α-Ferrocenylvinylacetylenes

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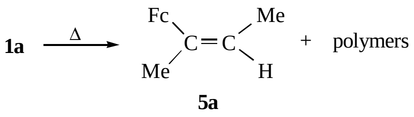
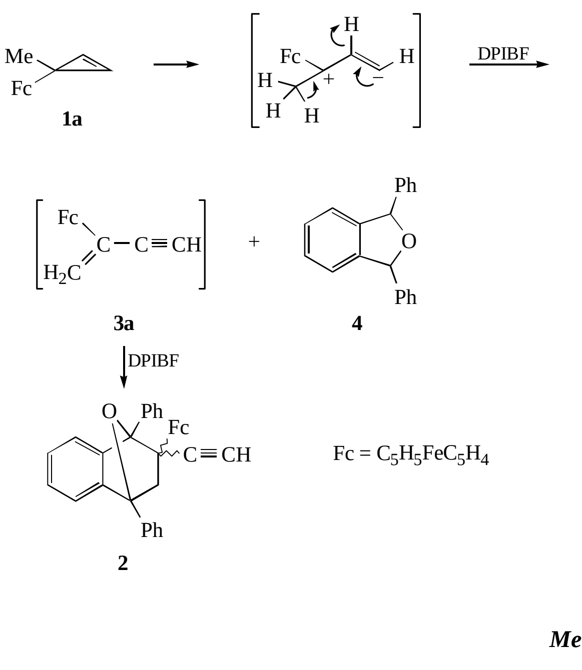
Thermolysis of 3-isopropyl- and 3-cyclobutyl-3-ferrocenylcyclopropenes results in the formation of 3-alkylidene-3-ferrocenylpropynes and (*Z*,*E*)-1-alkyl-1-ferrocenylpropenes; 2,2-dibromo-1-methyl-, 2,2-dibromo-1-isopropyl- and 2,2-dibromo-1-cyclobutylferrocenylcyclopropanes are converted into ferrocenylvinylacetylenes on treatment with Bu^tOK in THF.

It is well known that the introduction of a ferrocenyl substituent into a cyclopropane or cyclopropene ring substantially alters its properties. The transformations of *gem*-dihalo(ferrocenyl)cyclopropanes into 1,2- and 1,3-dienes under the action of BuLi or Na_2CO_3 in ethanol[1–3] and of 2,2-dibromo-1-alkyl-1-ferrocenylcyclopropanes into monobromides, cyclopropenes and retrocyclization products upon treatment with Bu^tOK in DMSO are the examples.[4] 3-Aryl-3-ferrocenylcyclopropanes easily undergo intramolecular transformations with small-ring opening followed by retrocyclization involving the aryl fragment.[5–8] The reaction of 3-ferrocenyl-3-methylcyclopropene **1a** with 1,3-diphenylisobenzofuran (DPIBF) also proceeds in an unusual way, the main product being compound **2**, *viz*., an adduct of DPIBF with 3-ferrocenylbut-3-ene-1-yne **3a** formed upon small-ring opening under reaction conditions, as depicted in the scheme.[9]

All attempts to identify 3-ferrocenylbut-3-ene-1-yne **3a** under conditions of cyclopropene **1a** thermolysis (refluxing in dry benzene, toluene or xylene in an inert atmosphere), without DPIBF or any other trap for expected **3a** were unsuccessful. The only product isolated from the reaction mixture was 2-ferrocenylbut-2-ene **5a**, supposedly, as the *trans*-isomer. In addition, some other polymeric products of unknown structures were isolated.



There are only two reports available in the literature concerning the synthesis of α-ferrocenyl-substituted vinylacetylenes, namely, 3-ferrocenyl-3-cyclohexylidenepropyne.[1,3] This compound was synthesised by prolonged refluxing of 1,1-dibromo-2-cyclohexyl-2-ferrocenylcyclopropane in ethanol (18% yield) or acetonitrile (48% yield) in the presence of Na_2CO_3. The absence of other data on the chemical properties of ferrocenylenynes and on convenient methods of their synthesis indicates that this class of compounds has not been adequately studied. On the other hand, these compounds can be used for the synthesis of ferrocene derivatives and for studies of the influence of a bulky ferrocenyl substituent on the reactions of conjugated enynes.



We examined the preparation of this compounds by thermolysis of 3-alkyl-3-ferrocenylcyclopropenes with secondary alkyl substituents [alkyl = isopropyl (**1b**) or cyclobutyl (**1c**)].[†] We found that these compounds, in contrast to 3-ferrocenyl-3-methylcyclopropene **1a**, afford 3-alkylidene-3-ferrocenylpropynes (**3b**,**c**)[‡] and (*Z*,*E*)-1-alkyl-1-ferrocenylprop-1-enes (**5b**,**c**)[§] as the main products on refluxing in benzene, together with small amounts of methyl vinyl ketones (**6b**,**c**),[¶,††] respectively.

The structures of the compounds obtained were established on the basis of the ^1H and ^{13}C NMR spectra and elemental analysis data.

Thermolysis of cyclopropenes **1b**,**c** in the presence of DPIBF[††] leads to the formation of Diels–Alder adducts **7b**,**c** and compounds **3b**,**c**, **4**, **5b**,**c** and **6b**,**c**. The Diels–Alder adducts were obtained as mixtures of two structural isomers **7b**$_1$ and **7b**$_2$ or **7c**$_1$ and **7c**$_2$ (~3:1),[‡‡] as was found by ^1H NMR spectroscopy. The X-ray analysis of the major isomers formed indicates that their structures correspond to *exo*-1,5-diphenyl-3-*anti*-ferrocenyl-3-*syn*-isopropyl(or cyclobutyl)-6,7-benzo-8-oxatricyclo$[3.2.1.0^{2,4}]$-oct-6-enes (**7b**$_1$,**c**$_1$). The structures of minor isomers have not been established as yet.

It is quite obvious that in this case heterolysis of a C–C bond of the cyclopropane ring leads to carbenoids **8b**,**c**. We believe

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[†] *gem*-Dibromocyclopropanes **9b**,**c** and cyclopropenes **1b**,**c** were synthesised according to the published procedures.[4,7–9]

1b: yield 61%, orange crystals, mp 62–63 °C. ^1H NMR (hereinafter, $CDCl_3$) δ: 0.79 (d, 6H, Me, *J* 6.73 Hz), 2.41 (m, 1H, CH, *J* 6.73 Hz), 4.12 (s, 5H, C_5H_5), 4.02 (s, 4H, C_5H_4), 6.95 (s, 2H, CH=). ^{13}C NMR (hereinafter, $CDCl_3$) δ: 20.70 (Me), 29.91 (CH), 34.90 (C), 66.95 (C_5H_4), 68.01 (C_5H_5), 98.73 ($C_{ipso}Fc$), 110.59 (CH=). Found (%): C, 72.29; H, 7.03; Fe, 21.08. Calc. for $C_{16}H_{18}Fe$ (%): C, 72.21; H, 6.81; Fe, 20.98.

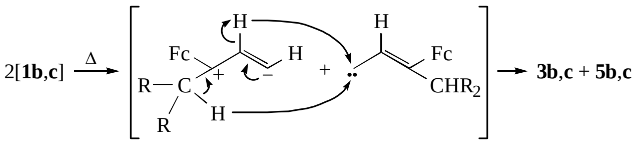
1c: yield 52%, orange crystals, mp 66°C. ^1H NMR, δ: 1.60–2.25 (m, 6H, CH_2), 2.85 (m, 1H, CH), 4.11 (s, 5H, C_5H_5), 3.97 (m, 2H, C_5H_4), 4.02 (m, 2H, C_5H_4), 7.05 (d, 2H, CH=, *J* 0.8 Hz). ^{13}C NMR, δ: 14.67, 16.97 (CH_2), 29.99 (CH), 33.98 (C), 66.91 (C_5H_4), 68.00 (C_5H_5), 98.65 ($C_{ipso}Fc$), 109.93 (CH=). Found (%): C, 73.56; H, 6.38; Fe, 20.14. Calc. for $C_{17}H_{18}Fe$ (%): C, 73.40; H, 6.52; Fe, 20.08.

[‡] **3a**: yield 52%, orange oil. ^1H NMR, δ: 3.01 (s, 1H, CH=), 4.16 (s, 5H, C_5H_5), 4.24 (m, 2H, C_5H_4), 4.51 (m, 2H, C_5H_4), 5.47 (d, 1H, CH_2, *J* 0.9 Hz), 5.60 (d, 1H, CH_2, *J* 0.9 Hz). ^{13}C NMR, δ: 66.67, 69.09 (C_5H_4), 69.65 (C_5H_5), 76.51 (CH=), 82.93 ($C_{ipso}Fc$), 89.97 (C=), 118.15 (CH_2=), 128.42 (C). Found (%): C, 71.33; H, 4.99; Fe, 23.54. Calc. for $C_{14}H_{12}Fe$ (%): C, 71.22; H, 5.12; Fe, 23.66.

3b: yield 61%, orange oil. ^1H NMR, δ: 1.85 (s, 3H, Me), 2.02 (s, 3H, Me), 2.89 (s, 1H, CH≡), 4.12 (s, 5H, C_5H_5), 4.15 (m, 2H, C_5H_4), 4.19 (m, 2H, C_5H_4). Found (%): C, 72.87; H, 6.03; Fe, 21.19. Calc. for $C_{16}H_{16}Fe$ (%): C, 72.75; H, 6.11; Fe, 21.14.

3c: yield 53%, orange oil. ^1H NMR, δ: 1.81–2.53 (m, 6H, CH_2), 3.01 (s, 1H, CH≡), 4.14 (s, 5H, C_5H_5), 4.18 (m, 2H, C_5H_4), 4.29 (m, 2H, C_5H_4). Found (%): C, 73.85; H, 6.05; Fe, 20.07. Calc. for $C_{17}H_{16}Fe$ (%): C, 73.93; H, 5.84; Fe, 20.23.

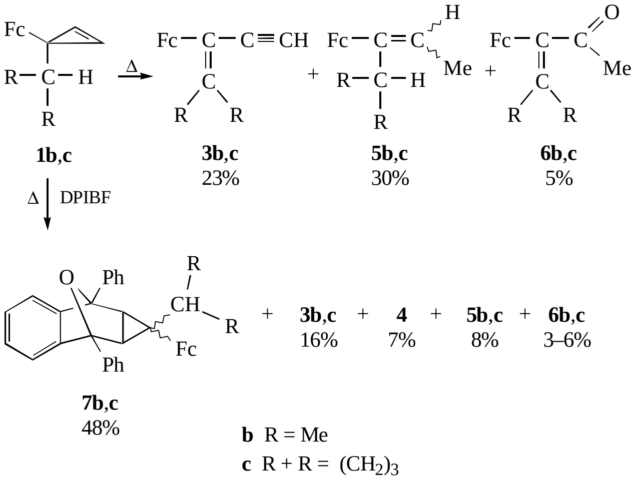
that compounds **3b**,**c** and **5b**,**c** result from disproportionation of carbenoids **8b**,**c** according to the following scheme:



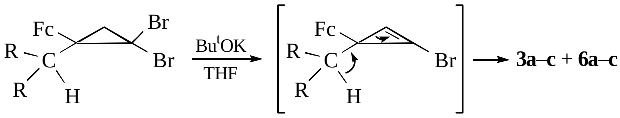
8b,**c**

Methyl vinyl ketones **6b**,**c** are formed upon hydration of acetylenes **3b**,**c** during chromatographic separation of the reaction mixtures.

The fact that 1,3-dihydro-1,3-diphenylisobenzofuran **4** is formed during the thermolysis of cyclopropenes **1a**[9] and **1b**,**c** in the presence of DPIBF indicates that 1,3-diphenylisobenzofuran can act as a partner in the disproportionation of carbenoids **8a**–**c** and in the generation of enynes **3a**–**c**.



Further, we have found that Bu^{t}OK in THF, unlike Bu^{t}OK in DMSO,[4,10,11] is a convenient reagent[1] for the preparation of ferrocenylvinylacetylenes from corresponding *gem*-dibromocyclopropanes **9a**–**c**,[§§] the yields of acetylenes **3a**–**c** can be as high as 52–63%.[††] However, the formation of methyl vinyl ketones **6a**–**c** (8–15%) during isolation and purification cannot be avoided:



9a–**c**

10a–**c**

a R = H
b R = Me
c R + R = $(CH_2)_3$

The reaction seems to occur *via* intermediate 3-alkyl-1-bromo-3-ferrocenylcyclopropenes **10a**–**c**, although these cannot be captured when the reaction was carried out in the presence of 1,3-dienes.

[§] **5a**: yield 28%, orange oil. ^{1}H NMR, δ: 1.44 (d, 3H, Me, *J* 6.67 Hz), 1.78 (s, 3H, Me), 4.06 (s, 5H, C_5H_5), 4.01 (m, 2H, C_5H_4), 4.23 (m, 2H, C_5H_4), 5.52 (q, 1H, CH=, *J* 6.67 Hz). Found (%): C, 69.87; H, 6.93; Fe, 23.41. Calc. for $C_{14}H_{16}Fe$ (%): C, 70.02; H, 6.72; Fe, 23.26.

(*Z*,*E*)-**5b** (2:1), R_f = 0.75 (hexane), yield 30.5%, orange oil. ^{1}H NMR for (*Z*)-**5b**, δ: 1.17 (d, 6H, Me, *J* 6.8 Hz), 1.81 (d, 3H, Me, *J* 6.6 Hz), 2.40 (m, 1H, CH, *J* 6.8 Hz), 4.05 (s, 5H, C_5H_5), 4.00 (m, 1H, C_5H_4), 4.20 (m, 2H, C_5H_4), 4.27 (m, 1H, C_5H_4), 5.51 (q, 1H, CH=, *J* 6.6 Hz); for (*E*)-**5b**, δ: 1.19 (d, 6H, Me, *J* 6.75 Hz), 1.70 (d, 3H, Me, *J* 6.62 Hz), 2.75 (m, 1H, CH, *J* 6.75 Hz), 4.03 (s, 5H, C_5H_5), 3.75 (m, 1H, C_5H_4), 4.02 (m, 1H, C_5H_4), 4.18 (m, 1H, C_5H_4), 4.43 (m, 1H, C_5H_4), 5.83 (q, 1H, CH=, *J* 6.62 Hz). Found for (*Z*,*E*)-**5b** (%): C, 71.52; H, 7.65; Fe, 20.98. Calc. for $C_{16}H_{20}Fe$ (%): C, 71.66; H, 7.51; Fe, 20.83.

(*Z*,*E*)-**5c** (2.5:1), R_f = 0.71 (hexane), yield 28.1%, orange oil. ^{1}H NMR for (*Z*)-**5c**, δ: 1.48 (d, 3H, Me, *J* 6.8 Hz), 1.63–2.40 (m, 6H, CH_2), 2.85 (m, 1H, CH), 4.12 (s, 5H, C_5H_5), 4.02 (m, 2H, C_5H_4), 4.16 (m, 2H, C_5H_4), 5.84 (q, 1H, CH=, *J* 6.8 Hz); for (*E*)-**5c**, δ: 1.76 (d, 3H, Me, *J* 7.3 Hz), 1.82–2.40 (m, 6H, CH_2), 2.55 (m, 1H, CH), 4.15 (s, 5H, C_5H_5), 3.86 (m, 2H, C_5H_4), 4.07 (m, 2H, C_5H_4), 5.50 (q, 1H, CH=, *J* 7.3 Hz). Found for (*Z*,*E*)-**5c**, (%): C, 72.74; H, 7.27; Fe, 20.06. Calc. for $C_{17}H_{20}Fe$ (%): C, 72.87; H, 7.19; Fe, 19.94.

[¶] **6a**: yield 8%, violet crystals, mp 67–68 °C. ^{1}H NMR, δ: 1.98 (s, 3H, Me), 4.18 (s, 5H, C_5H_5), 4.25 (m, 2H, C_5H_4), 4.47 (m, 2H, C_5H_4), 5.71 (s, 1H, CH_2), 5.89 (s, 1H, CH_2). Found (%): C, 66.24; H, 5.32; Fe, 22.04. Calc. for $C_{14}H_{14}FeO$ (%): C, 66.17; H, 5.55; Fe, 21.98.

6b: yield 15%, violet crystals, mp 71–72 °C. ^{1}H NMR, δ: 1.74 (s, 3H, Me), 1.96 (s, 3H, Me), 2.05 (s, 3H, Me), 4.23 (s, 5H, C_5H_5), 4.32 (m, 2H, C_5H_4), 4.54 (m, 2H, C_5H_4). Found (%): C, 68.29; H, 6.27; Fe, 19.93. Calc. for $C_{16}H_{18}FeO$ (%): C, 68.11; H, 6.43; Fe, 19.7.

6c: yield 12%, violet crystals, mp 74–75 °C. ^{1}H NMR, δ: 1.93 (s, 3H, Me), 1.98–2.68 (m, 6H, CH_2), 4.21 (s, 5H, C_5H_5), 4.31 (m, 2H, C_5H_4), 4.46 (m, 2H, C_5H_4). Found (%): C, 69.66; H, 6.04; Fe, 18.78. Calc. for $C_{17}H_{18}FeO$ (%): C, 69.41; H, 6.20; Fe, 19.00.

[††] *Synthesis of 3-alkylidene-3-ferrocenylpropynes* **3a**–**c**. *gem*-Dibromoferrocenylcyclopropanes **9a**–**c** (2 mmol) were added to a solution of Bu^{t}OK (0.56 g, 5 mmol) in dry THF (50 ml) with stirring under dry argon at 5–10 °C. Stirring was continued for 2–3 h at room temperature, and then water (50 ml) was added. The organic layer was separated, dried with $CaCl_2$ and concentrated. The residue was chromatographed on a plate with neutral alumina (Brockmann activity III) in hexane.

Thermolysis of 3-alkyl-3-ferrocenylcyclopropenes **1a**–**c**. A solution of 1 mmol of cyclopropenes **1a**–**c** in 50 ml of dry benzene was boiled for 3–5 h until the disappearance of the initial cyclopropenes (TLC, hexane). Following the removal of the solvent, the residue was subjected to preparative TLC on silica gel (hexane).

Reaction of cyclopropenes **1b**,**c** *with 1,3-diphenylisobenzofuran*. A solution of 0.56 g (2 mmol) of DPIBF and of 0.41 g (1.5 mmol) of cyclopropenes **1b**,**c** in 60 ml of dry benzene was refluxed for 5 h (monitoring by TLC on silica gel, as in the previous experiment). Then, the solvent was removed, and TLC on SiO_2 (hexane–benzene, 2:1) was carried out. The following compounds were separated: 1,3-dihydro-1,3-diphenylisobenzofuran **4**,[9] alkenes **5b**,**c**, propynes **3b**,**c**, vinyl ketones **6b**,**c** and Diels–Alder adducts **7b**,**c** (mixture of isomers, 3:1).

Reaction of propyne **3a** *with 1,3-diphenylisobenzofuran*. A mixture of 3-ferrocenylbut-3-ene-1-yne **3a** (0.24 g, 1 mmol) and 1,3-isobenzofuran (0.27 g, 1 mmol) in 50 ml of dry benzene was stirred at room temperature for 10 h. Then, the solvent was removed in a vacuum, and TLC on SiO_2 (hexane–benzene, 2:1) was carried out. The following compounds were separated: *endo*-**2a**, R_f = 0.27, yield 46%, mp 205 °C; *exo*-**2b**, R_f = 0.32, yield 22%, mp 195–196 °C.[9]

[‡‡] **7b**$_1$: R_f = 0.29 (hexane–benzene, 2:1), yield 34%, yellow crystals, mp 226–227 °C. ^{1}H NMR, δ: 0.39 (d, 6H, Me, *J* 6.68 Hz), 2.45 (s, 2H, CH), 2.95 (m, 1H, CH, *J* 6.68 Hz), 4.07 (s, 5H, C_5H_5), 3.91 (s, 4H, C_5H_4), 6.95–7.83 (m, 14H, 3Ar). Found (%): C, 80.42; H, 5.94; Fe, 10.54. Calc. for $C_{36}H_{32}FeO$ (%): C, 80.60; H, 6.01; Fe, 10.41.

7b$_2$: R_f = 0.19 (hexane–benzene, 2:1), yield 10%, yellow crystals, mp 234–235 °C. ^{1}H NMR, δ: 0.42 (d, 6H, Me, *J* 6.7 Hz), 2.40 (s, 2H, CH), 2.72 (m, 1H, CH, *J* 6.7 Hz), 3.97 (s, 5H, C_5H_5), 4.11 (s, 4H, C_5H_4), 7.05–7.81 (m, 14H, 3Ar). Found (%): C, 80.76; H, 6.24; Fe, 10.18. Calc. for $C_{36}H_{32}FeO$ (%): C, 80.60; H, 6.01; Fe, 10.41.

7c$_1$: R_f = 0.32 (hexane–benzene, 2:1), yield 36%, yellow crystals, mp 218–219 °C. ^{1}H NMR, δ: 1.42–2.05 (m, 6H, CH_2), 2.41 (s, 2H, CH), 2.92 (m, 1H, CH), 4.05 (s, 5H, C_5H_5), 4.01 (s, 4H, C_5H_4), 7.00–7.91 (m, 14H, 3Ar). Found (%): C, 80.93; H, 5.65; Fe, 10.23. Calc. for $C_{37}H_{32}FeO$ (%): C, 81.02; H, 5.88; Fe, 10.18.

7c$_2$: R_f = 0.32 (hexane–benzene, 2:1), yield 11%, yellow crystals, mp 231–232 °C. ^{1}H NMR, δ: 1.75–2.35 (m, 6H, CH_2), 2.46 (s, 2H, CH), 3.15 (m, 1H, CH), 4.08 (s, 5H, C_5H_5), 3.94 (m, 2H, C_5H_4), 4.04 (m, 2H, C_5H_4), 7.15–7.76 (m, 14H, 3Ar). Found (%): C, 81.14; H, 5.92; Fe, 10.19. Calc. for $C_{37}H_{32}FeO$ (%): C, 81.02; H, 5.88; Fe, 10.18.

[§§] **9b**: yield 74%, orange crystals, mp 123–124 °C. ^{1}H NMR, δ: 0.98 (d, 3H, Me, *J* 6.8 Hz), 1.15 (d, 3H, Me, *J* 6.8 Hz), 1.75 (d, 1H, CH_2, *J* 7.2 Hz), 2.11 (d, 1H, CH_2, *J* 7.2 Hz), 2.17 (m, 1H, CH), 4.16 (s, 5H, C_5H_5), 4.21 (m, 2H, C_5H_4), 4.25 (m, 2H, C_5H_4). Found (%): C, 44.85; H, 4.34; Fe, 13.70; Br, 37.63. Calc. for $C_{16}H_{18}Br_2Fe$ (%): C, 45.09; H, 4.26; Fe, 13.10; Br, 37.55.

9c: yield 72%, orange crystals, mp 127–128 °C. ^{1}H NMR, δ: 1.56 (s, 1H, CH_2), 1.87 (s, 1H, CH_2), 1.70–2.55 (m, 6H, CH_2), 2.58 (m, 1H, CH), 4.15 (s, 5H, C_5H_5), 3.46 (m, 1H, C_5H_4), 4.03 (m, 1H, C_5H_4), 4.13 (m, 1H, C_5H_4), 4.21 (m, 1H, C_5H_4). Found (%): C, 46.71; H, 4.28; Fe, 12.52; Br, 36.63. Calc. for $C_{17}H_{18}Br_2Fe$ (%): C, 46.60; H, 4.14; Fe, 12.74; Br, 36.52.

Further, we have found that 3-ferrocenyl-4-methylpent-3-en-1-yne **3b** and 3-cyclobutylidene-3-ferrocenylpropyne **3c**, respectively, do not react with DPIBF even on refluxing in *m*-xylene. This is in contrast to the behaviour of 3-ferrocenylbut-3-en-1-yne **3a**,‡ which gave a Diels–Alder adduct as a mixture of *endo*- and *exo*-isomers (**2a**:**2b** ~ 2:1) in an almost quantitative yield.[9]

α-Ferrocenylvinylacetylenes **3a**–**c** readily add water upon dissolution in wet solvents and upon chromatographing on alumina (Brockmann activity III). When stored under ordinary conditions, they undergo rapid polymerization and resinification.

References

1 W. M. Horspool, R. G. Sutherland and B. J. Thomson, *J. Chem. Soc. (C)*, 1971, 1554.

2 W. M. Horspool, R. G. Sutherland and B. J. Thomson, *J. Chem. Soc. (C)*, 1971, 1558.

3 W. M. Horspool, R. G. Sutherland and B. J. Thomson, *J. Chem. Soc. (C)*, 1971, 1563.

4 E. I. Klimova, N. N. Meleshonkova, T. B. Klimova, M. G. Martinez and C. T. Alvarez, *Mendeleev Commun*., 1997, 242.

5 A. J. Fray, P. S. Jain and R. L. Krieger, *J. Organomet. Chem*., 1981, **214**, 381.

6 A. J. Fray, R. L. Krieger, I. Agranat and E. Aharon-Shalom, *Tetrahedron Lett*., 1976, **32**, 4803.

7 E. I. Klimova, T. B. Klimova, L. Ruiz Ramirez, M. G. Martinez, C. T. Alvarez, P. G. Espinova and A R. Toscano, *J. Organomet. Chem*., 1997, **545**, 191.

8 E. I. Klimova, M. G. Martinez, T. B. Klimova, C. T. Alvarez, Ar R. Toscano, R. Moreno Esparza and L. Ruiz Ramirez, *J. Organomet. Chem*., 1998, **566**, 175.

9 E. I. Klimova, L. Ruiz Ramirez, T. B. Klimova, M. G. Martinez, N. N. Meleshonkova and A. V. Churakov, *J. Organomet. Chem*., 1998, **559**, 1.

10 T. C. Shields and W. E. Billups, *Chem. Ind.*, 1967, **25**, 1999.

11 T. C. Shields, W. E. Billups and A. N. Kurtz, *Angew. Chem., Int. Ed. Engl*., 1968, **7**, 209.

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