Journal of Organometallic Chemistry, 179 (1979) 197—204

ELECTRON-RICH HEPTAFULVENEIRON TRICARBONYL COMPLEXES. SYNTHESIS AND REACTIONS OF 8-ALKOXYHEPTAFULVENE—$Fe(CO)_3$ DERIVATIVES

ZEEV GOLDSCHMIDT * and YITZHAK BAKAL

Department of Chemistry, Bar-Ilan University, Ramat Gan (Israel)

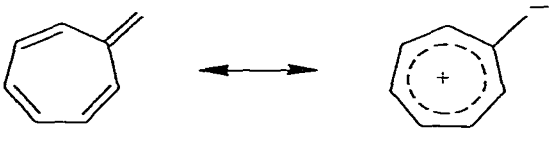
(Received April 30th, 1979)

Summary

The synthesis of a series of stable 8-alkoxyheptafulvene—$Fe(CO)_3$ complexes V, VI and VIII from the appropriate acycloheptatriene—$Fe(CO)_3$ complexes is described. Tetracyanoethylene cycloadds to complexes V and VIII in a 8 + 2 manner, giving X and XI respectively. Oxidation of X with cerium(IV) gives the tetrahydroazulene complex XIV. Similarly, *N*-phenyltriazolinedione reacts with V affording the imidoacetal adduct XII, which is readily hydrolyzed to form the water soluble imidoaldehyde complex XIII. ^{13}C NMR studies indicate that the exocyclic double bond has no significant polar character.

Introduction

The contribution of the dipolar resonance form of heptafulvene (Ib) to its ground state stability has been frequently challenged in recent years [1]. Despite spectroscopic and theoretical [1,2] indications that heptafulvene (I) should be a planar and stable molecule, it has been found experimentally to be a very labile compound [3]. Moreover, ^{13}C NMR studies of the charge distribution in 8-substituted heptafulvenes as reflected by the difference in the chemical shift of the exocyclic double bond carbons, indicated only a small contribution of a polar structure [4—6]. This conclusion was supported by the successful synthesis [7] of a series of thermally labile heptafulvenes bearing electron-donating groups at the 8-position. These heptafulvenes again did not show any extraordinary polarity of the exocyclic double bond in the ^{13}C NMR spectrum [7].



(Ia) (Ib)

TABLE 1

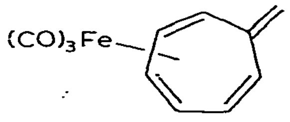
^{13}C NMR SPECTRA OF IRON TRICARBONYL COMPLEXES OF 8-METHOXYHEPTAFULVENES AND CYCLOHEPTATRIENES

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	Ligand		Δ(87)	δΔ
									CO	OMe		
Vc [a]	56.2	85.9	90.4	58.6	124.2	122.5	118.0	148.2	211.8	60.5	30.2	3.6
Vt [a]	64.0	85.3	91.1	57.9	127.5	116.9	116.7	145.3	211.8	60.4	28.6	1.7
							(113.9) [b]	(140.5)			(26.6)	
J_{CH}(Hz)	151	170	170	155	158	159	—	179	—	144		
multiplicity [c]	t	d	d	d	d	d	s	d	s	q		
VIIIc [a,d]	57.4	86.9	91.1	58.6	126.5	122.0	119.0	129.9	209.1	62.7	10.9	1.4
							(115.0) [b]	(124.5)			(9.5)	
XIII [e,h]	57.2*	53.5	92.2	99.4	58.5*	161.7	132.4**	191.5	209.9			
IV [f]	26.9	53.9	89.2	94.6	60.4	154.0	136.9	192.3	209.7			
CH_2=CHOMe	153.2 [g]	84.1										

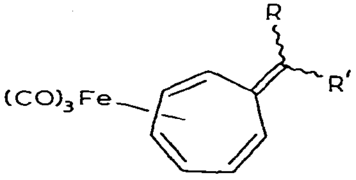
[a] $CDCl_3$, δ ppm from TMS. [b] Calculated from methyl vinyl ether. [c] s, singlet; d, doublet; t, triplet; q, quartet. [d] Aromatic signals at δ 128.2, 128.6, 130.2, 134.2 ppm [e] Acetone-d_6; aromatic signals at δ 126.7, 128.5, 129.6, 133.4** ppm; triazolidinedione carbonyls at δ 154.2, 155.0 ppm. [f] Ref. 16. [g] Ref. 19. [h] Asterisk(s) indicate that alternative assignments are possible.

Stabilization of heptafulvenes has been achieved with either electron-withdrawing substituents at the 8-position [1] or by transition metal complexation [8—12]. The parent iron tricarbonyl complex II, apparently a non-planar molecule [13], readily dimerizes [14,15]. Other alkyl and aryl derivatives are thermally stable [8—11]. It was thus interesting to attempt the synthesis of heptafulvene complexes with reversed electron demand [12].

This paper relates the simple access to 8-alkoxyheptafulvene—$Fe(CO)_3$ complexes III and describes some of their properties and reactions.



(II)

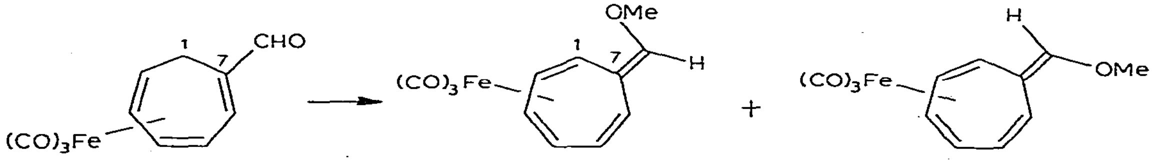


(III)

(R = H, Ph ;
R' = OMe, OEt)

Results and discussion

Aldehyde IV [16] readily reacts at room temperature with trimethylorthoformate in methanol containing a catalytic amount of HCl to give an air sensitive oil consisting of a mixture of the two isomers of 8-methoxyheptafulvene—$Fe(CO)_3$, Vc and Vt, in 60% yield. The isomers could not be separated. They decomposed during attempted distillation and were best kept in solution under N_2.



(IV) (Vc) (Vt)

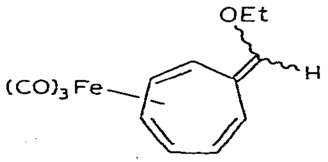
The ^1H NMR spectrum of V (in $CDCl_3$) resembles that of previously prepared heptafulvene complexes. It is characterized by a pair of methoxy singlets for Vc and Vt at δ 3.70 and 3.64 ppm, respectively, in ca. 1/3 ratio. In addition, there appear signals at δ 3.22 (H(4)), 3.7 (H(1) of Vt), 4.22 (H(1) of Vc), 5.1—6.0 (H(2), H(3), H(5), H(6)), 6.19 (H(8) of Vc) and 6.24 (H(8) of Vt) ppm. Both mass and IR spectra confirmed the presence of iron tricarbonyl group. The absence of a carbonyl band in the 1680 cm^{-1} region confirmed the structural assignment.

The ^{13}C NMR spectra of V (in $CDCl_3$) was of particular analytical value. In addition to a typical ligand carbonyl signal at δ 211.8 ppm it displayed two sets of nine distinct carbon signals. A careful analysis of both coupled and uncoupled spectra led to the assignment summarized in Table 1. The *cis-trans* configuration around the C(7)—C(8) double bond was assigned by comparison with the ^1H and ^{13}C NMR spectra of 6-substituted pentafulvenes [17]. The key to the isomeric identification in the proton NMR spectrum was the paramagnetic shift of H(1) of the major isomer, expected for a *cis* configuration (Vc), due to intramolecular Van der Waals repulsion. This assignment is confirmed by the observed diamagnetic shift of C(1) in the ^{13}C spectrum caused by steric interaction [17].

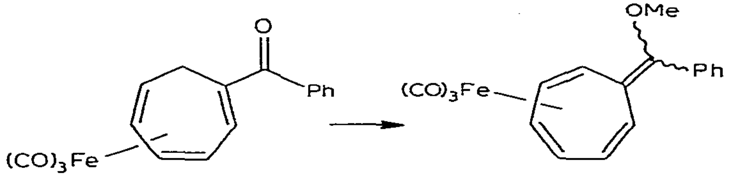
The assessment of the extra polar character of the heptafulvene complexes is based on the constitutive additivity method of Savitzki and Namikava [18], which has been applied to free fulvenes [17,4]. In this way the chemical shifts of the exocyclic double bond carbons (C(7) and C(8) in heptafulvenes) are calculated by summing up the estimated constitutive bond parameters. The difference between the calculated and experimental values ($\delta\Delta$ in Table 1) measures the extent of excess polarity.

Thus, for the constitutive bond parameter of the $=CH-OCH_3$ group a value of —19.2 ppm (with respect to 128.5 ppm for benzene) is calculated using the experimental chemical shifts for methyl vinyl ether [19]. This leads to calculated values of 113.9 and 140.5 ppm (from TMS) for C_7 and C_8 of 8-methoxyheptafulvenes respectively. As seen for the $\delta\Delta$ values of Table 1, the deviations are of the order of only 2.2—5.5%. Clearly, it can be concluded that complexes V and VIII, like other fulvenes [4—7,17], lack substantial aromatic character.

That the fulvenation reaction involved in the transformation of IV to V is a general process has been demonstrated by two additional examples: (a) aldehyde IV reacts with triethylorthoformate in acidic ethanol to give VI; and (b) benzoylcycloheptatriene complex VII [16], afforded the heptafulvene complex VIII with trimethylorthoformate in acidic methanol. The spectroscopic characteristics of VI and VIII are similar to that of V (see Experimental). ^{13}C NMR data for the major isomer VIIIc (*cis*) are included in Table 1.

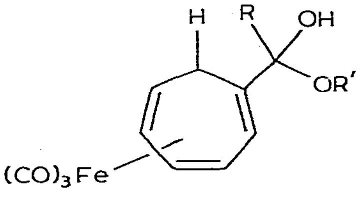


(VI)



(VII) (VIII)

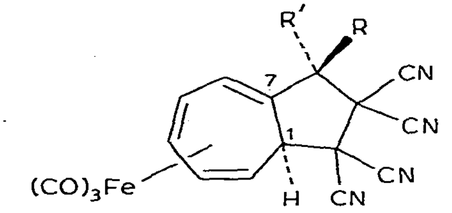
A reasonable mechanism for the formation of heptafulvene complexes involves the intermediate production of the corresponding hemiacetals IX followed by a formal 1,8 acid-catalyzed dehydration. Analogous dehydrations of cycloheptatriene—$Fe(CO)_3$ carbinols were previously utilized for the synthesis of heptafulvene complexes [8,9].



(IX) (R = H, Ph;
R' = Me, Et)

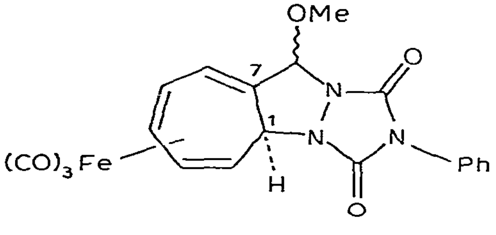
Cycloaddition reactions

Heptafulvenes [3,6], as well as their iron tricarbonyl complexes [11,20], generally undergo periselective 8 + 2 cycloadditions with strong dienophiles, forming the condensed azulene skeleton. 8-Alkoxyheptafulvene complexes are no exception. Thus, tetracyanoethylene (TCNE) readily cycloadds to V affording the unseparated isomeric mixture of X in a *cis-trans* ratio of ca. 4/5. This ratio, which does not correspond to the *cis-trans* ratio found in the substrate V, suggests a mechanism involving a nonconcerted cycloaddition. The analytical and spectroscopic data are consistent with the structural assignment. In particular, the ^{1}H NMR spectrum displays characteristic signals of the cycloheptatriene vinylic protons at δ 2.97 (m, H(2), H(5)), 5.74 (m, H(3), H(4)) and 6.33 (ddd, H(1), *J* 8, 2, 2 Hz) ppm. The other resonances occur for the *trans* (major) isomer at δ 3.46 (s, OMe) 3.9 (m, H(1)) and 4.62 (bs, H(8)) ppm and for the *cis* (minor) isomer at 3.68 (s, OMe and H(1)) and 4.33 (s, H(8)) ppm. Similarly, cycloaddition of VIII with TCNE afforded adduct XI.

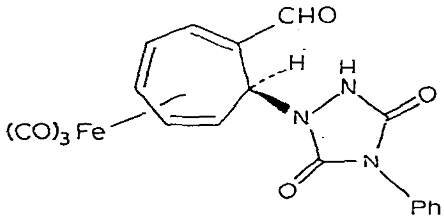


(Xc R = H, R' = OMe;
Xt R = OMe, R' = H;
XIc R = Ph, R' = OMe;
XIt R = OMe, R' = Ph)

N-Phenyltriazolinedione (NPTD) [21], reacts as expected with V to give adduct XII. This is an interesting imidoacetal (at C(8)), which is very readily hydrolysed to give a water soluble imino-aldehyde XIII. The structure of XIII was inferred from its elemental analysis and IR spectrum (1685 cm^{-1}). The ^{1}H NMR of XIII closely resembles that of IV except for the absence of the *trans*-proton absorption at C(7) and a paramagnetic shift of the *cis*-proton resonance to δ 5.44 ppm (d, *J* = 5 Hz). The ^{13}C NMR spectrum of XIII is also conclusive, especially when compared to the corresponding aldehyde complex IV (Table 1).



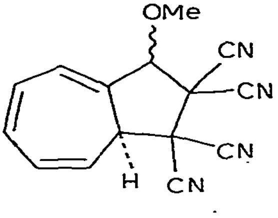
(XII)



(XIII)

Finally we attempted to release the organic ligand from its complex. Oxidation of X with cerium(IV) gave a low yield of an oily product whose analytical and spectroscopical data matched that of structure XIV.

In summary, a novel one step synthesis of 8-alkoxyheptafulvene—Fe(CO)$_3$ from the corresponding acylcycloheptatriene complexes has been demonstrated. The fulvenes thus obtained undergo a regiospecific 8 + 2 cycloaddition with dienophiles. Oxidation can eventually lead to the tetrahydroazulene system. The ^{13}C NMR spectrum of the complexes reveals that these heptafulvenes form a group of cross-conjugated olefins which show no extraordinary polarization.



(XIV)

Experimental

General

^1H and ^{13}C NMR spectra were recorded on Varian HA-100 spectrometer and Varian CFT-20 instruments, using TMS as internal standard. IR spectra were measured with a Perkin—Elmer 257 spectrometer. Mass spectra were determined with a Hitachi Perkin—Elmer RMU-6 spectrometer at an ionizing energy of 70 eV. All the reactions were conducted under nitrogen.

8-Methoxyheptafulveneiron tricarbonyl (V). To a solution of 500 mg (1.82 mmol) of aldehyde complex IV in absolute methanol [22] was added 0.7 cm^3 of trimethylorthoformate and two drops of concentrated HCl. The solution was kept at room temperature for 24 h, H_2O (200 cm^3) was added, and the mixture extracted with ether (3 X 25 cm^3). The combined ethereal solution was washed with 5% aq. Na_2CO_3 then H_2O, and dried over $MgSO_4$. Removal of the solvent left a yellow oil which was chromatographed on silica gel. Elution with hexane afforded 300 mg (58% yield) of an uncrystallizable oil which decomposed readily if not kept in solution under N_2. IR (neat) 2040, 1980, 1965, 1955 cm^{-1}; *m/e* 274 (M^+), 246, 218, 190. ^1H NMR ($CDCl_3$) shows a 3/1 mixture of Vc/Vt. δ 3.22 (m, H(4)), 5.1—6.0 (H(2), H(3), H(5), H(6)) ppm. Additional signals for Vc at δ 3.7 (s, OMe), 4.22 (bd, H(1) *J* 8 Hz), 6.19 (s, H(8)) ppm. Vt: δ 3.64 (s, OMe, ~3.7 (H(1), hidden under OMe signal), 6.24 (s, H(8)) ppm. For ^{13}C NMR see Table 1.

8-Ethoxyheptafulveneiron tricarbonyl (VI) was similarly obtained in 50% yield from IV and triethylorthoformate. ^1H NMR ($CDCl_3$) δ 1.37 (m, 3H, CH_3CH_2), 3.15 (m, 1H(4)), 3.5—4.3 (m, H(1), CH_2CH_3), 5.0—6.0 (m, H(2), H(3), H(5), H(6)), 6.18 (bs, H(8)) ppm.

8-Methoxy-8-phenylheptafulveneiron tricarbonyl (VIII) was similarly obtained in 60% yield from ketone VII and trimethylorthoformate. IR (Nujol) 2040, 1970, 1965 cm^{-1}; *m/e* 274 (M^+), 246, 218, 190. ^1H NMR ($CDCl_3$) a 4/1 mixture of VIIIc/VIIIt. δ 3.10 (m, H(4)), 5.2—5.8 (m, H(2), H(3), H(5), H(6)) ppm. Additional signals for VIIIc: δ 3.43 (s, OMe), 4.66 (m, H(1)) ppm. VIIIt: δ 3.32 (s, OMe), 3.86 (bd, H(1), *J* 8 Hz) ppm. ^{13}C NMR see Table 1.

Reaction with TCNE

General Procedure: Adducts were obtained by keeping a mixture of equimolar amounts of freshly sublimed TCNE and the corresponding fulvene complex in CH_2Cl_2 for 1 h at room temperature. Removal of solvent under reduced pressure and recrystallization from CH_2Cl_2/hexane gave the product.

Adduct X was obtained as a 4/5 mixture of *cis*/*trans* in 62% yield; m.p. 128°C (dec.). IR (Nujol) 2055, 2005, 1998 cm^{-1}; *m/e* 274 (*M* — TCNE), 246, 218, 190. Anal.: Found: C, 53.67; H, 2.36; N, 14.08. $C_{18}H_{10}FeN_4O_4$ calcd.: C, 53.73; H, 2.49; N, 13.93%. ^1H NMR ($CDCl_3$) δ 2.97 (m, H(2), H(5)), 5.74 (m, H(3), H(4)), 6.33 (ddd, H(6), *J* 8, 2, 2 Hz) ppm. Additional signals for Xt (major): δ 3.46 (s, OMe), 3.90 (m, H(1)), 4.62 (bs, H(8)) ppm. Xc (minor): δ 3.68 (s, OMe and H(1)), 4.33 (s, H(8)) ppm.

Adduct XI was similarly obtained in 26% yield; m.p. 146°C (dec.). IR (Nujol): 2068, 2003, 1995 cm^{-1}; *m/e* 350 (*M* — TCNE), 322, 294, 266; Anal.: Found: C, 60.10; H, 3.00; N, 11.64. $C_{24}H_{14}FeN_4O_4$ calcd.: C, 60.25; H, 2.93; N, 11.70%. ^1H NMR (acetone-d_6) δ 3.16 (s, OMe), 3.26 (m, H(5)), 3.45 (m, H(2)), 4.43 (m, H(1)), 6.08 (m, H(3), H(4)), 6.38 (dd, H(6), *J* 8, 3 Hz), 7.56 (m, 5H aromatic) ppm.

Adduct XII (The reaction of V with NPTD). A solution of V (274 mg, 1 mmol) in 10 cm^3 of CH_2Cl_2 was titrated with a CH_2Cl_2 solution of NPTD at —78°C. After stirring for 1 h the solvent was removed and the residual oil crystallized from CH_2Cl_2/hexane to give 112 mg of yellow crystals (25% yield), m.p. 125°C (dec.). IR (Nujol): 2040, 2005, 1770, 1710 cm^{-1}; *m/e* 274 (*M* — NPTD), 246, 218, 190, 134. Anal.: Found: C, 53.35; H, 3.43; N, 9.31. $C_{20}H_{15}FeN_3O_6$ calcd.: C, 53.45; H, 3.34; N, 9.13%. ^1H NMR ($CDCl_3$) δ 2.64 (t, H(5), *J* 7 Hz), 3.34 (s, OMe), 3.54 (m, H(2)), 5.06 (s, H(8)), 5.14 (m, H(1)), 5.66 (m, H(3), H(4)), 5.98 (dd, H(6), *J* 7, 2 Hz) 7.4 (m, 5H aromatic) ppm.

Aldehyde XIII (hydrolysis of XII). A CH_2Cl_2 solution of adduct XII (200 mg, 0.45 mmol) was absorbed on a silica gel column (50 g) and left for 24 h. Elution with ethyl acetate afforded 170 mg (85% yield) of yellow crystals, m.p. 175°C (dec.) from acetone/hexane. IR (Nujol): 2055, 1995, 1980, 1760, 1685 cm^{-1}; *m/e* 232 (*M* — NPTD — CO), 204, 176, 120. Anal.: Found: C, 52.34; H, 2.75; N, 9.71. $C_{19}H_{13}FeN_3O_6$ calcd.: C, 52.41; H, 2.98; N, 9.65%. ^1H NMR (acetone-d_6): δ 3.26 (m, H(2), H(5)), 5.44 (d, H(1), *J* 5 Hz), 6.18 (m, H(3), H(4)), 7.4 (m, H(6), 5H aromatic), 9.10 (s, H(8)) ppm. ^{13}C NMR see Table 1.

Oxidative decomplexation of adduct X (XIV). To a solution of 402 mg (1 mmol) of X in acetonitrile (50 cm^3) a solution of 1.75 g (3.2 mmol) cerium ammonium nitrate in acetonitrile (50 cm^3) was added dropwise at 0°C. The solution was stirred for 1 h, diluted with H_2O (500 cm^3), and extracted with CH_2Cl_2 (4 × 30 cm^3). The combined extracts were washed with H_2O and dried over $MgSO_4$. Removal of solvent and chromatography on silica gel (hexane elution) gave 170 mg (64% yield) of colorless oil which showed no IR signals between 2100—1900 cm^{-1}. *m/e* 262 (M^+), 134, 128, 119. Anal.: Found: C, 68.56; H, 3.84; N, 21.18. $C_{15}H_{10}N_4O$ calcd.: C, 68.7; H, 3.81; N, 21.37%. ^1H NMR ($CDCl_3$) δ 6.26—6.86 (H(3), H(4), H(5), H(6)). Additional signals for XIV-*trans* (major): δ 3.22 (m, H(1)), 3.54 (s, OMe), 4.98 (s, H(8)), 5.58 (dd, H(2), *J* 10, 4 Hz) ppm. XIV *cis* (minor): δ 3.49 (m, H(1)), 3.77 (m, OMe), 4.92 (bs, H(8)), 5.47 (dd, H(2), *J* 10, 4 Hz) ppm.

References

1 D.J. Bertelli, Top. Nonbenzenoid Aromat. Chem., 1 (1973) 29.
2 R. Thomas and P. Coppens, Acta Cryst., B, 28 (1972) 1800; A. Bauder, C. Keller and M. Neuenschwander, J. Mol. Spectrosc., 63 (1976) 281; J. Aihara, J. Amer. Chem. Soc., 98 (1976) 2750.
3 W. von E. Doering and D.W. Wiley, Tetrahedron, 11 (1960) 163; H.E. Zimmerman and L.R. Sousa, J. Amer. Chem. Soc., 94 (1972) 834.
4 R. Hollenstein, A. Mooser, M. Neuenschwander and W. von Philipsborn, Angew. Chem. Int. Ed. Eng., 13 (1974) 551.
5 L. Knothe and H. Prinzbach, Justus Liebigs Ann. Chem., (1977) 687.
6 K. Kamatzu, M. Fujimori and K. Okamoto, Tetrahedron, 33 (1977) 2791.
7 K.M. Rapp and J. Daub, Tetrahedron Lett., (1976) 2011; (1977) 227; K.M. Rapp, T. Burgemeister and J. Daub, Tetrahedron Lett., (1978) 2685.
8 B.F.G. Johnson, J. Lewis, P. McArdle and G.L.P. Randall, J. Chem. Soc. Chem. Commun., (1971) 177; J.A.S. Howell, B.F.G. Johnson, P.L. Josty and J. Lewis, J. Organometal. Chem., 39 (1972) 329.
9 B.F.G. Johnson, J. Lewis, P. McArdle and G.L.P. Randall, J. Chem. Soc. Dalton, (1972) 2076.
10 Z. Goldschmidt and S. Antebi, Tetrahedron Lett., (1978) 1225.
11 Z. Goldschmidt and Y. Bakal, J. Organometal. Chem., 168 (1979) 215.
12 R. Gompper and W. Reiser, Tetrahedron Lett., (1976) 1263.
13 Cf. R.P. Dodge, J. Amer. Chem. Soc., 86 (1964) 5429.
14 G.T. Rodeheaver, G.C. Farrant and D.F. Hunt, J. Organometal. Chem., 30 (1971) C22.
15 A. Eisenstadt, J.M. Guss and R. Mason, J. Organometal. Chem., 80 (1974) 245.
16 B.F.G. Johnson, J. Lewis, P. McArdle and J.L.P. Randall, J. Chem. Soc. Dalton, (1972) 456.
17 R. Hollenstein, W. von Philipsborn, R. Vögeli and M. Neuenschwander, Helv. Chim. Acta, 56 (1973) 847.
18 G.B. Savitzky and K. Namikawa, J. Phys. Chem., 68 (1964) 1956.
19 G.C. Levy and G.L. Nelson, Carbon-13 NMR for Organic Chemistry, Wiley-Interscience, New York, 1972, p. 63; K. Hatada, K. Nagata and H. Yuki, Bull. Chem. Soc. Japan, 43 (1970) 3195.
20 P. McArdle, J. Organometal. Chem., 114 (1978) C31.
21 R.C. Cookson, S.S.H. Gilani and I.D.R. Stevens, J. Chem. Soc. C, (1967) 1905.
22 A.I. Vogel, A Textbook of Practical Organic Chemistry, 3rd Ed., Longman, London, 1956, p. 169.