Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2010, **20**, 174–176
Mendeleev Communications

Ligand-displacement reactions as a powerful route to *closo*-ruthenacarboranes incorporating bidentate N-donor ligands

Dmitrii I. D'yachikhin, Fedor M. Dolgushin, Ivan A. Godovikov and Igor T. Chizhevsky*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 5085; e-mail: chizbor@ineos.ac.ru

DOI: 10.1016/j.mencom.2010.05.018

A facile ligand-exchange method based on the direct reaction of either three-bridge *exo-nido* complex [*exo*-5,6,10-{Cl(Ph_3P)$_2$Ru}-5,6,10-(μ-H)$_3$-10-H-*nido*-7,8-$C_2B_9H_8$] or its *closo* isomer [3,3-(PPh_3)$_2$-3-Cl-3-H-3,1,2-*closo*-$RuC_2B_9H_{11}$] with chelating N,N-donor ligands was employed to synthesize the *N*,*N*-diamine-*closo*-ruthenacarborane complexes [3,3-{κ^2-4,4′-R_2-2,2′-(C_5H_3N)$_2$}-3-PPh_3-*closo*-3,1,2-$RuC_2B_9H_{11}$] (R = H, Bu^t) and [3,3-{κ^2-phen}-3-PPh_3-*closo*-3,1,2-$RuC_2B_9H_{11}$].

Previously, we have shown that *exo-nido*-ruthenacarborane [*exo*-5,6,10-{Cl(Ph_3P)$_2$Ru}-5,6,10-μ-(H)$_3$-10-H-*nido*-7,8-$C_2B_9H_8$] **1** and its C,C′-dimethylated derivative,[1] as well as the *closo* isomer of **1**, [3,3-(PPh_3)$_2$-3-Cl-3-H-*closo*-3,1,2-$RuC_2B_9H_{12}$] **2**,[2,3] can serve as convenient precursors for the investigation of PPh_3-diphosphine displacement reactions. In particular, using this synthetic methodology, *closo* and *exo-nido* 18-electron diamagnetic and 17-electron paramagnetic *P*,*P*-diphosphine-ruthenacarborane complexes have been conveniently prepared,[3–6] some of which are efficient pre-catalysts for the atom-transfer radical polymerization (ATRP) of vinyl monomers.[3,7–9] Other known *exo-nido*-[10] and *closo*-ruthenacarboranes,[11,12] which have *exo*-polyhedrally heteroatom-substituted {*nido*-C_2B_9}-carborane ligands, have been extensively explored as active promotors for Kharasch chemistry. Herein, we describe the facile synthesis of *closo*-ruthenacarborane clusters with chelating N,N-donor ligands, such as 2,2′-bipyridyl derivatives and 1,10-phenanthroline (phen), where both species **1** and **2** were starting materials.

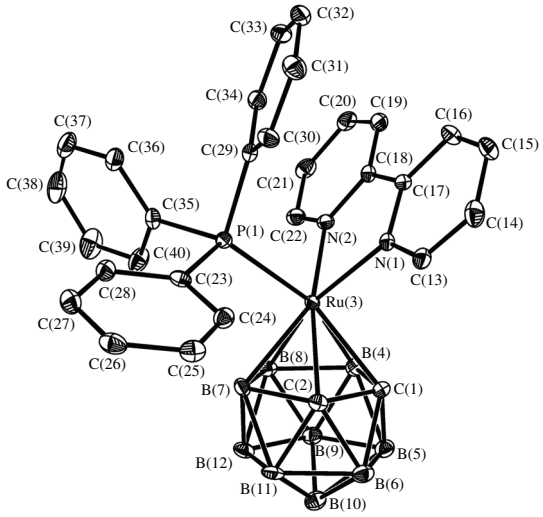
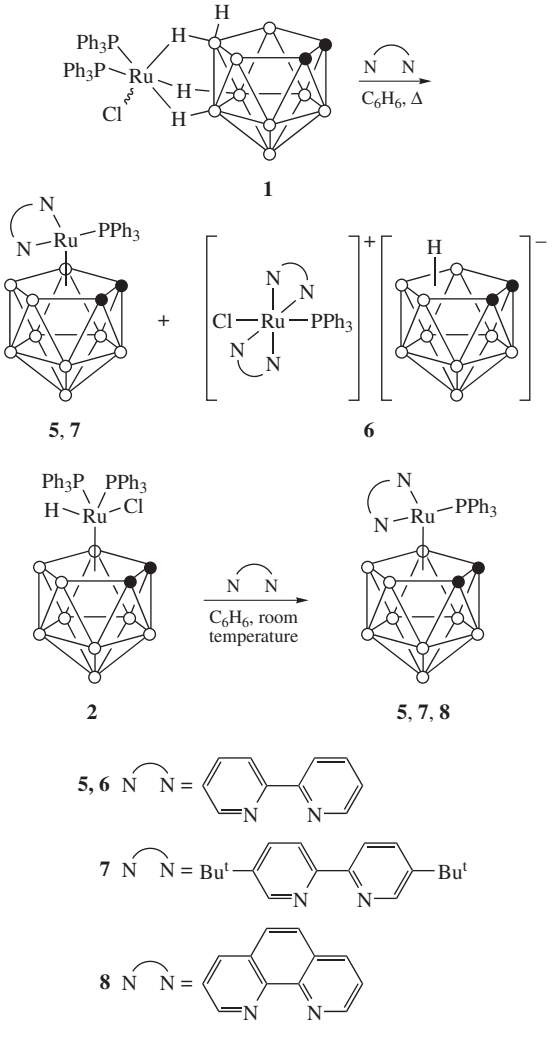


Figure 1 ORTEP representation of the molecular structure of complex **5** with thermal ellipsoids at a 50% probability level. Selected interatomic distances (Å) and angles (°): Ru(3)–P(1) 2.3400(7), Ru(3)–N(1) 2.1147(19), Ru(3)–N(2) 2.0865(19), Ru(3)–C(1) 2.200(2), Ru(3)–C(2) 2.181(2), Ru(3)–B(4) 2.252(3), Ru(3)–B(7) 2.178(3), Ru(3)–B(8) 2.266(3), C(1)–C(2) 1.625(3), C(1)–B(4) 1.696(3), C(2)–B(7) 1.741(4), B(4)–B(8) 1.803(4), B(7)–B(8) 1.794(4); N(1)–C(17)–C(18) 114.4(2), N(2)–C(18)–C(17) 114.4(2), N(2)–Ru(3)–N(1) 76.00(7).

The Ru^{II} complexes with electron-rich diamine-type ligands are of particular interest because of their potential physical and photophysical properties.[13] However, only a few complexes, which have both large-cage polyhedral borane or carborane and chelating diamine ligands, were described in the literature.[14–19] Jelliss and co-workers[19] reported the preparation of carbonyl-bearing *closo*-ruthenacarboranes with TMEDA, as well as



Scheme 1

4,4′-R_2-2,2′-bipyridyl derivatives [R = H (**3**), Bu^t (**4**), and *n*-nonyl] by double carbonyl substitution of [3,3,3-$(CO)_3$-*closo*-3,1,2-$RuC_2B_9H_{11}$] in the presence of Me_3NO as the CO-abstracting reagent. Looking for more simple and reliable synthetic routes to *N*,*N*-diamine-*closo*-ruthenacarborane clusters, we initially examined the reactions of isomeric complexes **1** or **2** with 2,2′-bipyridyl ligand **3**. Thus, the treatment of precursors **1** and **2** with a 20% molar excess of **3**, either on heating in benzene for 2 h (in the case of **1**) or by stirring their benzene solution at ambient temperature for 60 h (in the case of **2**), followed by column chromatography resulted in the isolation of complex [3,3-{κ^2-2,2′-$(C_5H_4N)_2$}-3-(PPh_3)-*closo*-3,1,2-$RuC_2B_9H_{11}$] **5** in 35 and 88% yields, respectively (Scheme 1). Note that target product **5** in the reaction of *exo-nido*-ruthenacarborane **1** with **3** is formed together with an amount of new ionic complex [$RuCl(PPh_3)${κ^2-2,2′-$(C_5H_4N)_2$}$_2$][*nido*-$C_2B_9H_{11}$] **6**, which exists in *cis* and *trans* isomeric forms. This fact together with some decomposition of products that occurs could be accounted for the moderate yield of *closo* compound **5** in this reaction. The structures of both complexes **5** and *trans*-**6** have been deduced on the basis of single-crystal X-ray diffraction data[†] (Figures 1 and 2, respectively) and confirmed by multinuclear NMR spectroscopy.[‡]

A single-crystal X-ray diffraction study of complex **5**[†] proved this species to be a mononuclear *closo*-ruthenacarborane with an 18-electron six-coordinate Ru^{II} atom, which adopts the piano stool structure (Figure 1). The ruthenium atom in **5** is bound to one PPh_3 group and ligated by one 2,2′-bipyridyl ligand in a chelating manner [Ru(3)–N(1) 2.115(2), Ru(3)–N(2) 2.087(2) Å]. Despite the almost symmetrical coordination of the ruthenium atom by the {*nido*-C_2B_9} ligand [C(1)–C(2) 1.625(3), Ru(3)–C_{cb} 2.19 (av.) and Ru(3)–B 2.23 (av.) Å], one of the Ru–B distances formally *trans*-oriented with respect to the strong diamine donor, namely Ru(3)–B(7) of 2.178(3) Å, proved to be noticeably shorter than the other two within the C_2B_3 open face [Ru(3)–B(4) 2.252(3) and Ru(3)–B(8) 2.266(3) Å]. The bidentate 2,2′-bipyridyl ligand in **5** remains essentially planar with the N(1)–C(14)–C(15)–N(2) torsion angle of 2.4(3)°.

Similarly, complex **2** readily reacted with substituted bipyridyl ligand **4** and 1,10-phenanthroline hydrate in benzene to afford two new more sterically demanded *N*,*N*-diamine-*closo*-ruthenacarboranes [3,3-{κ^2-4,4′-Bu$^t_2$-2,2′-$(C_5H_3N)_2$}-3-PPh_3-*closo*-3,1,2-$RuC_2B_9H_{11}$] **7** and [3,3-{κ^2-phen}-3-PPh_3-*closo*-3,1,2-$RuC_2B_9H_{11}$] **8** in 72 and 88% yields, respectively. It is noteworthy that all of the reactions with the use of *closo*-ruthenacarborane **2** as the starting reagent afford compounds **5**, **7** and **8** as the only carborane-containing products formed in high yields. Complexes **5**, **7** and **8** were isolated as air-stable crystalline solids. Analytical and NMR-spectroscopic data[‡] are entirely consistent with the

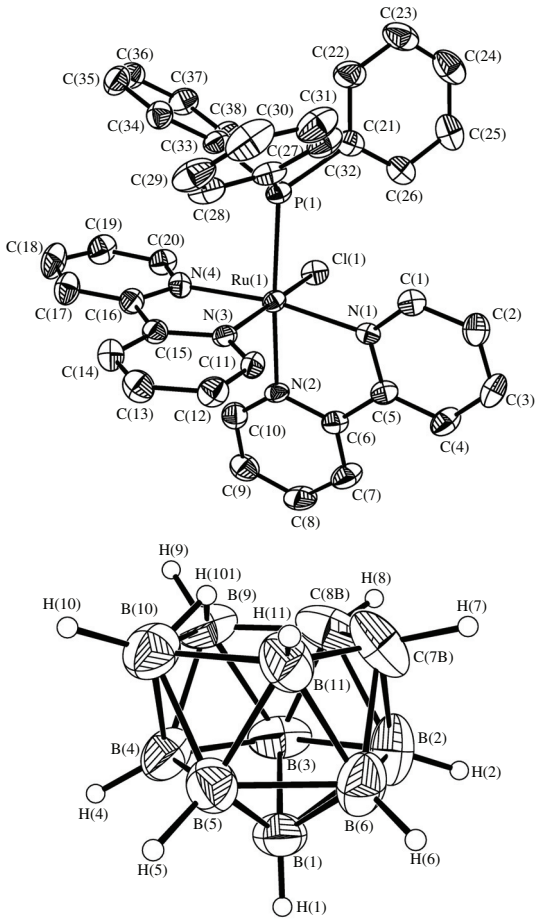


Figure 2 ORTEP representation of the molecular structure of complex **6** with thermal ellipsoids at a 50% probability level. Selected interatomic distances (Å) and angles (°): Ru(1)–Cl(1) 2.4272(9), Ru(1)–P(1) 2.3254(9), Ru(1)–N(1) 2.111(3), Ru(1)–N(2) 2.110(3), Ru(1)–N(3) 2.052(3), Ru(1)–N(4) 2.070(3), C(7B)–C(8B) 1.553(7), C(7B)–B(11) 1.580(8), C(8B)–B(9) 1.587(8), B(9)–B(10) 1.831(9), B(9)–H(101) 1.33, B(10)–H(101) 1.02; P(1)–Ru(1)–N(2) 174.30(8), Cl(1)–Ru(1)–N(3) 171.17(8), N(1)–Ru(1)–N(4) 170.6(1).

[†] *Crystal data for* **5**: $C_{30}H_{34}B_9N_2Ru{\cdot}C_3H_6O$, M = 710.00, monoclinic, space group $P2_1/n$, a = 11.0321(9), b = 19.768(2) and c = 15.841(1) Å, β = 96.566(2)°, V = 3432.0(5) Å^3, d_{calc} = 1.374 g cm^{-3}, Z = 4, MoKα radiation, λ = 0.71073 Å, μ = 0.534 mm^{-1}, T = 100(2) K, $2\theta_{max}$ = 60°, $R_1(F)$ = 0.0416 for 7475 reflections with $I > 2\sigma(I)$, and $wR_2(F^2)$ = 0.0909 for all 9993 unique reflections (R_{int} = 0.0655).

Crystal data for **6**: $C_{38}H_{31}ClN_4PRu{\cdot}C_2B_9H_{12}{\cdot}1.5(C_6H_6)$, M = 961.73, monoclinic, space group $P2_1/n$, a = 11.9780(5), b = 13.5873(6) and c = 28.926(1) Å, β = 93.435(1)°, V = 4699.2(4) Å^3, d_{calc} = 1.359 g cm^{-3}, Z = 4, MoKα radiation, λ = 0.71073 Å, μ = 0.465 mm^{-1}, T = 120(2) K, $2\theta_{max}$ = 56°, $R_1(F)$ = 0.0642 for 8511 reflections with $I > 2\sigma(I)$, and $wR_2(F^2)$ = 0.1559 for all 11303 unique reflections (R_{int} = 0.0435).

The SHELXTL program package[20] was used for the calculations.

CCDC 756382 and 756383 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2010.

[‡] For **5**: ^{1}H NMR (CD_2Cl_2) δ: 2.43 (s, 2H, CH_{carb}), 6.95 (t, 6H, PPh_3, J_t 8.6 Hz), 7.21 (t, 6H, PPh_3, J_t 7.2 Hz), 7.31 (m, 5H, PPh_3 + H$^{5,5'}$), 7.73 (t, 2H, H$^{4,4'}$, ^3J 7.6 Hz), 7.81 (d, 2H, H$^{3,3'}$, ^3J 8.3 Hz), 9.52 (d, 2H, H$^{6,6'}$, ^3J 6.4 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2) δ: 36.2 (s). ^{11}B NMR (CD_2Cl_2) δ: –27.4 (br. s, 2B), –9.95 (d, 2B, $J_{B,H}$ 132 Hz), –4.3 (br. s, 3B), 6.65 (br. s, 2B). IR (ν/cm^{-1}): 2523 (B–H). Found (%): C, 54.75; H, 5.16. Calc. for $C_{30}H_{34}B_9N_2PRu$ (%): C, 55.30; H, 5.22.

For *trans*-**6**: ^{1}H NMR (CD_2Cl_2) δ: –2.9 (br. s, 1H, H_{endo}), 1.84 (br. s, 2H, CH_{carb}), 6.94, 7.16, 7.69, 7.80 (t, 4×1H, H_{bpy}, J_t 6.7–8.0 Hz), 7.91, 7.94, 8.72, 8.91 (d, 4×1H, H_{bpy}, J_d 5.7–8.3 Hz), 7.0–7.5 (m, 23H, PPh_3 + H_{bpy}). ^{31}P{^{1}H} NMR (CD_2Cl_2) δ: 56.1 (s). ^{11}B NMR (CD_2Cl_2) δ: –37.1 (d, 1B, $J_{B,H}$ 149 Hz), –33.3 (d, 1B, $J_{B,H}$ 133 Hz), –22.1 (d, 2B, $J_{B,H}$ 153 Hz), –17.0 (d, 3B, $J_{B,H}$ 107 Hz), –11.1 (d, 2B, $J_{B,H}$ 136 Hz).

For *cis*-**6**: ^{1}H NMR (CD_2Cl_2) δ: –2.9 (br. s, 1H, H_{endo}), 1.80 (br. s, 2H, CH_{carb}), 6.77, 7.08, 7.23, 7.24, 7.70, 8.03 (t, 6×1H, H_{bpy}, J_t 6.7–7.8 Hz), 7.17 (m, 5H, PPh_3 + H_{bpy}), 7.34 (m, 12H, PPh_3), 7.91 (m, 2H, H_{bpy}), 8.12, 8.19, 8.27, 8.33, 9.16, 9.29 (d, 6×1H, H_{bpy}, J_d 5.4–8.3 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2) δ: 42.32 (s). ^{11}B NMR (CD_2Cl_2) δ: –37.1 (d, 1B, $J_{B,H}$ 149 Hz), –33.3 (d, 1B, $J_{B,H}$ 133 Hz), –22.1 (d, 2B, $J_{B,H}$ 153 Hz), –17.0 (d, 3B, $J_{B,H}$ 107 Hz), –11.1 (d, 2B, $J_{B,H}$ 136 Hz).

For **7**: ^{1}H NMR (CD_2Cl_2) δ: 1.36 (s, 18H, Bu^t), 2.70 (s, 2H, CH_{carb}), 7.12 (m, 12H, PPh_3), 7.28 (m, 5H, PPh_3 + H$^{5,5'}$), 7.59 (d-like, 2H, H$^{3,3'}$, ^3J 2.0 Hz), 9.10 (d, 2H, H$^{6,6'}$, ^3J 6.0 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2) δ: 44.84 (s). IR (ν/cm^{-1}): 2529 (B–H). Found (%): C, 60.18; H, 6.50; B, 13.06. Calc. for $C_{40}H_{50}B_9N_2PRu$ (%): C, 59.61; H, 6.80; B, 12.68.

For **8**: ^{1}H NMR (CD_2Cl_2) δ: 2.89 (s, 2H, CH_{carb}), 6.99 (m, 12H, PPh_3), 7.14 (t-like, 3H, PPh_3, ^3J 7.0 Hz), 7.62 (q-like, 2H, H^{3,8}), 7.71 (s, 2H, H^{5,6}), 8.15 (d, 2H, ^3J 5.4 Hz), 9.50 (d, 2H, ^3J 8.1 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2) δ: 44.97 (s). ^{11}B NMR (CD_2Cl_2) δ: –24.5 (d, 3H, $J_{B,H}$ 143 Hz), –11.92 (d, 2B, $J_{B,H}$ 145 Hz), –6 (br. t, 3H, $J_{B,H}$ 130 Hz), –2.7 (d, 1H, $J_{B,H}$ 126 Hz). IR (ν/cm^{-1}): 2512 (B–H). Found (%): C, 57.44; H, 5.85. Calc. for $C_{32}H_{34}B_9N_2PRu$ (%) C, 56.89; H, 5.04.

formulations of all three compounds. The ^{1}H NMR spectra of neutral *closo* complexes **5**, **7** and **8** are diagnostic in that they do not display a broad high-field resonance at *ca.* –2.5 ppm originating from the B–H–B *endo*-hydrogen of the {*nido*-C_2B_9} open face, as opposed to the spectrum of ionic complex **6**.‡ The ^{1}H NMR spectra of all the above *closo*-ruthenacarboranes show single-cluster CH resonances, as well as diamine, and PPh_3 ligand aromatic resonances with their overal integration corresponding to the *N*,*N*-diamine/PPh_3/carborane ligand ratio of 1:1:1. The ^{31}P{^{1}H} NMR spectra of **5**, **7** and **8** display a sharp singlet at δ 36.2, 44.84 and 44.97 ppm, respectively, that confirms the presence of the ruthenium-bound PPh_3 ligand.

This study was supported by the Russian Foundation for Basic Research (grant nos. 09-03-00211 and 07-03-00631) and, in part, by the Programme of Basic Research of the Division of Chemistry and Materials Science of the Russian Academy of Sciences.

References

1 I. T. Chizhevsky, I. A. Lobanova, V. I. Bregadze, P. V. Petrovskii, V. A. Antonovich, A. V. Polyakov, A. I. Yanovsky and Yu. T. Struchkov, *Mendeleev Commun*., 1991, 47.
2 E. H. S. Wong and M. F. Hawthorne, *Inorg. Chem*., 1978, **17**, 2863.
3 D. N. Cheredilin, F. M. Dolgushin, I. D. Grishin, E. V. Kolyakina, A. S. Nikiforov, S. P. Solodovnikov, M. M. Il'in, V. A. Davankov, I. T. Chizhevsky and D. F. Grishin, *Izv. Akad. Nauk, Ser. Khim*., 2006, 1120 (*Russ. Chem. Bull., Int. Ed*., 2006, **55**, 1163).
4 D. N. Cheredilin, R. Kadyrov, F. M. Dolgushin, E. V. Balagurova, I. A. Godovikov, S. P. Solodovnikov and I. T. Chizhevsky, *Inorg. Chem. Commun*., 2005, **8**, 614.
5 D. N. Cheredilin, E. V. Balagurova, I. A. Godovikov, S. P. Solodovnikov and I. T. Chizhevsky, *Izv. Akad. Nauk, Ser. Khim*., 2005, 2455 (*Russ. Chem. Bull., Int. Ed*., 2005, **54**, 2535).
6 D. N. Cheredilin, F. M. Dolgushin, A. A. Korlyukov, S. P. Godovikov, R. Kadyrov, E. V. Balagurova, S. P. Solodovnikov and I. T. Chizhevsky, *J. Organomet. Chem*., 2006, **691**, 3989.
7 E. V. Kolyakina, I. D. Grishin, D. N. Cheredilin, F. M. Dolgushin, I. T. Chizhevsky and D. F. Grishin, *Izv. Akad. Nauk, Ser. Khim*., 2006, 85 (*Russ. Chem. Bull., Int. Ed*., 2006, **55**, 89).
8 I. D. Grishin, E. V. Kolyakina, D. N. Cheredilin, I. T. Chizhevsky and D. F. Grishin, *Vysokomol. Soedin., Ser. A*, 2007, **49**, 1766 (*Polymer Sci., Ser. A*, 2007, **49**, 1079).
9 I. D. Grishin, I. T. Chizhevsky and D. F. Grishin, *Dokl. Akad. Nauk*, 2008, **423**, 340 [*Dokl. Chem*. (*Engl. Transl*.), 2008, **423**, 290].
10 F. Simal, S. Sebille, A. Demonceau, A. F. Noels, R. Núñez, M. Abad, F. Teixidor and C. Viñas, *Tetrahedron Lett*., 2000, **41**, 5347.
11 O. Tutusaus, C. Viñas, R. Núñez, F. Teixidor, A. Demonceau, S. Delfosse, A. F. Noels, I. Mata and E. Molins, *J. Am. Chem. Soc*., 2003, **125**, 11830.
12 O. Tutusaus, S. Delfosse, F. Simal, A. Demonceau, A. F. Noels, R. Núñez, C. Viñas and F. Teixidor, *Inorg. Chem. Commun*., 2002, **5**, 941.
13 V. Balzani and A. Juris, *Coord. Chem. Rev*., 2001, **211**, 97.
14 Y. Nie, C.-H. Hu, J.-M. Dou, H.-J. Yao, J. Sun, R.-S. Jin and P.-J. Zheng, *Acta Crystallogr., Sect. C*, 1998, **54**, 1813.
15 Á. Álvarez, R. Macías, M. J. Fabra, M. L. Martin, F. J. Lahoz and L. A. Oro, *Inorg. Chem*., 2007, **46**, 6811.
16 A. A. Erdman, Z. P. Zubreichuk, V. P. Prokopovich, A. V. Polyakov, A. I. Yanovsky, Yu. T. Struchkov, N. A. Maier and Yu. A. Ol'dekop, *Koord. Khim*., 1989, **15**, 122 (in Russian).
17 H. M. Colquhoun, T. J. Greenhough and M. G. H. Wallbridge, *J. Chem. Soc., Dalton Trans*., 1985, 761.
18 J.-S. Park, D.-H. Kim, S.-J. Kim, J. Ko, S. H. Kim, S. Cho, C.-H. Lee and S. O. Kang, *Organometallics*, 2001, **20**, 4483.
19 P. A. Jelliss, J. Mason, J. M. Nazzoli, J. H. Orlando, A. Vinson, N. P. Rath and M. J. Shaw, *Inorg. Chem*., 2006, **45**, 370.
20 *SHELXTL v.5.10, Structure Determination Software Suite*, Bruker AXS, Madison, Wisconsin, USA, 1998.

Received: 30th December 2009; Com. 09/3445