.02 (s, 9H, YCH₂Si(CH_3)₃), 1.53 (dd, $^2J_{HH} = 5.0$ Hz, $^2J_{YH} = 2.0$ Hz, 2H, YCH_2aryl), 1.71 (dd, $^2J_{HH} = 5.0$ Hz, $^2J_{YH} = 2.3$ Hz, 2H, YCH_2aryl), 2.00 (s, 6H, Mes-CH_3), 2.02 (s, 6H, Mes-CH_3), 2.03 (s, 6H, Mes-CH_3), 2.13 (s, 6H, Mes-CH_3), 2.26 (s, 6H, Mes-CH_3), 6.07 (d, 2H, $^3J_{HH} = 1.5$ Hz, Im-H), 6.08 (s, 2H, Mes-CH), 6.25 (d, 2H, $^3J_{HH} = 1.5$ Hz, Im-H), 6.41 (s, 2H, Mes-CH), 6.78 (s, 2H, Mes-CH), 6.92 (s, 2H, Mes-CH); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): $\delta = 4.85$ (YCH₂Si(CH_3)₃), 17.74 (Mes-CH_3), 18.06 (Mes-CH_3), 19.08 (Mes-CH_3), 20.98 (Mes-CH_3), 21.52 (Mes-CH_3), 30.13 (d, $^1J_{YC} = 37.3$ Hz, YCH_2SiMe₃), 48.94 (d, $^1J_{YC} = 18.2$ Hz, YCH_2Ph), 119.86 (Mes-CH), 120.38 (Im-C), 121.21 (Im-C), 124.95 (Mes-CH), 126.76

(Mes-C), 129.28 (Mes-CH), 129.38 (Mes-CH), 133.24 (Mes-C), 135.55 (Mes-C), 135.68 (Mes-C), 136.68 (Mes-C), 138.72 (Mes-C), 138.82 (Mes-C), 146.03 (Mes-C), 194.69 (d, $^1J_{YC} = 35.6$ Hz, carbene-C) ppm.

4.3. Synthesis of [Lu(CH₂SiMe₃)(IMes')₂] (**3-Lu**)

1-Lu (60 mg, 0.099 mmol) was treated with IMes (60 mg, 0.198 mmol) in toluene (2 mL) for 2 h at room temperature. Concentration of the solution in vacuo, addition of a few drops of pentane and storage at −30 °C gave **3-Lu** as light yellow powder (29 mg, 34%). ^{1}H NMR (400 MHz, C_6D_6): $\delta = -1.37$ (d, $^2J_{HH} = 10.8$ Hz, 1H, LuCH_2SiMe₃), −1.31 (d, $^2J_{HH} = 10.8$ Hz, 1H, LuCH_2SiMe₃), −0.02 (s, 9H, LuCH₂SiCH_3), 1.32 (d, $^2J_{HH} = 6.3$ Hz, 2H, LuCH_2aryl), 1.44 (d, $^2J_{HH} = 6.3$ Hz, 2H, LuCH_2Ph), 2.01 (s, 6H, Mes-CH_3), 2.04 (s, 6H, Mes-CH_3), 2.07 (s, 6H, Mes-CH_3), 2.15 (s, 6H, Mes-CH_3), 2.28 (s, 6H, Mes-CH_3), 6.07 (d, 2H, $^3J_{HH} = 1.5$ Hz, Im-H), 6.10 (s, 2H, Mes-CH), 6.29 (d, 2H, $^3J_{HH} = 1.5$ Hz, Im-H), 6.46 (s, 2H, Mes-CH), 6.79 (s, 2H, Mes-CH), 6.95 (s, 2H, Mes-CH); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): $\delta = 4.86$ (LuCH₂-Si(CH_3)₃), 17.88 (Mes-CH_3), 18.07 (Mes-CH_3), 19.28 (Mes-CH_3), 21.02 (Mes-CH_3), 21.48 (Mes-CH_3), 37.57 (LuCH_2SiMe₃), 54.68 (LuCH_2aryl), 120.21 (Im-C), 120.65 (Mes-CH), 121.59 (Im-C), 125.68 (Mes-CH), 127.52 (Mes-C), 129.35 (Mes-CH), 129.40 (Mes-CH), 131.95 (Mes-C), 135.60 (Mes-C), 135.76 (Mes-C), 136.95 (Mes-C), 138.18 (Mes-C), 138.72 (Mes-C), 145.77 (Mes-C), 201.51 (carbene-C) ppm.

4.4. Crystallographic data for **2-Lu**

The X-Ray diffraction measurement was performed on a Bruker AXS diffractometer with MoKα radiation using ω-scans. Absorption corrections were carried out with the multi-scan method using Mulabs as implemented in the program system Platon [10]. The structure was solved by direct methods (SIR-92) [11] and refined (SHELXL-97) [12] against all F^2 data. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included into calculated positions. For the graphical representation, the program ORTEP3 was used as implied in the program system WinGX [13]. Crystallographic data and refinement parameters of **2-Lu**: block, $0.17 \times 0.20 \times 0.23$ mm, $C_{33}H_{53}LuN_2OSi_2$, $M_r = 724.92$, $T = 130(2)$ K, space group $P2_1/c$, monoclinic, $a = 17.1475(11)$ Å, $b = 10.4971(7)$ Å, $c = 19.9850(13)$ Å, $\beta = 94.2124(10)°$, $V = 3587.6(4)$ Å^3, $Z = 4$, $D_{calc} = 1.342$, μ (Mo Kα) $= 2.844$ mm^{-1}, $F(000) = 1488$, θ range $= 2.19-30.60°$, index ranges $-23 \leq h \leq 23$, $-15 \leq h \leq 14$, $-28 \leq h \leq 27$, 52210 reflections collected, 10560 independent reflections ($R_{int} = 0.0641$), GOF (F^2) $= 0.907$, $R_1 = 0.0446$ and $wR_2 = 0.0606$ for all data, $R_1 = 0.0303$ and $wR_2 = 0.0571$ for $I > 2\sigma(I)$, largest residual densities 1.637 and −0.645 e Å^{-3}.

Acknowledgment

Appendix A. Supporting information

CCDC number 773563 contains the supplementary crystallographic data for the structural analysis of **2-Lu**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

References

[1] H. Schumann, D.M.M. Freckmann, S. Schutte, S. Dechert, M. Hummert, Z. Anorg. Allg. Chem. 633 (2007) 888–892.

[2] (a) P.L. Arnold, S.A. Mungur, A.J. Blake, C. Wilson, Angew. Chem. Int. Ed. 42 (2003) 5981–5984;
(b) S.T. Liddle, P.L. Arnold, Organometallics 24 (2005) 2597–2605;
(c) I.J. Casely, S.T. Liddle, A.J. Blake, C. Wilson, P.L. Arnold, Chem. Commun. (2007) 5037–5039;
(d) P.L. Arnold, S.T. Liddle, J. McMaster, C. Jones, D.P. Mills, J. Am. Chem. Soc. 129 (2007) 5360–5361;
(e) P.L. Arnold, I.J. Casely, Z.R. Turner, C.D. Carmichael, Chem.-Eur. J. 14 (2008) 10415–10422;
(f) P.L. Arnold, I.J. Casely, S. Zlatogorsky, C. Wilson, Helv. Chim. Acta 92 (2009) 2291–2303;
(g) Z.-G. Wang, H.-M. Sun, H.-S. Yao, Q. Shen, Y. Zhang, Organometallics 25 (2006) 4436–4438;
(h) Z.-G. Wang, H.-M. Sun, H.-S. Yao, Y.-M. Yao, Q. Shen, Y. Zhang, J. Organomet. Chem. 691 (2006) 3383–3390;
(i) B.L. Wang, D. Wang, D.M. Cui, W. Gao, T. Tang, X.S. Chen, X.B. Jing, Organometallics 26 (2007) 3167–3172;
(j) B.L. Wang, D.M. Cui, K. Lv, Macromolecules 41 (2008) 1983–1988;
(k) H.S. Yao, Y. Zhang, H.M. Sun, Q. Shen, Eur. J. Inorg. Chem. (2009) 1920–1925.

[3] R.H. Crabtree, J. Organomet. Chem. 690 (2005) 5451–5457.

[4] (a) W.A. Herrmann, C. Köcher, Angew. Chem. Int. Ed. Engl. 36 (1997) 2162–2187;
(b) W.A. Herrmann, Angew. Chem. Int. Ed. 41 (2002) 1290–1309;
(c) F.E. Hahn, M.C. Jahnke, Angew. Chem., Int. Ed. 47 (2008) 3122–3172; (d) S. Díez-González, N. Marion, S.P. Nolan, Chem. Rev. 109 (2009) 3612–3676.

[5] (a) K.C. Hultzsch, T.P. Spaniol, J. Okuda, Angew. Chem. Int. Ed. 38 (1999) 227–230;
(b) S. Arndt, P. Voth, T.P. Spaniol, J. Okuda, Organometallics 19 (2000) 4690–4700;
(c) S. Arndt, K. Beckerle, K.C. Hultzsch, P.-J. Sinnema, P. Voth, T.P. Spaniol, J. Okuda, J. Mol. Catal. A: Chem. 190 (2002) 215–223;
(d) K.C. Hultzsch, P. Voth, T.P. Spaniol, J. Okuda, Z. Anorg. Allg. Chem. 629 (2003) 1272–1276;
(e) M. Konkol, T.P. Spaniol, M. Kondracka, J. Okuda, Dalton Trans. (2007) 4095–4102;
(f) M. Ohashi, M. Konkol, I. Del Rosal, R. Poteau, L. Maron, J. Okuda, J. Am. Chem. Soc. 130 (2008) 6920–6921;
for reviews see: (g) J. Okuda, Dalton Trans. (2003) 2367–2378;
(h) M. Konkol, J. Okuda, Coord. Chem. Rev. 252 (2008) 1577–1591;
(i) M. Nishiura, Z. Hou, Nat. Chem. 2 (2010) 257–268.

[6] W. Fegler, T.P. Spaniol, J. Okuda, Dalton Trans. 39 (2010) 6774–6779.

[7] R. Shannon, Acta Crystallogr. A32 (1976) 751–767.

[8] (a) J.W. Connolly, G. Urry, Inorg. Chem. 2 (1963) 645–646;
(b) M.F. Lappert, R. Pearce, J. Chem. Soc. Chem. Commun. (1973) 126;
(c) H. Schumann, D.M.M. Freckmann, S. Dechert, Z. Anorg. Allg. Chem. 628 (2002) 2422–2426.

[9] L. Hintermann, Beilstein J. Org. Chem. 3 (2007) 22.

[10] (a) A.L. Spek, Acta Crystallogr. A46 (1990) C34;
(b) A.L. Spek, J. Appl. Crystallogr. 36 (2003) 7–13.

[11] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, J. Appl. Crystallogr. 26 (1993) 343–350.

[12] G.M. Sheldrick, Acta Crystallogr A64 (2008) 112–122.

[13] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837–838.