Simple and efficient synthesis of *closo*-rhoda- and *closo*-iridacarboranes with π-ligands based on cyclic dienes

T. V. Zinevich, A. V. Safronov, E. V. Vorontsov, P. V. Petrovskii, and I. T. Chizhevsky★

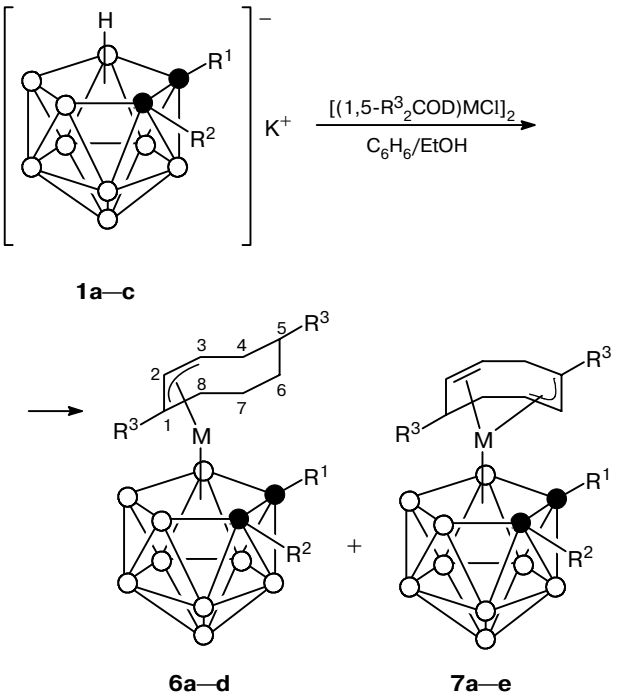
A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow, Russian Federation. Fax: (095) 135 5085. E-mail: chizbor@ineos.ac.ru

Closo- and *exo-nido*-rhodacarboranes with cyclic π-hydrocarbon ligands based on dienes, for example, of the η^3-allyl or $\eta^{3,2}$-allylalkene type, exhibit high catalytic activity in homogeneous catalysis.[1,2] Data on *closo*-iridacarboranes containing η-enyl/dienyl ligands are lacking in the literature. Known procedures for the preparation of rhodium *closo*-complexes of this type,[3,4] which contain no heteroatomic susbtitutents in the carborane fragments, generally involve many steps and often require isolation and purification of intermediates at each stage, which sometimes leads to a noticeable decrease in the yields of the target products. In this connection, the development of a simple, efficient, and versatile procedure for the synthesis of these compounds assumes great importance.

The procedure proposed in the present study allows one to substantially simplify the synthesis of *closo*-rhodacarboranes containing $\eta^{1,2}$-cycloalkene, η^3-cycloallyl, or $\eta^{3,2}$-cycloallylalkene ligands and to prepare these compounds in high or moderate yields by one-step reactions with the use of available reagents. It also opens up the way to the synthesis of structurally similar *closo*-iridacarborane complexes. This method is based on the reactions of K salts of *nido*-dicarbaundecaborates $[nido\text{-}7\text{-}R^1\text{-}8\text{-}R^2\text{—}C_2B_9H_{10}]^-$ (**1**, R^1 and R^2 = H, Alk, or ArAlk) with the $[(\eta^4\text{-diene})RhCl]_2$ dimers under specific conditions, which have been used previously for the preparation of the known *exo-nido*-bis(phosphine)rhodacarboranes.[5]

The reactions of compounds **1a**—**d** (see Scheme 1; R^1 = Me, R^2 = Ph for **1d**)) or $[nido\text{-}7,9\text{-}C_2B_9H_{12}]^-K^+$ (**2**) with the dimers $[(\eta^4\text{-diene})RhCl]_2$ (diene is dicyclopentadiene (DCPD), 2-(hydroxymethyl)norbornadiene (HMNBD), 2-(2-hydroxyprop-2-yl)norbornadiene (HPNBD), cycloocta-1,5-diene (COD), or 1,5-dimethylcycloocta-1,5-diene (DMCOD)) or $[(\eta^4\text{-COD})IrCl]_2$ in the C_6H_6—EtOH mixture (4 : 1) (0.5—12 h) afforded *closo*-3,3,3-$(\eta^{1,2}\text{-}C_{10}H_{13})$-1-$R^1$-2-$R^2$-3,1,2-$RhC_2B_9H_9$ (**3a**,**b**, R^1 = R^2 = H (**a**) or Me (**b**)); *closo*-3,3-$(\eta^{3,2}\text{-}C_7H_7\text{-}2\text{-}CR^3_2)$-1-$R^1$-2-$R^2$-3,1,2-$RhC_2B_9H_9$ (**4a**—**d**, R^1 = R^2 = R^3 = H (**a**); R^1 = R^2 =Me, R^3 = H (**b**); R^1 = R^2 = R^3 =Me (**c**); R^1 = Me, R^2 = Ph, R^3 = H (**d**)) or *closo*-2,2-$(\eta^{3,2}\text{-}C_7H_7\text{-}2\text{-}CH_2)$-2,1,7-$RhC_2B_9H_{11}$ (**5**); or *closo*-3-$(\eta^3\text{-}1,5\text{-}R^3_2\text{—}C_8H_{11})$-1-$R^1$-2-$R^2$-3,1,2-$MC_2B_9H_9$ (**6a**—**d**) and *closo*-3,3-$(\eta^{3,2}\text{-}1,5\text{-}R^3_2\text{—}C_8H_9)$-1-$R^1$-2-$R^2$-3,1,2-$RhC_2B_9H_9$ (**7a**—**d**) (see Table 1). Under these conditions, η^3-allylic complexes **6a**—**c** were obtained along with less common complexes **7a**—**c** (see, for example, **7a** [6]). In all cases, the mixtures obtained were readily separated into individual compounds by column chromatography on silica gel. The reactions of salts **1b** or **1c** with $[(\eta^4\text{-COD})RhCl]_2$ in the presence of COD proceeded selectively to form either exclusively compound **7a** (the yield was 67%) or a mixture of complexes **6c** and **7c** in a ratio of ~1 : 6, respectively. In addition, the reaction of **6d** with $[(\eta^4\text{-COD})IrCl]_2$ in the presence of COD afforded $\eta^{3,2}$-allylalkene complex

Scheme 1



1a: R^1 = R^2 = H
1b: R^1 = R^2 = Me
1c: R^1, R^2 = *o*-$(CH_2)_2C_6H_4$

6a, 7a: M = Rh; R^1 = R^2 = Me, R^3 = H
6b, 7b: M = Rh; R^1, R^2 = *o*-$(CH_2)_2C_6H_4$, R_3 = H
6c, 7c: M = Rh; R^1 = R^2 = R^3 = Me
6d: M = Ir; R^1 = R^2 = Me, R^3 = H
7d: M = Rh; R^1 = R^2 = R^3 = H
7e: M = Ir; R^1 = R^2 = Me, R^3 = H

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Table 1. Reagents and the yields of the products in the reactions of salts **1a**—**d** and **2** with $[(\eta^4\text{-diene})MCl]_2$

Starting salt	$[(\eta^4\text{-diene})MCl]_2$		τ/h[a]	Product	Yield (%)
	L	M			
1a	DCPD	Rh	0.5	**3a**[8]	79
	HMNBD	Rh	1.0	**4a**[9]	89
	COD	Rh	12.0	**7d**	44
1b	DCPD	Rh	2.5	**3b**[8]	90
	HMNBD	Rh	2.0	**4b**[9]	75
	HPNBD	Rh	4.0	**4c**[10]	71
	COD	Rh	12.0	**6a**[3,7]	35
				7a[6]	24
		Ir	0.25	**6d**	84
			0.5	**7e**	40
	DMCOD	Rh	1.0	**6c**	81
				7c	5
1c	COD	Rh	3.0	**6b**	29
				7b	31
1d	HMNBD	Rh	5.0	**4d**	34 [b]
2	HMNBD	Rh	4.0	**5**	43

[a] τ is the reaction time.
[b] A 1 : 1 mixture of diastereomers.

7e in 40% yield. It should be noted that protonation of [*closo*-3,3-(η⁴-COD)-1,2-Me_2-3,1,2-$RhC_2B_9H_9$]PPN with TFA[3] or the reaction of **1b** with $[(\eta^4\text{-COD})RhCl]_2$ in CH_2Cl_2[7] performed previously afforded exclusively η³-cycloallylic complex **6a**.

Complexes **3a**,**b** and **6b**,**c** are feachered by the presence of the agostic C—H...Rh interaction. In complexes **6c** and **6b**, these interactions involve respectively one or two competing aliphatic CH_2 groups of the η³-cyclooctenyl ligand, which are located in the α positions with respect to the allylic fragment. Correspondingly, the signals for the hydrogen atoms involved in the C—H...Rh bond are observed in the ^1H NMR spectra of compounds **6c** and **6b** as multiplets at δ_H 0.08 and −0.24 with the intensities of one and two protons, respectively (Table 2). The 2D EXSY ^1H-^1H NMR spectrum (22 °C) of complex **6b**, which was fluctional in solution, revealed evidences of the exchange between the terminal and central protons of the allylic group, between the terminal protons of the allylic group and the adjacent aliphatic *exo*-protons, and between the *endo*-protons involved in the C—H...Rh bond and the aliphatic *endo*-protons at positions 5 or 7 of the ligand. All these data are indicative of the 1,2-migration of the allylic fragment in complex **6b** with respect to the carbon sceleton of the ligand.

The compositions and the structures of the new *closo*-rhodacarborane complexes were confirmed by the data from elemental analysis and the ^1H, $^{13}C\{^1H\}$, and $^{11}B/^{11}B\{^1H\}$ NMR spectra (see Table 2) (the assign-

Table 2. Data of elemental analysis and the ^1H NMR spectra ($CDCl_3$, 400.13 MHz) of complexes **4d**, **6b**—**d**, and **7b**—**e**

Compound	Found / Calculated (%)			Molecular formula	δ (*J*/Hz)[a]
	C	H	B		
4d	47.31 47.43	6.03 6.04	—	$C_{17}H_{26}B_9Rh$	Mixture of A and B diastereomers: 7.63—7.13 (two d + m, 10 H, Ph_A, Ph_B, J = 8.1); 5.36 (s, 1 H, $H_A^{syn}(8)$); 5.21 (s, 1 H, $H_B^{syn}(8)$); 4.97 (m, 1 H, $H_A(5)$); 4.75 (m, 1 H, $H_B(5)$); 4.27 (m, 1 H, $H_B(3)$); 4.12 (m, 1 H, $H_A(3)$); 4.02 (s, 1 H, $H_A^{anti}(8)$); 4.09 (s, 1 H, $H_B^{anti}(8)$); 3.68 (m, 2 H, $H_A(4)$, $H_B(4)$); 3.62 (m, 2 H, $H_A(6)$, $H_B(6)$); 3.40 (m, 1 H, $H_A(1)$); 3.33 (m, 1 H, $H_B(1)$); 2.46 (s, 3 H, Me—B); 2.07 (s, 3 H, Me—A); 1.81 (dm, 1 H, $H_B(7\alpha)$ or $H_B(7\beta)$), J_{AB} = 10.2); 1.79 (m, 2 H, $H_A(7\alpha)$, $H_A(7\beta)$); 1.68 (dt, 1 H, $H_B(7\beta)$ or $H_B(7\alpha)$), J_{AB} = 10.2, J_t = 1.6)
6b	48.52 48.41	6.80 6.72	—	$C_{18}H_{30}B_9Rh$	7.15 (m, 2 H, *m*-C_6H_4); 6.98 (m, 2 H, *o*-C_6H_4); 5.86 (q*, 2 H, H(1), H(3), $J \approx 8.4$); 4.43 (t, 1 H, H(2), J = 7.6); 3.87 (d, 2 H, $C\underline{H}_AH_BC_6H_4$, J_{AB} = 16.8); 3.78 (d, 2 H, $CH_A\underline{H}_BC_6H_4$, J_{AB} = 16.8); 2.03 (m, 2 H, $H_{exo}(4)$, $H_{exo}(8)$); 1.53 (m, 3 H, $H_{exo}(5)$, $H_{exo}(6)$, $H_{exo}(7)$); 1.24 (m, 2 H, $H_{endo}(5)$, $H_{endo}(7)$); 1.08 (m, 1 H, $H_{endo}(6)$); −0.24 (m, 2 H, $H_{endo/agost}(4)$, $H_{endo/agost}(8)$)
6c	41.98 41.99	7.99 7.99	24.39 24.29	$C_{14}H_{32}B_9Rh$	5.18 (q*, 1 H, H(3), $J_{H(3),H(4)} = J_{H(3),H(2)} \approx 8.9$); 4.62 (d, 1 H, H(2), J = 8.0); 2.48 (ddd, 1 H, $H_{exo}(4)$, J_{AB} = 15.0, $J_{H(4exo),H(3)}$ = 8.9, $J_{H(4exo),H(5)}$ = 2.4); 2.26, 2.18, 2.15 (all s, 3 H each, C(1)—Me, 2 Me_{carb}); 2.16 (m, 1 H, $H_{exo}(8)$); 2.06 (m, 1 H, $H_{endo}(4)$); 1.90 (m, 2 H, H(5), H(7)); 1.77 (m, 1 H, H(7)); 1.45 (m, 2 H, H(6)); 1.03 (d, 3 H, C(5)—Me, J_{gem} = 6.8); 0.08 (m, 1 H, $H_{endo/agost}(8)$)
6d [b,c]	31.03 31.20	6.25 6.06	20.97 21.06	$C_{12}H_{28}B_9Ir$	5.31 (m, 1 H, H(2)); 5.20 (q*, 2 H, H(1), H(3), $J \approx 8.4$); 2.34 (m, 2 H, $H_{exo}(4)$, $H_{exo}(8)$); 2.24 (s, 6 H, Me); 1.72 (m, 5 H, H(5), $H_{exo}(6)$, H(7)); 1.26 (br.d, 1 H, $H_{endo}(6)$, J_{gem} = 12.0); 0.82 (m, 2 H, $H_{endo/agost(?)}(4)$, $H_{endo/agost(?)}(8)$)[d]

(*to be continued*)

Table 2 (*continued*)

Compound	Found / Calculated (%)			Molecular formula	δ (*J*/Hz)[a]
	C	H	B		
7b [e]	48.31 48.63	6.30 6.30	—	$C_{18}H_{28}B_9Rh$	7.27 (m, 2 H, *m*-C_6H_4); 7.12 (d, 1 H, *o*-C_6H_4, J = 6.8); 7.03 (d, 1 H, *o*-C_6H_4, J = 6.8); 5.85 (q*, 1 H, H(1), $J \approx$ 8.0); 5.65 (t*, 1 H, H(6), $J \approx$ 7.6); 4.16 (t, 1 H, H(2), J = 7.6); 3.83, 3.70, 3.60, 3.22 (all d, 1 H each, $C\underline{H}_2C_6H_4$, J_{AB} = 18.0); 3.32 (q*, 1 H, H(3), $J \approx$ 7.6); 2.73 (m, 3 H, H(5), H(7)); 2.50, 2.30 (both m, 1 H each, H(4)); 2.18, 1.77 (both m, 1 H each, H(8))
7c [c]	42.96 42.20	7.89 7.53	—	$C_{14}H_{30}B_9Rh$	5.54 (q*, 1 H, H(1), $J \approx$ 7.2); 5.41 (t*, 1 H, H(6), $J \approx$ 6.9); 4.32 (d, 1 H, H(2), J = 8.1); 3.69 (q*, 1 H, H(5), $J \approx$ 8.1); 3.47 (m, 1 H, H(4)); 3.22 (m, 1 H, H(7)); 2.86 (dd, 1 H, H(4), J_{AB} = 14.3, $J_{H(4),H(5)} = J_{H(4),H(3)}$ = 8.6); 2.42, 1.80 (both m, 1 H each, H(8)); 2.22, 2.00 (both s, 3 H each, Me_{carb}); 1.90 (s, 3 H, C(3)—Me); 1.03 (d, 3 H, C(7)—Me, J_{gem} = 6.9)
7d [e]	34.93 35.08	6.57 6.43	28.48 28.41	$C_{10}H_{22}B_9Rh$	6.02 (q*, 1 H, H(1), $J \approx$ 8.0); 5.37 (t*, 1 H, H(6), $J \approx$ 7.2); 4.64 (q*, 1 H, H(3), $J \approx$ 7.6); 4.49 (t, 1 H, H(2), J = 7.6); 3.74 (q*, 1 H, H(5), $J \approx$ 8.4); 3.49, 3.04 (both br.s, 1 H each, H_{carb}); 3.24 (m, 1 H, H(4)); 2.54 (dd, 1 H, H(4), J_{AB} = 16.6, $J_{H(4),H(5)} = J_{H(4),H(3)}$ = 7.2); 2.45, 2.11 (both m, 1 H each, H(8))
7e	—	—	—	—	5.57 (q*, 1 H, H(3), $J \approx$ 7.6); 4.96 (t*, 1 H, H(6), $J \approx$ 6.7); 4.15 (t, 1 H, H(2), J = 7.3); 3.85 (q*, 1 H, H(1), $J \approx$ 6.6); 3.65 (m, 1 H, H(8)); 3.38 (m, 2 H, H(7), H(8)); 2.82 (dd, 1H, H(5), J_{AB} = 14.9, ^2J = 7.2); 2.67 (m, 1H, H(5)); 2.54 (s, 3 H, Me); 2.48 (q*, 1 H, H(4)); 1.95 (c, 3 H, Me); 1.80 (m, 1 H, H(4))

[a] Quadruplet-like (q*) and triplet-like (t*) multiplet signals.
[b] The ^{1}H NMR spectrum was recorded at −93 °C.
[c] The ^{1}H NMR spectrum was measured in CD_2Cl_2.
[d] The participation of the H atom in the formation of the C—H...Ir bond was not unambiguously confirmed.
[e] The assignment of the signals was made by comparing with the ^{1}H NMR spectra of compounds **7a**,[6] **7c**, and **7e**.

ment of the signals in the ^{1}H and ^{13}C NMR spectra was made using the correlation ^{1}H-^{1}H and ^{13}C{^{1}H}-^{1}H NMR spectra).

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