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Chromium tricarbonyl complexes with biphenylene as η^6 ligand: synthesis, structure, dynamic behaviour in solid state and thermal η^6,η^6-haptotropic rearrangements. Experimental (NMR) and theoretical (DFT) studies

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Abstract

The reaction of biphenylene (**1**) with $Cr(CO)_3Py_3/BF_3 \cdot OEt_2$ at 25 °C gives a mixture of two known isomeric complexes: tricarbonyl(1-4,4a,8b-η^6-biphenylene)chromium (**2**) (yield 62%) and hexacarbonyl(μ-η^6:η^6-biphenylene)bis-chromium (**3**) (yield 4%). Complexes **2** and **3** were separated by thin layer chromatography on silica and characterised by ^1H and ^{13}C, as well as ^{13}C CP MAS-NMR. X-ray structure analysis for **3** proved *trans*-orientation of the chromium tricarbonyl groups. A novel regioselective method for the synthesis of (η^6-biphenylene)chromium tricarbonyl complexes bearing a substituent R (D (**4**), CH_3 (**5**)) in position 1 of the coordinated ring was proposed. The kinetics of η^6,η^6-inter-ring haptotropic rearrangement (IRHR) for **4** in inert, noncoordinating C_6F_6 was investigated by $^2H-\{^1H\}$-NMR spectroscopy. Density function theory (DFT) calculations for ground, intermediate and transition states were done and fitted well with experiment. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Biphenylene; Tricarbonyl chromium complexes; Haptotropic rearrangements; X-ray structure analysis; ^1H and ^{13}C high-resolution and CP MAS-NMR spectroscopy; Kinetics; Density function theory; Quantum chemical calculations

1. Introduction

π-Complexes of transition metals with unsaturated and aromatic ligands including polycyclic aromatic hydrocarbons (PAH), in which only a part of the ligand positions accessible for coordination is involved in bonding with a metal atom, are characterised by high lability [1]. This is manifested in a variety of dynamic processes that take place in these compounds. Among these are intramolecular inter-ring haptotropic rearrangements (IRHR), which occur with migration of the metal atom from one position of the ligand to another [2].

Synthesis of the new π-complexes of transition metals with PAH and investigation of plausible IRHR in such compounds are thus of a great challenge and interest for organometallic chemists. Biphenylene represents in this aspect quite an intriguing molecule owing to the fact that two six-membered rings in this planar molecule are separated by the four-membered ring. It appears interesting to compare activation parameters of IRHR for this system with the corresponding parameters of IRHR of some already investigated related systems.

Thermally induced IRHR were found and thoroughly investigated for different transition metal complexes with PAH [3], in particular, for chromium tricarbonyl complexes of substituted naphthalenes [4–7] (Scheme 1), biphenyls [8] (Scheme 2) and some other PAH [9]. In

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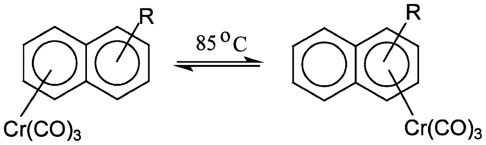
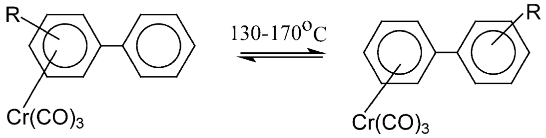


1- or 2-R=Me_3Sn, Me_3Si, Me, Br, Cl, D

Scheme 1.



R=m, p-Me, p-Me_3Sn, o,p-Br, o,m,p-D

Scheme 2.

such complexes dissolved in inert, noncoordinating solvents (e.g. decane or C_6F_6) $Cr(CO)_3$ group during IRHR intramolecularly shifts along the π-system of the ligand between different aromatic rings at 80–170 °C with the activation barrier of ca. 27–33 kcal mol^{-1} (η^6,η^6-rearrangements). This was proved by cross-experiment [5] as well as by the retention of stereochemistry [10] and optical activity [11] in the course of IRHR. Reactions proceeding with such rates could be monitored by methods of stationary kinetics (e.g. HPLC [12] and NMR [5]).

To our knowledge all the attempts to prove the existence of degenerate IRHR (η^6,η^6-rearrangement) in transition metal complexes of unsubstituted symmetric PAH by means of dynamic NMR without introducing a substituent-label into one of the six-membered rings of the ligand were unsuccessful. Thus, on heating ^1H- and ^{13}C-NMR spectra of the samples of η^6-acenapthyleneCr$(CO)_3$ [2], η^6-$C_{10}H_8Cr(CO)_3$ [13], $[(\eta^6\text{-}C_{10}H_8)Ir(C_5Me_5)]^{2-}(PF_6)_2$, (70 °C, CF_3COOH) [14], $(\eta^6\text{-}C_{10}H_8)_2Cr$ (130 °C, C_6D_6) [15] did not manifest the dynamic behaviour.

Only recently rearrangements fast on NMR time scale were found for the nickel complex of naphthalene $(\eta^2\text{-}C_{10}H_8)Ni(Pr_2NCH_2CH_2NPr_2)$ [16] and anthracene [17]. Solid state ^{13}C CP MAS-NMR and solution dynamic NMR was used to investigate these processes in the course of which the metal has been shifted both between double bonds inside one aromatic ring and between the two six-membered rings of the ligands (η^2,η^2-rearrangement).

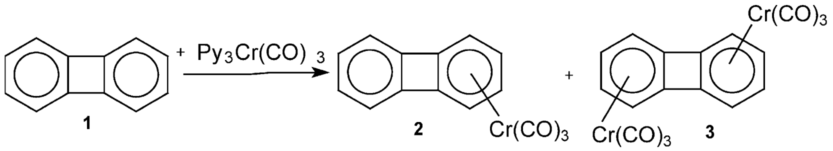
These facts determined our strategy of searching of IRHR in biphenylene complexes which involves:

1) synthesis of chromium tricarbonyl complex of biphenylene;
2) introducing a substituent-label into the activated [18] coordinated ring;
3) investigation of IRHR in this systems by the methods of stationary kinetics (NMR spectroscopy);
4) comparison of activation parameters obtained with the corresponding parameters for related annelated plane naphthalene system and an open twisted biphenyl system;
5) investigation of ground and transition states of this IRHR by means of quantum chemical calculations (DFT).

2. Results and discussion

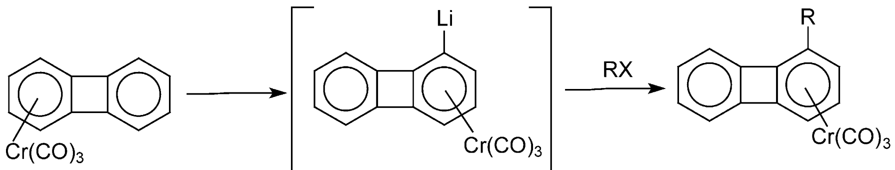
2.1. Synthesis of chromium tricarbonyl complexes of biphenylene

The reaction of biphenylene (**1**) with $Cr(CO)_3Py_3$/$BF_3\cdot OEt_2$ under condition of Öfele reaction [19] gives a mixture of chromium tricarbonyl complex **2** and bis-chromium tricarbonyl complex **3** in a 66% yield (Eq. (1)). Complexes **2** and **3** were separated by TLC on silica (ratio **2**/**3** is 15.5). Earlier, compounds **2** and **3** were first synthesised by Moser and Rausch and later on by Venzo, Ceccon et al. by the reaction of **1** with $(NH_3)_3Cr(CO)_3$ in boiling dioxane [20,21].



(1)

Metallation of **2** with BuLi in THF at −70 °C, followed by the treatment with electrophiles RX (CH_3I, D_2O) proceeds regioselectively and gives only complexes **4** and **5**, respectively, substituted in the coordinated ring of the ligand in position 1 (Eq. (2)) in contrast to chromium tricarbonyl complexes of naphthalenes [5,6] and biphenyls [22] where these reactions proceed unselectively.



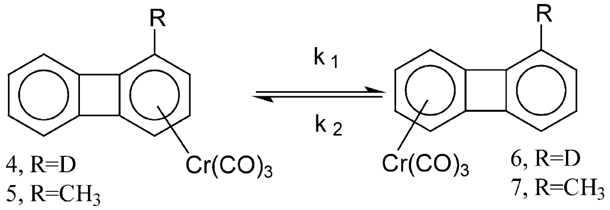
2

4, R=D; 5, R=Me

(2)

IRHR for biphenylene complexes **4** and **5** (Eq. (3)) starts in thoroughly degassed decane at temperatures above 115 °C and proceeds with the rate convenient for the observation by NMR at 130 °C. Equilibrium $\mathbf{4}\rightleftharpoons\mathbf{6}$ is reached after ca. 20 h ($K_{eq} = [\mathbf{4}]/[\mathbf{6}] = 1$). Further heating does not change the isomer ratio according to ^{2}D-NMR spectra.

Rearrangement $\mathbf{5}\rightleftharpoons\mathbf{7}$ takes place a little bit slowly: After 40 h the isomer ratio [**5**]/[**7**] is 5.8 and after 56 h—3.2 according to ^{1}H-NMR. Unfortunately, in this case, equilibrium was not reached due to a high degree of decomposition of the complexes during prolonged heating at 130 °C.



(3)

2.2. X-ray analysis of complex 3 structure

The X-ray structure for **2** was reported earlier [23] but for the corresponding bis-chromium complex **3** such an analysis was accomplished for the first time. Ligand 1 is coordinated by two $Cr(CO)_3$ moieties which are situated at different sides of the ligand plane (*trans*-coordination).

The $Cr(CO)_3$ group have a staggered conformation with respect to six-memebered cycle (Fig. 1). The geometry of **1** in the complex is quite typical [23]. The C–C bonds lengths alternate with the elongation of C(1)–C(2), C(3)–C(4) and C(5)–C(6). In general, our data fit well the data for corresponding bis-$Mo(CO)_3$ complex of biphenylene [24].

Projection of the $Cr(CO)_3$ on the ligand plane is presented in Fig. 2. Bond lengths and angles for **3** are listed in Table 1. The crystallographic data for **3** are given in Table 2.

An analysis of crystal packing of **3** have revealed that molecules are assembled into layers parallel to crystallographic plane bc by C–H···O contacts (Fig. 3).

2.3. The study of the kinetic of IRHR in the complexes 4 and 5

For the deuterium labeled complex **4**, the kinetics of IRHR $\mathbf{4}\rightleftharpoons\mathbf{6}$ were investigated in detail in C_6F_6 at

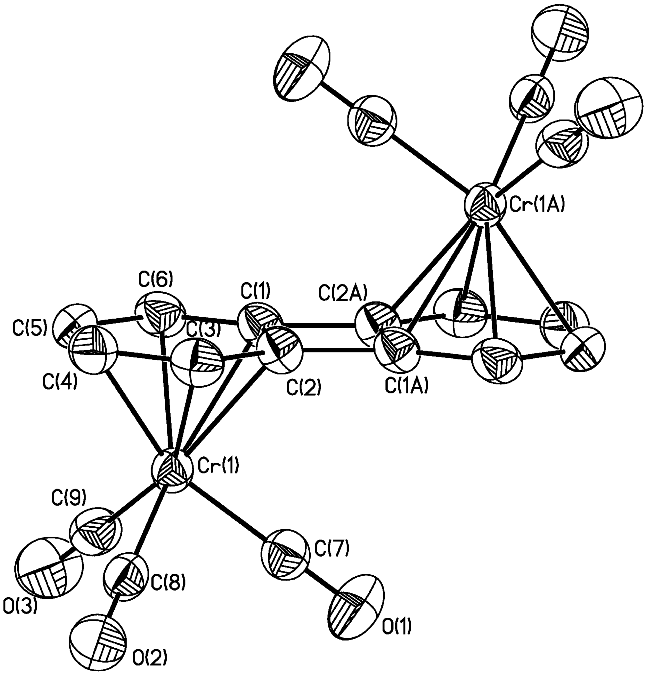


Fig. 1. Crystallographic structure of **3**.

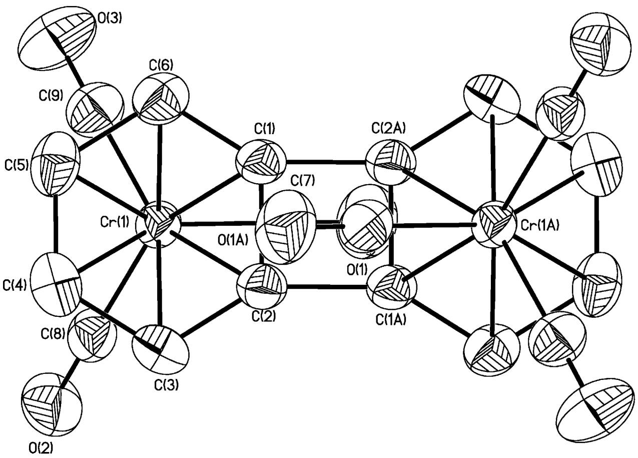


Fig. 2. $Cr(CO)_3$-group projection on biphenylene plane.

Table 1
Selected bond lengths (Å) and bond angles (°) in **3**

Bond lengths			
Cr(1)–C(1)	2.212(4)	Cr(1)–C(9)	1.863(4)
Cr(1)–C(2)	2.210(3)	C(1)–C(2)	1.445(5)
Cr(1)–C(3)	2.238(4)	C(2)–C(3)	1.374(5)
Cr(1)–C(4)	2.201(4)	C(3)–C(4)	1.436(5)
Cr(1)–C(5)	2.197(4)	C(4)–C(5)	1.395(6)
Cr(1)–C(6)	2.245(4)	C(5)–C(6)	1.427(6)
Cr–X [a]	1.711	C(1)–C(6)	1.385(5)
Cr(1)–C(7)	1.851(4)	C(1)–C(2A) [b]	1.504(5)
Cr(1)–C(8)	1.854(4)		
Bond angles			
C(2)–C(1)–C(6)	121.5(3)	C(5)–C(6)–C(1)	116.1(4)
C(1)–C(2)–C(3)	122.5(3)	C(2)–C(1)–C(2A) [b]	90.7(3)
C(2)–C(3)–C(4)	116.0(3)	Cr(1)–C(7)–O(1)	179.9(4)
C(3)–C(4)–C(5)	121.6(4)	Cr(1)–C(8)–O(2)	178.8(4)
C(4)–C(5)–C(6)	122.2(4)	Cr(1)–C(9)–O(3)	179.4(3)
Pseudotorsion angles			
C(7)–Cr(1)–X–C(1)	32.1	C(9)–Cr(1)–X–C(5)	29.0
C(8)–Cr(1)–X–C(3)	29.3		

[a] X denotes the center of the six-membered cycle.

[b] Atom is obtained from base one by symmetry transformation $1-x+1$, $-y$, $-z$.

Table 2
Crystal data and structure refinement for **3**

	3
Molecular formula	$C_{18}H_8Cr_2O_6$
Formula weight	424.24
Color, shape	Red, prism
Dimension (mm)	0.35 × 0.20 × 0.20
Diffractometer	Siemens P3/PC
Temperature (K)	298
Crystal system	Monoclinc
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	9.946(2)
b (Å)	11.293(2)
c (Å)	7.1721(14)
β (°)	89.91(3)
V (Å^3)	803.7(3)
Z	2
$F(000)$	424
ρ_{calc} (g cm^{-1})	1.753
Radiation, λ (Mo–K$_\alpha$) (Å)	0.71072
Linear absorption, μ (cm^{-1})	23.85
Scan type	$\theta-2\theta$
θ Range (°)	2.05–25.02
Measured	1502
Unique	1418 ($R_{int}=0.0123$)
Width [$I > 2\sigma(I)$]	5955
Parameters	134
Final R (F_{hkl}): R_1	0.0477
wR_2	0.1316
GOF	1.079
ρ_{max}/ρ_{min} (e Å^{-3})	0.678/−0.727

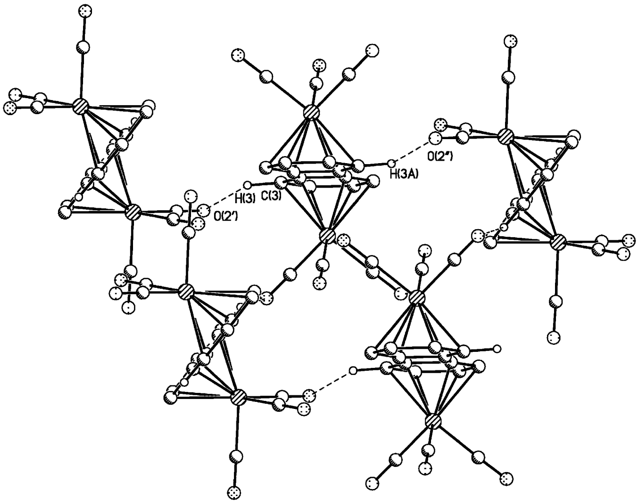


Fig. 3. The scheme illustrating the formation of the C–H···O bonded layers. The parameters of C–H···O contact are H(3)···O(2′) 2.51 Å, C(3)H(3)O(2′) 134°, C(3)···O(2′) 3.351(6) Å.

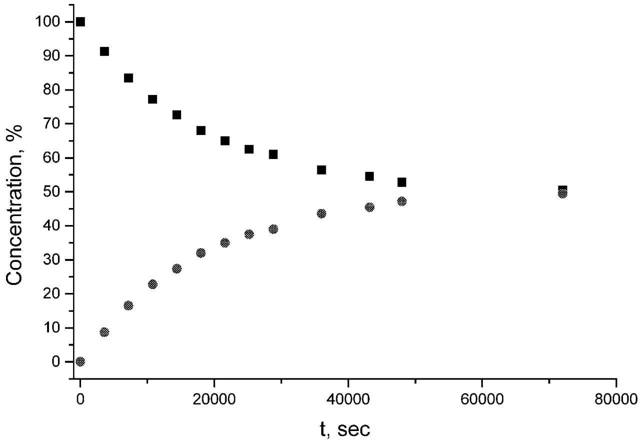
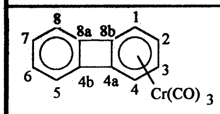
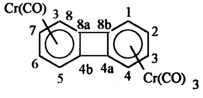
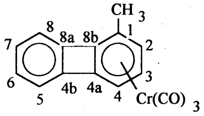
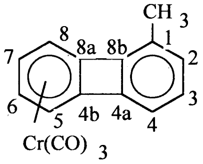


Fig. 4. Kinetic curves of isomerisation of isotopomeric chromium tricarbonyl complexes of 1-D-biphenylene **4** (■) and **6** (●) starting from **4** in C_6F_6 at 130 °C.

130 °C. To determine concentrations of the isomers in the course of isomerization $^2H\{^1H\}$-NMR spectroscopy was used and a ^{19}F signal of C_6F_6 served for locking as described in Ref. [25]. The solubility of the complexes was high enough to measure precisely the concentrations of isomers even at very high degrees of interconversion. Special measures were taken to purify C_6F_6 and to prepare samples in order to avoid minor traces of oxygen and moisture (see Section 5). Kinetic curve for the interconversion of the complexes **4** and **6** is shown in Fig. 4. The rate constant was calculated by using a least-squares program for reversible degenerate first-order reaction described by equation ln $(D_0-D_{eq}/D_t-D_{eq}) = 2k_{obs}t$ (Fig. 4).

It is noteworthy to mention that in thoroughly degassed C_6F_6 the appearance of the free biphenylene was observed only in minor quantities (less than 5%) even after a prolonged heating (20 h). This is the evidence that in C_6F_6 at 130 °C the reaction proceeds mainly intramolecularly. A minor partial decomposition

Table 3
NMR-parameters ^1H and ^{13}C (δ in ppm, J in Hz) for chromium tricarbonyl complexes of biphenylenes in C_6D_6. Note that the carbon atoms numeration for the ligand differs from corresponding numeration for the X-ray structure

Compound	Coordinated ring	Non-coordinated ring, carbonyls
 **2**	H_1,H_4: δ4.62, m; J(2,3)=5.9; H_2, H_3: δ4.28, m; J(3,4)=5.9; AA'BB'- system; C_1-C_4: 88.14; 91.86; C_{4a}, C_{8b}: 119.12;	H_5,H_8: δ6.34, m, H_6,H_7: δ6.54, m; AA'BB' - system; C_5-C_8: 118.46, 131.20; C_{4a}, C_{8f}: 148.20;
 *3	H_1 , H_4, H_5, H_8: δ5.92, m; H_2 , H_3, H_6, H_7: δ5.65, m; AA'BB' - system C_1-C_8: 87.46; 91.94; C_{4a}, C_{4b}:, C_{8a}, C_{8b}: 119.26;	
 **5**	H_2: δ4.18, d; J(2-3)=5.9; H_4: δ4.56, d, J(3-4)=5.9; H_3: δ4.44, t	H_5,H_8: δ6.54-6.58; m, H_6: δ6.27, t; J(6-7) = 7.90 H_7: δ6.41, t CH_3: δ1.62, s;
 ** **7**	H_6, H_7: δ5.17, m; J(5-6)=J(7-8)=5.9; J(6-7)=6.5; H_5: δ5.44, d; H_8: δ5.41, d;	H_2: δ6.63, d; J(2-3)=7.6; H_4: δ6.98, d, J(3-4)=5.9; H_3: 6.90, t;

*Bis-chromium complex **3** is insoluble in C_6D_6 and only slightly soluble in acetone d_6. **In contrast to C_6D_6 signals of **5** and **7** in $CDCl_3$ are not superimposed and ^1H NMR signals of **7** in the mixture with **4** after IRHR could be easily separated in this solvent.

of the complexes must not affect the calculation supposing the rates of decomposition of isotopomers **4** and **6** are equal.

The rate constant $k_{obs} = (2.85 \pm 0.04)\ 10^{-5}\ s^{-1}$ and $\Delta G^{\#} = 32.24$ kcal mol^{-1} were calculated. Thus, the free activation energy for IRHR in chromium tricarbonyl complexes of biphenylene is higher than that for the analogous rearrangement in planar naphthalene (28.5 kcal mol^{-1}) [5] but much lower than that of biphenyl chromium tricarbonyl complexes (35.1 kcal mol^{-1}) [26], respectively, taking into account the corresponding temperature of IRHR. This can be associated with the larger distance between the two six-membered rings in the biphenylene complex and the twist of the phenyl rings in the biphenyl complex, respectively.

2.4. High resolution ^1H- and ^{13}C-NMR investigation of chromium tricarbonyl complexes of biphenylene

All the complexes were characterized by means of ^1H- and ^{13}C-NMR spectroscopy. Data for **2** and **3** are already known from earlier works [21,27], those for **5** and **7** are also summarised in Table 3.

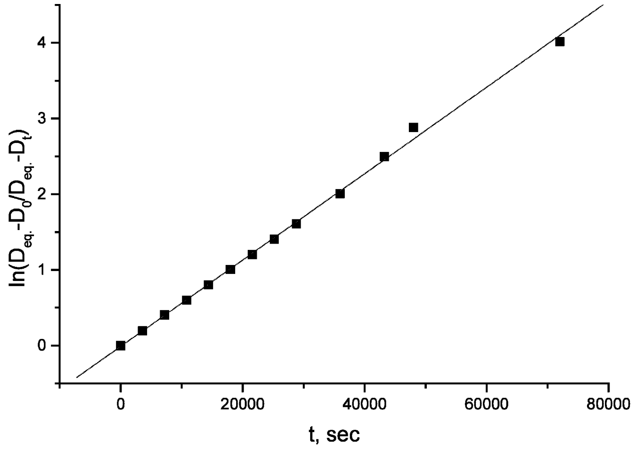
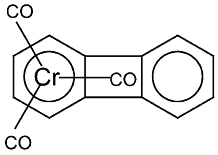


Fig. 5. First-order kinetic plot for the haptotropic rearrangement **4**$\rightleftharpoons$**6** (Eq. (5)) starting from **4**.

2.5. Solid state (CP) MAS-NMR investigation of chromium tricarbonyl complexes

The crystalline powder of **2** was also investigated by ^{13}C CP MAS-NMR (Fig. 5) From the spectrum one can obtain approximately the same information as from a high-resolution spectrum. The carbon signals of the coordinated ring are shifted upfield (90–110 ppm), whereas carbons of the non-coordinated ring are on their usual places (125–140 ppm). The quaternary carbons could be assigned by the use of sequence non-quaternary suppression (NQS) [28], which allows observing the signals of only quaternary carbons. Very often, including the case presented, the number of carbon signals in ^{13}C CP MAS-NMR spectrum exceeds the number which could be deduced from the symmetry of the molecule. This fact could be explained by a different environment of the molecule in the crystal lattice. In general, this considerably complicates the interpretation of ^{13}C CP MAS spectra interpretation.

In contrast to a high-resolution ^{13}C-NMR spectrum of **2** in, which due to the free rotation of $Cr(CO)_3$-group only one sharp carbonyl signal is observed, in the corresponding ^{13}C CP MAS of crystalline **2** at ca. 230 ppm one can observe three carbonyl signals (two of three signals are quite close to each other) with the intensities ratio 1:1:1 (Fig. 6). It is characteristic for metal carbonyl complexes that the side bands from carbonyl signals in low field (ca. 315 ppm) are more intensive than main signals. This fact could be explained by a considerable chemical shift anisotropy of carbonyl groups. According to an X-ray structure analysis of the molecule **2** it has a structure in which two of three carbonyls are equivalent [23].



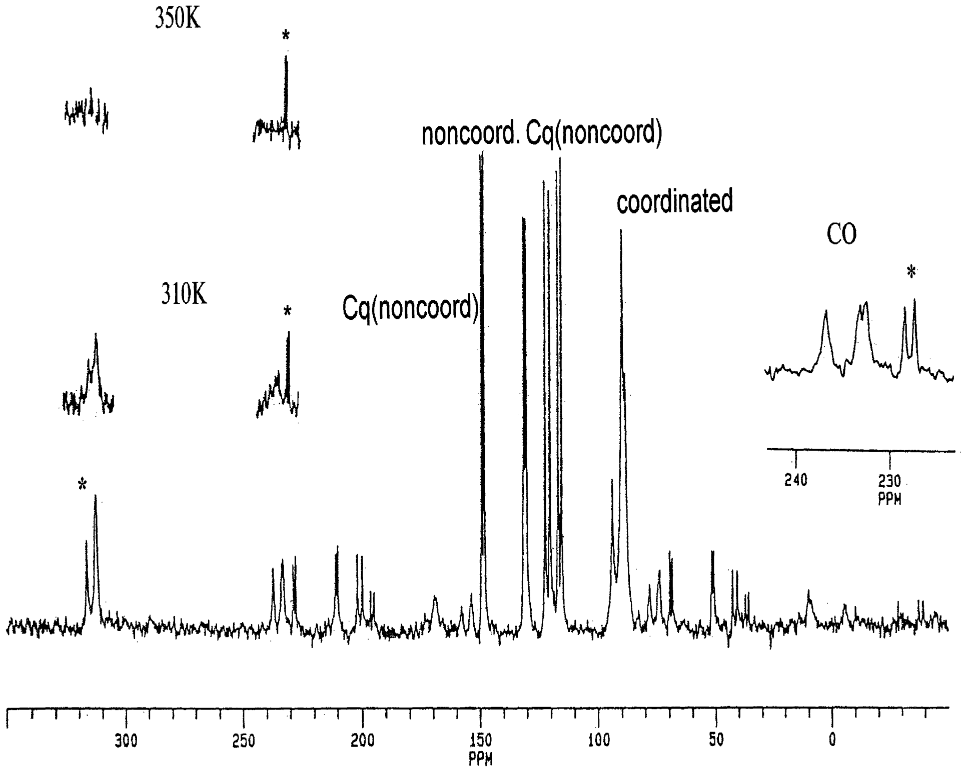


Fig. 6. ^{13}C-NMR CP MAS of polycrystalline η^6-biphenylene tricarbonyl chromium (**2**). Spinning rate ~6 kHz. *, spinning sidebands.

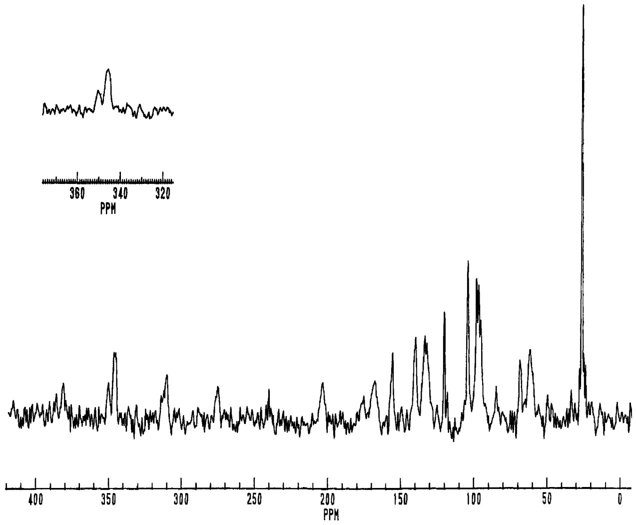


Fig. 7. ^{13}C-NMR CP MAS of polycrystalline η^6-toluene tricarbonyl chromium at 203 K.

Data obtained confirm that in the solid state at room temperature the rotation of the $Cr(CO)_3$-group around the Cr–ligand axis stops, which means that (a) a sufficiently high activation barrier exists for this process in the solid state in comparison to that in liquid and (b) environment of the $Cr(CO)_3$-group in the crystallographic unit is not completely symmetric.

Usually the $Cr(CO)_3$-group rotation in arene complexes in solution proceeds with very low activation barriers (<3 kcal mol^{-1}) and even at very low temperatures cannot be ‘frozen’ in high-resolution ^{13}C-NMR spectra of chromium tricarbonyl complexes of polycyclic arenes [29] except some exotic cases [30]. Thus, for **2** only one signal of carbonyl groups (Table 3) in solution could be observed.

Heating of the sample leads to a gradual broadening of carbonyl signals in ^{13}C CP MAS-NMR spectra and to final coalescence of these signals at 350 K. For the corresponding aromatic ring carbon signals some broadening was also observed. All these changes are reversible. Taking into consideration that two of three signals are quite close and using the equation below for the approximation for a two-site instead of a three-site exchange [31], activation barrier for the $Cr(CO)_3$-group rotation in the solid state for **2** was estimated as $\Delta G^{\#} = 15.9$ kcal mol^{-1}. Previously, such approach was used by Hanson et al. for the estimation of activation barrier for $Mo(CO)_3$ group rotation in $(CH_3{-}C_6H_5)Mo(CO)_3$ [32]

$$\Delta G^{\#} = RT_c[22.96 + \ln(T_c/\delta\nu)] \text{ (kcal mol}^{-1})$$

where $\delta\nu$ is the chemical shift difference for the carbonyl groups, T_c is the coalescence temperature and $R = 1.987$ kcal mol^{-1}.

A more adequate and correct approach for calculating the activation barrier consists in signals lineshape simulation by means of dynamic spectra calculation program [33], e.g. DISPARDNMR [34]. Such approach is not fully correct for analysis of solid state CP MAS dynamic spectra due to some contribution of side-bands to the dynamic behavior but nevertheless it approximately fits the real situation. Such a calculation was done for the three-site exchange in **2**, which results in $\Delta G^{\#} = 16.1$ kcal mol^{-1}. The value remarkably fits with the estimation obtained above.

In our case it was not possible to raise the temperature above 370 K and to obtain one carbonyl signal which corresponding to the rapid rotation (up to this temperature we observed only the base line) because of some temperature restrictions for the MAS probe. But we did obtain a full picture for the temperature evolution of the carbonyl signals for the corresponding monocyclic η^6-chromium tricarbonyl complex of toluene. At 203 K (-70 °C), one can observe two signals with intensity ratio 2:1 in spinning sideband region of carbonyl groups at ca. 340 ppm (Fig. 7). Unfortunately, we failed to accumulate the carbonyl signals themselves with a sufficient signal–noise ratio.

Increasing the temperature leads to a coalescence of the signals in the base line and upon further increase of the temperature, to the appearing and gradual sharpening of the carbonyl signal. At 360 K one sharp carbonyl signal (Fig. 8) can be evidenced which is consistent with the rapid rotation of the carbonyl group in solid state at elevated temperatures.

Such dynamic behavior for chromium tricarbonyl complex of monocyclic arenes is in accordance with the results of Barrie et al. [35] obtained for some other chromium tricarbonyl complexes of monocyclic arenes. A typical temperature evolution of ^{13}C CP MAS spectra in carbonyl region (230 ppm) for $Cr(\eta^6\text{-}C_6H_2Me_4\text{-}1,2,4,5)(CO)_3$ is presented at Fig. 9. At 253 K two signals with intensity ration 2:1 observed which turned to be broadened and approached each other on increasing the temperature. These signals coalescence at 317K. The subsequent temperature increase to 362 K leads to the appearance of a sharp singlet.

These findings may be considered as the evidence that activation barriers for the rotation of chromium tricarbonyl group in complexes of PAH are generally higher than those for monocyclic arenes (e.g. for η^6-toluene tricarbonyl chromium the corresponding activation barrier of 15.5 kcal mol^{-1} was calculated from ^{13}C MAS-NMR [32]).

It is worth of noting that for complex **2** the chemical shift anisotropy of carbonyl groups decreases with increasing temperature, which manifests itself in decreasing of the intensities of side bands at elevated temperatures. These data are also in agreement with the results of Barrie et al. [35,36], Hanson et al. [32] and Harris and coworkers [37] and prove an increase in the rate of chromium tricarbonyl group rotation. The latter conclusion contradicts in some aspects the data of Braga

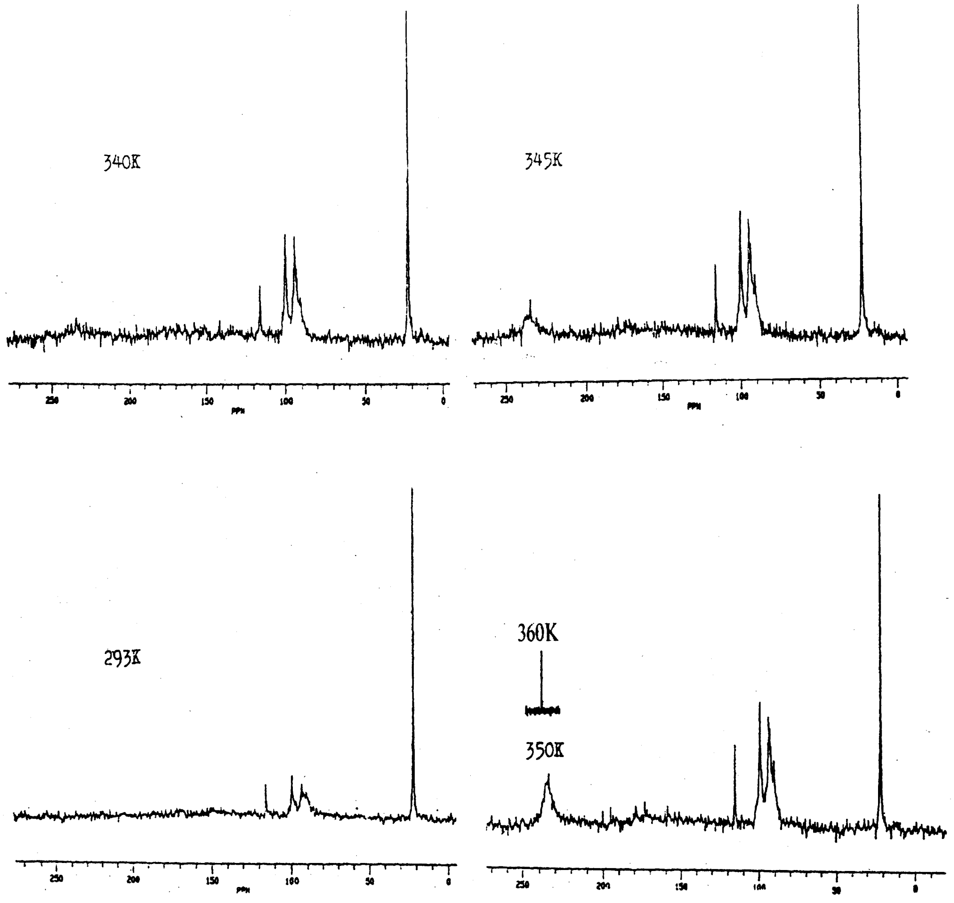


Fig. 8. ^{13}C-NMR CP MAS of polycrystalline η^6-toluene tricarbonyl chromium at different temperatures.

[38] who calculated these activation barriers and demonstrated that due to the packing effect such a barrier should be sufficiently high to prevent the observed dynamic behavior. Rapid tripod rotation is also in line with a temperature-dependent X-ray study of (η^6-C_6HMe_5)$Cr(CO)_3$ [35]. For this complex complete and correct structure investigation was achieved only at low temperatures (below 150 K) which found an explanation in the fast rotation of chromium tricarbonyl groups at ambient temperature.

But except for the molecular factors, determining the activation barrier of tripod rotation, a considerable influence has also the molecular packing in the crystallographic unit as well as the contribution of small amplitude (librational) oscillations of molecular fragments [38] which generally could also lead to averaging the carbonyl signals. This reduces in some aspects the value of the information concerning only a few estimated barriers of the chromium tricarbonyl group rotation in solid state because it represents complicated task to differentiate between influence on such barriers of pure molecular properties and packing effects in crystallographic unit.

Additionally CP MAS-NMR demonstrates a high potential for the investigation of substances insoluble in usual solvents (in such a case this method is indispensable) and sparingly soluble substances. In the Fig. 10 a high-resolution ^{13}C-NMR of **3**, only slightly soluble in most of organic solvents, is shown. It takes the overnight accumulation with 400 MHz superconducting spectrometer to obtain the spectrum from the saturated solution in acetone-d_6 with acceptable signal-noise ratio, whereas sufficiently good ^{13}C CP MAS-NMR spectrum was obtained after only 1 h from the solid. The analysis of the spectrum shows that we really deal with bischromium complex of biphenylene **3** (one can observe only upfield signals of the coordinated carbons and no signals from free aromatic carbons). Once again three carbonyl signals were observed as a result of unsymmetric surroundings of the $Cr(CO)_3$-group in the crystallographic unit (Fig. 3, cf. with the symmetric $Cr(CO)_3$-group projection on biphenylene plane from X-ray analysis, Fig. 2).

In spite of the fact that CP MAS-NMR spectra are very useful for the investigation of organometallic substances (especially of less soluble or even insoluble and unstable complexes and clusters), high-resolution NMR is actually employed more often for studying of such derivatives. It could probably be explained of difficulties with the interpretation due to the fact that

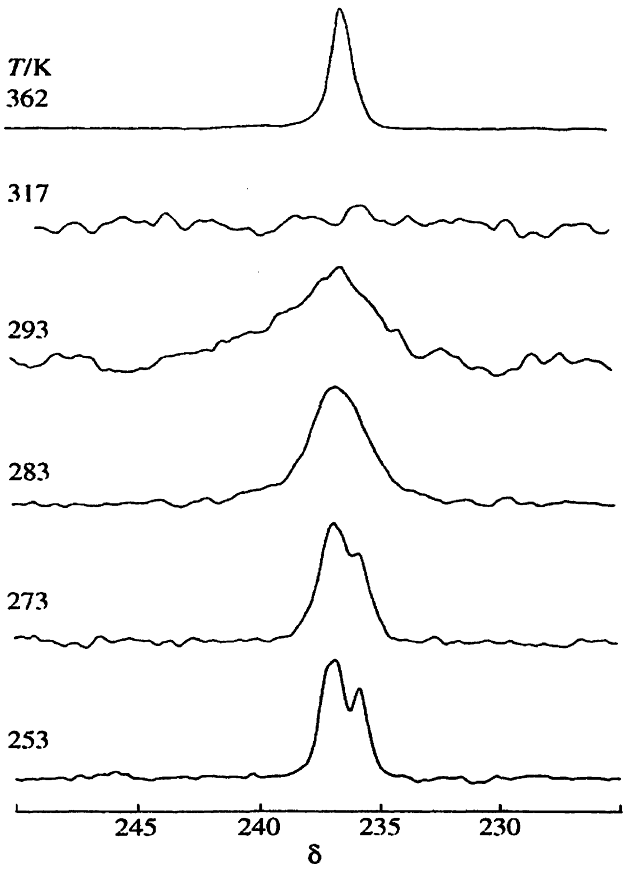


Fig. 9. ^{13}C CP MAS-NMR spectra of Cr(η^6-$C_6H_2Me_4$-1,2,4,5)$(CO)_3$ in carbonyl region at the temperatures indicated [35].

signals in CP MAS-NMR spectra are usually considerably broader and their number could exceed the number deduced from symmetry of the molecule.

These difficulties could be at least partially overcome by recording the spectra for the complexes supported on silica gel. It is well known that substances adsorbed on silica gel considerably increase their mobility [39] that leads to a considerable decrease of cross polarization. As the result signals in MAS-NMR spectra become narrower and informational quality of the spectra considerably increased. In this regards, a lack of side bands as a consequence of high mobility of the molecule adsorbed on silica gel that eliminates the chemical shift anisotropy, should be mentioned. Such spectra could even compete with the high-resolution spectra. In contrast, due to a negligible cross polarization no ^{13}C CP MAS-NMR spectra were detected in this case. Therefore, on the next experimental stage we have for the first time investigated MAS-NMR spectra of the chromium tricarbonyl complexes of PAH supported on silica gel. Previously such an approach was used by Günther et al. [40] for the investigation of PAH. In Fig. 11 ^{13}C MAS-NMR spectrum of **2** supported on silica is presented.

Additional advantages of this approach are that: (1) one needs no expensive deuterated solvents; (2) it is possible to investigate complexes directly after TLC without their intermediate separation that could be considered as an analytical tool as well as; (3) to investigate reactions on support surfaces [41] which is quite important in catalysis.

Carbon signals are quite narrow (<15 Hz) and completely resolved. It should be emphasized that the use of cross-polarization only deteriorates the quality of the spectra. This was explained by the considerable mobility of absorbed molecules and sharp decrease of dipole dipole interactions ^{1}H, ^{13}C.

Complex **2** has intermediate stability being supported on silica gel in comparison with few other investigated chromium tricarbonyl complexes of PAH such as naphthalene, biphenyl, 1,6-methano[10]annulene, etc. [42]. We observed a gradual decomposition of **2** at room temperature (25 °C) after preliminary heating of the adsorbed complex at 50 °C for 1 h in order to overcome the activation barrier of adsorption. During 8 h of heating the sample completely decomposed to form biphenylene and $Cr(CO)_6$ (the corresponding signal at 212 ppm was assigned by supporting of the pure chromium hexacarbonyl on silica gel).

Qualitative kinetic data of such decomposition are presented in Fig. 12a–d. An excess of the chromium was probably oxidized to Cr_2O_3 thus coloring silica gel in green. The rate of complex **2** decomposition depends on the silica gel pretreatment. For instance, degassing and storing silica under the argon atmosphere considerably increased the stability of adsorbed complexes.

For the complex **2** supported on silica gel sufficiently good resolved ^{1}H MAS-NMR was measured (Fig. 13). Signals belonging to (1) α- and to (2) β-protons of both coordinated and noncoordinated rings are separated.

Useful information (e.g. for assignment) for supported complexes, in general, could be obtained from the two-dimensional shift correlation spectra ^{13}C, ^{1}H (HETCOR) (Fig. 14). Corresponding HETCOR spectrum of **2** contains all the predicted peaks. The assignments of ^{1}H and ^{13}C spectra were done from solution spectra of deuterated complexes **4** and **6** and from solid state HETCOR and are consistent with previous assignments of Ceccon et al. [41].

Unfortunately, all the attempts to obtain ^{13}C and ^{1}H MAS-NMR spectra for **3** were ineffective. This can be explained with low mobility of this complex on silica and/or its low adsorption, which may be caused by the fact that both sides of the π system are now substituted by a chromium tricarbonyl group and a free molecular surface is absent. Further experiments will be done (changing of support, solvent for digestion etc) to overcome this problem.

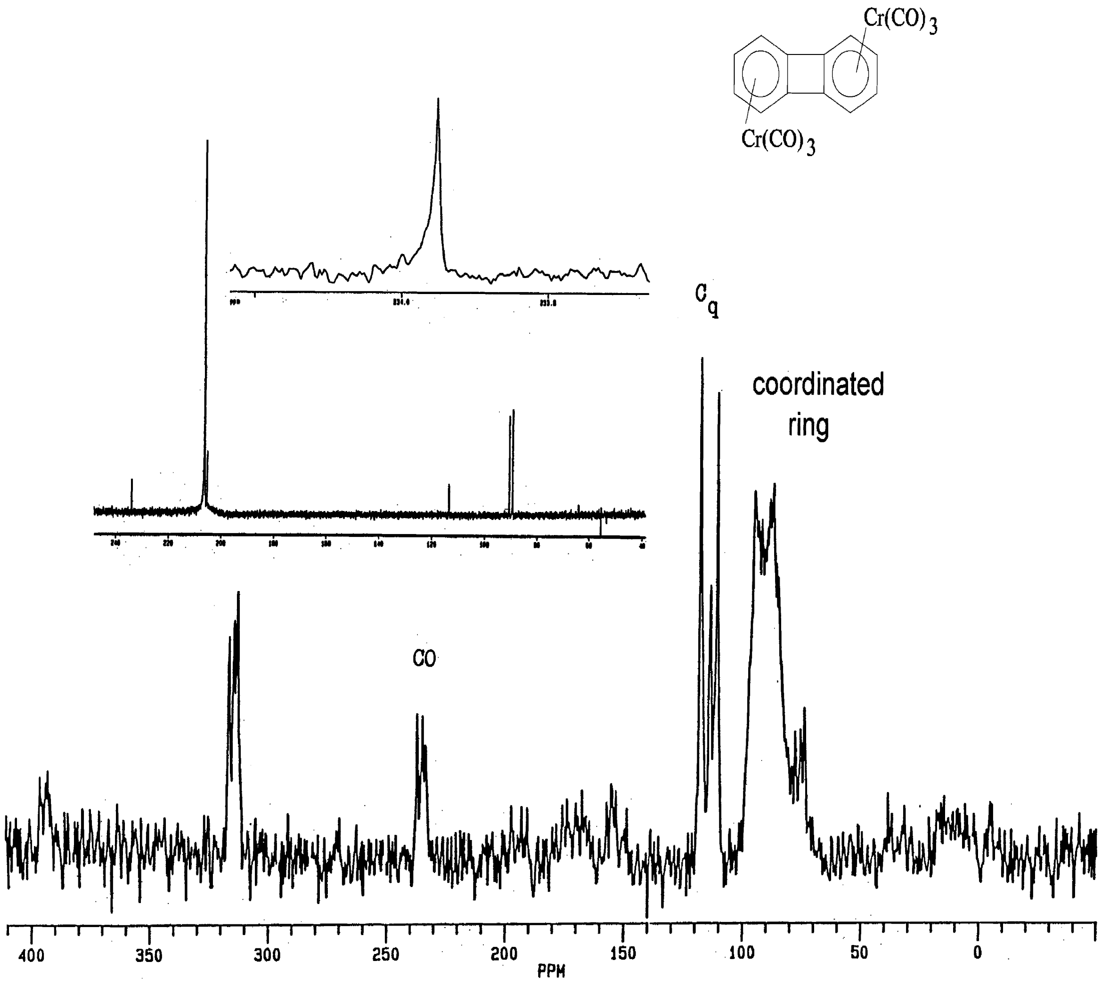


Fig. 10. ^{13}C CP MAS-NMR of polycrystalline **3**. An inset is a high-resolution ^{13}C-NMR spectrum of **3** in acetone-d_6.

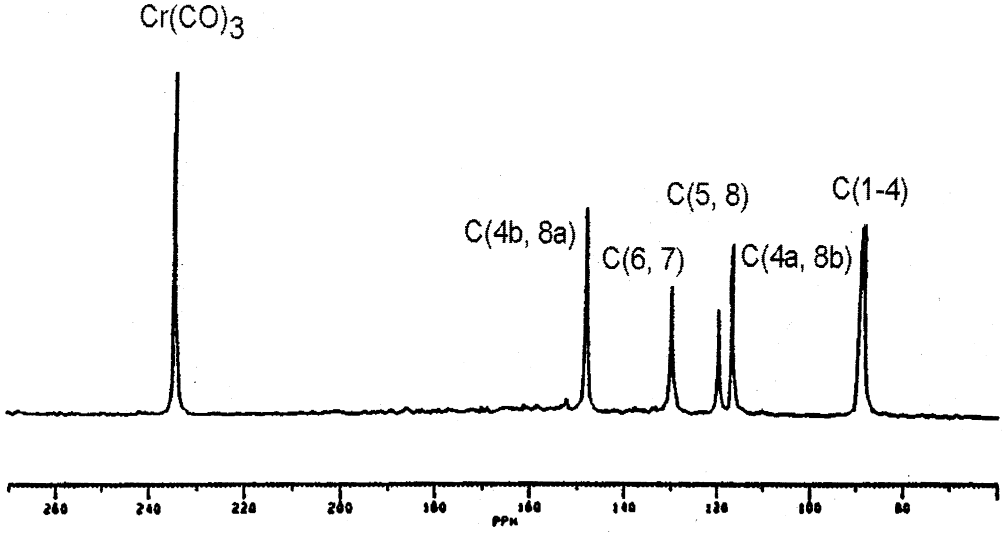


Fig. 11. ^{13}C MAS-NMR of **2** supported on silica gel.

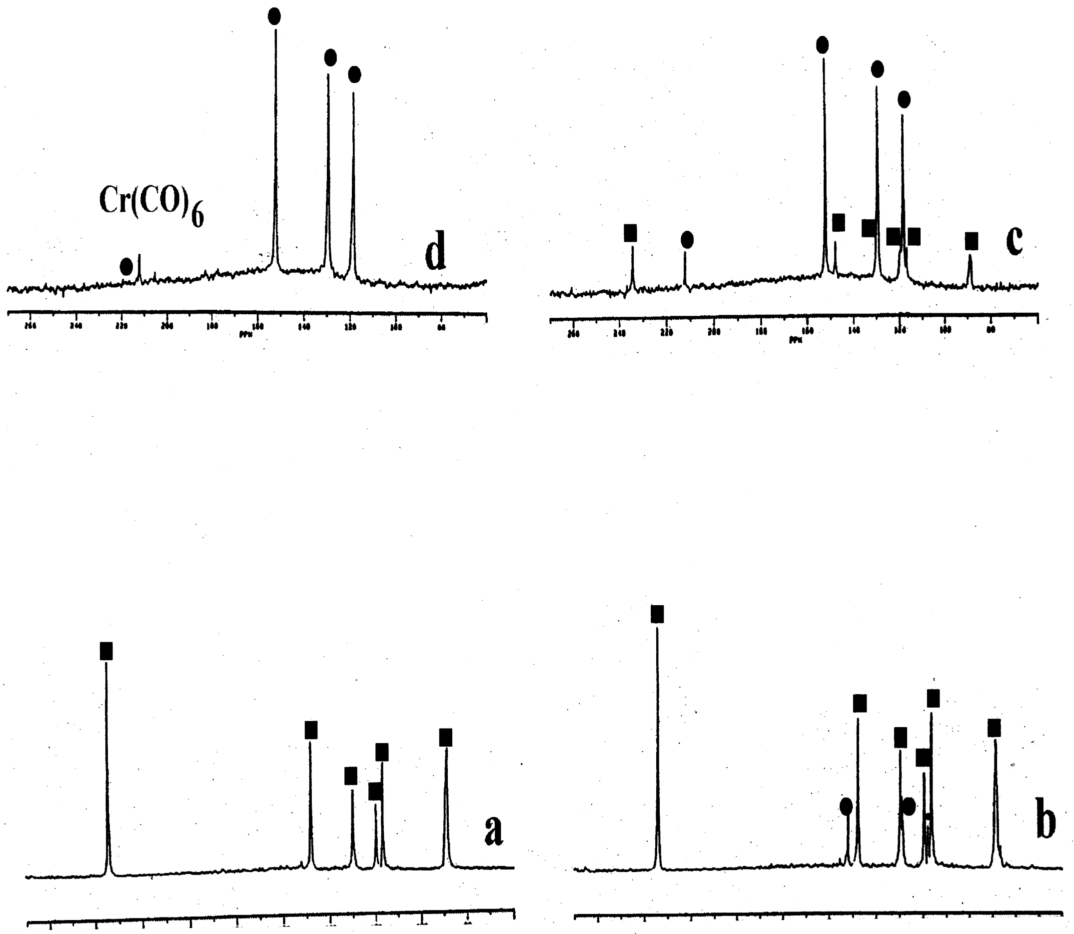


Fig. 12. ^{13}C MAS-NMR of (a) complex **2** supported on silica and kinetic of their decomposition at 25 °C, (b) after 4 h, (c) after 12 h, (d) after 24 h (pure biphenylene **1** and Cr(CO)$_6$:), ■ signals of the complex, ● signals of biphenylene and Cr(CO)$_6$.

3. The investigation of the mechanism of η^6,η^6-haptotropic rearrangements in biphenylene chromium tricarbonyls by means of density function theory (DFT)

Reasonable activation barrier for η^6,η^6-IRHR $\mathbf{4} \rightleftharpoons \mathbf{6}$ was obtained in the course of a detailed mechanistic investigation of the rearrangement by DFT. Recently it was shown that this method, which requires only very modest calculation expenditures [43] gives results qualitatively quite similar to the results of ab initio calculations. For calculations we used a program [44] with extended basis sets (triple-ζ basis) and approximation for exchange correlation energy (PBE functional [45]).

In this paper it was demonstrated that the calculation results reproduce very well structural parameters in η^6-biphenylene chromium tricarbonyl (ground state) including such details as differences in bond lengths of Cr atom with coordinated ring carbons and even Cr(CO)$_3$-group conformation for the ground state. These data are presented in Table 4 and in Fig. 15.

Two symmetrically located degenerated reaction routes were observed on potential energy surface. Except product (ground state) there are two equivalent intermediates and four transition states. Due to degenerative character of the IRHR, there are only three different stationary points (ground, intermediate and transition state) which are presented in Figs. 15–17, correspondingly: inter-atomic distances and relative energies for stationary points are presented in Table 4. The intermediate has quasi η^4-butadiene structure with C_s-symmetry in which the Cr(CO)$_3$-group is shifted to the periphery of four-membered ring of the ligand. Transition state energy fits very well corresponding experimental free activation energy, has the unsymmetric pseudo η^6-structure with the different distances of Cr to the carbons of six-membered ring C1–C6 and organometallic group also slightly shifted to the ligand periphery. It is noteworthy that the least motion route of Cr(CO)$_3$ from one ring to another via the centre of C5–C6 bond is forbidden. On the qualitative level these results are in accordance with those of Albright and

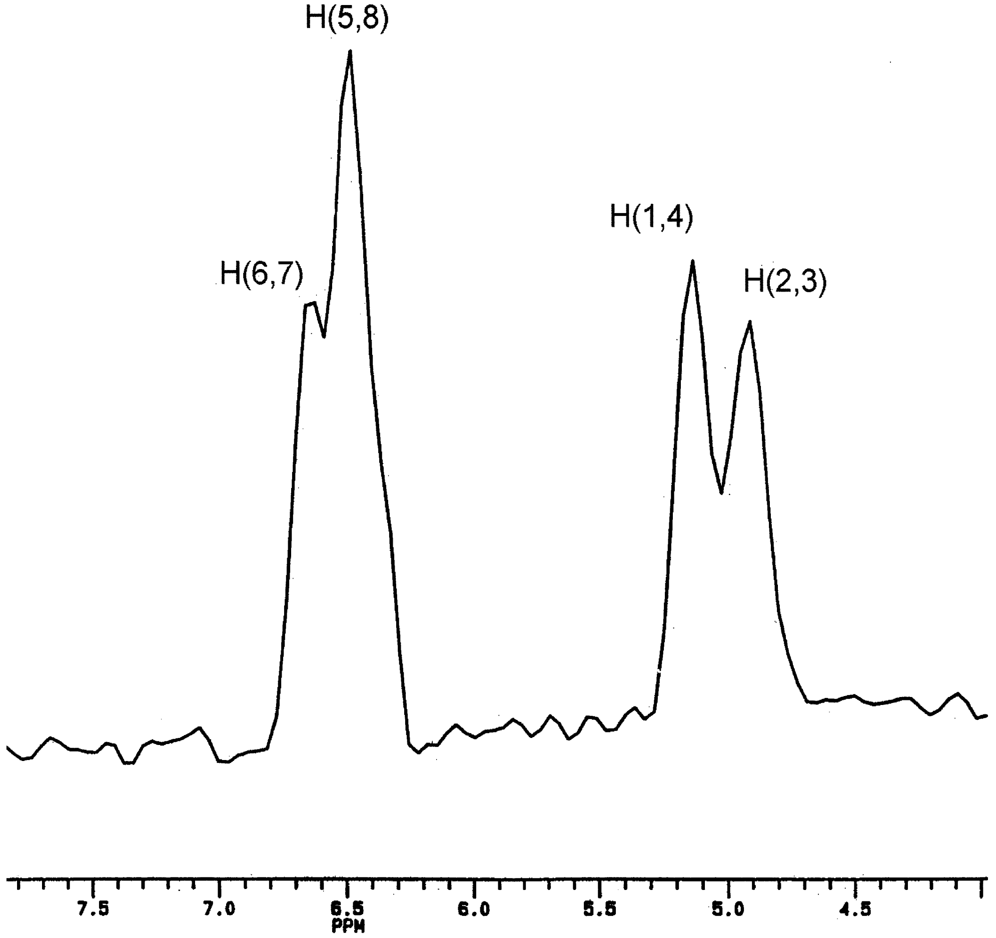


Fig. 13. ^{1}H MAS-NMR of **2** supported on silica gel (intensity deviation for the protons in non-coordinated ring could be explained by low digital resolution).

Hoffmann [2]. Relative energy of intermediate is decreased on 4 kcal mol^{-1} in comparison with transition state and is stabilised due to polycycle bending. It should be noted that potential energy surface near the locations of intermediate and transition state in the both directions (± 1 Å) are quite plane. This in some extent deteriorates the procedure of transition state localisation.

Considering the inherent approximations (approximation of isolated molecule, neglection of the difference of energies of zero vibration) the calculated activation barrier nevertheless is in good accordance with the experimentally determined $\Delta G^{\#}$.

4. Conclusions

A number of chromium tricarbonyl complexes of biphenylene were synthesized under stereoselective control and their IRHR rearrangements were investigated experimentally (NMR) and theoretically (DFT). Experimental activation barrier for IRHR fits very well with calculated theoretically.

As example for mono- and bis-chromium tricarbonyl complexes of biphenylene **2** and **3** it was shown that ^{13}C CP MAS-NMR spectroscopy is a very powerful method for the investigation of transition metal complexes of PAH which gives possibility to elucidate their structure, dynamic behavior and, in some instances, phase transitions. ^{1}H and ^{13}C MAS-NMR spectroscopy has additional advantages for studying of the complexes supported on inorganic oxides both for the elucidation of their structures and as the models for catalytic systems and for the investigation of adsorption processes in general. Besides there is a possibility to obtain the high-resolution spectra without using deuterated solvents immediately after thin layer or column chromatography. Some reactions of the substances supported on inorganic oxides as well as their kinetics could be investigated which is of great prospects in combinatorial chemistry [46].

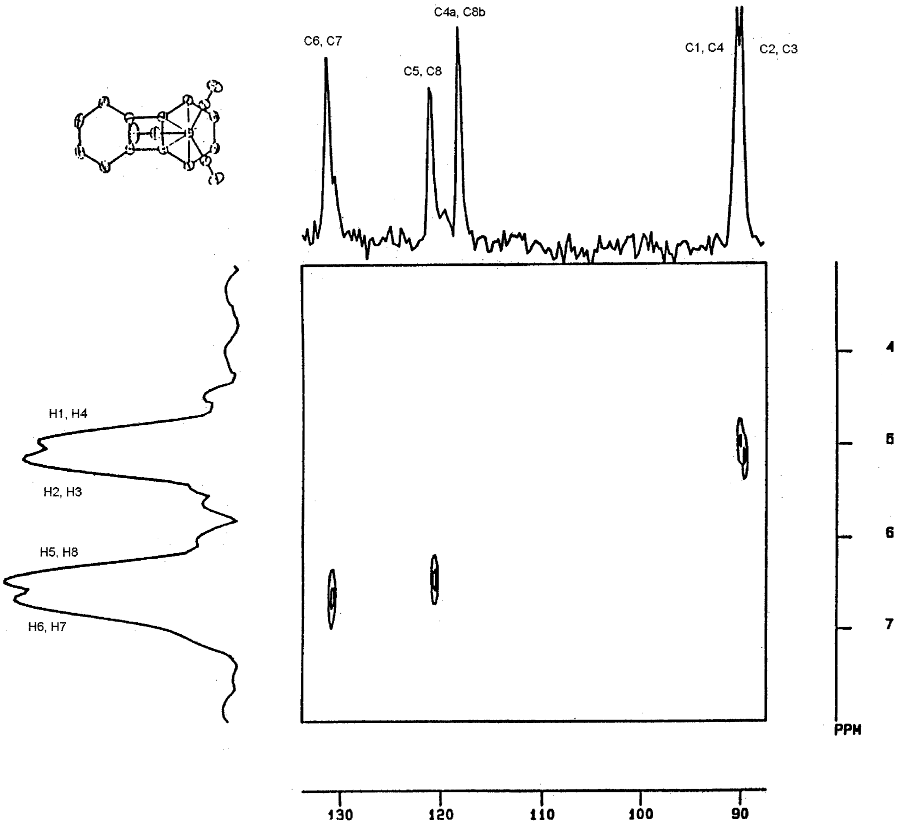


Fig. 14. 2D ^{13}C, ^{1}H-shift-correlation (HETCOR) of **2** adsorbed on silica.

Table 4
Relative energies and inter-atomic distances for stationary points on the potential energy surface of degenerate rearrangement **4**⇌**6** (for numeration see Figs. 15–17)

Parameters	Product	Transition state	Intermediate
ΔE (kcal mol^{-1})	0	33.3	29.4
R(Cr–C1)	2.262 (2.249) [a]	2.777	3.578
R(Cr–C2)	2.195 (2.199) [a]	2.947	3.917
R(Cr–C3)	2.195 (2.199) [a]	2.800	3.538
R(Cr–C4)	2.262 (2.249) [a]	2.481	2.671
R(Cr–C5)	2.252 (2.229) [a]	2.293	2.200
R(Cr–C6)	2.252 (2.229) [a]	2.447	2.703
R(Cr–C11)	3.345	3.059	2.200
R(Cr–C12)	3.345	3.215	2.703
R(Cr–C14)	4.546	4.118	2.671

[a] Experimental data [23].

5. Experimental

All operations, except TLC, were performed in a purified argon atmosphere. All solvents (ether, decane, THF, hexafluorobenzene) were purified by refluxing over K/Na alloy and distilled from it under argon just prior use. If not specially mentioned chromatography was carried out on silica 40/100 μ Chemapol (Bratislava). IR spectra were recorded on a spectrometer UR-20 Carl Zeiss in heptane. High resolution NMR spectra were recorded on a spectrometer Varian VXR-400 (400 Hz for ^{1}H). The assignments of the signals in ^{1}H-NMR spectra were done with the help of double resonance (in some cases COSY techniques was used) and Overhauser effect measurements by means of the NOEDIF procedure which is included in the software of the spectrometers. The assignment of the signals in ^{13}C-NMR spectra were done with the help of DEPT and by the comparison with the spectra of model compounds. All the solid state spectra were recorded with a Bruker MSL-300 spectrometer operating at ^{1}H frequency of 300.13 MHz and ^{13}C frequency of 75.5 MHz using a 4-mm o.d. ZrO_2 rotor. Chemical shifts were measured with respect to the spectrometer reference frequency which was calibrated for ^{1}H spectra by the high-field signal of adsorbed naphthalene which was set to 7.3 ppm, for ^{13}C spectra by the 38.4 ppm signal ($^{13}CH_2$ resonance) of adamantane as standard. Mass spectra were recorded on MAT-112S under electron impact of 70 eV. Grinding of the complex **2** with silica gel (35–70 mesh, ASTM, product no. 7733, Merck, Darmstadt), a ratio from 1:4 to 1:10 (w/w)) gives samples suitable for ^{13}C CP MAS-NMR.

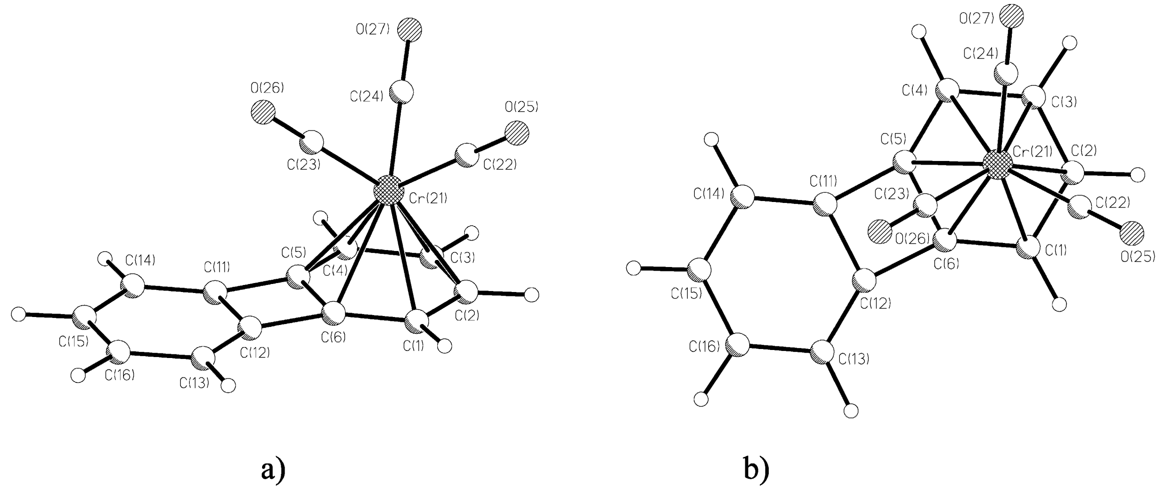


Fig. 15. A side (a) and a top (b) view and numbering system in **2**. Please note that numeration differs from those accepted in Tables 1 and 2 (X-ray) and Table 3 (NMR).

5.1. Synthesis of the complexes (1–4,4a,8b-η^6-biphenylene)chromium tricarbonyl (2) and (μ-η^6:η^6-biphenylene)bis-(chromium tricarbonyl) (3)

Freshly distilled $BF_3 \cdot OEt_2$ (3.90 g, 34.6 mmol) was added to a mixture of 1.12 g (7.4 mmol) of biphenylene and 2.28 g (6.1 mmol) $Cr(CO)_3Py_3$ in 50 ml of ether at −10 °C. After the stirring at 25 °C for 30 min solution was filtrated and washed three times with water and dried over anhydrous $MgSO_4$. After the ether was removed in vacuo the residue was chromatographed on 3×40 silica gel column using petroleum ether/benzene mixture as eluent. First zone was eluted with benzene–petroleum ether. After recrystallization from benzene/heptane 1.10 g of **2** (62%) was obtained as orange–red crystals, m.p. 144–146 °C. Mass spectra: *m*/*e* 288 (22%, $[M]^+$); 260 (3%, [M−CO]); 232 (12%, [M−2CO]); 204 (50%, [M−3CO]), 152 (7%, [M−$Cr(CO)_3$]) 52 (100%, Cr). IR spectra: (ν_{CO}): 1974, 1917, 1907 cm^{-1} (heptane). ^1H- and ^{13}C-NMR data are presented in Table 3. Anal. Found: C, 62.35; H, 2.90; Cr, 18.20; O, 16.55. Calc. for $C_{15}H_8CrO_3$: C, 62.51; H, 2.80; Cr, 18.04; O, 16.65%.

The second zone was eluted with benzene. After recrystallization from benzene/heptane 0.10 g of **3** (4%) was obtained as orange–red crystals, m.p. 255–258 °C (dec.). Mass spectra: *m*/*e* 424 (8%, $[M]^+$); 368 (5%, [M−2CO]); 340 (12%, [M−3CO]); 312 (2%, [M−4CO]), 284 (14%, [M−5CO]), 256 (30%, [M−6CO]), 204 (23%, [M−$Cr(CO)_6$]), 152 (6%, [M−$2Cr_2(CO)_6$]), 52 (100, Cr). IR spectra: (ν_{CO}): 1973, 1917, 1906 cm^{-1} (heptane). ^1H- and ^{13}C-NMR data are presented in

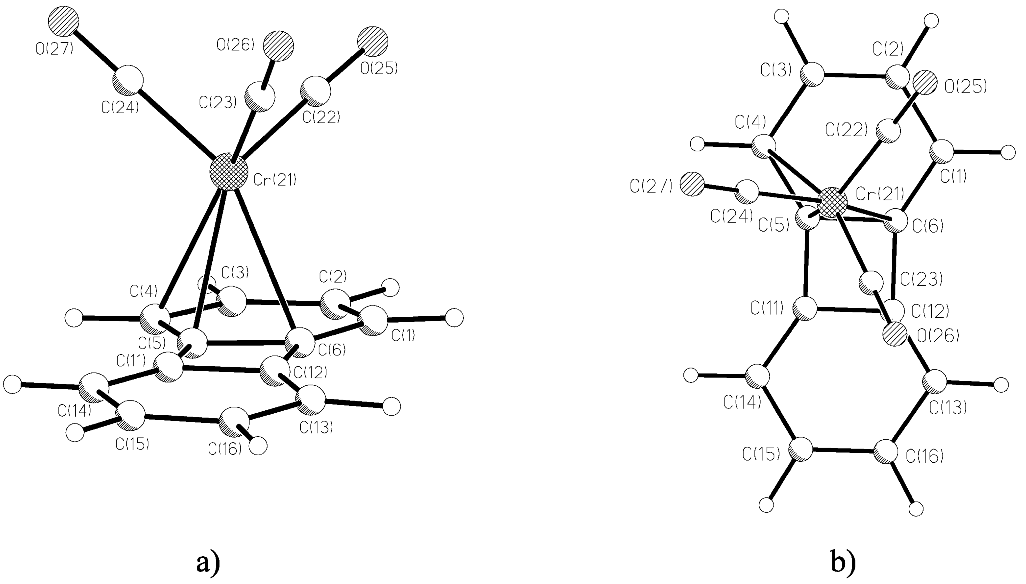


Fig. 16. A side (a) and a top (b) view and numbering system in transition state for the rearrangement $\mathbf{4} \rightleftharpoons \mathbf{6}$.

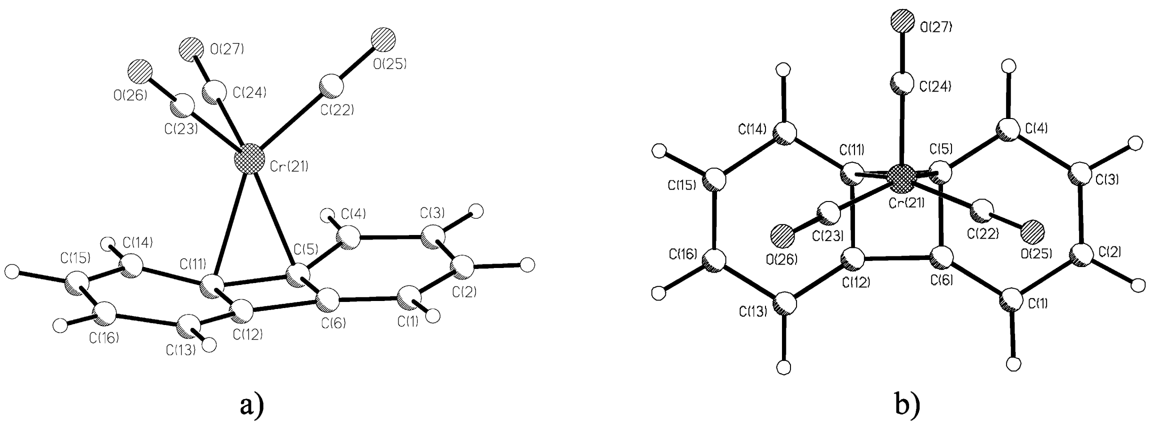


Fig. 17. A side (a) and a top (b) view and numbering system in intermediate for the rearrangement **4**⇌**6**.

Table 3. Anal. Found: C, 50.90; H, 2.00; Cr, 24.95; O, 22.15%. Calc. for $C_{15}H_8Cr_2O_6$: C, 50.90; H, 1.90; Cr, 24.51; O, 22.63%.

*5.2. Synthesis of the complexes (1-deuterio-1-4,4a,8b-η^6-biphenylene) chromium tricarbonyl (**4**) and (1-methyl-1-4,4a,8b-η^6 -biphenylene) chromium tricarbonyl (**5**)*

A solution of **3** in THF was treated by *n*-BuLi in hexane at −70 °C. The ratio of **3**/BuLi was 1:2. After stirring for 5 min temperature was slowly increased to −60 °C and solution coloured in red. After stirring for 30 min reaction mixture was treated with D_2O or CH_3I in THF and stirred for 30 min. After solvent at 0 °C was removed in vacuo, the residue was chromatographed on 3 × 40 silica gel column using petroleum ether/benzene mixture as eluent. Complexes were recrystallized from benzene/heptane.

For **4**: from 0.20 g (0.70 mmol) of **2** in 30 ml THF and 0.1 ml D_2O in 5 ml of THF 0.14 g (70%) of **4** was obtained, m.p. 140–142 °C. Mass spectra: *m/e* 289 (100%, $[M]^+$); 261 (8%, [M−2CO]); 233 (13%, [M−3CO]); 153 (3%, $[M-Cr(CO)_3]$), 52 (15, Cr). IR spectra: (ν_{CO}): 1974, 1917, 1907 cm^{-1} (heptane).

For **5**: from 0.15 g (0.52 mmol) of **2** in 30 ml THF and 1.5 g of freshly distilled CH_3I (10 mM) 0.11 g (75%) of **5** was obtained, m.p. 159–161 °C. Mass spectra: *m/e* 302 (70%, $[M]^+$); 274 (2%, [M−CO]); 246 (20%, [M−2CO]); 218 (38%, [M−3CO]), 166 (100%, $[M-Cr(CO)_3]$), 52 (48, Cr). IR spectra: (ν_{CO}): 1981, 1924, 1911 cm^{-1} (heptane). ^1H- and ^{13}C-NMR data are presented in Table 3. Anal. Found: C, 63.62; H, 3.20; Cr, 17.06; O, 16.00. Calc. for $C_{16}H_{10}CrO_3$: C, 63.58; H, 3.30; Cr, 17.22; O, 15.89%.

6. Supplementary material

Supplementary tables are available from the author upon request.

Acknowledgements

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