3-Cyclobutyl-3-ferrocenylcyclopropene and 3-cyclobutylidene-3-ferrocenylpropyne. Synthesis and chemical properties

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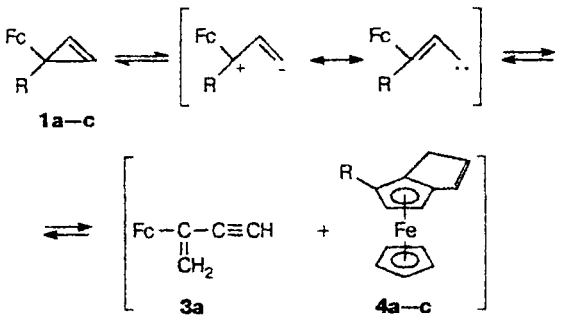
3-Cyclobutyl-3-ferrocenylcyclopropene was synthesized by the reactions of mono- or dibromoferrocenylcyclopropanes with Bu^{t}OK in DMSO. Treatment of dibromoferrocenylcyclopropane with Bu^{t}OK in THF afforded 3-cyclobutylidene-3-ferrocenylpropyne in 52% yield. Heterolysis of the C—C bond in the three-membered ring of 3-cyclobutyl-3-ferrocenylcyclopropene at low and high temperatures was studied. Hydrolysis yielded 3-cyclobutyl-1*H*-cyclopentaferrocene and products with linear structures, *viz.*, 3-cyclobutylidene-3-ferrocenylpropene, *E*- and *Z*-1-ferrocenyl-1-cyclobutylpropenes, and 1-cyclobutylidene-1-ferrocenylacetone. Cyclopropene reacts with 1,3-diphenylisobenzofuran to form two Diels—Alder adducts, while the enyne does not react with 1,3-diphenylbenzofuran.

Key words: 3-cyclobutyl-3-ferrocenylcyclopropene, cyclopropene, cyclopropane, cyclobutane, ferrocenyl-substituted dienes, heterolysis, enynes, cyclopentaferrocene.

It is known that the introduction of the ferrocene substituent into a three-membered ring leads to a substantial change in the properties of the latter.[1—8] Examples of changes in the properties of the small carbocycle are intramolecular transformations of 3-alkyl-3-ferrocenylcyclopropenes (**1a—c**) upon their condensation with 1,3-diphenylisobenzofuran (**2**).[9] It appeared that the major products were products of conversions of the initial cyclopropenes upon heating, *viz.*, 2-ferrocenylbut-1-en-3-yne (**3a**) and 3-alkylcyclopentaferrocene (**4a—c**), rather than classical Diels—Alder adducts, as in the case of 3,3-dialkyl- and 3-alkyl-3-arylcyclopropenes.[10—12] Compounds **3a** and **4a—c** were obtained as a result of heterolysis of the C—C bond of the small ring.



Fc = $C_5H_5FeC_5H_4$; R = Me (**a**); Bu^t (**b**); Ad (**c**)

The formation of alkylation products of the ferrocene fragment suggests that the ferrocenyl substituent in compounds **1a—c** has a nonbisector orientation with respect to the three-membered ring, like the aryl groups in 3-aryl-3-ferrocenylcyclopropenes.[13,14] At the same time, the formation of linear butenyne **3a** and polymeric compounds in substantial amounts casts some doubt on this conclusion.

With the aim of determining the conformations of 3-alkyl-3-ferrocenylcyclopropenes, we synthesized 3-ferrocenyl-3-cyclobutylcyclopropene (**5**) starting from

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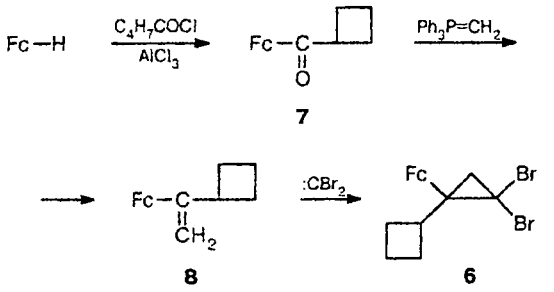
1,1-dibromo-2-cyclobutyl-2-ferrocenylcyclopropane (**6**). The latter was prepared according to the following scheme:

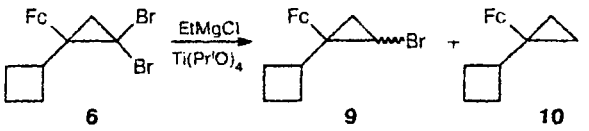


Compounds **6**—**8** were formed without complications in 60—75% yields. Dibromide **6** was reduced with a mixture of ethylmagnesium chloride and titanium tetraisopropylate.[15] 1-Bromo-2-cyclobutyl-2-ferrocenylcyclopropane (**9**) was obtained as a mixture of the *Z* (**9a**) and *E* isomers (**9b**) in a ratio of 4 : 1 (the yield was 66%). The assignment of the isomeric monobromides was made based on the ^{1}H NMR spectral data (Table 1) taking into account the NMR criteria found previously for the determination of *Z* and *E* geometric isomers of monobromoferrocenylcyclopropanes (see Refs. 5—9, 12, and 13). In addition to monobromide **9**, the product of complete reduction, *viz.*, 1-cyclobutyl-1-ferrocenyl-

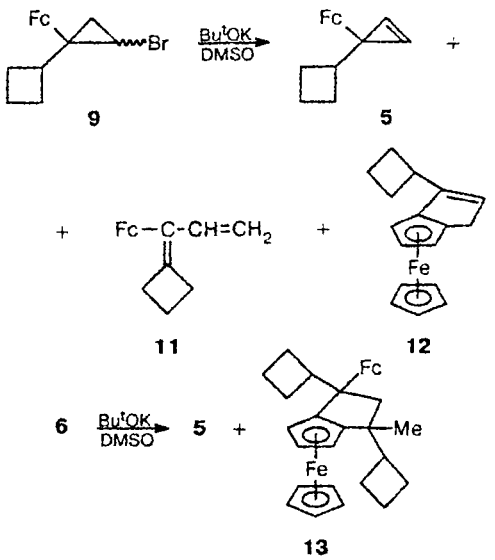
Table 1. Data of ^{1}H NMR spetroscopy for the synthesized compounds (δ, *J*/Hz)

Compound	C_5H_5 (s, 5 H)	C_5H_4 (m)	CH_2	CH	CH_3, Ar
5	4.11	3.97 (2 H), 4.02 (2 H)	1.60—2.25 (m, 6 H)	2.85 (m, 1 H), 7.05 (d, 1 H, J = 0.8)	—
6	4.15	4.03 (1 H), 4.13 (1 H), 4.21 (2 H)	1.56 (s, 1 H), 1.87 (s, 1 H), 1.70—2.55 (m, 6 H)	3.46 (m, 1 H)	—
7	4.06	4.18 (2 H), 4.35 (2 H)	1.75—2.30 (m, 6 H), 4.89 (t, 1 H, J = 1.40), 5.24 (t, 1 H, J = 1.36)	3.30 (m, 1 H)	—
8	4.15	4.47 (2 H), 4.71 (2 H)	1.80—2.50 (m, 6 H)	3.64 (m, 1 H)	—
***Z*-9**	4.14	4.00—4.20 (4 H)	1.52 (ddd, 1 H), 2.06 (ddd, 1 H, J_{gem} = 6.4, J_{trans} = 5.1, J_{cis} = 7.6), 1.81—2.53 (m, 6 H)	3.24 (m, 1 H), 3.70 (dd, 1 H, J = 5.1; 7.6)	—
***E*-9**	4.17	4.10 (2 H), 4.25 (2 H)	1.74 (ddd, 1 H), 1.95 (ddd, 1 H, J_{gem} = 6.26, J_{trans} = 5.0, J_{cis} = 7.2), 1.78—2.30 (m, 6 H)	3.20 (m, 1 H), 3.52 (dd, 1 H, J = 5.0; 7.2)	—
10	4.12	4.07 (s, 4 H)	0.66 (m, 2 H), 0.76 (m, 2 H), 1.50—2.10 (m, 6 H)	2.76 (m, 1 H)	—
11	4.14	3.97 (1 H), 4.16 (2 H), 4.22 (1 H)	1.87—2.48 (m, 6 H), 5.04 (ddd, 1 H), 5.15 (ddd, 1 H, J_{gem} = 0.8, J_{trans} =17.4, J_{cis} =10.6)	6.05 (dd, 1 H, J = 17.4; 10.6)	—
12	4.12	4.20 (1 H), 4.26 (1 H), 4.30 (1 H)	1.80—2.50 (m, 6 H), 4.28 (d, 2 H, J = 6.8)	2.98 (m, 1 H), 5.98 (t, 1 H, J = 6.8)	—
13	4.07, 4.10	4.03 (1 H), 4.14 (2 H), 4.20 (1 H), 4.25 (2 H), 4.37 (1 H)	1.68—2.70 (m, 12 H), 2.05 (d, 1 H, J = 9.2), 2.44 (d, 1 H, J = 9.2)	2.76 (m, 1 H), 2.89 (m, 1 H)	1.58 (s, 3 H)
14a	4.05	4.01 (4 H)	1.40—2.05 (m, 6 H)	2.40 (s, 2 H), 2.93 (m, 1 H)	7.15 (m, 4 H), 7.4—7.65 (m, 6 H), 7.72—7.90 (m, 4 H)
14b	4.08	3.94 (2 H), 4.04 (2 H)	1.75—2.30 (m, 6 H)	2.46 (s, 2 H), 3.15 (m, 1 H)	6.90—7.12 (m, 4 H), 7.25—7.56 (m, 6 H), 7.64—7.72 (m, 4 H)
15	4.21	4.32 (2 H), 4.46 (2 H)	1.97—2.68 (m, 6 H)	—	1.93 (s, 3 H)
16a	4.12	4.05 (2 H), 4.16 (2 H)	1.63—2.40 (m, 6 H)	2.85 (m, 1 H), 5.84 (q, 1 H, J = 6.8)	1.48 (d, 3 H, J = 6.8)
16b	4.15	3.86 (2 H), 4.07 (2 H)	1.82—2.40 (m, 6 H)	2.55 (m, 1 H), 5.50 (q, 1 H, J = 7.3)	1.76 (d, 3 H, J = 7.3)
19	4.14	4.18 (2 H), 4.29 (2 H)	1.81—2.53 (m, 6 H)	3.01 (s, 1 H)	—

cyclopropane (**10**), was isolated from the reaction mixture.



The target cyclopropene **5** was synthesized according to two procedures, *viz.*, by dehydrobromination of monobromocyclopropane **9** under the action of a 5% excess of Bu^{t}OK in DMSO and by treatment of dibromocyclopropane **6** with two equivalents of Bu^{t}OK in DMSO.[13]



In the first case, 3-cyclobutylidene-3-ferrocenylpropene (**11**) and 3-cyclobutyl-1*H*-cyclopentaferrocene (**12**) were obtained as by-products, while in the second case, 1,3-dicylobutyl-3-ferrocenyl-1-methyl-1,2-dihydrocyclopentaferrocene (**13**) was formed as a by-product which is, apparently, associated with opening of the small ring in the starting mono- and dibromides (for more details, see Refs. 6—9).

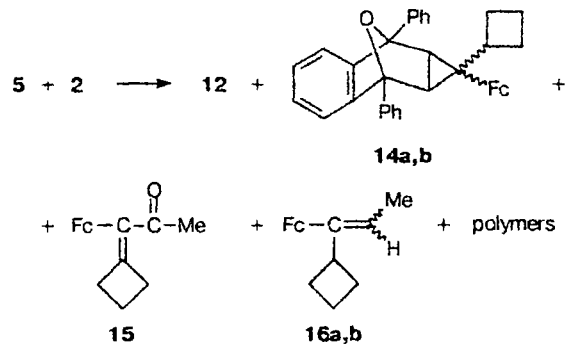
Cyclopropene **5** is a low-melting crystalline compound, which rapidly decomposes upon storage under normal conditions. In solutions, cyclopropene **5** is gradually isomerized even in the cold (0 °C) to form compound **12** (in a yield of up to 31%) and polymeric products, whose structures were not established.

Freshly prepared ferrocenylcyclopropene **5** reacted with 1,3-diphenylisobenzofuran **2** upon boiling in benzene to form two isomeric Diels—Alder adducts **14** (in a ratio of 3.2 : 1). Compounds **12**, **15**, and **16a,b** were also isolated from the reaction mixture.

Isomer **14a**, which was obtained in a larger amount, was isolated in the individual state. The ^{1}H and ^{13}C NMR spectra of compound **14a** are given in Tables 1 and 2, respectively. However, we failed to grow crystals and to perform X-ray diffraction analysis with the aim of establishing the spatial structure of **14a**.

Table 2. Data of ^{13}C NMR spectroscopy for compounds **5**, **14a**, and **19** (δ)

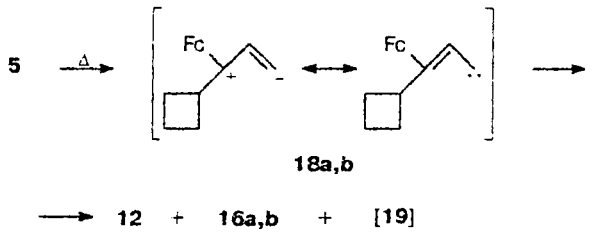
Group or atom	5	14a	19
C_5H_5	68.0	68.4	68.6
C_5H_4	66.9	65.4, 67.1	66.7, 69.0
CH_2	14.7, 17.0	16.3, 17.5	17.3, 22.1
CH	30.0	19.2, 41.1	76.5
C	34.0	39.1	89.7, 121.2, 129.4
Fc_{ipso}	98.7	91.1	82.9
C—O	—	95.9	—
CH=	109.9	—	—
C_{ipso}	—	142.1, 154.2	—
Ar	—	121.2, 125.9, 127.8, 128.1, 129.0	—



Based on a comparison of the spectral data for compound **14a** and 3-methyl-3-*anti*-ferocenyl-*exo*-1,5-diphenyl-6,7-benzo-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene (**17**),[9] which has been prepared previously and whose spatial structure has been established by X-ray diffraction analysis, the structure of 3-cyclobutyl-3-*anti*-ferrocenyl-*exo*-1,5-diphenyl-6,7-benzo-8-oxatricyclo-[3.2.1.0^{2,4}]oct-6-ene was assigned to adduct **14a**. By analogy,[10—11] adduct **14b** has, apparently, the *exo* structure with the ferrocenyl substituent in the *syn* orientation with respect to the bridging oxygen atom.

Compound **12**, 1-cyclobutylidene-1-ferrocenylacetone (**15**), and 1-ferrocenylpropenes (**16a,b**) were apparently formed as a result of the opening of the small ring in the course of the reaction and subsequent conversions of intermediates **18a,b**. Compound **12** was formed as a result of intramolecular alkylation in carbene **18b**. Ketone **15** was obtained as a product of hydration of 3-cyclobutylidene-3-ferrocenylpropyne (**19**) and propenes **16a** and **16b** were obtained due to intermo-

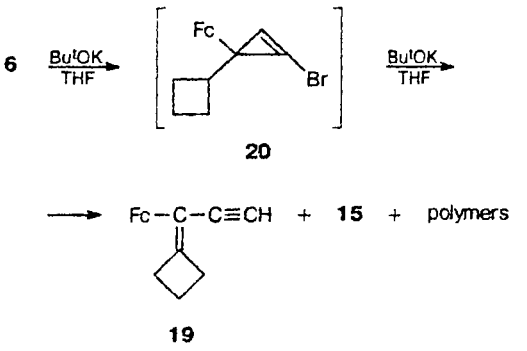
lecular disproportionation of intermediates **18a,b** to form intermediate enyne **19** and alkenes **16**.



We succeeded in synthesizing enyne **19** in 52% yield by treating dibromocyclopropane **6** with Bu^{t}OK in THF at low temperature (0 °C). In addition to compound **19**, ketone **15** (~15%) and polymeric products were isolated from the reaction mixture.

In this case, the reaction proceeded, apparently, through intermediate formation of 1-bromo-3-cyclobutyl-3-ferrocenylcyclopropene (**20**).[14] However, attempts to detect intermediate monobromocyclopropene by performing the reaction in the presence of dienes failed.

It appeared that vinylacetylene **19** readily added water to form ketone **15** both upon chromatography on



aluminum oxide and in moist solvents. Compound **19** was rapidly polymerized upon storage but did not form diene adducts with 1,3-diphenylisobenzofuran upon boiling in benzene.

Hence, the results obtained did not allow us to unambiguously infer the conformation of 3-cyclobutyl-3-ferrocenylcyclopropene. A large number of products with linear structures, which were formed as a result of the opening of the small ring, is indicative of the absence of interactions through space between the mo-

Table 3. The yields and the physicochemical characteristics of the synthesized compounds

Compound	M.p. /°C	Yield (%)	Found / Calculated (%)				Molecular formula
			C	H	Fe	Br	
5	66	52	73.56 73.40	6.38 6.52	20.14 20.08	—	$C_{17}H_{18}Fe$
6	127—128	73	46.71 46.60	4.28 4.14	12.58 12.74	36.63 36.52	$C_{17}H_{18}Br_2Fe$
7	106—107	63	72.11 72.20	6.73 6.81	21.06 20.99	—	$C_{16}H_{18}Fe$
8	62—63	76	67.25 67.18	5.82 6.00	20.77 20.82	—	$C_{15}H_{16}FeO$
9 (*Z*, *E*)[a]	87—89	66	57.03 56.85	5.19 5.33	15.67 15.55	22.39 22.27	$C_{17}H_{18}BrFe$
10	Oil	16	72.73 72.87	7.26 7.19	19.82 19.94	—	$C_{17}H_{20}Fe$
11	Oil	19	73.32 73.40	6.63 6.52	19.93 20.08	—	$C_{17}H_{18}Fe$
12	83—84	9	73.58 73.40	6.35 6.52	20.15 20.08	—	$C_{17}H_{18}Fe$
13	218—219	46	72.33 72.20	6.74 6.81	21.08 20.99	—	$C_{32}H_{36}Fe_2$
14a,b[b]	204—205	39	80.93 81.02	5.65 5.88	10.23 10.18	—	$C_{37}H_{32}FeO$
15	74—75	17	69.66 69.41	6.04 6.20	18.78 19.00	—	$C_{17}H_{18}FeO$
16a,b[c]	Oil	19	72.74 72.87	7.27 7.19	20.06 19.94	—	$C_{17}H_{20}Fe$
19	Oil	52	73.85 73.93	6.05 5.84	20.07 20.23	—	$C_{17}H_{18}Fe$

[a] The *Z*/*E* ratio is ~ 4 : 1. [b] The **14a/14b** ratio is ~ 3.2 : 1. [c] The *Z*/*E* ratio is ~ 3 : 1.

lecular orbitals of the ethylene fragment and of the substituted cyclopentadienyl ring of the ferrocene fragment in compound **5**, which is possible in the case of the bisector orientation of the ferrocenyl substituent. This problem calls for further investigation.

Experimental

The ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini spectrometer (200 and 50 MHz) for solutions in $CDCl_3$ with tetramethylsilane as the internal standard (see Tables 1 and 2, respectively). The results of elemental analysis, the yields, and the melting points of the synthesized compounds are given in Table 3. Column chromatography was performed with the use of Al_2O_3 (Brockmann III).

Ferrocenyl cyclobutyl ketone (7) was prepared by Friedel—Crafts acylation of ferrocene with cyclobutanecarboxylic acid chloride in the presence of $AlCl_3$.[16]

1-Cyclobutyl-1-ferrocenylethylene (8) was synthesized according to Wittig[17] from ketone **7** and methylenetriphenylphosphorane under an atmosphere of dry argon.

1,1-Dibromo-2-cyclobutyl-2-ferrocenylcyclopropane (6) was prepared from alkene **8** according to a known procedure.[18]

Reduction of dibromide 6 was performed as described previously[8]; the reaction afforded cyclopropane **10** and monobromide **9** (a 4 : 1 mixture of *Z* and *E* isomers).

3-Cyclobutyl-3-ferrocenylcyclopropene (5). *A.* Dehydrobromination of monobromide **9** was performed according to a standard procedure.[9] Chromatography on Al_2O_3 (hexane as the eluent) afforded cyclopropene **5**, diene **11**, and compound **12** (Table 3).

B. Dibromide **6** (1.75 g, 4 mmol) was added to a solution of Bu^tOK (6 mmol) in DMSO (50 mL) at 20 °C. The reaction mixture was stirred for 10 h and treated as described above. Chromatography on Al_2O_3 (hexane as the eluent) afforded cyclopropene **5** in a yield of 0.39 g (35%) and compound **13** in a yield of 0.49 g (46%).

Reaction of cyclopropene 5 with 1,3-diphenylisobenzofuran 2. A mixture of compounds **5** (0.42 g, 1.5 mmol) and **2** (0.56 g, 2 mmol) was refluxed in dry benzene (60 mL) for 5 h. The solvent was distilled off *in vacuo*. Chromatography of the residue on Al_2O_3 afforded compound **12** (hexane) in a yield of 0.05 g (11%), m.p. 74—75 °C; alkene **16** (a 3 : 1 mixture of *Z* and *E* isomers, hexane) in a yield 0.08 g (19%); ketone **15** (a 4 : 1 hexane—benzene mixture as the eluent) in a yield of 0.075 g (17%); and adduct **14a,b** (~3.2 : 1, a 2 : 1 hexane—benzene mixture as the eluent) in a yield of 0.32 g (39%) as yellow crystals (see Table 3). Adduct **14a,b** was chromatographed in a thin layer on silica gel (a 1 : 1 hexane—benzene mixture as the eluent). Compound **14a** was obtained in a yield of 0.11 g (R_f = 0.42, yellow powder, m.p. 218—219 °C) and a 1 : 1 mixture of compounds **14a** and **14b** was obtained in a yield of 0.15 g (R_f = 0.48, m.p. 207 °C).

3-Cyclobutylidene-3-ferrocenylpropyne (19). Dibromocyclopropane **6** (1.75 g, 4 mmol) was added to a solution of Bu^tOK (9 mmol) in anhydrous THF (150 mL) under an atmosphere of dry argon at 0 °C. The reaction mixture was stirred for 7 h and then benzene (50 mL) and water (50 mL) were poured into the reaction flask. The organic layer was separated from the aqueous layer, the solvent was evaporated *in vacuo*, and the residue was chromatographed on Al_2O_3. Vinylacetylene **19** was obtained in a yield of 0.57 g (52%) (hexane as the eluent) (see Table 3) and methyl vinyl ketone **15** was obtained in a yield of 0.17 g (15%) as violet crystals (hexane—benzene as the eluent).

References

1. A. J. Fry, P. S. Jain, and R. L. Krieger, *J. Organomet. Chem.*, 1961, **214**, 381.
2. A. J. Fry, R. L. Krieger, I. Agranat, and E. Aharon-Shalom, *Tetrahedron Lett.*, 1976, **32**, 4803.
3. I. Agranat, E. Aharon-Shalom, A. J. Fry, R. L. Krieger, and W. O. Krug, *Tetrahedron*, 1979, **35**, 733.
4. E. I. Klimova, A. N. Pushin, and V. A. Sazonova, *Zh. Obshch. Khim.*, 1987, **57**, 2336 [*J. Gen. Chem. USSR*, 1987, **57** (Engl. Transl.)].
5. E. I. Klimova, C. Alvarez Toledano, M. Martinez Garcia, Kh. Gomes Lara, N. N. Meleshonkova, and I. G. Bolesov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 652 [*Russ. Chem. Bull.*, 1996, **45**, 613 (Engl. Transl.)].
6. E. I. Klimova, L. Ruiz Ramirez, T. Klimova-Berestneva, M. Martinez Garcia, R. Moreno Esparsa, C. Alvarez Toledano, and A. Ruben Toscano, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 499 [*Russ. Chem. Bull.*, 1998, **47**, 482 (Engl. Transl.)].
7. E. I. Klimova, T. Klimova-Berestneva, L. Ruiz Ramirez, M. Martinez Garcia, C. Alvarez Toledano, and A. Ruben Toscano, *J. Organomet. Chem.*, 1997, **544**, 130.
8. E. I. Klimova, M. Martinez Garcia, T. Klimova, C. Alvarez, R. Toscano, R. Moreno, and L. Ruiz Ramirez, *J. Organomet. Chem.*, 1998, **566**, 175.
9. E. I. Klimova, L. Ruiz Ramirez, R. Moreno, T. Klimova, M. Martinez Garcia, N. N. Meleshonkova, and A. V. Churakov, *J. Organomet. Chem.*, 1998, **559**, 1.
10. L. T. Zaitseva, I. B. Avezov, V. V. Plemenkov, and I. G. Bolesov, *Zh. Org. Khim.*, 1974, **10**, 2227 [*J. Org. Chem. USSR*, 1974, **10** (Engl. Transl.)].
11. I. G. Bolesov, L. T. Zaitseva, V. V. Plemenkov, I. B. Avezov, and L. S. Surmina, *Zh. Org. Khim.*, 1978, **14**, 71 [*J. Org. Chem. USSR*, 1978, **14** (Engl. Transl.)].
12. V. N. Postnov, E. I. Klimova, N. N. Meleshonkova, and I. G. Bolesov, *Dokl. Akad. Nauk SSSR*, 1994, **339**, 362 [*Dokl. Chem.*, 1994 (Engl. Transl.)].
13. E. I. Klimova, C. Alvarez Toledano, T. Klimova-Berestneva, M. Martinez Garcia, A. R. Toscano, and L. Ruiz Ramirez, *Zh. Obshch. Khim.*, 1998, **68**, 999 [*Russ. J. Gen. Chem.*, 1998, **68** (Engl. Transl.)].
14. T. C. Shields, W. E. Billups, and A. N. Kurtz, *Angew. Chem., Int. Ed., Engl.*, 1968, **7**, 209.
15. V. V. Plemenkov, Kh. Z. Giniyatov, Ya. Ya. Villem, N. V. Villem, L. S. Surmina, and I. G. Bolesov, *Dokl. Akad. Nauk SSSR*, 1980, **254**, 895 [*Dokl. Chem.*, 1980 (Engl. Transl.)].
16. M. Rausch, H. Vogel, and H. Rosenberg, *J. Organomet. Chem.*, 1957, **22**, 903.
17. G. Wittig and U. Schollkopf, *Org. Syn.*, 1960, **40**, 66.
18. N. V. Bovin, L. S. Surmina, N. I. Yakushkina, and I. G. Bolesov, *Zh. Obshch. Khim.*, 1977, **13**, 1888 [*J. Gen. Chem. USSR*, 1977, **13** (Engl. Transl.)].

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