Trimethylammonium-containing rhodacarborane $[(9\text{-}NMe_3\text{-}7,8\text{-}C_2B_9H_{10})RhCl_2]_2$ as a catalyst for the annulation of arylcarboxylic acids with alkynes

A. P. Molotkov,[a] S. V. Timofeev,[a] and D. A. Loginov[a,b]★

[a]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow, Russian Federation. Fax: +7 (495) 135 5085. E-mail: dloginov@ineos.ac.ru*
[b]*Plekhanov Russian University of Economics, 36 Stremyanny per., 117997 Moscow, Russian Federation*

Rhodacarborane $[(9\text{-}NMe_3\text{-}7,8\text{-}C_2B_9H_{10})RhCl_2]_2$ exhibited moderate catalytic activity in the reaction of annulation of arylcarboxylic acids with alkynes, giving naphthalenes as the major products. Effects of the substituent at the carborane ligand, as well as the nature of organic substrates, on the catalytic activity and selectivity of the reaction were estimated. In particular, it was revealed that a replacement of the NMe_3 group at the carborane ligand with the SMe_2 one leads to a significantly decreased activity of the catalyst.

Key words: homogeneous catalysis, metallacarboranes, oxidative coupling, rhodium.

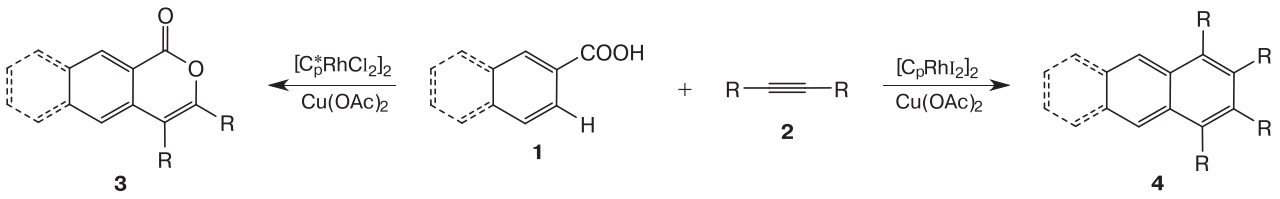
Annulation reactions of arylcarboxylic acids **1** with alkynes **2** in the presence of cyclopentadienyl complexes of rhodium are an efficient method for the synthesis of isocoumarins and polyaromatic hydrocarbons,[1—6] which are widely employed in medicine and photoelectronics.[7—12] We have recently demonstrated[10] that the reaction exhibits a unique chemoselectivity depending on the presence of methyl substituents in the cyclopentadienyl ligand (Scheme 1). For instance, in the case of complex bearing the pentamethylcyclopentadienyl ligand $[Cp^*RhCl_2]_2$, isocoumarins **3** were selectively formed upon the annulation with one molecule of an alkyne, while the reactions catalyzed by the methyl-free derivative $[CpRhI_2]_n$ were concerted with a decarboxylation and subsequent inclusion of two alkyne molecules to give corresponding naphthalenes **4**.

Rhoda- and iridacarboranes can also catalyze this important organic reaction.[13—16] The other examples of successful use of metallacarboranes in homogeneous catalysis include the reactions of radical polymerization of methyl methacrylate,[17,18] hydrogenation, isomerization, and metathesis of olefins,[19—21] as well as the cycloaddition of cyclopentadiene to activated alkenes.[22] Herein, we revealed that in contrast to cyclopentadienyl complexes, substituents in carborane ligands affect only on the catalytic activity of metallacarboranes in the annulation of aryl carboxylic acids with alkynes, but cause no effect on its selectivity.

Results and Discussion

Contrary to unsubstituted dicarbollide dianion $[7,8\text{-}C_2B_9H_{11}]^{2-}$, charge-compensated carborane ligands $[L\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (L = SMe_2, NMe_3, pyridine, *etc.*) are not only isolobal to the cyclopentadienide anion, but also possess the same charge, which provides the similarity of transition metal complexes based on them.[23—27] In particular, it was previously demonstrated that a simple replacement of Cp^- with a charge-compensated carborane

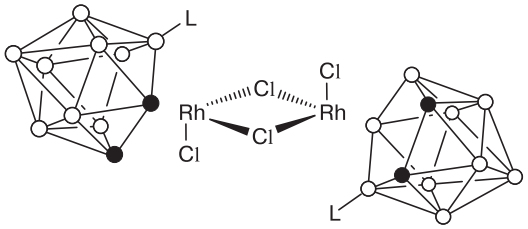
Scheme 1



Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 1922—1926, October, 2021.

anions in the synthesis of metallocenes leads to the formation of corresponding bis(carborane) sandwich complexes.[28,29] A similar approach was reported[30–32] for the synthesis of rhodacarborane halide complexes $[(9\text{-L-}7,8\text{-}C_2B_9H_{10})RhX_2]_2$ (X = Cl, Br, and I) that are structural analogs of catalysts for the CH activation of cyclopentadienyl derivatives $[(C_5R_5)RhX_2]_2$.

To estimate the catalytic activity of rhodacarborane halide complexes in the annulation of aryl carboxylic acids with alkynes, we selected complexes **5** and **6** containing either SMe_2 or NMe_3 group at the boron atom of carborane ligand.



5, 6

L = SMe_2 (**5**), NMe_3 (**6**)

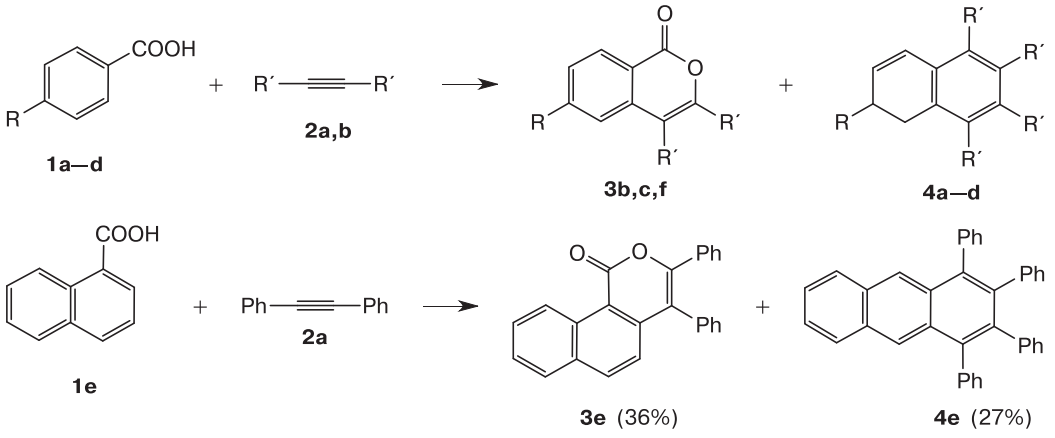
The coupling of benzoic acid with diphenylacetylene in boiling *o*-xylene in the presence of copper(II) acetate was selected as the model reaction. The copper salt is an oxidizing agent that is necessary for the regeneration of rhodium catalyst (see Ref. 4 for details). It emerged that dimethylsulfonium complex **5** (at the loading of 1 mol.%) catalyzes this reaction to give 1,2,3,4-tetraphenylnaphthalene (**4a**) as the only product in the yield of 30% (Scheme 2; Table 1, entry *1*), which was confirmed by GC/MS data showing that in addition to naphthalene **4a**, there was only unreacted diphenylacetylene. The replacement of the SMe_2 group with NMe_3 one in the carborane ligand of the catalyst led to a significantly increased yield of **4a** (up to 62% according to ^1H NMR data; see Table 1, entry *2*). The observed effect may be explained by the affinity of SMe_2 group to demethylation processes even in the presence of very weak nucleophiles (*e.g.*, halide ions) to give sulfide derivatives,[33] in which the SMe group can hinder the proceeding of catalytic processes. In particular, we have previously reported[34] that the iron methyl sulfide complex $(9\text{-SMe-}7,8\text{-}C_2B_9H_{10})Fe(C_6H_6)$ does not undergo arene exchange reactions due to the presence of an intramolecular S–Fe interaction in the intermediate $(9\text{-SMe-}7,8\text{-}C_2B_9H_{10})Fe$.

Table 1. Reaction of the annulation of arylcarboxylic acids with alkynes, catalyzed by rhodacarboranes **5** and **6**

Entry	Acid	Alkyne	Catalyst	Product	Yield of products* (%)
1	**1a**	**2a**	**5**	**4a**	(30)
2	**1a**	**2a**	**6**	**4a**	41 (62)
3	**1b**	**2a**	**6**	**3b**	3
				4b	22
4	**1c**	**2a**	**6**	**3c**	5
				4c	10
5	**1d**	**2a**	**6**	**4d**	Traces
6	**1e**	**2a**	**6**	**3e**	36
				4e	27
7	**1a**	**2b**	**6**	**3f**	16

* The yields are given for the isolated products. The yields estimated using ^1H NMR spectroscopy data are given in parentheses.

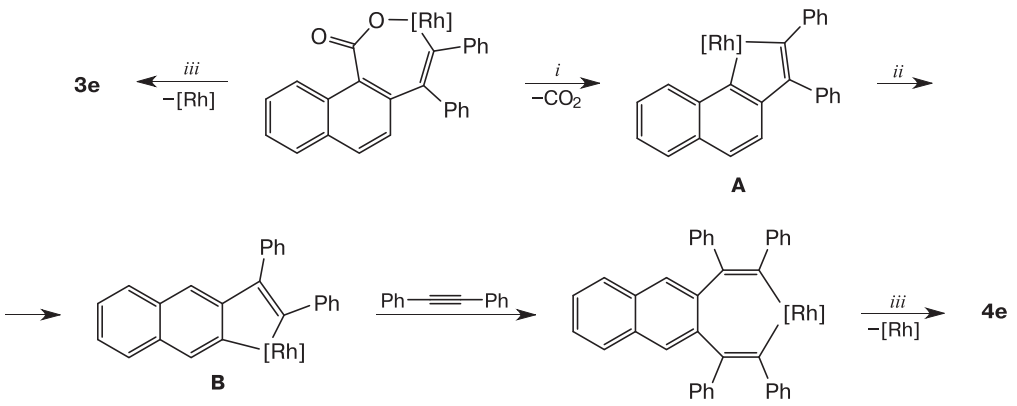
Scheme 2



1: R = H (**a**), Cl (**b**), CF_3 (**c**), NO_2 (**d**)
2: R′ = Ph (**a**), Et (**b**)

Conditions: [Rh]-catalyst (1 mol.%), $Cu(OAc)_2 \cdot H_2O$ (2 equiv.), *o*-xylene, 150 °C, 6 h.

Scheme 3



i. Decarboxylation. *ii*. Isomerization. *iii*. Reductive elimination.

For further evaluations of substrate specificity, we selected the most active trimethylammonium complex **6** as the catalyst (see Table 1, entries *3*—*7*). In particular, it was demonstrated that the selectivity of the reaction was maintained upon the introduction of substituents at the *para*-position of benzoic acid, and naphthalenes were the major products. However, in the case of strong electron-withdrawing substituents such as CF_3 and NO_2, yields of the target products were significantly reduced (see Table 1, entries *4* and *5*), which may be explained by a deactivation of the benzene ring.[35] At the same time, using of 1-naphthalenecarboxylic acid led to a high conversion under the reaction conditions to give a mixture of products, isocoumarin **3e** and naphthalene **4e** (see Table 1, entry *6*). It should be noted that compound **4e** according to NMR data contains a linear anthracene moiety in its structure, rather than a bent phenanthrene system. The formation of **4e** is apparently associated with the isomerization of intermediate **A** into a more thermodynamically stable intermediate **B** (Scheme 3).[5] Moreover, we revealed that using of dialkylacetylenes (*e.g.*, diethylacetylene) leads to a change in the direction of reaction with benzoic acid to give isocoumarin **3f** as the only product (see Table 1, entry *7*). Such a behavior is consistent with the redox character of the reaction and may be explained by a decrease in the oxidation potentials of key intermediates due to the appearance of electron-donating alkyl groups, which makes the decarboxylation process less favorable.

In summary, this work revealed that the catalytic activity of rhodacarborane halide complexes in the annulation of arylcarboxylic acids with alkynes depends on the nature of the charge-compensating substituent at the carborane ligand, while trimethylammonium complex **6** exhibited the greatest activity. Similarly to the cyclopentadienyl complex $[CpRhI_2]_n$, rhodacarborane **6** leads to the formation of naphthalenes as the major products. However, it was demonstrated that the selectivity depends also on the nature of substrates (arylcarboxylic acids and alkynes), while in the presence of electron-donating substituents, isocoumarins can be obtained. At the same time, strong electron-withdrawing groups in arylcarboxylic acids significantly reduce the activity of the catalysts considered in this work. Therefore, the further design of catalytic systems is an important task for subsequent studies in this field in order to overcome this problem.

Experimental

The reactions were carried out under an argon atmosphere. *o*-Xylene was purified by distillation over metallic Na. Operations associated with the isolation of products were performed in air. Complexes **5** (see Ref. 30) and **6** (see Ref. 32) were obtained according to known procedures. Silica gel (70—230 mesh, Merck) was used for column chromatography. ^{1}H NMR spectra were recorded on a Bruker Avance-400 instrument (400.13 MHz).

Annulation of arylcarboxylic acids with alkynes (general procedure). *o*-Xylene (2 mL) was added to a mixture of arylcarboxylic acid (0.6 mmol), alkyne (1.3 mmol), complex **6** (4.5 mg, 0.006 mmol), and $Cu(OAc)_2 \cdot H_2O$ (250.0 mg, 1.3 mmol). The reaction mixture was refluxed under vigorous stirring for 6 h. The formed precipitate was centrifuged and washed with dichloromethane. The solutions were combined, and the solvent was removed *in vacuo*. The residue was loaded onto a column (15×1 cm) filled with silica gel and petroleum ether. The unreacted alkyne was eluted off with the same solvent. Then, using a mixture of petroleum ether and dichloromethane as the eluent, the first yellow or colorless fraction containing the naphthalene product was collected. Increasing the dichloromethane fraction in the eluent, a second yellow fraction containing the isocoumarin product was collected. After evaporating the solvents in vacuo, the target products were isolated as colorless or light yellow crystalline substances. The yields are shown in Table 1.

Reaction of benzoic acid with diphenylacetylene. 1,2,3,4-Tetraphenylnaphthalene (4a) was isolated as a light yellow crystalline solid. The eluent was petroleum ether—dichloromethane (3 : 1), R_f = 0.47. ^{1}H NMR ($CDCl_3$), δ: 6.82—6.96 (m, 10 H, Ph); 7.18—7.35 (m, 10 H, Ph); 7.41—7.50 (m, 2 H); 7.68—7.74

(m, 2 H) (*cf.* Ref. 10). The corresponding isocoumarin product (3,4-diphenyl-1*H*-isochromen-1-one) was not detected.

Reaction of 4-chlorobenzoic acid with diphenylacetylene. 6-Chloro-1,2,3,4-tetraphenylnaphthalene (4b) was isolated as a light yellow crystalline solid. The eluent was petroleum ether—dichloromethane (3 : 1), R_f = 0.31. ^{1}H NMR ($CDCl_3$), δ: 6.86—6.87 (m, 10 H, Ph); 7.20—7.27 (m, 10 H, Ph); 7.32 (dd, 1 H, *J* = 9.8 Hz, *J* = 2.2 Hz); 7.61 (d, 1 H, *J* = 8.8 Hz); 7.64 (d, 1 H, *J* = 2 Hz) (*cf.* Ref. 10).

6-Chloro-3,4-diphenyl-1*H*-isochromen-1-one (3b) was isolated as a colorless crystalline solid. The eluent was petroleum ether—dichloromethane (1 : 1), R_f = 0.18. ^{1}H NMR ($CDCl_3$), δ: 7.16—7.26 (m, 6 H); 7.30—7.32 (m, 2 H); 7.43—7.49 (m, 4 H); 8.33 (d, 1 H, *J* = 8.4 Hz) (*cf.* Ref. 10).

Reaction of 4-(trifluoromethyl)benzoic acid with diphenylacetylene. 1,2,3,4-Tetraphenyl-6-(trifluoromethyl)naphthalene (4c) was isolated as a colorless crystalline solid. The eluent was petroleum ether—dichloromethane (4 : 1), R_f = 0.34. ^{1}H NMR ($CDCl_3$), δ: 6.86—6.89 (m, 10 H, Ph); 7.20—7.28 (m, 10 H, Ph); 7.54 (m, 1 H); 7.77 (d, 1 H, *J* = 8.8 Hz); 7.98 (s, 1 H) (*cf.* Ref. 1). ^{19}F NMR ($CDCl_3$), δ: −62.22.

3,4-Diphenyl-6-(trifluoromethyl)-1*H*-isochromen-1-one (3c) was isolated as a colorless crystalline solid. The eluent was petroleum ether—dichloromethane (2 : 1), R_f = 0.10. ^{1}H NMR ($CDCl_3$), δ: 7.16—7.28 (m, 5 H); 7.30—7.35 (m, 2 H); 7.44—7.46 (m, 4 H); 7.74 (d, 1 H, *J* = 8.4 Hz); 8.53 (d, 1 H, *J* = 8 Hz) (*cf.* Ref. 1). ^{19}F NMR ($CDCl_3$), δ: −63.37.

Reaction of naphthalene-1-carboxylic acid with diphenylacetylene. 1,2,3,4-Tetraphenylanthracene (4e) was isolated as a colorless crystalline solid. The eluent was petroleum ether—dichloromethane (3 : 1), R_f = 0.46. ^{1}H NMR ($CDCl_3$), δ: 6.80—6.99 (m, 10 H, Ph); 7.26—7.36 (m, 10 H, Ph); 7.41—7.44 (m, 2 H); 7.86—7.88 (m, 2 H); 8.25 (s, 2 H) (*cf.* Ref. 5).

3,4-Diphenyl-1*H*-benzo[*h*]isochromen-1-one (3e) was isolated as a colorless crystalline solid. The eluent was dichloromethane, R_f = 0.76. ^{1}H NMR ($CDCl_3$), δ: 7.12—7.33 (m, 6 H); 7.42—7.49 (m, 3 H); 7.51—7.55 (m, 2 H); 7.61—7.65 (m, 1 H); 7.77—7.81 (m, 1 H); 7.87 (d, 1 H, *J* = 8.0 Hz); 8.00 (d, 1 H, *J* = 8.8 Hz); 9.88 (d, 1 H, *J* = 8.4 Hz) (*cf.* Ref. 10).

Reaction of benzoic acid with diethylacetylene. The corresponding naphthalene product (1,2,3,4-tetraethylnaphthalene) was not detected. **3,4-Diethyl-1*H*-isochromen-1-one (3f)** was isolated as a light yellow crystalline solid. The eluent was petroleum ether—dichloromethane (1 : 1), R_f = 0.35. ^{1}H NMR ($CDCl_3$), δ: 1.21 (t, 3 H, Et, *J* = 7.6 Hz); 1.29 (t, 3 H, Et, *J* = 7.4 Hz); 2.60—2.69 (m, 4 H, Et); 7.46 (t, 1 H, *J* = 7.4 Hz); 7.55 (d, 1 H, *J* = 8.4 Hz); 7.72 (t, 1 H, *J* = 7.8 Hz); 8.32 (d, 1 H, *J* = 8 Hz) (*cf.* Ref. 10).

This work was financially supported by the Russian Science Foundation (Project No. 17-73-30036).

NMR expriments were carried out using the scientific equipment at the Center for the Study of the Molecular Structure at the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences and financially supported by the Ministry of Science and Higher Education of the Russian Federation. D. A. Loginov is grateful to the Plekhanov Russian University of Economics for providing access to electronic databases of scientific literature.

This paper does not contain descriptions of studies on animals or humans.

The authors declare no competing interests.

References

1. K. Ueura, T. Satoh, M. Miura, *J. Org. Chem.*, 2007, **72**, 5362; DOI: 10.1021/jo070735n.
2. E. Kudo, Y. Shibata, M. Yamazaki, K. Masutomi, Y. Miyauchi, M. Fukui, H. Sugiyama, H. Uekusa, T. Satoh, M. Miura, K. Tanaka, *Chem. Eur. J.,* 2016, **22**, 14190; DOI: 10.1002/chem.201603499.
3. Y. Honjo, Y. Shibata, E. Kudo, T. Namba, K. Masutomi, K. Tanaka, *Chem. Eur. J.*, 2018, **24**, 317; DOI: 10.1002/chem.201703928.
4. D. A. Loginov, V. E. Konoplev, *J. Organomet. Chem.* 2018, **867**, 14; DOI: 10.1016/j.jorganchem.2017.11.013.
5. Y. Inai, Y. Usuki, T. Satoh, *Synthesis*, 2021, **53**, 3029; DOI: 10.1055/a-1416-6997.
6. V. B. Kharitonov, S. A. Runikhina, Y. V. Nelyubina, D. V. Muratov, D. Chusov, D. A. Loginov, *Chem. Eur. J.*, 2021, **27**, 10903; DOI: 10.1002/chem.202100572.
7. Y. Yamashita, *Sci. Technol. Adv. Mater.* 2009, **10**, 024313; DOI: 10.1088/1468-6996/10/2/024313.
8. Z. Xiao, S.Chen, R. Cai, S. Lin, K. Hong, Z. She, *Beilstein J. Org. Chem.*, 2016, **12**, 2077; DOI: 10.3762/bjoc.12.196.
9. D. A. Loginov, A. P. Molotkov, N. E. Shepel, *J. Organomet. Chem.,* 2018, **867**, 67; DOI: 10.1016/j.jorganchem.2017.12.021.
10. A. P. Molotkov, M. A. Arsenov, D. A. Kapustin, D. V. Muratov, N. E. Shepel', Y. V. Fedorov, A. F. Smol'yakov, E. I. Knyazeva, D. A. Lypenko, A. V. Dmitriev, A. E. Aleksandrov, E. I. Maltsev, D. A. Loginov, *ChemPlusChem*, 2020, **85**, 334; DOI: 10.1002/cplu.202000048.
11. S. Qian, H. Zhang, J. Lan, Z. Bin, *Organic Electronics*, 2020, **84**, 105792; DOI: 10.1016/j.orgel.2020.105792.
12. M. R. Simić, S. Erić, I. Borić, A. Lubelska, G. Latacz, K. Kieć-Kononowicz, S. Vojnović, J. Nikodinović-Runić, V. Savic, *J. Serb. Chem. Soc.*, 2021, **86**, 639; DOI: 10.2298/JSC201201025S.
13. D. A. Loginov, A. O. Belova, A. R. Kudinov, *Russ. Chem. Bull.*, 2014, **63**, 983; DOI: 10.1007/s11172-014-0537-3.
14. D. A. Loginov, A. O. Belova, A. V. Vologzhanina, A. R. Kudinov, *J. Organomet. Chem.*, 2015, **793**, 232; DOI: 10.1016/j.jorganchem.2015.01.022.
15. A. P. Molotkov, M. M. Vinogradov, A. P. Moskovets, O. Chusova, S. V. Timofeev, V. A. Fastovskiy, Y. V. Nelyubina, A. A. Pavlov, D. A. Chusov, D. A. Loginov, *Eur. J. Inorg. Chem.*, 2017, **2017**, 4635; DOI: 10.1002/ejic.201700498.
16. M. M. Vinogradov, D. A. Loginov, *J. Organomet. Chem.*, 2020, **910**, 121135; DOI: 10.1016/j.jorganchem.2020.121135.
17. I. D. Grishin, N. A. Knyazeva, A. M. Penkal´, *Russ. Chem. Bull.*, 2020, **69**, 1520; DOI: 10.1007/s11172-020-2931-3.
18. D. F. Grishin, I. D. Grishin, *Russ. Chem. Rev.*, 2021, **90**, 231; DOI: 10.1070/RCR4964.
19. L. S. Alekseev, S. E. Lyubimov, F. M. Dolgushin, V. V. Novikov, V. A. Davankov, I. T. Chizhevsky, *Organometallics,* 2011, **30**, 1942; DOI: 10.1021/om101201e.
20. A. P. Y. Chan, J. A. Parkinson, G. M. Rosair, A. J. Welch, *Inorg. Chem.*, 2020, **59**, 2011; DOI: 10.1021/acs.inorgchem.9b03351.

21. Q. Xie, T. Wang, S. Wu, W. Guo, H. Zhang *J. Organomet. Chem.*, 2018, **865**, 95; DOI: 10.1016/j.jorganchem.2018.02.009.
22. R. J. Jeans, A. P. Y. Chan, L. E. Riley, J. Taylor, G. M. Rosair, A. J. Welch, I. B. Sivaev, *Inorg. Chem.*, 2019, **58**, 11751; DOI: 10.1021/acs.inorgchem.9b01774.
23. S.V. Timofeev, I. B. Sivaev, E. A. Prikaznova, V. I. Bregadze, *J. Organomet. Chem.*, 2014, **751**, 221; DOI: 10.1016/j.jorganchem.2013.08.012.
24. D. A. Loginov, D. V. Muratov, A. R. Kudinov, *Russ. Chem. Bull.*, 2008, **57**, 1; DOI: 10.1007/s11172-008-0001-3.
25. A. R. Kudinov, D. A. Loginov, *Russ. Chem. Bull.*, 2009, **58**, 600; DOI: 10.1007/s11172-009-0062-y.
26. D. A. Loginov, M. M. Vinogradov, Z. A. Starikova, P. V. Petrovskii, J. Holub, A. R. Kudinov, *Collect. Czech. Chem. Commun.*, 2010, **75**, 981; DOI: 10.1135/cccc2010052.
27. A. A. Telegina, D. A. Gruzdev, G. L. Levit, V. P. Krasnov, *Russ. Chem. Bull.*, 2021, **70**, 539; DOI: 10.1007/s11172-021-3121-7.
28. Y.-K. Yan, D. M. P. Mingos, D. J. Williams, *J. Organomet. Chem.*, 1995, **498**, 267; DOI: 10.1016/0022-328X(95)05533-U.
29. R. Núñez, O. Tutusaus, F. Teixidor, C. Viñas, R. Sillanpää, R. Kivekäs, *Chem. Eur. J.*, 2005, **11**, 5637; DOI: 10.1002/chem.200500288.
30. A. R. Kudinov, D. S. Perekalin, P. V. Petrovskii, K. A. Lyssenko, G. V. Grintselev-Knyazev, Z. A. Starikova, *J. Organomet. Chem.*, 2002, **657**, 115; DOI: 10.1016/S0022-328X(02)01382-7.
31. M. M. Vinogradov, Z. A. Starikova, D. A. Loginov, A. R. Kudinov, *J. Organomet. Chem.*, 2013, **738**, 59; DOI: 10.1016/j.jorganchem.2013.04.011.
32. S. V. Timofeev, O. B. Zhidkova, I. B. Sivaev, Z.A. Starikova, K. Yu. Suponitsky, H. Yan, V. I. Bregadze, *J. Organomet. Chem.*, 2018, **867**, 342; DOI: 10.1016/j.jorganchem.2017.11.014.
33. M. M. Vinogradov, Y. V. Nelyubina, D. A. Loginov, A. R. Kudinov, *J. Organomet. Chem.*, 2015, **798**, 257; DOI: 10.1016/j.jorganchem.2015.04.007.
34. M. M. Vinogradov, Y. V. Nelyubina, M. Corsini, F. F. de Biani, A. R. Kudinov, D. A. Loginov, *Eur. J. Inorg. Chem.*, 2017, **2017**, 4627; DOI: 10.1002/ejic.201700333.
35. T. P. Pabst, P. J. Chirik, *Organometallics*, 2021, **40**, 813; DOI: 10.1021/acs.organomet.1c00030.

Received January 13, 2021;
in revised form June 1, 2021;
accepted June 23, 2021