

-Ferrocenylnylacetylenes

Elena I. Klimova,^{*a} Marcos Martinez Garcia,^b Tatiana Klimova,^a Lena Ruiz Ramirez^a and Jose Manuel Mendez Stivalet^a

^a Department of Chemistry, National Autonomous University of Mexico, CP 04510 Mexico DF, Mexico.

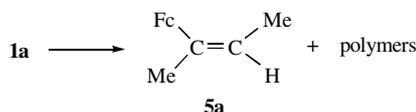
Fax: +5 25 622 5366; e-mail: klimova@servidor.unam.mx

^b Institute of Chemistry, National Autonomous University of Mexico, CP 04510 Mexico DF, Mexico. Fax: +525 616 2203

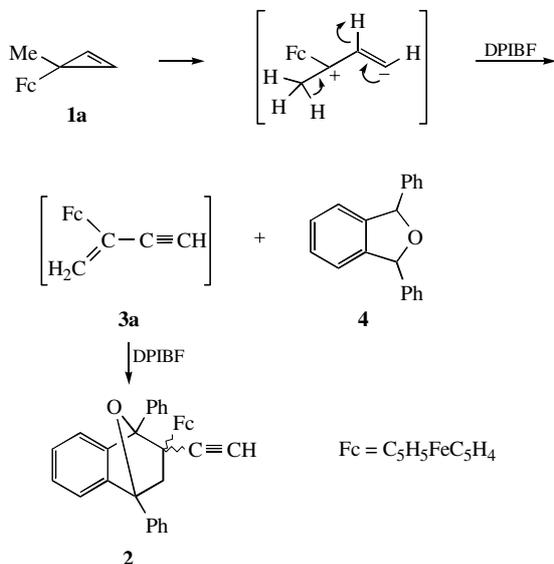
Thermolysis of 3-isopropyl- and 3-cyclobutyl-3-ferrocenylcyclopropanes results in the formation of 3-alkylidene-3-ferrocenylpropynes and (*Z,E*)-1-alkyl-1-ferrocenylpropenes; 2,2-dibromo-1-methyl-, 2,2-dibromo-1-isopropyl- and 2,2-dibromo-1-cyclobutylferrocenylcyclopropanes are converted into ferrocenylnylacetylenes 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 Na₂CO₃ 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 -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 Na₂CO₃. The



absence of other data on the chemical properties of ferrocenylnylacetylenes 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 these compounds by thermolysis of 3-alkyl-3-ferrocenylcyclopropanes 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 ¹³C 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 **7b₁** and **7b₂** or **7c₁** and **7c₂** (~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 (**7b₁,c₁**). 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

[†] *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, CDCl₃) δ: 0.79 (d, 6H, Me, *J* 6.73 Hz), 2.41 (m, 1H, CH, *J* 6.73 Hz), 4.12 (s, 5H, C₅H₅), 4.02 (s, 4H, C₅H₄), 6.95 (s, 2H, CH=). ¹³C NMR (hereinafter, CDCl₃) δ: 20.70 (Me), 29.91 (CH), 34.90 (C), 66.95 (C₅H₄), 68.01 (C₅H₅), 98.73 (C_{ipso}Fc), 110.59 (CH=). Found (%): C, 72.29; H, 7.03; Fe, 21.08. Calc. for C₁₆H₁₈Fe (%): C, 72.21; H, 6.81; Fe, 20.98.

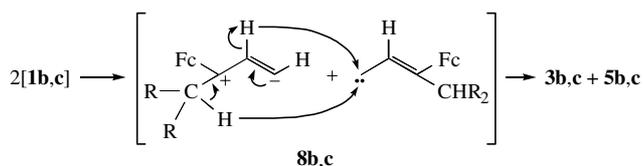
1c: yield 52%, orange crystals, mp 66 °C. ¹H NMR, δ: 1.60–2.25 (m, 6H, CH₂), 2.85 (m, 1H, CH), 4.11 (s, 5H, C₅H₅), 3.97 (m, 2H, C₅H₄), 4.02 (m, 2H, C₅H₄), 7.05 (d, 2H, CH=, *J* 0.8 Hz). ¹³C NMR, δ: 14.67, 16.97 (CH₂), 29.99 (CH), 33.98 (C), 66.91 (C₅H₄), 68.00 (C₅H₅), 98.65 (C_{ipso}Fc), 109.93 (CH=). Found (%): C, 73.56; H, 6.38; Fe, 20.14. Calc. for C₁₇H₁₈Fe (%): 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, C₅H₅), 4.24 (m, 2H, C₅H₄), 4.51 (m, 2H, C₅H₄), 5.47 (d, 1H, CH₂, *J* 0.9 Hz), 5.60 (d, 1H, CH₂, *J* 0.9 Hz). ¹³C NMR, δ: 66.67, 69.09 (C₅H₄), 69.65 (C₅H₅), 76.51 (CH=), 82.93 (C_{ipso}Fc), 89.97 (C=), 118.15 (CH₂=), 128.42 (C). Found (%): C, 71.33; H, 4.99; Fe, 23.54. Calc. for C₁₄H₁₂Fe (%): 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, C₅H₅), 4.15 (m, 2H, C₅H₄), 4.19 (m, 2H, C₅H₄). Found (%): C, 72.87; H, 6.03; Fe, 21.19. Calc. for C₁₆H₁₆Fe (%): C, 72.75; H, 6.11; Fe, 21.14.

3c: yield 53%, orange oil. ¹H NMR, δ: 1.81–2.53 (m, 6H, CH₂), 3.01 (s, 1H, CH=), 4.14 (s, 5H, C₅H₅), 4.18 (m, 2H, C₅H₄), 4.29 (m, 2H, C₅H₄). Found (%): C, 73.85; H, 6.05; Fe, 20.07. Calc. for C₁₇H₁₆Fe (%): 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:



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**

§ **5a**: yield 28%, orange oil. ¹H NMR, δ: 1.44 (d, 3H, Me, *J* 6.67 Hz), 1.78 (s, 3H, Me), 4.06 (s, 5H, C₅H₅), 4.01 (m, 2H, C₃H₄), 4.23 (m, 2H, C₃H₄), 5.52 (q, 1H, CH=, *J* 6.67 Hz). Found (%): C, 69.87; H, 6.93; Fe, 23.41. Calc. for C₁₄H₁₆Fe (%): C, 70.02; H, 6.72; Fe, 23.26.

(*Z,E*)-**5b** (2:1), *R*_f = 0.75 (hexane), yield 30.5%, orange oil. ¹H 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, C₅H₅), 4.00 (m, 1H, C₃H₄), 4.20 (m, 2H, C₃H₄), 4.27 (m, 1H, C₃H₄), 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, C₅H₅), 3.75 (m, 1H, C₃H₄), 4.02 (m, 1H, C₃H₄), 4.18 (m, 1H, C₃H₄), 4.43 (m, 1H, C₃H₄), 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 C₁₆H₂₀Fe (%): 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. ¹H NMR for (*Z*)-**5c**, δ: 1.48 (d, 3H, Me, *J* 6.8 Hz), 1.63–2.40 (m, 6H, CH₂), 2.85 (m, 1H, CH), 4.12 (s, 5H, C₅H₅), 4.02 (m, 2H, C₃H₄), 4.16 (m, 2H, C₃H₄), 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, CH₂), 2.55 (m, 1H, CH), 4.15 (s, 5H, C₅H₅), 3.86 (m, 2H, C₃H₄), 4.07 (m, 2H, C₃H₄), 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 C₁₇H₂₀Fe (%): C, 72.87; H, 7.19; Fe, 19.94.

¶ **6a**: yield 8%, violet crystals, mp 67–68 °C. ¹H NMR, δ: 1.98 (s, 3H, Me), 4.18 (s, 5H, C₅H₅), 4.25 (m, 2H, C₃H₄), 4.47 (m, 2H, C₃H₄), 5.71 (s, 1H, CH₂), 5.89 (s, 1H, CH₂). Found (%): C, 66.24; H, 5.32; Fe, 22.04. Calc. for C₁₄H₁₄FeO (%): C, 66.17; H, 5.55; Fe, 21.98.

6b: yield 15%, violet crystals, mp 71–72 °C. ¹H NMR, δ: 1.74 (s, 3H, Me), 1.96 (s, 3H, Me), 2.05 (s, 3H, Me), 4.23 (s, 5H, C₅H₅), 4.32 (m, 2H, C₃H₄), 4.54 (m, 2H, C₃H₄). Found (%): C, 68.29; H, 6.27; Fe, 19.93. Calc. for C₁₆H₁₈FeO (%): C, 68.11; H, 6.43; Fe, 19.7.

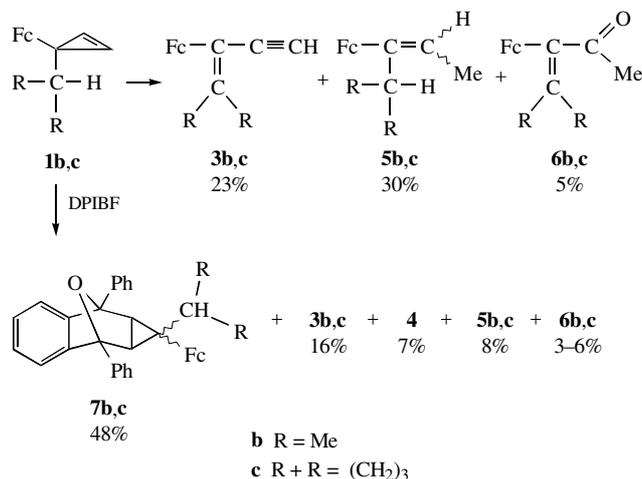
6c: yield 12%, violet crystals, mp 74–75 °C. ¹H NMR, δ: 1.93 (s, 3H, Me), 1.98–2.68 (m, 6H, CH₂), 4.21 (s, 5H, C₅H₅), 4.31 (m, 2H, C₃H₄), 4.46 (m, 2H, C₃H₄). Found (%): C, 69.66; H, 6.04; Fe, 18.78. Calc. for C₁₇H₁₈FeO (%): C, 69.41; H, 6.20; Fe, 19.00.

¶ *Synthesis of 3-alkylidene-3-ferrocenylpropynes 3a-c.* *gem*-Dibromoferrrocenylcyclopropanes **9a-c** (2 mmol) were added to a solution of Bu^tOK (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 CaCl₂ 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).

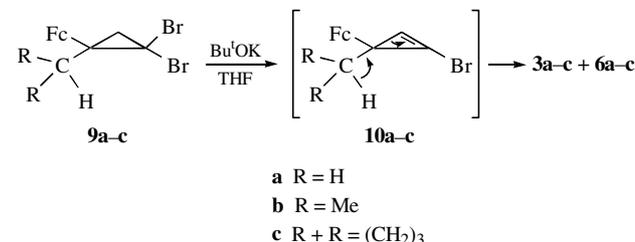
Reaction of cyclopropenes 1b,c with 1,3-diphenylisobenzofuran. A solution of 0.56 g (2 mmol) of DPIBF and of 0.41 g (1.5 mmol) of cyclopropenes **1b,c** in 60 ml of dry benzene was refluxed for 5 h (monitoring by TLC on silica gel, as in the previous experiment). Then, the solvent was removed, and TLC on SiO₂ (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 SiO₂ (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



and in the generation of enynes **3a-c**.

Further, we have found that Bu^tOK in THF, unlike Bu^tOK in DMSO,^{4,10,11} is a convenient reagent¹ for the preparation of ferrocenylvinylacetylenes from corresponding *gem*-dibromocyclopropenes **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:



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.

¶ **7b**: *R*_f = 0.29 (hexane–benzene, 2:1), yield 34%, yellow crystals, mp 226–227 °C. ¹H 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, C₅H₅), 3.91 (s, 4H, C₅H₄), 6.95–7.83 (m, 14H, 3Ar). Found (%): C, 80.42; H, 5.94; Fe, 10.54. Calc. for C₃₆H₃₂FeO (%): C, 80.60; H, 6.01; Fe, 10.41.

7b: *R*_f = 0.19 (hexane–benzene, 2:1), yield 10%, yellow crystals, mp 234–235 °C. ¹H 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, C₅H₅), 4.11 (s, 4H, C₅H₄), 7.05–7.81 (m, 14H, 3Ar). Found (%): C, 80.76; H, 6.24; Fe, 10.18. Calc. for C₃₆H₃₂FeO (%): C, 80.60; H, 6.01; Fe, 10.41.

7c: *R*_f = 0.32 (hexane–benzene, 2:1), yield 36%, yellow crystals, mp 218–219 °C. ¹H NMR, δ: 1.42–2.05 (m, 6H, CH₂), 2.41 (s, 2H, CH), 2.92 (m, 1H, CH), 4.05 (s, 5H, C₅H₅), 4.01 (s, 4H, C₅H₄), 7.00–7.91 (m, 14H, 3Ar). Found (%): C, 80.93; H, 5.65; Fe, 10.23. Calc. for C₃₇H₃₂FeO (%): C, 81.02; H, 5.88; Fe, 10.18.

7c: *R*_f = 0.32 (hexane–benzene, 2:1), yield 11%, yellow crystals, mp 231–232 °C. ¹H NMR, δ: 1.75–2.35 (m, 6H, CH₂), 2.46 (s, 2H, CH), 3.15 (m, 1H, CH), 4.08 (s, 5H, C₅H₅), 3.94 (m, 2H, C₅H₄), 4.04 (m, 2H, C₅H₄), 7.15–7.76 (m, 14H, 3Ar). Found (%): C, 81.14; H, 5.92; Fe, 10.19. Calc. for C₃₇H₃₂FeO (%): C, 81.02; H, 5.88; Fe, 10.18.

§§ **9b**: yield 74%, orange crystals, mp 123–124 °C. ¹H NMR, δ: 0.98 (d, 3H, Me, *J* 6.8 Hz), 1.15 (d, 3H, Me, *J* 6.8 Hz), 1.75 (d, 1H, CH₂, *J* 7.2 Hz), 2.11 (d, 1H, CH₂, *J* 7.2 Hz), 2.17 (m, 1H, CH), 4.16 (s, 5H, C₅H₅), 4.21 (m, 2H, C₃H₄), 4.25 (m, 2H, C₃H₄). Found (%): C, 44.85; H, 4.34; Fe, 13.70; Br, 37.63. Calc. for C₁₆H₁₈Br₂Fe (%): C, 45.09; H, 4.26; Fe, 13.10; Br, 37.55.

9c: yield 72%, orange crystals, mp 127–128 °C. ¹H NMR, δ: 1.56 (s, 1H, CH₂), 1.87 (s, 1H, CH₂), 1.70–2.55 (m, 6H, CH₂), 2.58 (m, 1H, CH), 4.15 (s, 5H, C₅H₅), 3.46 (m, 1H, C₅H₄), 4.03 (m, 1H, C₅H₄), 4.13 (m, 1H, C₅H₄), 4.21 (m, 1H, C₅H₄). Found (%): C, 46.71; H, 4.28; Fe, 12.52; Br, 36.63. Calc. for C₁₇H₁₈Br₂Fe (%): 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-ferrocenyl-but-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

-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. Agrat 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.

Received: 2nd June 1999; Com. 99/1509