

Half-sandwich rhodium complexes containing both N-heterocyclic carbene and *ortho*-carborane-1,2-dithiolate ligands

Xu-Qiong Xiao, Guo-Xin Jin *

Shanghai Key Laboratory of Molecular Catalysis and Innovative Material, Department of Chemistry, Fudan University, Shanghai 200433, China

Received 19 September 2007; received in revised form 31 October 2007; accepted 6 November 2007

Available online 13 November 2007

Abstract

A new route was used to synthesize half-sandwich rhodium complexes containing both N-heterocyclic carbenes (NHC) and carborane ligands. The rhodium carbene complexes $\text{Cp}^*\text{Rh}(\text{L})[\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]$ (Cp^* = pentamethylcyclopentadienyl, L = 1,3-dimethylimidazolin-2-ylidene; **4**) can be obtained from the reaction of $\text{Cp}^*\text{Rh}(\text{L})\text{Cl}_2$ (**2**) with $\text{Li}_2\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_{10})$ or from the reaction of $\text{Cp}^*\text{Rh}[\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]$ (**3**) with silver–NHC complex prepared by direct reaction of an imidazolium precursor and Ag_2O . Complexes **2** and **4** were characterized by IR, NMR spectroscopy, element analysis and X-ray structure analyses.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Rhodium; N-heterocyclic carbenes (NHC); Carborane; Half-sandwich complexes; Molecular structures

1. Introduction

N-heterocyclic carbenes (NHC) have emerged as an important class of ligands in organometallic chemistry and homogenous catalysis due to their strong σ -donor electronic properties and ease of changing steric bulk in recent years [1,2]. Many efforts have been made in the design of NHC complexes bearing functionalized groups, including pyridine, picoline and lutidine [3]. Therefore, the design of NHC complexes containing new ligands is of important.

During the past decades, considerable attention has been devoted to metal complexes containing chelating 1,2-dicarbido-*closo*-dodecarborane because of both their fundamental properties and wide-ranging potential applications [4]. Our group and Herberhold et al. have reported on the synthesis of 16-electron metal complexes and suggested that these complexes show rich coordination chemistry due to their unsaturation at a metal atom, which has allowed the addition reaction at the metal atom in a dichalcogenolato metal heterocycle [5]. Recently, our group has

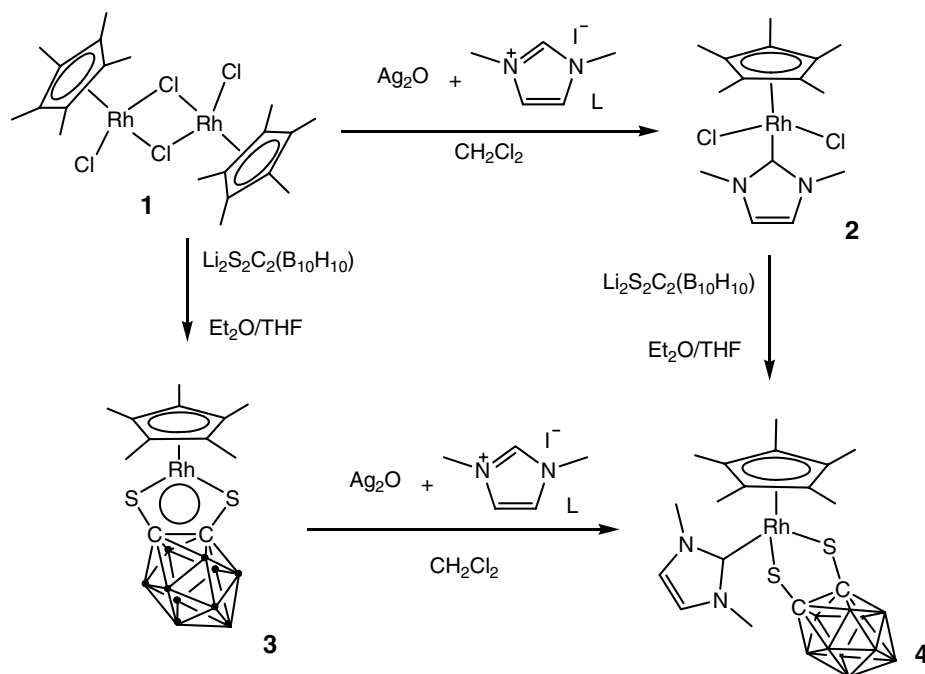
reported the synthesis of half-sandwich monometallic and dimetallic transition-metal complexes bearing both NHC and carborane ligands from the reaction of Ag carbene precursors and 16-electron “pseudo-aromatic” complexes $[\text{Cp}^*\text{MS}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]$ (M = Rh, Ir) [6]. Herein, another strategy was used to synthesize rhodium carbene complexes containing both NHC and carborane ligands (Scheme 1).

2. Results and discussion

A solution of **1** in CH_2Cl_2 was added to the filtrate of 1,3-dimethylimidazolium iodide (L) and silver oxide, to afford yellow $\text{Cp}^*\text{Rh}(\text{L})\text{Cl}_2$ (L = 1,3-dimethylimidazol-2-ylidene, **2**) in a yield of 78%, which has been characterized by NMR, elemental analysis and X-ray structure analyses.

The ^1H NMR spectrum of complex **2** shows no signal at δ 10–11 ppm, where the imidazolium $\text{C}_2\text{--H}$ signals of precursors were found ($\delta = 10.18$ ppm). The ^{13}C NMR spectroscopic data of **2** reveal that metalation of the carbene had occurred, as evidenced by presence of signals at $\delta = 164.9$ ppm (**2**) in the ^{13}C NMR spectrum, which is typical for the carbon of metal-carbene [7].

* Corresponding author. Tel.: +86 21 6564 3776; fax: +86 21 6564 1740.
E-mail address: gxjin@fudan.edu.cn (G.-X. Jin).



Scheme 1. Synthesis of complexes 2–4.

Single crystals suitable for X-ray crystallography of **2** were obtained by slow diffusion of hexane into dichloromethane solution of **2**. The metal centre of complex **2** adopts a distorted three-legged stool geometry (Fig. 1). The Rh–C_{carbene} bond length (2.052(3) Å) are typical for Rh–C σ bonds with very little back-donation [8]. The bond angle C_{cent}–Rh–C_{carbene} (C_{cent} is the central point of the Cp^{*}) is 126.2°, thus minimizing the repulsion between the

Cp^{*} and the imidazole ring. The Rh–C_{carbene} band is almost perpendicular to the Rh–Cl(1)–Cl(2) plane with an angle of 85.5°. As usual, the C–C distance in the imidazole unit is short (ca. 1.324(6) Å), which points to enhanced C=C double-bond character.

The complexes Cp^{*}Rh(L)[S₂C₂(B₁₀H₁₀)] (**4**) were obtained by treatment of **2** with the dilithium 1,2-dithiolate carborane cluster in THF solution or from the reaction of Cp^{*}Rh[S₂C₂(B₁₀H₁₀)] (**3**) with silver–NHC complex prepared by direct reaction of an imidazolium precursor and silver oxide (Scheme 1).

The ¹H NMR spectrum of complex **4** also shows no signal at δ 10–11 ppm, which is typical for the imidazolium C₂–H signals of precursors. The ¹³C NMR spectroscopic data of **4** exhibits signal at δ = 164.4 ppm, which can be unequivocally assigned for the metal–carbene carbon. The ¹¹B NMR spectrum of **4** show signals at δ = –7.3, –8.1, –8.7, –10.8, –11.6 ppm. The infrared spectrum of complexes **4** in the solid state exhibits intense B–H stretching of carborane at about 2580 cm^{–1}.

Single crystals suitable for X-ray crystallography of **4** were also obtained by slow diffusion of hexane into dichloromethane solution of **4**. The ORTEP diagram of **4** is presented in Fig. 2, which establishes that there is a pseudo mirror plane going through the Rh–C_{carbene} bond. The metal centre is in a distorted octahedral environment with Cp^{*} as three-coordinated ligand, chelating *ortho*-carborane dithiolate and monodentate NHC. Due to the coordination of the carbene to the metal centre, the “pseudo-aromatic” metalladithiolate heterocyclic system is destroyed and bent with a dihedral angle (168.0°) along the S··S vector, compared to 180° in [Cp^{*}RhS₂C₂(B₁₀H₁₀)] [9]. The Rh–S distance (2.36 Å) at the formally 18-electron metal centre is

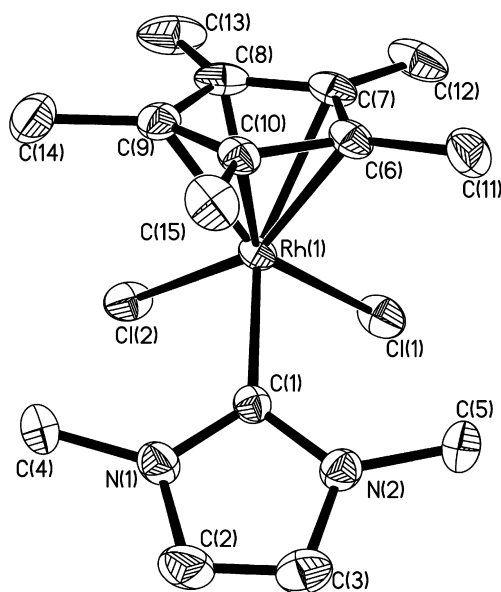


Fig. 1. Molecular structure of **2** (hydrogen atoms are omitted for clarity, ellipsoids set at the 30% probability level). Selected bond lengths (Å) and angles (°): Rh(1)–C(1) 2.052(3), Rh(1)–Cl(1) 2.4168(10), Rh(1)–Cl(2) 2.4232(11); C(1)–Rh(1)–Cl(1) 92.10(9), C(1)–Rh(1)–Cl(2) 94.08(9), Cl(1)–Rh(1)–Cl(2) 86.67(4), N(1)–C(1)–N(2) 103.6(3).

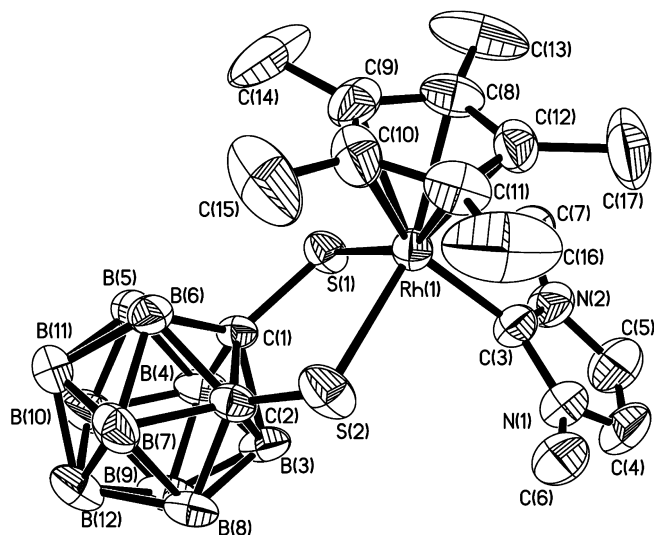


Fig. 2. Molecular structure of **4** (hydrogen atoms are omitted for clarity, ellipsoids set at the 30% probability level). Selected bond lengths (Å) and angles (°): Rh(1)–C(3) 2.044(6), Rh(1)–S(1) 2.3637(15), Rh(1)–S(2) 2.3667(16); C(3)–Rh(1)–S(1) 90.40(17), C(3)–Rh(1)–S(2) 93.44(17), S(1)–Rh(1)–S(2) 89.72(5).

significantly longer than that of 16-electron $[\text{Cp}^*\text{RhS}_2\text{C}_2\text{-(B}_{10}\text{H}_{10})]$, which is due to π -orbital donation of the lone pairs from the sulfur atoms to the electron-deficient metal centre. The Rh–C_{carbene} bond length (2.044 Å) is identical to that of **2**, which is typical for Rh–C σ bonds with very little back-donation. The bond angle C_{cent}–Rh–C_{carbene} (C_{cent} is the central point of the Cp*) is 127.7°, similar to that of **2**, which also minimize the repulsion between the Cp* and the imidazole ring. The C–C distance in the imidazole unit is about 1.335 Å, similar to that of **2**, which points to enhanced C=C double-bond character.

3. Conclusion

In summary, a different method to synthesize half-sandwich rhodium complexes containing both NHC and *ortho*-carborane-1,2-dithiolate ligands was found. We believe that this exploration may provide a guide to understand the chemistry of transition-metal complexes containing both NHC and *ortho*-carborane-1,2-dithiolate ligands.

4. Experimental

4.1. General procedure

Manipulation of air-sensitive compounds was performed under a controlled dry argon atmosphere using standard Schlenk techniques or inert-gas gloveboxes. Solvents were purified by standard methods prior to use. 1-methylimidazole was purchased from Acros. 1,3-dimethylimidazolium iodide (L) and Cp* $\text{Rh}[\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]$ (**3**) were prepared according to the reported literatures [10]. ^1H NMR (500 M), ^{13}C NMR (125 M) and ^{11}B NMR (160 M) spectra were recorded on a Bruker DMX 500

Spectrometer at room temperature in CDCl_3 solutions, using TMS (^1H NMR, ^{13}C NMR) and $\text{BF}_3 \cdot \text{OEt}_2$ (^{11}B NMR) as an internal standard. IR spectra were recorded on a Nicolet AVATAR-360 IR spectrometer. Elemental analyses were carried out on an Elementar III Vario EI Analyzer.

4.2. Synthesis of Cp* $\text{Rh}(\text{L})\text{Cl}_2$ (**2**)

A mixture of **1** (112 mg, 0.5 mmol) and silver (I) oxide (70 mg, 0.3 mmol) was taken up in 15 mL CH_2Cl_2 and stirred overnight. The resulting gray suspension was filtered through Celite, and the filtrate was added to a solution of $[\text{Cp}^*\text{Rh}_2\text{Cl}_2(\mu_2\text{-Cl})_2]$ (155 mg, 0.25 mmol) in CH_2Cl_2 (10 mL). The solution was stirred for 10 h at room temperature and filtered. After evaporating the solvent under reduced pressure, the yellow residue was washed with ether and then dried in a vacuum. Light yellow crystals suitable for X-ray diffraction analysis were grown by diffusion of hexane (6 mL) into a saturated solution of **2** in CH_2Cl_2 (4 mL) at room temperature. Yield: 158 mg (78%). ^1H NMR (500 MHz, CDCl_3): 6.93 (d, 2H, H_{im}), 3.97 (s, 6H, CH₃), 1.64 (s, 15H, C₅Me₅) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ 164.9 (C_{carbene}–Rh), 123.4 (C_{im}), 92.2 (C₅Me₅), 37.6 (NCH₃), 9.21 (C₅Me₅) ppm. Anal. Calc. for C₁₅H₂₃N₂Cl₂Rh (405.16): C, 44.47; H, 5.72; N, 6.91. Found: C, 43.69; H, 5.63; N, 7.02%.

4.3. Synthesis of Cp* $\text{Rh}(\text{L})[\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]$ (**4**)

Route 1: *o*-Carborane, H₂C₂(B₁₀H₁₀) (72 mg, 0.5 mmol), was dissolved in 10 ml of diethyl ether and lithiated by addition of 0.7 ml (1.1 mmol) of the commercially available 1.6 M hexane solution of *n*-butyl lithium. The addition of 35 mg (1.1 mmol) sulfur gave a colorless solution of Li₂[S₂C₂(B₁₀H₁₀)]. Then the solution was added with **2** (202 mg, 0.5 mmol) in a mixture of CH_2Cl_2 and THF. After stirring for 10 h at room temperature, a red solution of **3** was obtained. After removal of the solvent, the residue was extracted with CH_2Cl_2 , then washed with ether and dried in a vacuum. Crystals suitable for X-ray diffraction analysis were grown by diffusion of hexane (6 mL) into a saturated solution of **4** in CH_2Cl_2 (4 mL) at room temperature. Yield: 190 mg (70%). ^1H NMR (500 MHz, CDCl_3): 7.04 (d, 2H, H_{im}), 3.81 (s, 6H, CH₃), 1.57 (s, 15H, Cp*) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ 164.4 (C_{carbene}–Rh), 123.8 (C_{im}), 98.8 (C₅(CH₃)₅), 93.1 (C₂B₁₀H₁₀), 39.5 (NCH₃), 9.42 (C₅(CH₃)₅) ppm. ^{11}B NMR (160 MHz, CDCl_3): –7.3, –8.1, –8.7, –10.8, –11.6 ppm. IR (KBr disk): 2580 cm^{–1} ($\nu_{\text{B-H}}$). Anal. Calc. for C₁₇H₃₃N₂S₂B₁₀Rh (540.59): C, 37.77; H, 6.15; N, 5.18. Found: C, 37.59; H, 6.24; N, 5.05%.

Route 2: A mixture of **1** (112 mg, 0.5 mmol) and silver (I) oxide (70 mg, 0.3 mmol) was taken up in 15 mL CH_2Cl_2 and stirred overnight. The resulting gray suspension was filtered through Celite, and the filtrate was added to a solution of Cp* $\text{Rh}[\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]$ (222 mg, 0.5 mmol) in

CH₂Cl₂. The color of the solution changed from dark blue to red immediately. The solution was stirred for 4 h at room temperature and filtered. The resulting solid was washed with diethyl ether, and then dried in vacuo. Yield: 201 mg (74%). ¹H NMR (500 MHz, CDCl₃): 7.09 (d, 2H, H_{im}), 3.85 (s, 6H, CH₃), 1.62 (s, 15H, Cp*) ppm. IR (KBr disk): 2580 cm⁻¹ (ν_{B-H}). Anal. Calc. for C₁₇H₃₃N₂S₂B₁₀Rh (540.59): C, 37.77; H, 6.15; N, 5.18. Found: C, 36.97, H, 6.09; N, 5.39%.

4.4. X-ray crystallography

Suitable crystals of **2** and **4** were grown by slow diffusion from dichloromethane/hexane solution. Single crystals of these two complexes were mounted by gluing onto the end of a thin glass fiber. X-ray intensity data were collected on a CCD-Bruker SMART APEX system. All the determinations of unit cell and intensity data were performed with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). All the data were collected at room temperature and the structures were solved by direct meth-

ods and subsequently refined on F² by using full-matrix least-squares techniques (SHELXL [11]). All atoms except for hydrogen were refined with anisotropic thermal parameters. All the hydrogen atoms were included but not refined. All the calculations were carried out with the SHELXT program. Crystal data, data collection parameters and the results of the analyses of complexes **2** and **4** are listed in Table 1.

5. Supplementary material

CCDC 661508 and 661509 contains 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.

Acknowledgements

Financial support by the National Science Foundation of China (20531020, 20421303 and 20771028), by Shanghai Leading Academic Discipline project (B108), and by Shanghai Science and Technology Committee (05DZ22313 and 06XD14002) is gratefully acknowledged.

Table 1
X-ray crystallographic data and processing parameters for **2** and **4**

	2	4
Empirical formula	C ₁₅ H ₂₃ Cl ₂ N ₂ Rh	C ₁₇ H ₃₃ N ₂ S ₂ B ₁₀ Rh
Formula weight	405.16	540.58
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/c
a (Å)	8.389(3)	11.210(4)
b (Å)	26.640(8)	19.680(6)
c (Å)	15.008(5)	11.910(4)
α (°)	90	90
β (°)	96.450(4)	93.134(5)
γ (°)	90	90
Volume (Å ³)	3333.1(18)	2623.7(15)
Z	8	4
D _{calcd} (Mg/m ³)	1.615	1.369
Absorption coefficient (mm ⁻¹)	1.337	0.820
F(000)	1648	1104
Theta range for data collection (°)	1.53–27.23	2–27.15
Limiting indices	–10, 10, –34, 29, –19, 17	–14, 10, –25, 22, –15, 15
Reflections collected/ unique (R _{int})	16694/7390 (0.0357)	13108/5716 (0.0422)
Completeness to theta (°)	27.23 (99.2%)	27.15 (98.3%)
Maximum and minimum transmission	0.8779, 0.7758	0.9225, 0.8869
Data/restraints/parameters	7390/0/375	5716/0/306
Goodness-of-fit on F ²	1.044	1.040
Final R indices [I > 2σ(I)] ^a	R ₁ = 0.0353, wR ₂ = 0.0883	R ₁ = 0.0587, wR ₂ = 0.1363
R indices (all data)	R ₁ = 0.0456, wR ₂ = 0.0927	R ₁ = 0.0947, wR ₂ = 0.1565
Largest difference peak and hole (e/Å ³)	0.646 and –0.592	1.238 and –0.759

^a R₁ = ∑||F_o| – |F_c|| / ∑|F_o|;
wR₂ = [∑w(|F_o|² – |F_c|²)² / ∑w|F_o|²]^{1/2}.

References

- [1] (a) A.H. Wolfgang, *Angew. Chem., Int. Ed. Engl.* 41 (2002) 1290; (b) E. Peris, R.H. Crabtree, *Coord. Chem. Rev.* 248 (2004) 2239; (c) F.E. Hahn, *Angew. Chem., Int. Ed. Engl.* 45 (2006) 1348; (d) F.E. Hahn, L. Wittenbecher, Duc Le Van, R. Frohlich, *Angew. Chem., Int. Ed. Engl.* 39 (2000) 541; (e) F.E. Hahn, M.C. Jahnke, T. Pape, *Organometallics* 26 (2007) 150; (f) F.E. Hahn, M.C. Jahnke, V. Gomez-Benitez, D. Morales-Morales, T. Pape, *Organometallics* 24 (2005) 6458.
- [2] (a) X. Wang, G.X. Jin, *Organometallics* 23 (2004) 6319; (b) X. Wang, S. Liu, G.X. Jin, *Organometallics* 23 (2004) 6002; (c) X. Wang, S. Liu, L.H. Weng, G.X. Jin, *Organometallics* 25 (2006) 3565.
- [3] (a) A.A. Danopoulos, A.A.D. Tulloch, S. Winston, G. Eastham, M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.* 24 (2003) 1009; (b) D.S. McGuinness, K.J. Cavell, *Organometallics* 19 (2000) 741; (c) S. Grundemann, A. Kovacevic, M. Albrecht, J.W. Faller, R.H. Crabtree, *J. Am. Chem. Soc.* 124 (2002) 10473.
- [4] (a) G.X. Jin, *Coord. Chem. Rev.* 248 (2004) 587; (b) S. Liu, Y.F. Han, G.X. Jin, *Chem. Soc. Rev.* 36 (2007) 1543; (c) Z.W. Xie, *Acc. Chem. Res.* 36 (2003) 1.
- [5] (a) J.Q. Wang, C.X. Ren, G.X. Jin, *Chem. Commun.* (2005) 4738; (b) G.X. Jin, J.Q. Wang, C. Zhang, L.H. Weng, M. Herberhold, *Angew. Chem., Int. Ed.* 44 (2005) 259; (c) S.Y. Cai, X.F. Hou, L.H. Weng, G.X. Jin, *J. Organomet. Chem.* 690 (2005) 910.
- [6] X. Wang, S. Liu, L.H. Weng, G.X. Jin, *Chem. Eur. J.* 13 (2007) 188.
- [7] (a) E. Mas-Marza, E. Peris, I. Castro-Rodriguez, K. Meyer, *Organometallics* 24 (2005) 3158; (b) F.E. Hahn, M.C. Jahnke, T. Pape, *Organometallics* 25 (2006) 5927.
- [8] (a) E. Mas-Marza, J.A. Mata, E. Peris, *Angew. Chem., Int. Ed. Engl.* 46 (2007) 3729; (b) E. Mas-Marza, M. Sanau, E. Peris, *Inorg. Chem.* 44 (2005) 9961.
- [9] (a) J.Q. Wang, C.X. Ren, L.H. Weng, G.X. Jin, *Chem. Commun.* (2006) 162; (b) Q.G. Kong, G.X. Jin, S.Y. Cai, L.H. Weng, *Chin. Sci. Bull.* 48 (2003) 1733;

- (c) S. Liu, X. Wang, G.X. Jin, *J. Organomet. Chem.* 691 (2006) 261.
- [10] (a) C.G. Overberger, J.C. Salamone, S. Yaroslavsky, *J. Org. Chem.* 30 (1965) 3580;
(b) B.L. Benac, E.M. Burgess, A.J. Arduengo, *Org. Synth.* 64 (1986) 92;
- (c) M. Herberhold, G.-X. Jin, H. Yan, W. Milius, B. Wrackmeyer, *J. Organomet. Chem.* 587 (1999) 252;
(d) M. Herberhold, G.-X. Jin, H. Yan, W. Milius, B. Wrackmeyer, *Eur. J. Inorg. Chem.* (1999) 873.
- [11] Sheldrick, SHELXT-97, Universität Göttingen, Germany, 1997.