Journal of Organometallic Chemistry, 319 (1987) 229–237
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

SYNTHESIS AND CRYSTAL STRUCTURE OF NONAMETHYLRUTHENOCENYLCARBENIUM HEXAFLUOROPHOSPHATE

A.Z. KREINDLIN, P.V. PETROVSKII, M.I. RYBINSKAYA*, A.I. YANOVSKII
and YU. T. STRUCHKOV

A.N. Nesmeyanov Institute of Organoelement Compounds, Academy of Sciences,
28 Vavilov Street, 117813 Moscow (U.S.S.R.)

(Received June 19th, 1986)

Summary

The hitherto unknown functional derivatives of decamethylruthenocene (I), viz. $(C_5Me_5)RuC_5Me_4CHO$ (II), and $C_5Me_5RuC_5Me_4CH_2OH$ (III) have been synthesized. The interaction of III with acids results in $C_5Me_5RuC_5Me_4CH_2{}^+$ X^- (IV, $X = BF_4$, PF_6) which contain the carbocationic center stabilized by direct interaction with the Ru atom. NMR and X-ray structural data for the salt IV ($X = PF_6$) indicate the strong $Ru \cdots C^+$ interaction (the $Ru \cdots C^+$ distance is 2.603 Å).

Earlier, we reported the synthesis and properties of the nonamethylferrocenylcarbenium ion [1,2]. The present investigation was undertaken so as to compare this ion with its analogs. Synthesis of the nonamethylruthenocenylcarbenium ion * from decamethylruthenocene was carried out using the method for obtaining ferrocene derivatives [1].

Decamethylruthenocene (I) was obtained by a modified method [3]. Oxidation of methyl groups by $BaMnO_4$, as in ref. 1 results in a mixture of mono- and dialdehydes, $C_5Me_5RuC_5Me_4CHO$ (II) and $C_{18}H_{24}Ru(CHO)_2$. According to mass spectroscopy and NMR data the main component of the mixture of dialdehydes is the homoannular 1,2-isomer. The oxidation of I requires more rigorous conditions than decamethylferrocene [1].

Reduction of II by $LiAlH(OBu^t)_3$ results in $C_5Me_5RuC_5Me_4CH_2OH$ (III). Compounds II and III were identified by elemental analysis, IR, NMR and mass spectra (Tables 1 and 2).

Treatment of the carbinol III with acids (CF_3SO_3H, HBF_4 and HPF_6) yields the salts of nonamethylruthenocenylcarbenium. $C_5Me_5RuC_5Me_4CH_2{}^+$ X^- (IV). Solid

---

* Preliminary results have been published in [4,5]. While the X-ray structural study was in progress another synthetic route to this ion was reported [6].

0022-328X/87/$03.50

TABLE 1

PROPERTIES OF COMPOUNDS

Compound	Yield (%)	m.p. (°C)	IR spectrum (cm^{-1})	Analysis (%)		Empirical formula	Calcd. (%)		Mass spectrum, (relative intensity, %)
				C	H		C	H	
$C_5Me_5RuC_5Me_5$	32	308–311	–	–	–	$C_{20}H_{30}Ru$	–	–	372 M^+ (100)
$C_5Me_5RuC_5Me_4CHO$	38	296–298	1670 (ν(CO))	62.70	7.31	$C_{20}H_{28}ORu$	62.31	7.32	386 M^+ (100), 358 [M–CO]$^+$ (70), 357 [M–CHO]$^+$ (73)
$C_5Me_5RuC_5Me_4CH_2OH$	72	263–265	3620 (ν(OH))	62.24	7.63	$C_{20}H_{30}ORu$	61.99	7.80	388 M^+ (100), 372 [M–O]$^+$ (27) 370 [M–H_2O]$^+$ (37)
$C_{18}H_{24}Ru(CHO)_2$	5	248–250				$C_{20}H_{26}O_2Ru$	–	–	400 M^+ (100) 372 [M–CO]$^+$ (40), 371 [M–CHO]$^+$ (61), 344 [M–2CO]$^+$ (95), 343 [M–CO–CHO]$^+$ (99), 342 [M–2CHO]$^+$ (67)
$C_5Me_5RuC_5Me_4CH_2{}^+$ $BF_4{}^-$	84	180–230		50.98	6.91	$C_{20}H_{29}BF_4Ru$	52.53	6.39	

TABLE 2

NMR SPECTRA OF COMPOUNDS

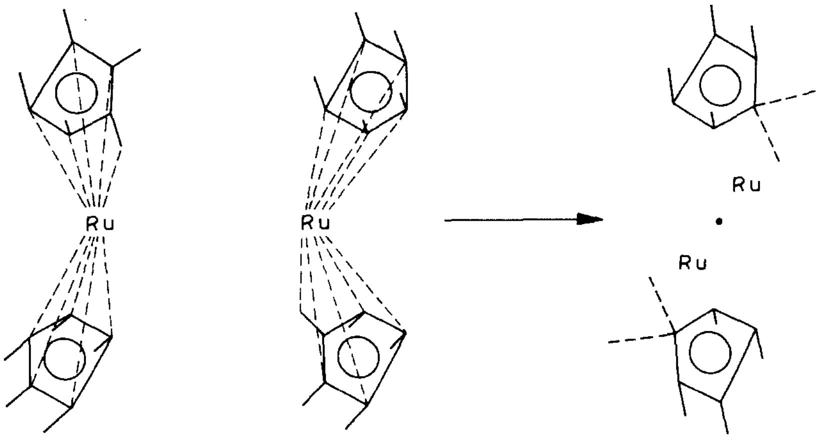
Compound	Chemical shifts (ppm)		
	Protons of functional groups	Me protons of C_5Me_4X-ring	Me-protons of C_5Me_5-ring
$C_5Me_5RuC_5Me_4CHO$ [a]	9.639(1) [b] (CHO)	1.910(6) 1.700(6)	1.643(15)
$C_5Me_5RuC_5Me_4CH_2OH$ [a]	4.013(1) (OH) 3.896(2) (CH_2)	1.791(6) 1.607(6)	1.653(15)
$C_5Me_5RuC_5Me_4CH_2{}^+$ $CF_3SO_3{}^-$ [c]	4.378(2) ($CH_2{}^+$)	1.861(6) 1.538(6)	1.773(15)
$C_5Me_5RuC_5Me_4CH_2{}^+$ BF_4^- [d]	4.748(2) ($CH_2{}^+$)	1.959(6) 1.630(6)	1.860(15)
$C_{18}H_{24}Ru(CHO)_2$ [e]	9.936(CHO) 9.640 (CHO) 9.737 (CHO)	2.019 1.173	1.657 1.647

[a] In $CDCl_3$. [b] Values of integral intensities of signals are given in brackets. [c] Solution of II in $CDCl_3/CF_3SO_3H$. [d] In $(CD_3)_2CO$. [e] Isomer mixture. ^{13}C Spectrum $C_5Me_5RuC_5Me_4CH_2{}^+$ $PF_6{}^-$ (in CH_2Cl_2): 107.201, 105.361, 97.215, 96.924 – $\mathit{C}_5Me_4CH_2{}^+$, C_5Me_5; 77.768 (triplet, ^1J(CH) 165 Hz) – $\mathit{C}H_2{}^+$; 8.735 (quadruplet, ^1J(CH) 129 Hz); 8.012 (quadruplet ^1J(CH) 163 Hz) – $C_5\mathit{Me}_4CH_2{}^+$; 9.514 (quadruplet, ^1J(CH) 129 Hz) – $C_5\mathit{Me}_5$.

tetrafluoroborate and hexafluorophosphate were isolated. The NMR data indicate that the signals of the protons and those of the carbon nucleus of the $CH_2{}^+$ group in IV are shifted up-field by 0.5–0.8 ppm (^{1}H NMR) and 16 ppm (^{13}C NMR) (see Table 2) relative to similar signals in the spectra of $C_5Me_5FeC_5Me_4CH_2{}^+$ X^- (V) [1]. These data are indicative of more considerable shielding of the corresponding ^{1}H and ^{13}C nuclei in IV, i.e. a much greater stabilization of the carbenium center by the Ru atom. The results of the X-ray studies of IV ($X = PF_6$) confirm this assumption.

Structural studies, of compounds in which the carbocationic center is stabilized by the metallocenyl fragment, are numerous [7–9]. The geometrical parameters of molecules in such compounds are of interest with regard to the stability of carbocations of this type and, in particular, to the possibility of the stabilization of the cationic centre by direct interaction with the metal atom. The synthesis and analysis of IV not only extends the number of different metals for which complexes of this kind have been structurally characterized (the majority of those cited above were derivatives of Fourth Period metals) but also allows elucidation of specific features of the carbocations obtained from polyalkylated cyclopentadienyl ligands. In this connection it is noteworthy that IV is the first example of a stable primary carbenium ion in the metallocene series which has been isolated as an individual solid compound.

Analysis of the geometry of cation IV is complicated by disorder found in the structure (see the Experimental section). This disorder is likely to be caused by the asymmetric cation $Ru(C_5Me_5)(C_5Me_4CH_2)^+$ having a symmetric "external" shape and the shift of the metal towards one of the ligands "inside the cation" should have an insignificant effect on the interionic distances in the structure. Thus the observed disorder originates from the statistical superposition of two orientations of



the cation IV related to each other by an inversion center. In the structural study, this superposition is manifested as the disorder of the Ru atom and one of the carbon atoms (C(6) in Fig. 1)..

It should be noted that such disorder of the metal atom in a π-complex sandwich system was observed earlier in a structural study of beryllocene [10] where the Be atom is η^5 bonded to one of Cp rings and η^1 bonded to the other. Crystals of this non-symmetric molecule occupy a special position at the inversion center (space group $P2_1/n$, $Z = 2$), with the ordered atoms of the Cp rings and the Be atom disordered over two positions related by the inversion center.

The disorder of atom C(6) in the cation IV has not been resolved in the present study. Therefore, the experimentally found position of C(6) should be regarded as an intermediate location between the methyl group carbon atom in the penta-

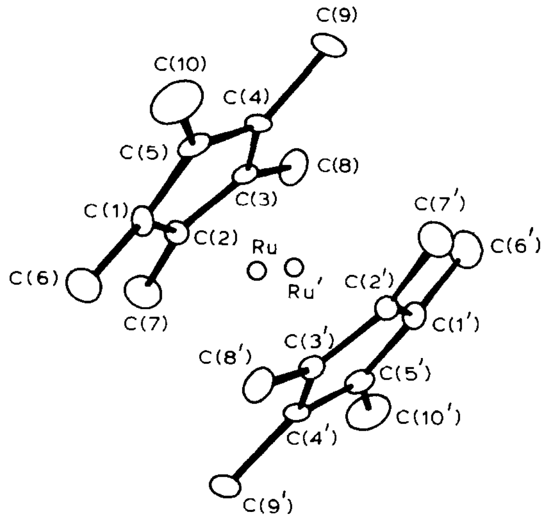


Fig. 1. The structure of cation IV.

methylcyclopentadienyl ligand and the actual location of the carbocationic atom C in $(Me_5C_5)Ru(C_5Me_4CH_2)$.

Despite these complications the geometrical parameters of cation IV clearly indicate the existence of direct metal-carbocationic center interaction. This interaction gives rise to a shift of the metal atom towards C(6) resulting in considerable variations in the Ru ··· C(Cp) distances (Table 4) * and a significant displacement of the C(6) atom (0.393(9) Å) from the Cp ring which is planar to within 0.01 Å. Unlike carbon atoms of Me groups C(7)–C(10) which are displaced from the Cp plane by 0.06–0.09 Å away from the metal atom, as is common for alkylcyclopentadienyl complexes [11–13], the carbocationic atom C(6) deviates from this plane in the direction of the Ru atom (the C(1)–C(6) bond is inclined by 14.4° to the Cp-ring plane). The short C(1)–C(6) bond length of 1.424(8) Å shows the specific nature of the C(6) atom and may be regarded as evidence of the partial fulvene character of the ligand (the lengths of other exocylic bonds are within the range 1.516–1.537 Å). Yet the distribution of the C–C bond lengths in the cycle (Table 4) does not fully support this assumption.

The metal atom shift, on the one hand, and the displacement of the C(6) atom from the Cp ring plane, on the other, result in a rather short Ru ··· C(6) distance of 2.603(8) Å (the distances from the Ru atom to the other Me group carbon atoms lie in the range 3.20–3.47 Å). This value is considerably smaller than the $M \cdots C^+$ distances found in a number of carbocations stabilized by the ferrocenyl group (2.715 Å in $C_5H_5FeC_5H_4CPh_2{}^+BF_4{}^-$ [8], 2.78 Å in $(C_5H_5FeC_5H_4CHC_5H_4FeC_5H_5)^+\ BF_4{}^-$ [7], and is close to the value of 2.55 Å obtained for the chromium fulvene complex $(OC)_3CrC_5H_4CPh_2$ [9]. Owing to the disorder discussed above, the experimental deviation of the C(6) atom from the Cp-ring plane is somewhat smaller, and the observed Ru–C(6) distance is greater than the actual values, and it may be assumed that of all the structures of complexes with a carbocationic center stabilized by a π-cylopentadienyl ligand the $M–C^+$ interaction in complex IV is strongest. This conclusion, prompted by the geometric parameters of cation IV, is in good agreement with the data obtained from the comparison of the reactivity and chemical behaviour of its salts and other carbocationic complexes.

Reduction of the salts of IV with $NaBH_4$ leads to decamethylruthenocene (I). Unlike its ferrocene analog V [1,2], solutions of IV or solid samples left to stand at 20°C for several months or at 80°C for 2–3 h do not yield paramagnetic products or dimeric 1,2-bis(ruthenocenyl)ethanes.

The relative stability of the salts (IV) is likely to be due to a decreased susceptibility of ruthenium derivatives to oxidation compared with their iron analogs **. The oxidative potential of the Ru atom in I (+0.55 V) is significantly higher than that of the Fe atom in $(C_5Me_5)_2Fe$ (−0.08 V) [3]. Besides, the stability of ruthenocenylcarbenium ions may be associated with a more effective interaction of the carbenium center with the Ru atom as compared with the similar interaction

---

* Despite a considerable scatter of the Ru–C(Cp) bond lengths in cation IV (1.877–2.351 Å), the mean value of 2.186 Å is in good agreement with the mean Ru–C distances in ruthenocene [14] and decamethylruthenocene [13] (2.186 and 2.176 Å respectively).

** The ability of ferrocenylcarbenium ions to dimerize in contrast to the analogous ruthenocene derivatives has been discussed in the literature [15].

in the ferrocene derivative owing to the greater dimensions and polarizability of the Ru atom. Unlike their ferrocene analogs, the higher stability of ruthenocenylcarbenium ions is likely to be responsible for the inability of these ions to undergo a singlet → triplet transition.

Experimental

Mass spectra were recorded with AEI-MS spectrometer, ^1H and ^{13}C NMR spectra were recorded with a Bruker WP-200 SY spectrometer, at 200.13 and 50.31 MHz, respectively. Chemical shifts (δ) were measured relative to internal TMS. C_5Me_5H was obtained by the procedure described in [16].

Preparation of the compounds

Preparation of I (A). 0.7 g of zinc dust (washed with aqueous HCl, water and alcohol) was added to a solution of 2.7 g (20 mmol) of C_5Me_5H, 0.7 g (3.4 mmol) of $RuCl_3$ in 50 ml of MeOH at 45°C. The mixture was stirred for 5 h at the same temperature and then filtered. The solid residue on the filter and the flask were washed repeatedly with benzene. All organic extracts were combined and the volume reduced, the dark oil obtained was dissolved in acetone and cooled. Crystals of I were separated and recrystallized from acetone. The yield was 0.4 g (1.08 mmol, 32%), m.p. 309–311°C.

Preparation of I (B). A solution of 0.5 g of $NaBH_4$ in 10 ml of 50% aqueous alcohol was slowly added dropwise to a solution of 2.7 g (20 mmol) of C_5Me_5H and 0.7 g of $RuCl_3$ (3.4 mmol) in 50 ml of 90% aqueous alcohol at 45°C. The mixture was stirred at the same temperature for 5 h and treated as for (A). 0.4 g I (32%) was obtained.

Preparation of II. A solution of 1.9 g (5.1 mmol) of I in 300 ml of dry benzene was refluxed with stirring for 8 h with 20 g of $BaMnO_4$. The solution was separated from the precipitate, evaporated and chromatographed on silica gel. I was eluted by benzene and 0.4 g was recovered. Monoaldehyde II was eluted by a benzene : ether mixture (19 : 1, 15 : 1), the yield was 0.6 g (1.5 mmol, 38%). The substance was recrystallized from a benzene : hexane mixture. The mixture of dialdehydes was eluted by a benzene : ether mixture (5 : 1, 4 : 1). The yield was 0.08 g.

Preparation of III. A solution of 3.3 g (45 mmol) of t-BuOH in 15 ml of dry ether was added dropwise to a suspension of 0.6 g (15 mmol) of $LiAlH_4$ in 50 ml of dry ether, during 15 min. The mixture was stirred for another 10 min and then a solution of II 0.8 g (2.1 mmol) in 50 ml of dry ether was added dropwise during 0.5 h. The mixture was stirred for 2 h at 20°C, and then under reflux for another 15 min. The excess of reducing agent was decomposed by careful addition of water. The ether layer was removed and the water layer was extracted with ether. Organic extracts were washed with water, dried over Na_2SO_4 and evaporated to dryness. The residue was recrystallized from a benzene : hexane mixture. The yield was 0.6 g (1.5 mmol, 72%).

Preparation of IV ($X = BF_4$, PF_6). A solution of 0.8 ml of 48% aqueous HBF_4 or 70% HPF_6 in 3 ml of $(CF_3CO)_2O$ and 10 ml of dry ether was added dropwsie during 5 min to 30 ml of an ether solution of 0.3 g (0.8 mmol) of III containing 0.5 ml of $(CF_3CO)_2O$. The yellow precipitate was separated by filtration, washed with dry ether, dissolved in 5 ml of CH_2Cl_2 and precipitated again by 50 ml of dry ether and

TABLE 3

ATOMIC COORDINATES AND THEIR EQUIVALENT ISOTROPIC TEMPERATURE FACTORS

Atom	x	y	z	$B_{\text{iso}}^{\text{eq.}}$ ($\times$Å^2)
Ru [a]	0.48849(5)	0.47109(6)	0.50360(5)	3.20(1)
P [a]	1/2	1/2	0	5.15(3)
F(1A) [a]	0.5987(8)	0.525(1)	0.0911(6)	11.9(3)
F(1B) [a]	0.5584(6)	0.3409(8)	0.0524(6)	9.8(2)
F(2A) [a]	0.4615(7)	0.6767(8)	0.0179(6)	11.1(2)
F(2B) [a]	0.5869(9)	0.600(1)	0.0691(1)	17.0(2)
F(3)	0.3796(4)	0.4721(4)	0.0752(3)	10.8(1)
C(1)	0.5061(4)	0.2446(6)	0.5127(4)	6.6(1)
C(2)	0.5982(4)	0.3078(6)	0.5853(3)	5.34(9)
C(3)	0.6966(3)	0.3892(5)	0.5326(3)	4.80(8)
C(4)	0.6702(4)	0.3781(5)	0.4273(3)	5.61(9)
C(5)	0.5531(5)	0.2858(6)	0.4130(3)	6.2(1)
C(6)	0.3749(6)	0.192(1)	0.5368(8)	12.7(2)
C(7)	0.5937(7)	0.282(1)	0.7010(4)	11.2(2)
C(8)	0.8168(5)	0.4699(7)	0.5807(6)	9.2(2)
C(9)	0.7618(6)	0.4458(9)	0.3437(5)	11.2(2)
C(10)	0.4902(8)	0.235(1)	0.3120(5)	13.0(2)

[a] Site occupation factor $G = 0.5$.

filtered. 0.3 g (84%) of tetrafluoroborate or 0.35 g (85%) of hexafluorophosphate was obtained.

Reduction of IV. 0.2 g (0.44 mmol) of IV was added to a solution of 0.3 g of $NaBH_4$ in 50 ml of THF. The reaction proceeded immediately. The mixture was poured into water and extracted with ether. 0.15 g (92%) of I was obtained (m.p. 308–309°C; the admixture probe showed no depression).

X-Ray analysis

Crystals of IV are monoclinic, at +20°C a 10.045(1), b 8.233(1), c 13.125(2) Å, β 90.06(1)°, V 1085.5 Å^3, space group $P2_1/n$, $Z = 2$, d_{calc} 1.577 g/cm^3. The cell parameters and intensities of 1435 independent reflections with $F^2 \geqslant 5\sigma$ were measured with an Enraf–Nonius CAD-4 diffractometer (+20°C, λMo-K_α graphite monochromator, ω/θ scan, the scanning rate ratio $\omega/\theta = 6:5$, $\theta \leqslant 26°$).

The structure was solved by the heavy-atom technique. The coordinates of Ru and P atoms which occupy special positions in the inversion centers were found from Patterson syntheses. Other non-hydrogen atoms were located by electron density synthesis; two of the three independent F atoms proved to be disordered in two positions. This indicates that the disorder of the PF_6 anion about the two positions differs by a rotation of $\sim 60°$ around the F(3) $\cdots$ F(3′) axis. The refinement of the structure by the full-matrix least-squares technique in the anisotropic approximation resulted in discrepancy factors of $R = 0.064$ and $R_w = 0.075$. Refinement showed that one of the terminal (exocyclic) carbon atoms, viz. C(6) formed a considerably shorter bond with the Cp ring compared with other C(Cp)–C(Me) bonds. In contrast to other C–C exocyclic bonds, this bond is inclined to the Cp-ring plane towards the metal atom (see above). In the difference Fourier synthesis the highest peak was located 0.3 Å away from the Ru atom. This peak was shifted towards the "peculiar" terminal C atom. When this peak was

TABLE 4

BOND LENGTHS (Å)

Ru–C(1)	1.877(5)	C(1)–C(6)	1.424(8)
Ru–C(2)	2.041(4)	C(2)–C(7)	1.534(7)
Ru–C(3)	2.229(3)	C(3)–C(8)	1.516(7)
Ru–C(4)	2.219(4)	C(4)–C(9)	1.537(7)
Ru–C(5)	2.041(4)	C(5)–C(10)	1.526(8)
Ru–C(6)	2.603(8)	P–F(1A)	1.566(7)
C(1)–C(2)	1.426(6)	P–F(1B)	1.591(7)
C(2)–C(3)	1.380(6)	P–F(2A)	1.524(7)
C(3)–C(4)	1.410(6)	P–F(2B)	1.506(9)
C(4)–C(5)	1.412(6)	P–F(3)	1.579(4)
C(5)–C(1)	1.432(7)		

included in the refinement, with site occupation factor $G = 0.5$ instead of the previously used Ru atom located at the inversion center, a considerable decrease in the discrepancy factors (to $R = 0.035$, $R_w = 0.047$) and a significant increase in the accuracy of geometrical parameters were achieved. Further attempts to improve the structure (by locating the H atoms and resolving the disorder of C(6) (see above)) failed. Attempts to refine the structure in different space groups with higher or lower symmetry also proved unsuccessful. Although refinement in the space group *Pn* resulted in sufficiently low *R*-values ($R = 0.038$, $R_w = 0.042$), this refinement, however, did not provide an opportunity to avoid the disorder of the Ru atom and yielded unacceptable values for a number of geometrical parameters. The attempts to refine the structure in the orthorhombic * space groups $P2_1nm$ or *Pmnm* did not give useful results either.

All calculations were carried out using the SDP-PLUS program package [17] on a PDP-11/23 PLUS computer. The atomic coordinates and the temperature factors are given in Table 3, the bond lengths are listed in Table 4. The structure of cation IV is shown in Fig. 1.

References

1 A.Z. Kreindlin, S.S. Fadeeva and M.I. Rybinskaya, Izv. Akad. Nauk SSSR, Ser. Khim., (1984), 403.

2 E.I. Fedin, A.L. Blumenfeld, P.V. Petrovskii, A.Z. Kreindlin, S.S. Fadeeva and M.I. Rybinskaya, J. Organomet. Chem., 292 (1985) 257.

3 U. Koelle and A. Salzer, J. Organomet. Chem., 243 (1983) C27.

4 A.Z. Kreindlin and S.S. Fadeeva, Abstracts of Reports of the 3rd All-Union Conference on Organometallic Chemistry, Ufa (1985) Vol. II, No. 228, p. 126.

5 A.Z. Kreindlin, P.V. Petrovskii, M.I. Rybinskaya, A.I. Yanovskii and Yu.T. Struchkov, Izv. Akad. Nauk SSSR, Ser. Khim., (1986) 493.

6 U. Koelle and A. Salzer, J. Organomet. Chem., 289 (1985) 133.

7 M. Cais, S. Dani, F.H. Herbstein and M. Kapon, J. Am. Chem. Soc., 100 (1978) 5554.

8 U. Behrens, J. Organomet. Chem., 182 (1979) 89.

9 V.G. Andrianov and Yu.T. Struchkov, Zh. Strukt. Khim., 18 (1977) 318.

10 K.W. Nugent, J.K. Beatic, T.W. Hambley and M.N. Snow, Austral. J. Chem., 37 (1984) 1601.

11 R.G. Teller and J.M. Williams, Inorg. Chem., 19 (1980) 2770.

---

* The pseudo-orthorhombic character of crystal IV is indicated by a monoclinic angle close to 90° and the atomic coordinates showing an approximate mirror plane normal to the Z axis.

12 Yu.T. Struchkov, V.G. Andrianov, T.N. Sal'nikova, I.R. Lyatifov and R.B. Materikova, J. Organomet. Chem., 145 (1978) 213.
13 D.C. Liles, A. Shaver, E. Singleton and M.B. Wiege, J. Organomet. Chem., 288 (1985) C23.
14 P. Seiler and J.D. Dunitz, Acta Crystallogr., B36 (1980) 2946.
15 W.E. Watts, J. Organomet. Chem., Libr., 7 (1979) 399.
16 R.S. Threlkel and J.E. Bercaw, J. Organomet. Chem., 136 (1977) 1.
17 B.A. Frenz in Eds. H. Schenk, R. Olthof-Hazelkamp, H. Konigsveld and G.C. Bassi, Computing in Crystallography, Delft Univ. Press, Delft, Holland, 1978, p. 64.