DOI: 10.1002/ejic.200700816

# Alkylmagnesium Complexes with the Rigid dpp-bian Ligand {dpp-bian = 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene}

# Igor L. Fedushkin,\*<sup>[a]</sup> Alexander G. Morozov,<sup>[a]</sup> Markus Hummert,<sup>[b]</sup> and Herbert Schumann\*<sup>[b]</sup>

Keywords: Magnesium / N ligands / Alkyl complexes / Structure elucidation

The reactions between equimolar amounts of (dpp-bian)Na- $(Et_2O)_x$  (1) {dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene} and MeMgBr, EtMgBr and Me\_3SiCH\_2MgCl in Et\_2O afford the corresponding alkylmagnesium complexes [(dpp-bian)MgMe]\_2 (2), (dpp-bian)MgEt(Et\_2O) (3) and (dppbian)MgCH\_2SiMe\_3(Et\_2O) (4), respectively. Compound 2 and *t*BuOH react with elimination of methane and the formation of [(dpp-bian)MgOtBu]\_2 (5). Compounds 2–5, all of which contain the dpp-bian ligand in its radical monoanionic form, were characterised by elemental analysis, IR spectroscopy, as

### Introduction

Recently, we reported on the successful preparation of monomeric alkylaluminium complexes of the type **A**, **B** and **C**, all of which contain the dpp-bian ligand in its radical monoanionic  $(\mathbf{A})^{[1]}$  or dianionic state (**B** and **C**) (Scheme 1).<sup>[2]</sup> Although these complexes are very sensitive to air and moisture, they are thermally stable and do not decompose in solution over the course of several weeks. In contrast, the magnesium complex (dpp-bian)Mg(*i*Pr)-





1584

- [a] G. A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, Tropinina 49, 603950 Nizhny Novgorod, GSP-445, Russia Fax: +7-831-4627497
  - E-mail: igorfed@iomc.ras.ru
- [b] Institut für Chemie der Technischen Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany Fax: +49-30-3142-2168 E-mail: schumann@chem.tu-berlin.de

© 2008 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

well as by single-crystal X-ray diffraction. Molecular structure determination revealed that the magnesium atoms in 2-5 are four-coordinate. The magnesium atoms of complexes 2and 5 reach the coordination number four by dimerisation through bridging Me and *t*BuO groups, respectively, whereas compounds 3 and 4 reach it by coordination of one molecule of diethyl ether.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2008)

 $(Et_2O)_2$  containing radical monoanionic dpp-bian is truly stable in hexane and  $Et_2O$ , but it decomposes immediately when it is dissolved in THF with reductive elimination of isopropyl radicals (Scheme 2).<sup>[3]</sup>



Scheme 2.

This result demonstrates that reductive elimination processes can be realised even with complexes of main group metals that are not able to change their oxidation state. To make such processes possible, one has to use ligands that are able to change their "oxidation state", as is the case with the dpp-bian ligand. To get a deeper insight into the structural peculiarities and the special solution behaviour of alkylmagnesium complexes coordinated by the dpp-bian radical anion, we investigated magnesium derivatives of the type (dpp-bian)MgR (R = Me, Et, tBu, CH<sub>2</sub>=CMeCH<sub>2</sub> and CH<sub>2</sub>SiMe<sub>3</sub>). The present work demonstrates that complexes with alkyl groups that are less bulky than the isopropyl moiety are stable, whereas *tert*-butyl- and 2-methylallylmagnesium complexes undergo alkyl radical elimination before they can be isolated.



Scheme 3.

#### **Results and Discussion**

# Synthesis of [(dpp-bian)MgMe]<sub>2</sub> (2), (dpp-bian)MgEt(Et<sub>2</sub>O) (3), (dpp-bian)MgCH<sub>2</sub>SiMe<sub>3</sub>(Et<sub>2</sub>O) (4) and [(dpp-bian)-MgOtBu]<sub>2</sub> (5)

Compounds 2–4 were prepared by salt elimination reactions between the in situ generated sodium complex (dppbian)Na(Et<sub>2</sub>O)<sub>x</sub> (1) and the Grignard reagents MeMgBr, EtMgBr and Me<sub>3</sub>SiCH<sub>2</sub>MgCl conducted in diethyl ether (Schemes 3 and 4). The solution of the starting sodium complex 1, as well as those of compounds 2–4, are red, which thus proves the presence of species containing the dpp-bian radical monoanion.





Whereas the methyl derivative 2 is readily soluble in diethyl ether and has to be isolated by crystallisation from toluene, compounds 3 and 4 crystallise after separation of the precipitated sodium halide from the clear and concentrated reaction solutions. Compounds 2–4 are thermally rather stable. They do not decompose, neither in THF at room temperature nor in boiling toluene.

In contrast to the above reactions, the treatment of **1** with *t*BuMgCl or CH<sub>2</sub>=CMeCH<sub>2</sub>MgBr in diethyl ether causes a change in the colour of the solution from red to green, which is thus unambiguously indicative of the formation of dianionic dpp-bian species. As in the case of the reaction of **1** with *i*PrMgCl,<sup>[3]</sup> the magnesium complex (dpp-bian)Mg(Et<sub>2</sub>O)<sub>2</sub> containing the dpp-bian dianion precipitates from the reaction mixture as green crystals.

As to be expected, complexes 2-4 are sensitive towards acidic substances. Thus, treatment of 2 with *tert*-butyl alcohol causes liberation of methane and formation of the corresponding alkoxide 5 in a yield of 65% (Scheme 5).



Scheme 5.

Compounds 2–5 were characterised by elemental analysis, IR spectroscopy and single-crystal X-ray analysis. The paramagnetism of all these compounds caused by the presence of the radical dpp-bian anion prevented NMR spectroscopic investigations.

In contrast to 1–4, complex 5 is an effective catalyst for the ring-opening polymerisation of cyclic esters, especially of *rac*- and L-lactide. When the polymerisation of *rac*-lactide with 5 was carried out in a 200:1 molar ratio in THF at room temperature the conversion of 95% was achieved within several minutes. The gel-permission chromatography has proved the formation of a high molecular weight polymer ( $M_{\rm W} = 7.5 \times 10^4$ , PDI 1.36).

#### Molecular Structures of 2-5

The molecular structures of 2, 3, 4 and 5 were determined by single-crystal X-ray diffraction and are depicted in Figures 1, 2, 3 and 4, respectively. Suitable crystals were obtained from toluene (2, 5) and diethyl ether (3, 4). Selected bond lengths and bond angles of the four compounds are shown in Table 1, and the crystal data collections and structure refinement data of the respective molecules are listed in Table 2.

Complexes 2–5 represent four-coordinate magnesium species with the dpp-bian radical anion acting as a chelating ligand. In the case of complexes 2 and 5, the coordination number 4 of magnesium is reached by formation of dimeric molecules through bridging methyl and *tert*-butoxy groups, respectively, and in the case of the monomeric complexes 3 and 4 by additional coordination of one molecule of diethyl ether. The shortening of the Mg–N distances in complex 2 (av. 2.0584 Å) relative to those in 3 (av. 2.103 Å), 4 (av. 2.096 Å) and 5 (av. 2.109 Å) reflects a strengthening of the metal-to-ligand interactions, which thus compensates for the somewhat higher electron deficiency at the Mg atoms in 2 relative to the situation in 3, 4 and 5. In general, all the



Figure 1. Molecular structure of 2. The hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at 30% probability.



Figure 2. Molecular structure of **3**. The hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at 30% probability.



Figure 3. Molecular structure of 4. The hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at 30% probability.

observed Mg–N bond lengths correspond well with those in other magnesium complexes containing the dpp-bian radical anion.<sup>[4]</sup> The bite angles N(1)–Mg–N(2) of all four molecules lie in the narrow range from 82.3 to 84.8°. As to be expected, the Mg–C(alkyl) bond lengths decrease on going from dimeric **2** (av. 2.284 Å) to the monomeric molecules **3** [2.220(3)/2.1161(4) Å] and **4** [2.124(4) Å], but they



Figure 4. Molecular structure of 5. The hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at 30% probability.

Table 1. Selected bond lengths [Å] and angles [°] for complexes 2-5.

Compound	2	<b>3</b> <sup>[a]</sup>	4	5
Mg(1)–N(1)	2.0550(18)	2.100(3)	2.106(3)	2.133(3)
Mg(1)–N(2)	2.0618(18)	2.107(3)	2.085(3)	2.084(3)
Mg(1)–O(1)		2.055(3)	2.061(3)	1.953(2)
Mg(1)–O(1a)				1.953(2)
Mg(1)-C(37)	2.314(2)	2.220(3)	2.124(4)	
Mg(1)-C(37a)	2.254(3)			
N(1)-C(1)	1.343(3)	1.338(4)	1.333(4)	1.342(4)
N(2)-C(2)	1.337(2)	1.337(5)	1.326(5)	1.339(4)
C(1)-C(2)	1.431(3)	1.445(5)	1.452(5)	1.437(5)
Mg(1)-N(1)-C(1)	107.27(13)	106.7(2)	108.6(2)	104.4(2)
Mg(1)-N(2)-C(2)	107.06(13)	106.3(2)	109.1(2)	105.6(2)
O(1)-Mg(1)-N(1)		114.73(12)	104.77(13)	122.81(12)
O(1)-Mg(1)-N(2)		109.10(12)	107.47(12)	118.25(11)
O(1)-Mg(1)-C(1)		128.33(12)	109.58(12)	123.42(10)
N(1)-Mg(1)-N(2)	84.75(7)	82.33(12)	82.76(13)	83.19(11)
N(1)-Mg(1)-C(37)	113.11(8)	123.44(13)	124.00(14)	
N(2)-Mg(1)-(C37)	118.92(8)	119.77(12)	119.79(15)	

[a] For one of two crystallographically independent molecules.

all fit well in the series of Mg-C(alkyl) distances of the following N-ligand supported magnesium compounds: [CH(8- $C_9H_6NP(iPr_2)=N(tBu)MgEt$  [2.183(14)Å],<sup>[5a]</sup> {CH[C- $(Me)N(2,6-iPr_2C_6H_3)]_{2}MgCH_2Ph(THF) [2.1325(18) Å]_{3}$ [PhTptBu]MgEt [PhTptBu = phenyltris-(3-tert-butylpyrazolyl)borato] [2.163(2) Å]<sup>[5c]</sup> and {2,6-N(R)C<sub>5</sub>H<sub>3</sub>[ArN=C- $(Me)_{2}MgR$  (R = Me, Et, *i*Pr) [2.122(2)–2.157(2) Å].<sup>[5d]</sup> The Mg–O(*t*Bu) bond lengths in **5** [1.963(3) and 1.953(3) Å] are fairly similar as the Mg-O distances in dimeric magnesium ketiminate [{CH[C(Me)NC<sub>6</sub>H<sub>4</sub>-2-OMe]<sub>2</sub>}MgOtBu]<sub>2</sub> [1.944(2) and 1.965(2) Å].<sup>[6]</sup> As in other metal complexes of the dpp-bian radical anion,<sup>[4]</sup> the C(1)-N(1) and C(2)-N(2)bond lengths in 2-5 [1.324(6)-1.343(3) Å] are longer than in free dpp-bian [both 1.282(4) Å]<sup>[7]</sup> and in metal complexes containing neutral dpp-bian ligands, for example, (dppbian)SnCl<sub>4</sub> [1.291(8) and 1.286(8) Å]<sup>[8]</sup> and (dpp-bian)SnCl<sub>2</sub> [1.283(1) and 1.269(1) Å].<sup>[9]</sup>

#### Conclusions

In this study we demonstrated that dpp-bian alkylmagnesium complexes with less bulky alkyl groups such as Me, Et and Me<sub>3</sub>SiCH<sub>2</sub> (**2–4**, respectively), are stable both in solution and in the solid state. However, dpp-bian-supported alkylmagnesium complexes with the bulky *tert*-butyl or 2-methylallyl group are just as unstable as the recently published (dpp-bian)Mg(*i*Pr)(Et<sub>2</sub>O)<sub>2</sub> (**1**)<sup>[3]</sup> and are prone to undergo reductive elimination of the respective alkyl radicals. As we could demonstrate by the reaction of [(dpp-bian)-MgMe]<sub>2</sub> (**2**) with *tert*-butyl alcohol yielding [(dpp-bian)-MgOtBu]<sub>2</sub> (**5**), the reactions of the stable complexes **2–4** with hydrogen acidic substrates may be a suitable method for the synthesis of novel magnesium complexes supported by the radical anionic dpp-bian ligand.

### **Experimental Section**

**General Remarks:** All manipulations were carried out in vacuo or under an atmosphere of nitrogen gas by using Schlenk techniques. The solvents Et<sub>2</sub>O and toluene were distilled from sodium/benzophenone prior to use. Melting points were measured in sealed capillaries. IR spectra were recorded with an FTIR FSM-1201 spectrometer.

(**dpp-bian**)Na(Et<sub>2</sub>O)<sub>x</sub> (1): A suspension of dpp-bian (1.0 g, 2.0 mmol) in Et<sub>2</sub>O (40 mL) was added to sodium metal (0.05 g, 2.14 mmol). Vigorous stirring of the mixture at room temperature for 4 h resulted in the formation of a clear red solution of 1. This solution was used in situ for the syntheses of 2, 3 and 4. Their yields were calculated on the basis of the amount of dpp-bian used in this reaction.

Table 2. Crystal data and structure refinement details for 2-5.



**[(dpp-bian)MgMe]<sub>2</sub> (2):** To the ethereal solution of **1**, prepared as described above, was added a solution of MeMgBr (0.5 M in diethyl ether, 4 mL, 2.0 mmol). After stirring the mixture at room temperature for 1 h, the solvent was removed from the red solution under reduced pressure. Repeated extraction of the remaining solid with hot toluene (ca. 500 mL) afforded **2** as deep-red prismatic crystals (0.79 g, 73%). M.p. >200 °C. IR (nujol):  $\tilde{v} = 1655$  (m), 1630 (w), 1588 (m), 1522 (s), 1461 (s), 1380 (s), 1365 (m), 1319 (m), 1253 (m), 1188 (m), 1103 (w), 1080 (w), 1057 (w), 1042 (w), 934 (w), 865 (m), 815 (s), 799 (s), 769 (s), 757 (vs), 730 (s), 699 (s), 669 (m), 607 (m), 522 (s), 457 (m) cm<sup>-1</sup>. C<sub>74</sub>H<sub>86</sub>Mg<sub>2</sub>N<sub>4</sub> (1080.08): calcd. C 82.29, H 8.03; found C 81.95, H 8.00.

(**dpp-bian**)**MgEt(Et<sub>2</sub>O)** (3): To the ethereal solution of 1, prepared as described above, was added a solution of EtMgBr (1.5 M in diethyl ether, 1.4 mL, 2.0 mmol). After stirring the mixture at room temperature for 1 h, the red solution was filtered off from precipitated NaBr and was then reduced in volume to 15 mL by evaporation of the solvent in vacuo. Crystallisation at room temperature gave 0.68 g (54%) of 3 as deep-red crystals. M.p. >200 °C. IR (nujol):  $\tilde{v} = 1670$  (m), 1627 (w), 1540 (m), 1530 (s), 1458 (s), 1373 (m), 1350 (m), 1310 (m), 1248 (m), 1090 (w), 1076 (w), 920 (w), 853 (w), 807 (s), 764 (s), 750 (vs), 731 (s), 690 (m), 601 (w), 527 (m) cm<sup>-1</sup>. C<sub>42</sub>H<sub>55</sub>MgN<sub>2</sub>O (628.19): calcd. C 80.30, H 8.82; found C 80.07, H 8.69.

(dpp-bian)MgCH<sub>2</sub>SiMe<sub>3</sub>(Et<sub>2</sub>O) (4): Similar to the preparation of 3, the ethereal solution of 1, prepared as described above, was treated with a solution of Me<sub>3</sub>SiCH<sub>2</sub>MgCl (2 M in diethyl ether, 2 mL, 2.0 mmol). From the red solution, reduced in volume to 5 mL by evaporation in vacuo, 4 crystallised at room temperature within a few days as large deep-red prismatic crystals. Yield 1.04 g (76%).

Compound	2	3	4	5
Empirical formula	$C_{74}H_{86}Mg_2N_4$	C42H55MgN2O	C44H61MgN2OSi	C <sub>94</sub> H <sub>114</sub> Mg <sub>2</sub> N <sub>4</sub> O <sub>2</sub>
Formula weight	1080.09	628.19	686.35	1380.51
Crystal system	monoclinic	monoclinic	orthorhombic	triclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_{1}2_{1}2_{1}$	ΡĪ
a [Å]	16.2591(2)	22.4481(6)	12.3084(3)	10.9989(5)
b [Å]	12.4590(1)	17.1710(4)	15.9415(4)	13.6483(7)
c [Å]	16.3895(2)	21.4873(6)	21.3489(5)	14.6897(7)
	_	_	90	99.036(2)
β[°]	93.018(1)	114.406(1)	90	105.320(2)
γ [°]	_	_	90	103.652(2)
Volume [Å <sup>3</sup> ]	3315.45(6)	7542.3(3)	4188.96(18)	2009.28(17)
Ζ	4	8	4	1
$D_{\text{calcd.}} [\text{g cm}^{-3}]$	1.082	1.106	1.088	1.141
Absorption coefficient [mm <sup>-1</sup> ]	0.079	0.080	0.104	0.081
F(000)	1164	2728	1492	746
Crystal size [mm]	$0.78 \times 0.37 \times 0.18$	$0.56 \times 0.52 \times 0.12$	$0.58 \times 0.30 \times 0.02$	$0.35 \times 0.34 \times 0.15$
$\theta$ range for data collection [°]	1.72 to 25.00	1.58 to 25.00	1.59 to 25.00	2.01 to 25.00
Index ranges	$-19 \le h \le 19$	$-26 \le h \le 26$	$-14 \le h \le 12$	$-13 \le h \le 13$
	$-14 \le k \le 14$	$-20 \le k \le 17$	$-17 \le k \le 18$	$-16 \le k \le 10$
	$-16 \le l \le 19$	$-23 \le l \le 25$	$-25 \le l \le 25$	$-17 \le l \le 17$
Reflections collected	19949	45125	25822	12631
Independent reflections	5835 [ $R_{\rm int.} = 0.0657$ ]	$13253 [R_{int.} = 0.0968]$	7354 [ $R_{\rm int.} = 0.1326$ ]	7060 [ $R_{\rm int} = 0.0775$ ]
Max/min transmission	0.9859/0.9408	0.9905/0.9566	0.9938/0.9576	0.9880/0.9722
Data/restraints/parameters	5835/3/378	13253/11/873	7354/0/456	7060/0/512
Goodness-of-fit on $F^2$	1.037	1.056	1.001	0.959
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0535$	$R_1 = 0.0814$	$R_1 = 0.0661$	$R_1 = 0.0673$
	$wR_2 = 0.1359$	$wR_2 = 0.2169$	$wR_2 = 0.1113$	$wR_2 = 0.1435$
R indices (all data)	$R_1 = 0.0820$	$R_1 = 0.1527$	$R_1 = 0.1278$	$R_1 = 0.1606$
	$wR_2 = 0.1520$	$wR_2 = 0.2615$	$wR_2 = 0.1312$	$wR_2 = 0.1810$
Absolute structure parameter	_	_	0.2(2)	_
Largest diff. peak/hole $[e Å^{-3}]$	0.382/-0.424	1.119/-0.410	0.268/-0.337	0.262/-0.328

# FULL PAPER

M.p. 151–153 °C. IR (nujol):  $\tilde{v} = 1680$  (m), 1641 (m), 1595 (s), 1536 (m), 1462 (m), 1368 (m), 1340 (w), 1325 (w), 1270 (s), 1080 (w), 910 (m), 860 (s), 839 (m), 802 (vs), 780 (s), 760 (s), 641 (w), 516 (s), 484 (w) cm<sup>-1</sup>. C<sub>44</sub>H<sub>61</sub>MgN<sub>2</sub>OSi (686.35): calcd. C 77.00, H 8.96; found C 76.75, H 8.81.

**[(dpp-bian)(MgOrBu)]**<sub>2</sub> (5): To a suspension of 2 (0.62 g, 0.57 mmol) in toluene (50 mL), cooled to ca. -70 °C, was added *t*BuOH (0.093 g, 1.13 mmol) by condensation in vacuo. Slow warming of the reaction mixture to ambient temperature was accompanied with liberation of methane and formation of a clear red solution, which was reduced in volume to ca. 15 mL by evaporation in vacuo at 80 °C. Crystallisation at ambient temperature gave 0.51 g (65%) of **5** as deep-red crystals. M.p. >200 °C. IR (nujol):  $\tilde{v} = 1676$  (m), 1658 (w), 1606 (s), 1588 (w), 1575 (m), 1384 (s), 1363 (s), 1313 (s), 1293 (m), 1136 (m), 1057 (s), 856 (s), 692 (s), 666 (s), 632 (m) cm<sup>-1</sup>. C<sub>94</sub>H<sub>114</sub>Mg<sub>2</sub>N<sub>4</sub>O<sub>2</sub> (1380.51): calcd. C 81.78, H 8.32; found C 81.15, H 8.03.

X-ray Crystallographic Study of 2-5: The crystal data and details of the data collections are listed in Table 2. The data were collected by using a SMART CCD diffractometer (graphite-monochromated Mo- $K_{\alpha}$  radiation,  $\omega$ -scan technique,  $\lambda = 0.71073$  Å) at 173 K. The structures were solved by direct methods with the use of SHELXS- $97^{[10]}$  and were refined on  $F^2$  by using all reflections with the SHELXL-97 program.<sup>[11]</sup> SADABS<sup>[12]</sup> was used to perform areadetector scaling and absorption corrections. The absolute structure of the noncentrosymmetric space groups was determined by using SHELXL-97 according to Flack.<sup>[13]</sup> All non-hydrogen atoms were refined anisotropically. All hydrogen atoms except those of the CH<sub>3</sub>Mg groups of compound 2 were placed in calculated positions by using a riding model. The positions of the hydrogen atoms of the  $CH_3Mg$  groups in 2 were deduced from the electron density map. The coordinated diethyl ether molecule in 3 was refined isotropically because of its high disorder. CCDC-654640 (for 2), -654641 (for 3), -654642 (4) and -654643 (for 5) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

## Acknowledgments

This work was supported by the Alexander von Humboldt Foundation (Partnership Project between the IOMC RAS and the Institut für Chemie der Technischen Universität Berlin), the Russian Foundation for Basic Research (Grant No. 07-03-00545), the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft (H. S.).

- a) H. Schumann, M. Hummert, A. N. Lukoyanov, I. L. Fedushkin, *Organometallics* 2005, 24, 3891–3896; b) A. N. Lukoyanov, I. L. Fedushkin, M. Hummert, H. Schumann, *Russ. Chem. Bull.* 2006, 55, 422–428.
- [2] a) A. N. Lukoyanov, I. L. Fedushkin, M. Hummert, H. Schumann, Z. Anorg. Allg. Chem. 2006, 632, 1471–1476; b) H. Schumann, M. Hummert, A. N. Lukoyanov, I. L. Fedushkin, Chem. Eur. J. 2007, 13, 4216–4222.
- [3] I. L. Fedushkin, A. A. Skatova, M. Hummert, H. Schumann, Eur. J. Inorg. Chem. 2005, 1601–1608.
- [4] a) I. L. Fedushkin, A. A. Skatova, V. K. Cherkasov, V. A. Chudakova, S. Dechert, M. Hummert, H. Schumann, *Chem. Eur. J.* 2003, 9, 5778–5783; b) I. L. Fedushkin, A. A. Skatova, A. N. Lukoyanov, V. A. Chudakova, S. Dechert, M. Hummert, H. Schumann, *Russ. Chem. Bull. Int. Ed.* 2004, 53, 2751–2762; c) I. L. Fedushkin, N. M. Khvoinova, A. Yu. Baurin, G. K. Fukin, V. K. Cherkasov, M. P. Bubnov, *Inorg. Chem.* 2004, 43, 7807; d) I. L. Fedushkin, A. A. Skatova, S. Y. Ketkov, O. V. Eremenko, A. V. Piskunov, G. K. Fukin, *Angew. Chem.* 2007, 119, 4380–4383; *Angew. Chem. Int. Ed.* 2007, 46, 4302–4305; e) I. L. Fedushkin, A. N. Lukoyanov, S. Y. Ketkov, M. Hummert, H. Schumann, *Chem. Eur. J.* 2007, 13, 7050–7056.
- [5] a) Z.-X. Wang, C.-Y. Qi, Organometallics 2007, 26, 2243–2251;
  b) P. J. Bailey, R. A. Coxall, C. M. Dick, S. Fabre, L. C. Henderson, C. Herber, S. T. Liddle, D. Loronno-Gonzalez, A. Parkin, S. Parsons, Chem. Eur. J. 2003, 9, 4820–4828; c) J. L. Kisko, T. Fillebeeen, T. Hascall, G. Parkin, J. Organomet. Chem. 2000, 596, 22–26; d) I. J. Blackmore, V. C. Gibson, P. B. Hitchcock, C. W. Rees, D. J. Williams, A. J. P. White, J. Am. Chem. Soc. 2005, 127, 6012–6020.
- [6] M. H. Chisholm, J. C. Gallucci, K. Phomphrai, *Inorg. Chem.* 2005, 44, 8004–8010.
- [7] I. L. Fedushkin, V. A. Chudakova, G. K. Fukin, S. Dechert, M. Hummert, H. Schumann, *Russ. Chem. Bull.* 2004, 53, 2744– 2750.
- [8] N. J. Hill, G. Reeske, J. A. Moore, A. H. Cowley, *Dalton Trans.* 2006, 4838–4844.
- [9] I. L. Fedushkin, N. M. Khvoinova, A. Yu. Baurin, V. A. Chudakova, A. A. Skatova, V. K. Cherkasov, G. K. Fukin, E. V. Baranov, *Russ. Chem. Bull.* 2006, 55, 74–83.
- [10] G. M. Sheldrick, SHELXS-97: Program for the Solution of Crystal Structures, University of Göttingen, 1990.
- [11] G. M. Sheldrick, SHELXL-97: Program for the Refinement of Crystal Structures, University of Göttingen, 1997.
- [12] G. M. Sheldrick, SADABS: Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, 1996.
- [13] a) H. D. Flack, *Acta Crystallogr., Sect. A* 1983, *39*, 876; b) G.
   Bernardinelli, H. D. Flack, *Acta Crystallogr., Sect. A* 1985, *41*, 500.

Received: August 2, 2007 Published Online: February 18, 2008