Journal of Organometallic Chemistry, 174 (1979) 67—75

MIGRATION OF HYDROGEN ATOMS FROM CYCLOPENTADIENYL RINGS TO METAL AND HYDROGEN EXCHANGE REACTIONS UPON THERMAL DECOMPOSITION OF DICYCLOPENTADIENYL COMPOUNDS OF TITANIUM AND ZIRCONIUM

G.A. RAZUVAEV
Institute of Chemistry, U.S.S.R. Academy of Science, Gorky (U.S.S.R.)

V.P. MAR'IN * and Yu.A. ANDRIANOV
Chemical Research Institute, Gorky State University, Gorky (U.S.S.R.)

(Received February 6th, 1979)

Summary

Thermal decomposition of Cp_2MR_2-d_{10} (M = Ti, Zr; R = CH_3, C_6H_5) has been studied. It has been shown that upon thermolysis of Cp_2MR_2 the migration of hydrogen atoms from Cp rings to the metal occurs which leads to destruction of the cyclopentadienyl group and hydrogen exchange reactions. Upon thermal decomposition of $Cp_2Zr(CH_3)_2$ exchange between the hydrogens of the Cp and R groups has been observed. The thermolysis of Cp_2MR_2 in the presence of Cp_2V-d_{10} leads to the formation of RD and vanadocene of d_0—d_9 forms. Zirconium compounds are the most active ones in hydrogen exchange reactions. There is no hydrogen exchange upon thermal decomposition of Cp_2VR_2 (R = CH_3) in the presence of Cp_2V-d_{10}.

Introduction

The first studies on thermal decomposition of transition metal compounds of π-Cp_2M-σ-R_2 were conducted with titanium derivatives (R = CH_3, C_6H_5, $CH_2C_6H_5$ in various solvents at the beginning of the 1960's [1,2]. It was established that thermolysis of these compounds results in the cleavage of carbon—titanium σ-bonds and the reduction of titanium. In later studies [3—8] with the use of deuterated compounds and solvents, several paths of RH formation were shown to exist for Cp_2TiR_2 derivatives, in which hydrogen atom donors are both σ-bonded ligands and π-Cp rings and on some other cases a solvent.

Thermal decomposition of deuterated zirconium compounds has not been studied. Nevertheless the investigated decomposition products of Cp_2ZrR_2

($R = CH_3$, C_6H_6) points to an analogy with decomposition paths of titanium derivatives [9]. Thermolysis of vanadium compounds Cp_2VR_2 ($R = CH_3$) and $Cp_2V(R)Cl$ ($R = CH_3$) proceeds with conservation of the Cp_2V structure and migration of the R group to the Cp ring. Decomposition of vanadium derivatives differs essentially from thermolysis of titanium subgroup compounds [10,11].

The present study involves investigations of thermal decomposition of titanium and zirconium compounds Cp_2MR_2 ($R = CH_3$, C_6H_5) with the use of labelled ligands. Special attention is paid to the role of Cp ligands in decomposition.

Results and discussion

In previous studies [4,9] thermal decomposition of Cp_2MR_2 (M = Ti, Zr; $R = CH_3$, C_6H_5) was shown to proceed with evolution of the main volatile product RH (1.6—1.8 mol per mol of parent compound) and with destruction of the original Cp_2M structure. In addition to investigations of titanium compounds [4] we studied thermolysis of zirconium derivatives (Table 1).

The main thermal decomposition products of Cp_2ZrR_2-d_{10} ($R = CH_3$, C_6H_5) compounds as well as those of analogous titanium derivatives are RD, RH and $R_{-H}D_2$.

Isotope composition of the decomposition products of Cp_2MR_2-d_{10} (M = Ti, Zr) leads us to the conclusion that independently of the nature of the central atom there are two paths of RH formation and hydrogen atom donors may be both: π-Cp and σ-R groups.

Decomposition routes of Cp_2TiR_2 compounds with participation of hydrogen atoms of σ-bonded ligands have been discussed later widely. When the source of hydrogen for RH elimination is an adjacent R group thermo- and photo-decomposition of Cp_2TiR_2 proceeds via intermediate formation of a complex which contains a carbon ($R = CH_3$) or benzene ($R = C_6H_5$) coordinated to the metal [3,5,12—16]. The formation of CH_4 and CH_2D_2 on decomposition

TABLE 1

THERMAL DECOMPOSITION OF Cp_2MR_2-d_{10}

Compound	Decomposition conditions	Isotope composition of the decomposition products (%)				
		CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
$Cp_2Ti(CH_3)_2$-d_{10}	Vacuum, 90°C, 30 min	54.0	41.0	4.1	0.9	—
$Cp_2Zr(CH_2)_2$-d_{10}	Vacuum, 230°C, 15 min	17.2	56.3	15.7	7.8	3.0
		C_6H_6	C_6H_5D	$C_6H_4D_2$	$C_6H_3D_3$	$C_6H_2D_4$/ C_6D_6
$Cp_2Ti(C_6H_5)_2$-d_{10}	Vacuum, 160°C 30 min	64.0	28.0	8.0	—	—
$Cp_2Zr(C_6H_5)_2$-d_{10}	Vacuum, 165°C, 30 min	65.7	12.7	11.0	6.0	4.6

of $Cp_2Zr(CH_3)_2$-d_{10} and of C_6H_6 and $C_6H_4D_2$ on decomposition of $Cp_2Zr(C_6H_5)_2$-d_{10} proves that thermolysis of zirconium compounds also proceeds via this route:

$$Cp_2MR_2 \rightarrow [Cp_2MR_{-H}] + RH \qquad (1)$$

$$[Cp_2MR_{-H}] \rightarrow C_{10}H_8M + RH \qquad (2)$$

The participation of Cp ligands in decomposition is of particular interest, since a hydrogen atom donated for RH formation leads to destruction of the cyclopentadienyl structure of a molecule. The evolution of substantial amounts of CH_3D and C_6H_5D on decomposition of Cp_2MR_2-d_{10} (M = Ti, Zr; R = CH_3, C_6H_5) and the destruction of the original π-Cp structure points to the existence of such a decomposition route:

$$(C_5D_5)_2MR_2 \rightarrow [C_{10}D_9MR] + RD$$

$$[C_{10}D_9MR] \rightarrow C_{10}D_8M + RD \qquad (3)$$

$$(M = Ti, Zr)$$

The destruction of the Cp structure on decomposition of Cp_2MR_2 (reaction 3) is probably more complicated than direct abstraction of a hydrogen atom from the ring by the R group.

In titanium, zirconium and niobium chemistry there are known cases of destruction of Cp structures by way of hydrogen transfer from a cyclopentadienyl ring to the metal. Thus it was previously shown that $Cp_2Ti(CH_3)_2$ reacts with hydrogen to afford the metastable titanocene form, which rearranges to dimeric hydride $[Cp(C_5H_4)TiH]_2$ [17]. A similar process occurs on reduction of metallocene dichlorides by sodium naphthalide in THF [18—20] and on decomposition of cyclopentadienyl hydrides [21].

It has been established that thermal decomposition of Cp_2MR_2 is also accompanied by migration of a hydrogen atom from a Cp ring to the metal. The hydrolysis of thermal decomposition products of Cp_2ZrR_2-d_{10} is one of the factors corroborating it (Table 2).

The reaction of thermal decomposition products of $Cp_2Zr(CH_3)_2$-d_{10} and $Cp_2Zr(C_6H_5)_2$-d_{10} with HCl in H_2O has essentially resulted in formation of HD and H_2; and treatment of thermal decomposition products of $Cp_2Zr(C_6H_5)_2$-d_{10} with D_2O leads mainly to the formation of D_2. The formation of HD in the first case and D_2 in the second one indicates that the thermal decomposition products contain hydrogen atoms bonded to metal and transferred from π-Cp ligands. It is interesting to note that Vol'pin [20] has obtained similar results. Hydrolysis of the mixture obtained from Cp_2TiCl_2-d_{10} and NpNa (Np = naphthyl) with H_2O gave D_2, HD and D_2.

That is why the degydrogenation process of Cp rings by R groups with RH formation (reactions 2 and 3) may occur not only via direct abstraction of hydrogen from a Cp ring but also via RH elimination with participation of a hydride hydrogen atom transferred to metal from a Cp ligand. Recently Bamford et al. [22] came to the same conclusion when they studied the photolysis of $Cp_2Ti(CH_3)_2$.

As a result of hydrogen migration hydrogen exchange reactions upon thermal

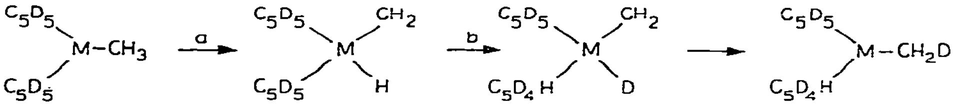
TABLE 2

HYDROLYSIS OF DECOMPOSITION PRODUCT OF Cp_2ZrR_2-d_{10}

Thermal decomposition products of	Agent (excess)	Isotope composition of the hydrolysis products (%)			
		Hydrogen		Methane	
$Cp_2Zr(CH_3)_2$-d_{10}	HCl/H_2O	H_2	41.1	CH_4	30.7
		HD	52.1	CH_3D	34.0
		D_2	6.8	CH_2D_2	25.3
				CHD_3	9.8
				CD_4	0.2
$Cp_2Zr(CH_3)_2$-d_{10}	D_2O	HD	15.4	CH_4	0.3
		D_2	84.6	CH_3D	15.5
				CH_2D_2	21.8
				CHD_3	30.3
				CD_4	32.1
$Cp_2Zr(C_6H_5)_2$-d_{10}	HCl/H_2O	H_2	38.9		
		HD	54.9		
		D_2	6.2		

decomposition of Cp_2MR_2 are found. It has appeared that there is hydrogen exchange between Cp rings and unchipped R groups in the thermolysis process of Cp_2MR_2. The isotope composition of methane, which forms as a result of HCl/H_2O hydrolysis of thermal decomposition products of $Cp_2Zr(CH_3)_2$-d_{10} is an evidence of this. Evolution of deuterated methane indicates that H/D exchange in a methyl ligand of a compound has occurred in the thermolysis process of $Cp_2Zr(CH_3)_2$-d_{10}.

Such an exchange is due to: (1) reversible transfer of a hydrogen atom from a σ-bonded ligand to the metal (eq. 4a), (2) rapid exchange between hydride atoms and hydrogen atoms of the Cp rings (eq. 4b).



(4)

The study on thermal transformation of Cp_2ZrAr_2 [23] points to the first process. A proof for the second process may be Brintzinger's study [24] on H/D exchange between the hydride form of titanocene and deuterium.

Evidently, the H/D exchange rate must be of a higher value than that of RH elimination.

The existence of such an exchange explains the formation of polydeuterated methanes and benzenes on decomposition of $Cp_2M(CH_3)_2$-d_{10} and $Cp_2M(C_6H_5)_2$-d_{10}, respectively (Table 1).

Hydrogen migration from Cp ligands to the metal is shown to cause intermolecular hydrogen exchange reactions. Thermal decomposition of Cp_2MR_2 (M = Ti, Zr) in the presence of Cp_2V-d_{10} proved this. Mass-spectrometric analysis of vanadocene after decomposition of $Cp_2Ti(CH_3)_2$ and $Cp_2Zr(CH_3)_2$ in the presence of Cp_2V-d_{10} showed, that H/D exchange in Cp ligands of vanadocene (Table 3) occurred in the course of reaction. Mass spectra contain lines relating to molecular ions of the d_0—d_{10} forms of vanadocenes. The greatest

TABLE 3

MASS SPECTROMETRIC ANALYSIS OF VANADOCENE AS A RESULT OF EXCHANGE REACTIONS

	Isotope forms of vanadocene (%)										
	$Cp_2V\text{-}d_{10}$	$Cp_2V\text{-}d_9$	$Cp_2V\text{-}d_8$	$Cp_2V\text{-}d_7$	$Cp_2V\text{-}d_6$	$Cp_2V\text{-}d_5$	$Cp_2V\text{-}d_4$	$Cp_2V\text{-}d_3$	$Cp_2V\text{-}d_2$	$Cp_2V\text{-}d_1$	Cp_2V
$Cp_2Ti(CH_3)_2 + Cp_2V\text{-}d_{10}$ Toluene, 100°C, 240 min	34.0	36.0	19.0	6.1	2.4	1.2	1.0	0.2	0.1	—	—
$Cp_2Zr(CH_3)_2 + Cp_2V\text{-}d_{10}$ Vacuum, 200°C, 30 min	12.2	24.2	26.8	19.6	10.5	4.2	1.7	0.5	0.2	0.1	—
Thermal decomposition products of $Cp_2Zr(CH_3)_2$ + $Cp_2V\text{-}d_{10}$	2.9	9.8	24.0	23.8	20.3	11.2	4.5	0.3	1.3	1.2	0.7
$[Cp(C_5H_4)TiH]_2 + Cp_2V\text{-}d_{10}$ Vacuum, 190°C, 60.min	5.7	15.6	21.1	21.1	17.0	10.7	5.3	2.4	0.7	0.3	0.1

degree of exchange was observed in $Cp_2Zr(CH_3)_2$ decomposition in the presence of Cp_2V-d_{10}. The quantitative determination of vanadocene after Cp_2MR_2 (R = Me, Ph) decomposition showed that vanadocene is consumed. Isotope composition of RH which is obtained upon decomposition of Cp_2MR_2 (R = CH_3, C_6H_5) in the presence of Cp_2V-d_{10} indicates that the products with partially deuterated ligands are formed for all derivatives (Table 4). The comparison of RH isotope composition upon decomposition of Cp_2MR_2 in the presence of Cp_2V-d_{10} suggests that, firstly, the greatest amounts of all deuterated products are formed on decomposition of zirconium compounds, secondly, methyl derivatives in these reactions are more active than phenyl derivatives.

In earlier investigations cyclopentadienyl complexes of $[Cp(C_5H_4)TiH]_2$, $[Cp(C_5H_4)NbH]_2$ and Cp_2TaH_3 were shown to be active catalysts for H/D exchange in a D_2/C_6H_6 system [25,26]. We checked the activity of "titanocene" obtained on reduction of $Cp_2Ti(CH_3)_2$ by hydrogen in hexane in a $[Cp(C_5H_4)$-$TiH]_2$ + Cp_2V-d_{10} system and showed that "titanocene" also takes part in hydrogen exchange (Table 3).

Evidently, the hydrogen atoms, transferred from Cp ligands to metal, take part in such exchange reactions. The fact that vanadocene has exchanged more than two hydrogen atoms of Cp rings in the reaction process indicates that reversible hydrogen exchange exists between hydrogen atoms of the Cp ligands of the compound, hydride atoms and hydrogen (deuterium) atoms of vanadocene upon thermal decomposition of Cp_2MR_2 in the presence of vanadocene. Such an exchange is of average statistical and probability character.

$$H_{CpM} \rightleftharpoons H_M \rightleftharpoons H_{CpV}$$

The exchange in Cp ligands of vanadocene probably occurs in a complex containing bridge hydrogen (deuterium) atoms of Cp_2MR_2 and Cp_2V-d_{10}.

In comparison with titanium derivatives, the high reactivity of zirconium

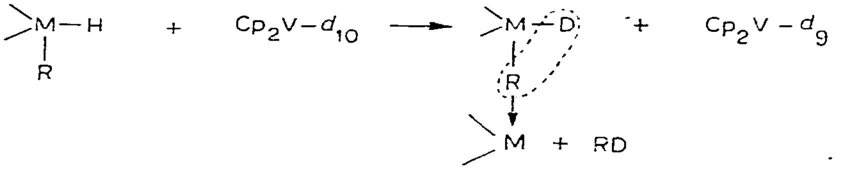
TABLE 4

THERMAL DECOMPOSITION OF Cp_2MR_2 (M = Ti, Zr) IN THE PRESENCE OF Cp_2V-d_{10} AT AN INITIAL COMPONENT RATIO 1/1

Compound	Reaction conditions	Isotope composition of RH (%)	Consumption degree of vanadocene
$Cp_2Ti(CH_3)_2$	Toluene, 100°C, 240 min	CH_4 90.6, CH_3D 9.3, CH_2D_2 0.1	0.26
$Cp_2Ti(C_6H_5)_2$	Toluene, 160°C, 60 min	C_6H_6 96.0, C_6H_5D 4.0	0.41
$Cp_2Ti(C_6H_5)_2$	Vacuum, 150°C 60 min	C_6H_6 91.0, C_6H_4D 8.2, $C_6H_4D_2$ 0.6, $C_6H_3D_3$ 0.2	not determined
$Cp_2Zr(CH_3)_2$	Vacuum, 200°C, 30 min	CH_4 43.2, CH_3D 50.5, CH_2D_2 4.1, CHD_3 1.8, CD_4 0.4	0.74
Thermal decomposition product of $Cp_2Zr(CH_3)_2$	Vacuum, 200°C 30 min		0.67
$Cp_2Zr(C_6H_5)_2$	Vacuum, 150°C, 60 min	C_6H_6 66.1, C_6H_5D 21.0 $C_6H_4D_2$ 12.9	0.57

compounds in exchange reactions characterizes a general tendency of zirconium compounds to form stronger bonds with hydrogen than in the case with the titanium analogue. A similar fact was mentioned by Samuel et al. [27] on photolysis of methyl-titanium and -zirconium derivatives.

Deuterated methane and benzene are formed upon decomposition of $Cp_2M(CH_3)_2$ and $Cp_2M(C_6H_5)_2$ in the presence of Cp_2V-d_{10} by way of RH elimination with the participation of a hydride hydrogen atom, after H/D exchange took place.



(5)

Direct exchange (eq. 6) can be neglected. An especially conducted experiment,

$$>M{-}D + RH \rightleftharpoons\ >M{-}H + RD \qquad (6)$$

heating of $Cp_2Zr(C_6H_5)_2$-d_{10} with CH_4 in a sealed ampule, indicates this (Table 5). Nevertheless, the fact itself, hydrogen atom exchange in methane, is of great interest and characterizes a high activity of hydride hydrogen atoms transferred from Cp ligands.

The hydrogen exchange in propylene proceeds with a greater rate than that in methane. Heating the thermodecomposition product of $Cp_2Zr(CH_3)_2$-d_{10} with propylene in a sealed ampule leads to formation of propylene with exchanged hydrogen atoms for deuterium and a small amount of propane (Table 5).

The use of a model system, thermal decomposition of a compound in the presence of Cp_2V-d_{10}, made it possible to reveal a great difference between the thermal decomposition route of Cp_2VR_2 and the thermal decomposition route of Cp_2TiR_2 and Cp_2ZrR_2. It is known that on thermal decomposition of Cp_2VR_2 ($R = CH_3$) the Cp_2V structure is destroyed only negligibly and decomposition occurs with migration of R groups to a Cp ring [10]. Thermolysis of an equimolar mixture of $Cp_2V(CH_3)_2$ and Cp_2V-d_{10} leads to formation of vanadocenes which contain exchanged Cp ligands (Table 6). However, lines corresponding

TABLE 5

THERMAL DECOMPOSITION OF Cp_2ZrR_2-d_{10} IN THE PRESENCE OF HYDROCARBONS AT AN INITIAL COMPONENT RATIO 1/1

System	Reaction conditions	Isotope composition of hydrocarbons (%)	
$CpZr(C_6H_5)_2$-d_{10} + CH_4	160°C, 45 min	CH_4 96.0, CH_3D 4.0	
Thermal decomposition products of $Cp_2Zr(CH_3)_2$-d_{10} + C_3H_6	200°C, 60 min	propane 2.3	propylene 97.7
		C_3H_8 17.5 C_3H_7D 39.5 $C_3H_6D_2$ 26.7 $C_3H_5D_3$ 16.3	C_3H_6 86.3 C_3H_5D 13.7

TABLE 6

MASS SPECTROMETRIC ANALYSIS OF VANADIUM PRODUCTS OF THERMAL DECOMPOSITION OF $Cp_2V(CH_3)_2$ IN THE PRESENCE OF Cp_2V-d_{10}

(Ratio 1/1, vacuum, 140°C, 1 h)

m/e of molecular ion	Product	Contents (%)
181	$(C_5H_5)_2V$	7.6
186	$(C_5H_5)(C_5D_5)V$	16.2
191	$(C_5D_5)_2V$	9.0
195	$(CH_3C_5H_4)(C_5H_5)V$	16.5
199	$(C_5H_5)(CH_3C_5D_5)V$	9.4
200	$(CH_3C_5H_4)(C_5D_5)V$	18.0
204	$(CH_3C_5D_4)(C_5D_5)V$	10.8
209	$(CH_3C_5H_4)_2V$	5.0
213	$(CH_3C_5H_5)(CH_3C_5D_4)V$	4.6
217	$(C_5D_4CH_3)_2V$	1.9
223	$[(CH_3)_2C_5H_3](CH_3C_5H_4)V$	0.6
227	$[(CH_3)_2C_5H_3](CH_3C_5D_4)V$	0.3
230	$[(CH_3)_2C_5D_3](CH_3C_5D_4)V$	0.1

to d_1—d_9 isotope vanadocene forms are absent in mass spectra as it takes place upon decomposition of $Cp_2Ti(CH_3)_2$ and $Cp_2Zr(CH_3)_2$ in the presence of Cp_2V-d_{10}. The absence of d_1—d_9 forms of vanadocenes indicates that upon thermodecomposition $Cp_2V(CH_3)_2$ the hydrogen exchange reaction does not occur and thermodecomposition of $Cp_2V(CH_3)_2$ is not accompanied by migration of hydrogen atoms to metal.

Thus, one of the pecularities of the thermolysis of dicyclopentadienyl-titanium and -zirconium compounds is easy transfer of hydrogen atoms from cyclopentadienyl rings to metal, leading to destruction of the cyclopentadienyl structure and a hydrogen exchange reaction; this differentiates the decomposition of these compounds from thermolysis of analogous vanadium derivatives.

Experimental

C_5D_6 was used for synthesis of compounds labelled by deuterium in cyclopentadienyl rings. C_5D_6 was obtained by hydrogen exchange reaction between C_5H_6 and D_2O. Isotopic purity of Cp_2MR_2-d_{10} compounds was checked by IR spectroscopy. In the IR spectra the absorption bands, corresponding to non-deuterated cyclopentadienyl ligands are absent. Cp_2V-d_{10} was taken as an example for quantitative determination of the degree of deuteration of the cyclopentadienyl groups; the determination was performed by mass spectrometry (see Table 7).

The calculation showed that the degree of deuteration was about 98% for the cyclopentadienyl groups of vanadocene.

Mass spectrometric measurements were conducted by an MI 1305 model at accelerating voltage 2 kV, electron energy 70 eV.

Exchange interactions of Cp_2MR_2 + Cp_2V-d_{10} were studied in evacuated molybdenum glass ampules supplied with an outlet for gaseous sampling and a special vacuum slice-system for vanadicene sublimation. Equimolar samples of

TABLE 7

MASS SPECTRUM OF Cp_2V-d_{10} IN THE m/e 181—191 REGION

m/e	Relative intensity (%)
191	100.00
190	10.73
189	1.16
188	0.09
187	0.54
186	0.86
185	0.46
184	0.04
183	0.08
182	0.01
181	0.01

compounds (50—150 mg) were taken for the experiments. The experimental conditions are given in the main part.

References

1 G.A. Razuvaev and V.N. Latyaeva, Uspekhi Khim., 34 (1965) 585.
2 G.A. Razuvaev, V.N. Latyaeva and L.I. Vyshinskaya, Trudy po khimii i khim teknologii, Gorky, vyp., 2 (1973) 3.
3 J. Dvorak, R.J. O'Brien and W. Santo, Chem. Commun., (1970) 411.
4 V.N. Latyaeva, L.I. Vyshinskaya and V.P. Mar'in, Zh. Osbhch. Khim., 46 (1976) 628.
5 C.P. Boekel, J.H. Teuben and H.J. de Liefde Meijer, J. Organometal. Chem., 81 (1974) 371.
6 C.P. Boekel, J.H. Teuben and H.J. de Liefde Meijer, J. Organometal. Chem., 102 (1975) 161.
7 C.P. Boekel, J.H. Teuben and H.J. de Liefde Meijer, J. Organometal. Chem., 102 (1975) 317.
8 G.J. Erskine, D.A. Wilson and J.D. McCowan, J. Organometal. Chem., 114 (1976) 119.
9 G.A. Razuvaev, L.I. Vyshinskaya and V.P. Mar'in, Dokl. Akad. Nauk SSSR, 225 (1975) 827.
10 G.A. Razuvaev, V.P. Mar'in, S.P. Korneva, L.I. Vyshinskaya, V.K. Cherkasov and O.N. Druzhkov, Dokl. Akad. Nauk SSSR, 231 (1976) 626.
11 G.A. Razuvaev, L.I. Vyshinskaya, S.P. Korneva, V.P. Mar'in and V.K. Cherkasov, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 700.
12 I.S. Kolomnikov, T.S. Lobeeva, V.V. Gorbachevskaya, G.G. Aleksandrov, Yu.T. Struchkov and M.E. Volpin, Chem. Commun., (1971) 972.
13 G.G. Aleksandrov and Yu.T. Struchkov, Zh. Struktur. Khim., 12 (1971) 667.
14 V.B. Shur, E.G. Berkovich and M.E. Volpin, Izv. Akad. Nauk SSSR, Ser. Khim., (1971) 2358.
15 M.E. Volpin, V.N. Shur, V.N. Latyaeva, L.I. Vyshinskaya and A.A. Shulgaister, Izv. Akad. Nauk SSSR, Ser. Khim., (1966) 385.
16 M.D. Rausch, W.H. Boon and H.G. Alt, J. Organometal. Chem., 141 (1977) 299.
17 R.H. Marvich and H.H. Brintzinger, J. Amer. Chem. Soc., 93 (1971) 2046.
18 C.W. Watt and F.O. Drummond, J. Amer. Chem. Soc., 92 (1970) 826.
19 C.W. Watt, L.J. Baye and F.O. Drummond, J. Amer. Chem. Soc., 88 (1966) 1138.
20 M.R. Volpin, A.A. Beji and V.B. Shur, J. Organometal. Chem., 27 (1971) C5.
21 F.N. Teble and G.W. Parshall, J. Amer. Chem. Soc., 93 (1971) 3793.
22 C.H. Bamford, R.J. Puddephatt and D.M. Slater, J. Organometal. Chem., 159 (1978) C31.
23 G. Erker, J. Organometal. Chem., 134 (1977) 139.
24 J.E. Bercaw, R.H. Marvich, L.G. Bell and H.H. Brintzinger, J. Amer. Chem. Soc., 94 (1972) 1219.
25 U. Klabude and G.W. Parshall, J. Amer. Chem. Soc., 94 (1972) 9081.
26 G.P. Pez and S.C. Kwam, J. Amer. Chem. Soc., 98 (1976) 7079.
27 E. Samuel, P. Mailard and C. Giannotti, J. Organometal. Chem., 142 (1977) 289.