2086 Russian Chemical Bulletin, International Edition, Vol. 53, No. 9, pp. 2086—2089, September, 2004

Letters to the Editor

Synthesis of cationic ruthenium diphosphine complexes with *nido*-dicarbaundecaborate anions. Molecular structure of $[RuCl(dppe)_2]^+[7,8\text{-}nido\text{-}C_2B_9H_{12}]^-$

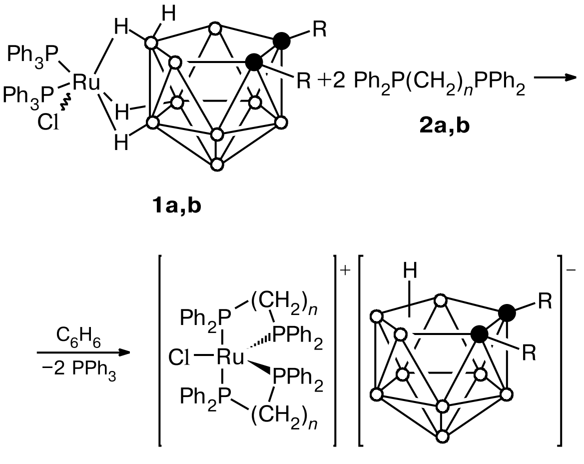
D. N. Cheredilin, F. M. Dolgushin, E. V. Balagurova, I. A. Godovikov, and I. T. Chizhevsky★

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: chizbor@ineos.ac.ru

In metallacarborane chemistry, 16- and/or 18-electron cationic complexes of the general formula $[M(L,L')_n]^+[7\text{-}R'\text{-}8\text{-}R''\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]^-$ (M = Rh; R′ and R″ = H, Alk, Ar, PhS, PPh_2; L and L′ = $P(Alk)_3$, PPh_3, $P(Alk)Ph_2$, *etc.*, n = 3 or 4; M = Ir, R′, R″ = H; L = η^4-COD, L′ = $(PAr_3)_2$, n = 0) have been represented earlier only by rhodium[1,2] and iridium[3] compounds. The only salt of this type with the complex *nido*-carborane anion, $[Rh(PPh_3)_3]^+[7\text{-}\{(1'\text{-}(closo\text{-}1',2'\text{-}C_2B_{10}H_{11})\}\text{-}7,8\text{-}nido\text{-}C_2B_9H_{11}]^-$, was structurally characterized[4] by X-ray diffraction. The aim of the present study was to synthesize new cationic ruthenium(II) diphosphine complexes with the *nido*-dicarbaundecaborate anions.

When studying the replacement of PPh_3 ligands in triply bridged *exo-nido*-ruthenacarboranes, *exo-nido*-5,6,10-$[RuCl(PPh_3)_2]$-5,6,10-μ-$(H)_3$-10-H-7,8-R_2-7,8-$C_2B_9H_6$ (**1:** R = H (**a**); R = Me (**b**)),[5] with the chelating diphosphine ligands $Ph_2P(CH_2)_nPPh_2$ (n = 2 (**2a**, dppe); 3 (**2b**, dppp)), we found that the reaction in benzene at 22 °C afforded predominantly the cationic complexes $[RuCl(Ph_2P(CH_2)_nPPh_2)_2]^+[7,8\text{-}R_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]^-$ (**3a**: R = H, n = 2; **3b**: R = H, n = 3; **3c**: R = Me, n = 3), in which the *nido*-dicarbaundecaborate anions serve as counterions.

Scheme 1



1a,b

2a,b

3a—c

Interestingly, in the course of the reactions of complexes **1a,b** with **2b** in a ratio of 1 : 1 not only **3b,c** but also intermediate diphosphine-substituted *exo-nido* complexes as mixtures of symmetrical (S) and asymmetrical (AS) isomers, *viz.*, *exo-nido*-5,6,10-[Cl(dppp)Ru]-5,6,10-μ-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 2000—2003, September, 2004.

Table 1. Elemental analysis data and yields of complexes **3a—c** and **4a,b**

Compound	Yield (%)	Found / Calculated (%)			Molecular formula
		C	H	B	
3a	95	60.86	5.67	9.12	$C_{54}H_{60}P_4B_9ClRu$
		60.81	5.63	9.13	
3b	78	58.24	5.55	8.50	$C_{56}H_{64}P_4B_9ClRu$
		58.03	5.60	8.25	$\cdot CH_2Cl_2$
3c	71	58.61	5.80	10.36	$C_{58}H_{68}P_4B_9ClRu$
		58.67	5.80	10.27	$\cdot CH_2Cl_2$
4a	58	50.86	5.17	14.21	$C_{29}H_{38}P_2B_9ClRu$
		51.05	5.57	14.27	
4b	59	50.06	5.52	8.50	$C_{32}H_{44}P_2B_9ClRu$
		50.92	5.79	8.34	$\cdot 1/2CH_2Cl_2$

$(H)_3$-10-H-7,8-R_2-7,8-$C_2B_9H_6$ (R = H (**4a**) or Me (**4b**)), were isolated by silica gel column chromatography. In a separate experiment, we demonstrated that the reaction of equimolar amounts of **4a** or **4b** with **2b** (C_6H_6, 22 °C) afforded complexes **3b** or **3c**, respectively, in 100% yields.

The compositions and structures of complexes **3a—c** and **4a,b** were confirmed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy and elemental analysis data (Tables 1 and 2). The structure of solvate complex **3a**$\cdot CH_2Cl_2$ was established by X-ray diffraction. According to the results of X-ray diffraction analysis, the coordination polyhedron of the ruthenium atom in the $[RuCl(dppe)_2]^+$ cation (Fig. 1) is a distorted trigonal bipyramid. Both bidentate ligands dppe occupy the axial and equatorial positions, and the chlorine atom is located in the equatorial plane. The distances from the ruthenium atoms to the axial P(1) and P(3) atoms are 2.398(1) and 2.391(1) Å, respectively, the P(1)—Ru(1)—P(3) angle is 175.85(5)°, the distances to the equatorial P(2) and P(4) atoms are 2.240(1) and 2.243(1) Å, respectively, and the Ru(1)—Cl(1) distance is 2.391(1) Å. Thus, the orientation of the ligands at the metal atom in the cationic fragment of complex **3a** is virtually identical to that observed earlier[6] in the known analog $[RuCl(dppe)_2]^+[PF_6]^-$. In both compounds, the main distortion of the trigonal-

Table 2. ^1H, $^{31}P\{^1H\}$, and ^{11}B NMR spectra of complexes **3a—c** and **4a,b**

Compound	Solvent (23 °C)	NMR (δ)		
		^1H	$^{31}P\{^1H\}$ ($J_{P,P}$/Hz)	^{11}B ($J_{B,H}$/Hz)
3a	$CDCl_3$	7.82—6.65 (m, 40 H, Ph); 2.66, 2.42, 1.60 (all br.s, 2 H + 4 H + 2 H, PCH_2CH_2P); 1.94 (br.s, 2 H, $C_{carb}H$); –2.71 (br.s, 1 H, H_{extra})	83.8, 56.4 (both t, 2 P + 2 P, *J* = 12)	–11.2 (d, 2 B, *J* = 135); –16.8, –17.5 (d+d, 2 B + 1 B, *J* = 132, *J* = 164); –21.9 (d, 2 B, *J* = 148); –33.0 (dd, 1 B, *J* = 174, $J_{B,H\ extra}$ = 90); –37.8 (d, 1 B, *J* = 138)
3b	$CDCl_3$	7.88—6.82 (m, 40 H, Ph); 5.31 (CH_2Cl_2); 2.77, 2.61, 1.91, 1.64 (all br.s, 2 H + 2 H + 2 H + 2 H, PCH_2); 2.25 (br.s, 4 H, CH_2); 1.91 (br.s, 2 H, $C_{carb}H$); –2.67 (br.s, 1 H, H_{extra})	44.3, –3.5 (both t, 2 P + 2 P, *J* = 31)	–11.1 (d, 2 B, *J* = 135); –16.8, –17.5 (d+d, 2 B + 1 B, *J* = 132, *J* = 164); –21.9 (d, 2 B, *J* = 148); –33.0 (dd, 1 B, *J* = 174, $J_{B\text{-}H\ extra}$ = 90); –37.7 (d, 1 B, *J* = 138)
3c	CD_2Cl_2	7.90—6.93 (m, 40 H, Ph); 5.31 (CH_2Cl_2); 2.68, 1.62 (both br.m, 4 H + 4 H, PCH_2); 2.27 (br.m, 4 H, CH_2); 1.36 (s, 6 H, Me); –2.57 (br.s, 1 H, H_{extra})	42.0, –2.9 (both t, 2 P + 2 P, *J* = 31)	–11.6 (br.d, 3 B, *J* = 131); –20.7 (d, 4 B, *J* = 140); –37.1 (dd, 1 B, *J* = 171, $J_{B,H\ extra}$ = 77); –39.2 (d, 1 B, *J* = 135)
4a*	$CDCl_3$	7.70—7.10 (m, Ph, S★+As★*); 3.46, 3.27, 2.61, 2.34, 1.60 (all br.m, $PCH_2CH_2CH_2P$, S★+As★); 2.27 (s, $C_{carb}H$, S★+As★); –1.32 (m, H_{extra}, S★+As★); –2.94, –5.20 (m+m, As★); –3.53 (m, S★); –15.88 (m, As★); –17.20 (m, S★)	51.6, 46.8 (both d, *J* = 50, As★); 49.0 (s, S★)	—
4b*	CD_2Cl_2	7.70—7.20 (m, Ph, S★+As★); 5.31 (CH_2Cl_2); 3.39, 3.22, 2.57, 2.46, 2.36, 1.74 (all br.m, $Ph_2PCH_2CH_2CH_2PPh_2$, S★+As★); 1.52, 1.46 (both s, Me, S★+As★); –1.16 (m, H_{extra}, S★+As★); –2.92, –5.30 (m+m, As★); –3.61 (m, S★); –15.92 (m, As★); –17.25 (m, S★)	51.6, 46.8 (both d, *J* = 50, As★); 49.0 (s, S★)	

* S★+As★ is a 2.5 : 1 mixture of symmetrical (S★) and asymmetrical (As★) isomers. The relative intensities of the signals of the S and As isomers are not given.

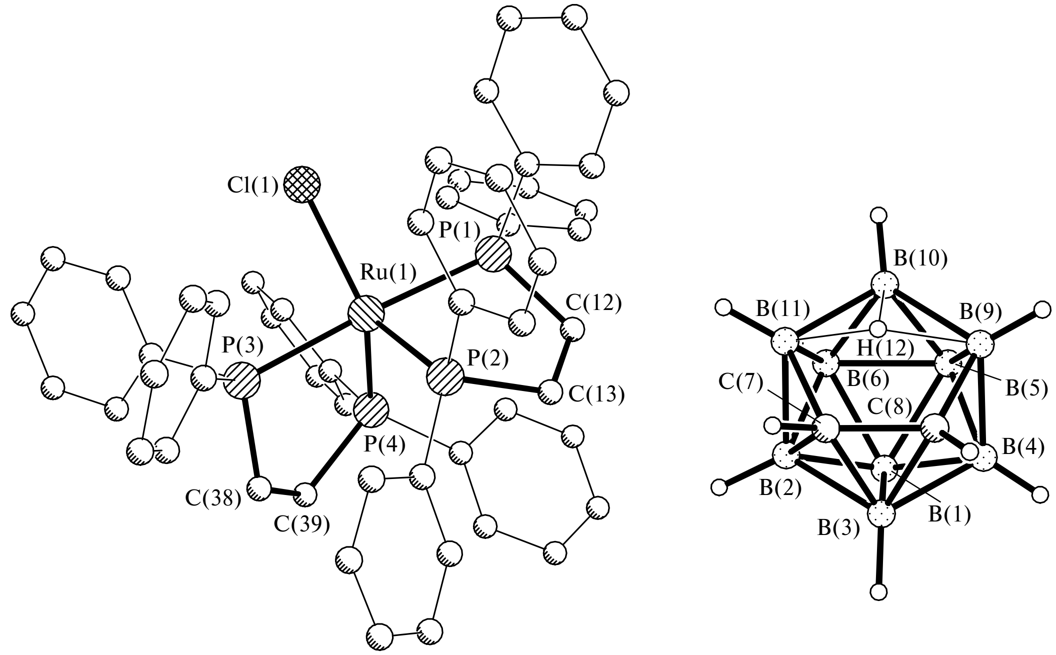


Fig. 1. Molecular structure of complex **3a**.

bipyramidal geometry is associated with the deviation of the angles in the equatorial plane from ideal values for a trigonal structure. In complex **3a**, P(2)—Ru(1)—P(4) is 96.69(5)°, P(2)—Ru(1)—Cl(1) is 133.41(5)°, and P(4)—Ru(1)—Cl(1) is 129.87(5)°. It should be noted that there are no specific interactions between the cations and anions in the crystal structure of **3a**.

In conclusion, it should be noted that three exo-polyhedral B—H...M bonds in *exo-nido*-metallacarboranes substantially stabilize this type of complexes.[7,8] This is why there is a sharp difference in the properties of triply and doubly bridged *exo-nido*-metallacarboranes. For example, the known reaction of the doubly bridged complex [*exo-nido*-$(PPh_3)_2Rh(7,8\text{-}\mu\text{-}(CH_2)_3\text{-}7,8\text{-}C_2B_9H_{10})$] with diphosphine **2a** (reagent ratio was 1 : 2)[1] afforded the $[Rh(dppe)_2]^+$[*nido*-$7,8\text{-}\mu\text{-}(CH_2)_3\text{-}7,8\text{-}C_2B_9H_{10}]^-$ salt along with [*closo*-$3,3\text{-}(dppe)\text{-}3\text{-}H\text{-}1,2\text{-}\mu\text{-}(CH_2)_3\text{-}3,1,2\text{-}RhC_2B_9H_9$] instead of the expected *exo-nido* complex structurally similar to complexes **4a,b**.

The reactions were carried out under argon using anhydrous solvents, which were prepared according to standard procedures. The reaction products were isolated by column chromatography in air. Chromatography was carried out on silica gel (Merck, 230—400 mesh). Phosphines were purchased from Strem Chemicals. The NMR spectra were recorded on a Bruker AMX-400 spectrometer (400.13 MHz for ^1H, 161.98 MHz for ^{31}P, 128.3 MHz for ^{11}B). Elemental analysis was carried out at the Laboratory of Microanalysis of the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences (Moscow).

Synthesis of complexes 3a—c (general procedure). ***A.*** A solution of chlorobis(triphenylphosphine)-*exo-nido*-[10-hydroorthocarborane-5,6,10-tris(hydrido)]ruthenium, *exo-nido*-5,6,10-$[RuCl(PPh_3)_2]\text{-}5,6,10\text{-}\mu\text{-}(H)_3\text{-}10\text{-}H\text{-}7,8\text{-}C_2B_9H_8$ (**1a**), (0.1 g, 0.13 mmol) in benzene (5 mL) was added to a solution of bis(diphenylphosphino)ethane (**2a**) (0.1 g, 0.25 mmol) in benzene (10—15 mL). The reaction mixture was stirred at 22 °C for 2—3 h until a dark-red precipitate formed. The precipitate was filtered off, washed with benzene (12—15 mL), and recrystallized from a CH_2Cl_2—hexane mixture to prepare analytically pure bis(1,2-diphenylphosphinoethane)chlororuthenium(II) *nido*-7,8-dicarbaundecaborate, $[RuCl(Ph_2P(CH_2)_2PPh_2)_2]^+$[7,8-*nido*-$C_2B_9H_{12}]^-$ (**3a**). Bis(1,3-diphenylphosphinopropane)chlororuthenium(II) *nido*-7,8-dicarbaundecaborate, $[RuCl(Ph_2P(CH_2)_3PPh_2)_2]^+$[7,8-*nido*-$C_2B_9H_{12}]^-$ (**3b**), and bis(1,3-diphenylphosphinopropane)chlororuthenium(II) *nido*-7,8-dimethyl-7,8-dicarbaundecaborate, $[RuCl(Ph_2P(CH_2)_3PPh_2)_2]^+[7,8\text{-}(CH_3)_2\text{-}7,8$-*nido*-$C_2B_9H_{10}]^-$ (**3c**), were synthesized according to an analogous procedure by the reacions of complex **1a** or chlorobis(triphenylphosphine)-*exo-nido*-[7,8-dimethyl-10-hydroorthocarborane-5,6,10-tris(hydrido)]ruthenium, *exo-nido*-5,6,10-$[RuCl(PPh_3)_2]$-$5,6,10\text{-}\mu\text{-}(H)_3\text{-}10\text{-}H\text{-}7,8\text{-}(CH_3)_2\text{-}7,8\text{-}C_2B_9H_6$ (**1b**), respectively, with bis(1,3-diphenylphosphino)propane (**2b**). The yields of products **3a—c**, elemental analysis data, and NMR spectra are given in Tables 1 and 2, respectively.

B. Benzene (10 mL) was added to a mixture of diphosphine **2b** (0.012 g, 0.029 mmol) and chlorobis(1,3-diphenylphosphinopropane)-*exo-nido*-[10-hydroorthocarborane-5,6,10-tris(hydrido)]ruthenium, *exo-nido*-5,6,10-[Cl(dppp)Ru]-$5,6,10\text{-}\mu\text{-}(H)_3\text{-}10\text{-}H\text{-}7,8\text{-}C_2B_9H_8$ (**4a**), (0.02 g, 0.029 mmol). The reaction mixture was stirred at 22 °C for 2—3 h until a precipitate formed. The precipitate was filtered off, washed with benzene (5 mL), and recrystallized from a CH_2Cl_2—hexane mixture to give complex **3b**. Complex **3c** was synthesized analogously starting from **2b** and chlorobis(1,3-diphenylphosphinopropane)-*exo-nido*-[7,8-dimethyl-10-hydroorthocarborane-5,6,10-tris(hydrido)]ruthenium, *exo-nido*-5,6,10-[Cl(dppp)Ru]-5,6,10-μ-$(H)_3$-10-H-7,8-$(CH_3)_2$-7,8-$C_2B_9H_6$ (**4b**).

X-ray diffraction study of complex 3a·CH_2Cl_2 was performed on a Bruker SMART 1000 CCD diffractometer, space group $P2_1/c$, at 120 K a = 12.7488(7) Å, b = 24.411(1) Å, c = 18.450(1) Å, β = 106.285(1)°, R_1 = 0.0613 for 5966 reflections with $I > 2\sigma(I)$).

Synthesis of complexes 4a,b (general procedure). Solid compound **1a** (0.1 g, 0.13 mmol) was added to a solution of diphosphine **2b** (0.05 g, 0.13 mmol) in benzene (15 mL). The reaction mixture was stirred at 22 °C until precipitation of salt **3b** started. The solution was concentrated *in vacuo*. The residue was chromatographed on a silica gel column, complex **4a** being eluted with a 1 : 1 CH_2Cl_2—hexane mixture. Rrecrystallization from the same solvent mixture afforded analytically pure complex **4a**. The residue of salt **3b** was eluted from a column using CH_2Cl_2, the solvent was evaporated, and salt **3b** was obtained in a yield of 0.03 g (38% with respect to **4a**). A mixture of complexes **4b** and **3c** was prepared from compounds **2b** and **1b** according to an analogous procedure.

This study was financially supported by the Russian Foundation for Basic Research (Project No. 03-03-32651) and the Foundation of the President of the Russian Federation (Federal Program for the Support of Leading Scientific Schools, Grant NSh-1060.2003.3).

References

1. J. A. Long, T. B. Marder, P. E. Behnken, and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1984, **106**, 2979.
2. C. Viñas, M. A. Flores, R. Núñez, F. Teixidor, R. Kivekäs, and R. Sillanpää, *Organometallics*, 1998, **17**, 2278.
3. J. A. Doi, R. G. Teller, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 1980, 80.
4. C. B. Knobler, T. B. Marder, E. A. Mizusawa, R. G. Teller, J. A. Long, P. E. Behnken, and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1984, **106**, 2990.
5. 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.
6. B. Chin, A. J. Lough, R. H. Morris, C. T. Schweitzer, and C. D´Agostino, *Inorg. Chem.*, 1994, **33**, 6278.
7. G. D. Kolomnikova, P. V. Petrovskii, P. V. Sorokin, F. M. Dolgushin, A. I. Yanovsky, and I. T. Chizhevskii, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 677 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 706 (Engl. Transl.)].
8. I. T. Chizhevskii, Dr. Sc. (Chem.) Thesis, A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences, Moscow, 1999 (in Russian).

Received June 25, 2004;
in revised form July 26, 2004