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^{1}H and ^{13}C NMR study of low-energy intramolecular transformations of coordinated propargyl cations $[(\mu\text{-}\eta^2,\eta^3\text{-}HCCCR_1R_2)Cp_2Mo_2(CO)_4]^+BF_4^-$

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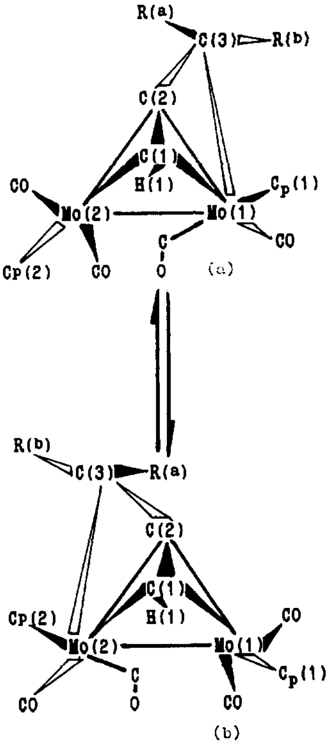
Abstract

Temperature dependencies of ^{1}H and ^{13}C NMR spectra of the solutions of coordinated propargyl cations $[(\mu\text{-}\eta^2,\eta^3\text{-}HCCCR_1R_2)Cp_2Mo_2(CO)_4]^+BF_4^-$, where $R_1 = R_2 = H$; $R_1 = H$, $R_2 = CH_3$; $R_1 = R_2 = CH_3$, along with their ^{13}C CP-MAS spectra in solid state have been investigated. Stereochemical non-rigidity of these cations is discussed.

Introduction

Interest in dinuclear cationic complexes with propargylic ligands is steadily growing due to their versatility as tools in organic synthesis [1,2], and to their intriguing fluxional behaviour in solution [3–10]. Two kinds of dynamic process have been proposed to rationalize the temperature dependencies of NMR spectra of alkynyldicobalthexacarbonyl cations [4]. For cations of alkynyl-bis-(cyclopentadienyl)tetracarbonylditungsten [5], and dimolbdenum [6] only a single dynamic process has been proposed to be involved in this dependence. For mestranyl-bis-(cyclopentadienyl)tetracarbonyldimolbdenum cations two dynamic processes were observed [10].

Earlier studies showed that in solutions of two series of compounds: $[(\mu\text{-}\eta^2,\eta^3\text{-}HC^1C^2C^3R_1R_2)Cp_2Mo_2(CO)_4]^+BF_4^-$, (M = Mo, W; $R_1 = R_2 = H$; $R_1 = H$, $R_2 = Me$; $R_1 = R_2 = Me$) there are also two distinct dynamic processes at work [9]. For the low-energy process $\Delta G^{\#}$ increases from the tertiary to primary cation [9], and such a trend in the variation of $\Delta G^{\#}$ is due to the stronger C(3)–Mo bond in the primary ion in comparison with that in the tertiary ion, and this is evident from



Scheme 1.

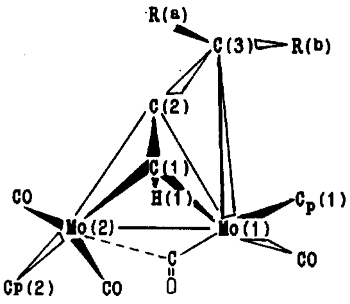
X-ray structural data of these compounds [11]. The high-energy process follows the same trend in $\Delta G^{\#}$ [9].

The low-energy process involves the rotation of the vector C(2)–C(3) relative to C(1)–C(2) (Scheme 1) and partial rotation around the Mo(1)–Mo(2) bond which brings Cp(2) to the position relative to the rotated vector C(2)–C(3) that was earlier occupied by Cp(1). Besides, the semibridging carbonyl at Mo(1) becomes terminal, and the terminal carbonyl at Mo(2) returns to a semibridging state (Scheme 1). The low-energy process leads to interconversion of Mo(1) and Mo(2), Cp(1) and Cp(2) and of the two pairs of carbonyl ligands, with the structures **a** and **b** being enantiomeric.

The high-energy process involves rotation around the C(2)–C(3) bond with the formation of diastereomeric structures.

The model of transition state of the low-energy process (enantiomerization) which has been put forward earlier for hexacarbonyldicobalt cations is of no use for cations of the bis-(cyclopentadienyl)tetracarbonyldimolbdenum series, since this model neglected the interconversion of terminal and bridging carbonyls, and the partial rotation around the Mo–Mo bond.

Earlier, two kinds of dynamic processes were suggested to explain fluxional behaviour of neutral compounds (μ-RC≡CR)$Cp_2Mo_2(CO)_4$ in solutions, one of which involves interconversion of Mo(1) and Mo(2), Cp(1) and Cp(2), and two pairs of carbonyls, and the other involves partial rotation around Mo–Mo bond [12]. Thus, similar to neutral compounds, the low-energy process (in further discussion



R(a)=R(b)= H (1)
R(a)= H , R(b)= CH_3 (2a)
R(a)= CH_3 , R(b)= H (2b)
R(a)=R(b)= CH_3 (3)

Scheme 2.

referred to as interconversion) in complexes with a coordinated propargyl cation can develop by two alternative paths: 1) the interconversion and the partial rotation around Mo–Mo bond occur synchronously through the same transition state, or 2) transition states of the two processes are different.

In the present article, this problem is investigated for the known cations **1**–**3** (Scheme 2) using high resolution ^{13}C and ^{1}H NMR spectroscopy in solution and ^{13}C NMR spectroscopy in the solid state (CP-MAS).

Results and discussion

Before discussion it is convenient to enumerate spectral features which would be observed for different cases of stereochemical non-rigidity of cations for R(a) = R(b) (Scheme 2):

1. Fast rotation around C(2)–C(3) bond without interconversion should have led to the observation of a single resonance for R(a) and R(b), two signals of Cp ligands, and four signals of CO ligands;
2. Fast interconversion and no rotation around C(2)–C(3) bond (enantiomerization) would give two resonances of R(a) and R(b), a single signal of Cp ligands, and two signals of CO ligands;
3. Fast rotation and interconversion-enantiomerization (or fast interconversion–diastereomerization) would give a single resonance for R(a) and R(b), single signal of Cp ligands, and two signals of CO ligands.

Cation 1

NMR data for cation **1** in solution and solid state are given in Tables 1 and 2.

Since the spectra of solutions in CD_2Cl_2 show two signals for protons at C(3), two signals of Cp protons, two signals of ^{13}Cp, and four signals of ^{13}CO at room temperature, the molecule is rigid in the NMR time scale [6,9]. Spin-lattice relaxation times (T_1) of protons have been measured for **1** at 193 K. Proton relaxation times are known to depend mainly on the number of adjacent protons, and on

Table 1

^{1}H NMR chemical shifts (δ ppm, from TMS), line width ($\Delta\nu$, Hz) and spin-lattice relaxation times (T_1, s) of cation **1** in CD_2Cl_2

T (K)	Parameter	H(1)	H(a)	H(b)	Cp	
293	δ	6.39	5.42	4.66	5.53	5.66
	$\Delta\nu$	6.0	2.4	1.2	1.6	1.7
233	δ	6.41	5.40	4.67	5.52	5.66
	$\Delta\nu$	12.0	–	3.4	4.0	1.2
193	δ	6.42	5.36 [a]	4.69	5.51	5.70
	$\Delta\nu$	2.0	3.0	2.0	1.4	1.4
	T_1	2.20	0.43	0.29	1.96	2.26

[a] $^4J(^1H-^aH) = 1.6$ Hz.

distances to them [13]. Therefore, these measurements, combined with X-ray data, can be used to assign resonance lines to protons at C(3) (Table 1), and attribute the observed $^4J = 1.6$ Hz to the splitting H(1)–H(a) (Scheme 2).

In the temperature range 293–193 K, in spite of the structural rigidity mentioned above, the ^{1}H NMR spectra of complex **1** is temperature dependent. This is most marked for H(1) and H(a) resonances, as well as for one of the Cp lines, which broaden, and then narrow again on cooling the sample (Table 1). Computer simulation of model spectra with spin exchange has shown that the observed temperature dependence corresponds to an exchange between at least two states, one of which is scarcely populated. Thus, these data can be considered as further evidence in favour of the occurrence in solutions of cation **1** of a weakly populated state (**1c**) which we have been not able to observe directly.

Cation 2

Both the overall pattern and the parameters of NMR spectra of solutions of **2** agree well with a previous report [9]. In ^{1}H NMR spectra at room temperature two groups of lines with relative intensity 1 : 5 occur, each including a single signal of Cp ligands. So, in the NMR time scale, the rotation around C(2)–C(3) is frozen. ^4J for H(1) equal to 1.6 Hz can be resolved for the more stable conformer at 192 K. This value, in agreement with the data given above, corresponds to the orientation of

Table 2

$^{13}C\{^1H\}$ NMR spectra of **1** in CD_2Cl_2 and in the solid state

T (K)	$\delta(^{13}C)$ (ppm from TMS)					
	C(1)	C(2)	C(3)		Cp	CO
294	78.1	117.2	74.0	92.8	91.7	225.0, 225.0, 217.6, 215.1
193	77.1	116.3	73.9	93.3	92.1	227.5, 226.4, 218.1, 215.7
294 [a]	77.1	117.2	74.6	94.6 [b]		229.5, 225.0, 223.2, 217.6

[a] Solid state. [b] Two signals of Cp-rings are unresolved.

Table 3

^{1}H NMR chemical shifts (δ, ppm, from TMS) of conformers **2** in CD_2Cl_2 at 187 K

Conformer	H(1)	H(a)	H(b)	Cp		CH_3
2a	6.13	6.36	–	5.70	5.75	1.95
2b	6.61	–	5.80	5.49	5.64	1.90
2c	6.67	7.29	–	5.86	5.55	1.90

CH_3 group in conformer **2a** (Scheme 2), and can be used to attribute the resonance lines to separate conformers (Tables 3 and 4).

In the temperature range 244–229 K the interconversion of the cluster system is frozen, and this is established by observation in ^{1}H NMR spectra of two separate lines of Cp ligands for each of the conformers. However, further cooling of the solution to 192 K leads to consecutive broadening and narrowing of lines, similar to that established for cation **1**. Here, one could also suggest exchange between two states, one of which is poorly populated. Indeed, this latter state (**2c**) could be directly observed at 187 K as a set of low-intensity ^{1}H NMR signals. Having applied the saturation transfer method at 203 K, we have been able to reveal that the observed states are indeed involved in position exchange. Spectral parameters of this new state (**2c**) ([**2a**]/[**2c**] = 11.5 at 187 K) are given in Table 3.

We demonstrated that 5-fold dilution of the CD_2Cl_2 solution and the use of a more polar solvent (CD_3CN) exert a negligible influence on the relative population of **2c**. The transitions between **2c** and **2a** are therefore obviously intramolecular.

No such state could be observed for the less stable conformer **2b** in NMR spectra.

Cation 3

Parameters of $^{13}C\{^1H\}$ NMR spectra of cation **3** in solid state and in CD_2Cl_2 solution are given in Table 5. At 294 K the solution spectra correspond to fast rotation around the C(2)–C(3) bond, and fast interconversion [9]. In the solid state at 294 K the interconversion is frozen (four resonance lines of CO groups are observed), but the rotation around the C(2)–C(3) bond is persistent [14]. The latter

Table 4

$^{13}C\{^1H\}$ NMR spectra of cations **2a**,**2b** in CD_2Cl_2 and in the solid state

T (K)	$\delta 9^{13}C)$ (ppm from TMS)					
	C(1)	C(2)	C(3)	Cp	CO	CH_3
294	75.7	110.4	99.4	92.1	221.9	21.9
193 (**2a**)	76.7	110.7	96.3	91.8, 92.3	227.6, 226.5, 217.9, 217.1	20.9
193 (**2b**)	–	109.2	94.6	90.3 91.4	229.5, 227.4, 218.7, 215.1	30.9
294 [a]	76.0	108.6	–	95.2, 92.6	229.9, 227.9, 223.0, 219.2	20.8

[a] Solid state.

Table 5

$^{13}C\{^1H\}$ NMR spectra of cations **3** and **3c** in CD_2Cl_2 and in the solid state

T (K)	$\delta(^{13}C)$ (ppm from TMS)					
	C(1)	C(2)	C(3)	Cp	CO	CH_3
294	75.8	104.8	147.5	94.4	223.2, 222.9	32.8
193 (3)	76.7	104.2	143.7	92.8, 93.7	227.2, 227.1, 218.9, 217.7	28.8, 36.2
193 (3c)	68.1	100.3	135.6	95.0, 93.9	228.1, 226.7, 219.8, 216.3	35.1, 27.3
163 (3)	76.0	104.2	142.4 [a]	93.1, 94.0, 92.8	227.6 [a], 219.1, 217.9 [a]	36.5 [a], 27.3
163 (3c)	67.9	100.0	–	95.1, 94.0	228.3, 227.0, 220.0, 216.5	
294	74.7	105.7	145.9	94.3	231.4, 229.1, 220.6, 215.7	32.1 [a]

[a] Wide signal. [b] Solid state.

process accounts for the observation of a broad signal of methyl groups in the spectrum of solid **3** at 294 K (Table 5). On cooling the solution to 203–193 K, the rotation around the C(2)–C(3) bond and interconversion of cluster system **3** are hindered. Moreover, the data of Table 5 show that a new set of low-intensity signals develops in the spectrum, that is indicative of a new state **3c** (relative population is about 9%). Thus, the spectra of the cation investigated also reveal an unknown, earlier intramolecular process, besides the interconversion and the rotation around the C(2)–C(3) bond.

As mentioned above the rotation around the C(2)–C(3) bond and the interconversion of the cluster system of **3**, **3c** are hindered at 193 K. However, from 193 to 162 K ^{13}C NMR spectra are still temperature dependent, and this is most marked for the signals of the state with the highest population (Fig. 1). In the solution overcooled to 162 K some of the signals are strongly broadened (C(1), C(2), C(3), low-field line of CH_3, CO), while the low-field line of Cp ligands is practically resolved into two lines. Thus, these spectra bear evidence of a new kind of structural non-rigidity of the tertiary cation, which has not been observed for cations **1** and **2**.

According to X-ray data [11] in cations **1** and **3** one of the Mo atoms is bonded to C(3), one of the carbonyls is semibridging, and Cp ligands occupy approximately *trans* positions (dihedral angle Cp(1)–Mo(1)–Mo(2)–Cp(2) is equal to 166° in **1**, and to 149° in **3**).

We have established that $^{13}C\{^1H\}$ NMR spectra of cation **1** in the solid state and in solution are practically identical (Table 2). For cation **3** this is valid only for the lines of the most populated state, observed at low temperatures (Table 5). So, the structures **1**, **3** (Scheme 2) occurring in solid state, are realized also in solution as the most stable forms.

Cation **2** has never previously been studied by X-ray methods. NMR spectra of cooled solutions show that the structure **2a** with "*cis*"-oriented CH_3- and Cp(1)-groups (Scheme 2) predominates. A fair agreement between the ^{13}C NMR spectra of conformer **2a** in solution and in the solid state (most apparent for the line of CH_3)

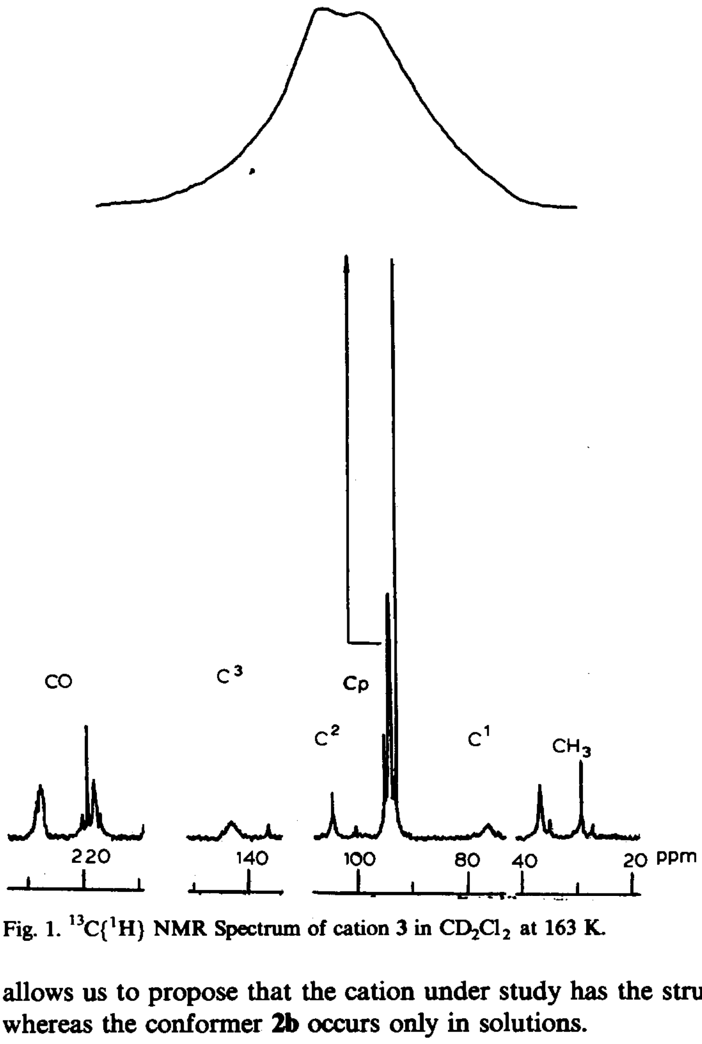
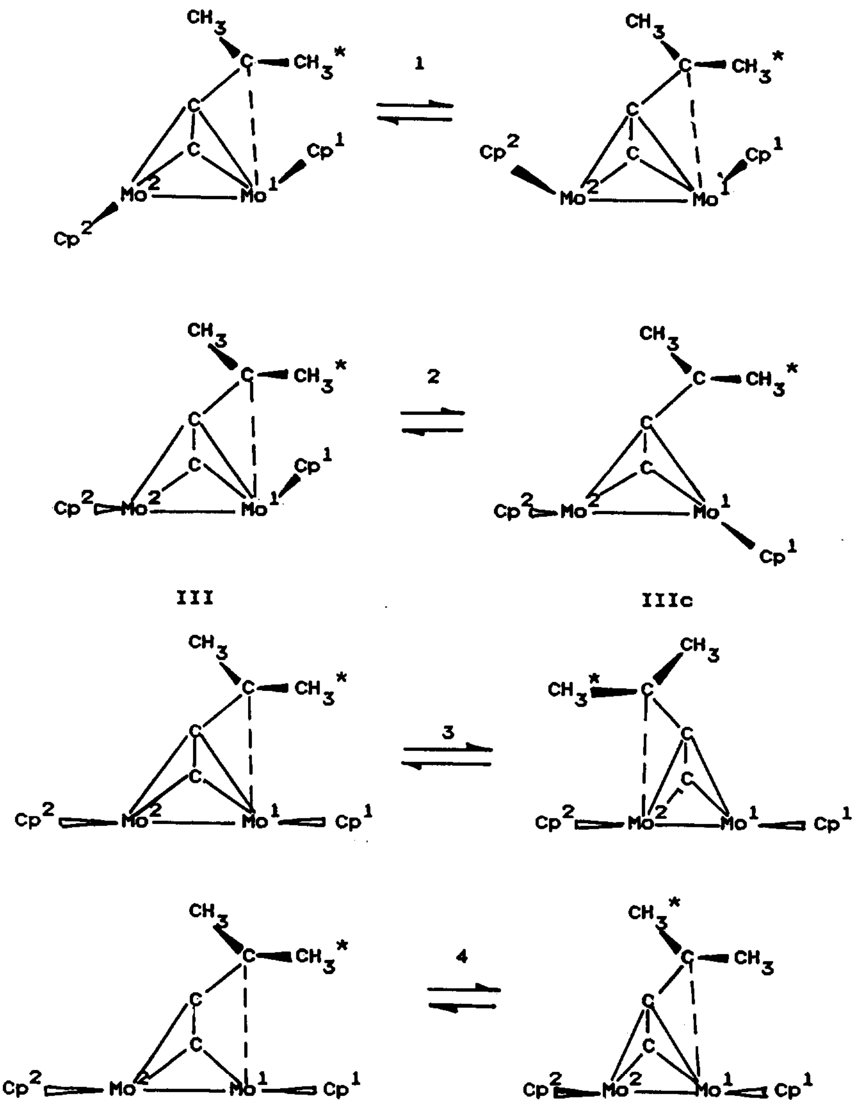


Fig. 1. $^{13}C\{^1H\}$ NMR Spectrum of cation 3 in CD_2Cl_2 at 163 K.

allows us to propose that the cation under study has the structure **2a** in solid state, whereas the conformer **2b** occurs only in solutions.

The NMR spectra made at low temperatures, when the interconversion and the rotation around C(2)–C(3) bond are frozen, reveal that complexes **1**, **2a**, and **3** are in equilibrium with the low-populated states **1c**, **2c**, and **3c**. The relative contents of the states follow the series **1c** < **2c** < **3c**. Since the distance Mo(1)–C(3) increases from the primary to the tertiary cation, the formation of the low-populated states is likely to be associated with the change in the orientation of Cp(1)-ring due to partial rotation around the bond Mo(1)–Mo(2) (the process 2 in Scheme 3). Such partial rotation around Mo–Mo bond leading to the position exchange for semibridging and terminal carbonyls at the same Mo atom has been earlier postulated to explain the temperature dependence of NMR spectra of neutral compounds (μ-$RC{\equiv}CR)Cp_2Mo_2(CO)_4$ [15].

According to NMR spectra cation **3** reveals some non-rigid behaviour even at very low temperatures (193–162 K, Fig. 1) when the interconversion, the rotation around C(2)–C(3) bond and the above mentioned process are frozen. We believe that such non-rigidity is valid for the other cations and corresponds to the Cp-ring at Mo(2) atom changing orientation.



Scheme 3.

The results of our study of temperature dependencies of NMR spectra of cations **1**–**3** can be summerized by Scheme 3. The partial rotation around the metal–metal bond with the change in spatial orientation of Cp(2)-ring (process 1) has the lowest energy requirements. The value of $\Delta G^{\#}$ for this process is estimated to be 7.4 kcal/mole for cation **3** at 163 K (the collapse of ^{13}Cp lines). For cations **1** and **2** this value is apparently lower, since process 1 is unobservable in NMR spectra. The values of $\Delta G^{\#}$ (298 K) of the internal rotation in the dimers $[\mathrm{CpM(CO)_3}]_2$ differ by 2.9 kcal/mole [16]. This energy difference corresponds to the difference (0.046 Å) between Cr–Cr and Mo–Mo distances [16]. The close difference is observed for the Mo(1)–Mo(2) distances of cations **1** and **3** (0.039 Å [11]). Consequently for process 1 in cation **1** the $\Delta G^{\#}$ value could be expected to be less than 5 kcal/mol at 163 K.

The change of Cp(1)-ring orientation (process 2) is superimposed over the faster process 1. For the cation **2** $\Delta G^{\#}$ of the transition **2c**–**2a** is estimated to be 11.0 kcal/mole at 239 K.

Process 3 involving interconversion of Mo(1) and Mo(2), Cp(1) and Cp(2), and of two pairs of carbonyls developes against the background of two faster processes 1 and 2. For cation **2a**, $\Delta G^{\#}$ of this process is estimated as 12.1 kcal/mole at 239 K.

And finally, the rotation around the C(2)–C(3) bond (process 4) has the greatest energy requirement. For cation **2a**, $\Delta G^{\#}$ value is equal to 14.6 kcal/mole at 239 K.

Conclusions

The results of the present work enable us to conclude that processes 1–4 accounting for the stereochemical non-rigidity of complexes $[(\mu\text{-}\eta^2,\eta^3\text{-HCCCR}_1\text{R}_2)\text{Cp}_2\text{Mo}_2(\text{CO})_4]^+\text{BF}_4^-$ in solution have different transition states and are asynchronous. The rotation around the C(2)–C(3) bond of the cation **3** and its tungsten analogue occurring without traces of any other process in the solid state [14] may be regarded as extra evidence in favour of the last conclusion.

Experimental

Cations **1**–**3** were obtained using published methods [17,18]. ^{1}H and ^{13}C NMR spectra of solutions of **1**–**3** have been obtained with Bruker WP-200 SY spectrometer using variable temperature unit VT-1000. Spin-lattice relaxation times were measured by inversion-recovery method. Solid state spectra were taken with a Bruker CXP-200 instrument. Magic angle spinning frequency was maintained at 3000–4000 Hz, and mixing time was 5 ms.

References

1 K.M. Nicholas, Acc. Chem. Res., 20 (1987) 207.
2 G.S. Mikaleian, A.S. Gybin, W.A. Smit and R. Caple, Tetrahedron Lett., 26 (1985) 1269.
3 S. Padmanabhan and K.M. Nicholas, J. Organomet. Chem., 212 (1984) C23; B.E.R. Schilling and R. Hoffman. J. Am. Chem. Soc., 100 (1978) 6274.
4 S.L. Schreiber, M.T. Klimas and T. Sammakia, J. Am. Chem. Soc., 109 (1987) 5749.
5 S.F.T. Froom, M. Green, K.R. Nagle and D.J. Williams. J. Chem. Soc., Chem. Commun., (1987) 1305.
6 A. Meyer, D.J. McCabe and M.D. Curtis, Organometallics, 6 (1987) 1491.
7 M.F.D'Agostino, C.S. Frampton and M.J. McClinchey, J. Organomet. Chem., 394 (1990) 145.
8 L.L. Troitskaya, V.I. Sokolov, V.I. Bakhmutov, O.A. Reutov, M. Gruselle, C. Cordier and G. Jaouen, J. Organomet. Chem., 364 (1989) 195.
9 I.V. Barinov, V.A. Chertkov and O.A. Reutov, J. Organomet. Chem., in press.
10 C. Cordier, M. Gruselle, G. Jaouen, V.I. Bakhmutov, M.V. Galakhov, L.L. Troitskaya, V.I. Sokolov, Organometallics, in press.
11 I.V. Barinov, O.A. Reutov, A.V. Polyakov, A.I. Yanovsky, Yu.T. Struchkov, J. Organomet. Chem., 418 (1991) C24.
12 W.I. Bailey, M.H. Chisholm, F.A. Cotton and L.A. Rankel, J. Am. Chem. Soc., 100 (1978) 5764.
13 S. Abragam, The principles of nuclear magnetism, Clarendon Press, Oxford, 1961.
14 M.V. Galakhov, V.I. Bakhmutov, I.V. Barinov., Magn. Reson. Chem., 29 (1991) 506.
15 J.A. Beck, S.A.R. Knox, R.F.D. Stansfield, F.G.A. Stone, M.J. Winter and P. Woodward, J. Chem. Soc., Dalton Trans., (1982) 195.
16 R.D. Adams, D.M. Collins and F.A. Cotton, Inorg. Chem., 13 (1974) 1086.
17 V.I. Sokolov, I.V. Barinov and O.A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., (1982) 1922.
18 O.A. Reutov, I.V. Barinov, V.A. Chertkov and V.I. Sokolov, J. Organomet. Chem., 297 (1985) C25.