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BASICITY OF CARBONYL COMPLEXES OF TRANSITION METALS

X *. INTERACTION OF (π-C_5H_5)Mn(CO)($Ph_2PCH_2CH_2PPh_2$) WITH APROTIC ACIDS IN SOLUTION

B.V. LOKSHIN*, E.B. NAZAROVA and A.G. GINZBURG
Institute of Organo-Element Compounds, USSR Academy of Sciences, Vavilova 28, Moscow B-312 (U.S.S.R.)

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Summary

The interaction of CpMn(CO)($Ph_2PCH_2CH_2PPh_2$) with some aprotic acids in solution has been studied by infrared, electronic and ESR spectroscopy and electroconductivity. It is shown, that reactions with π-acids and some π-complexes such as $CpTiX_3$, Cp_2MCl_2 (M = Ti, Zr, Hf, V) take place with oxidation of the manganese atom, electron transfer to the acceptor molecule and the formation of the cation-radical of the donor molecule. It is also shown that an increase in the oxidation state of the Mn atom occurs in the reactions with halides of Al, Ti, Sn and Hg and the structure of the products is discussed. Less basic complexes $CpMn(CO)_3$, $Et_5C_5Mn(CO)_3$ and $Et_5C_5Mn(CO)_2PPh_3$ are not oxidised in the presence of tetracyanoethylene but form charge-transfer complexes.

In previous parts of this study * we have shown that carbonyl and nitrosyl complexes of transition metals act as bases. In reactions with protic acids the proton attaches itself to the atom of the transition metal, i.e. these complexes are *d*-bases. Formation of adducts during interaction with Lewis acids may involve the transition metal or the ligands. In the latter case complex formation proceeds through the unshared electron pair of the oxygen of the CO or NO groups or of the σ-bonded ligand (halogen) [1,2]. With an increase in basicity of the central atom, the probability of interaction with Lewis acids through this atom increases. The higher the basicity of the metal atom the higher is the number of aprotic acids with which it may interact. From this point of view it is interesting to study the behavior of the diphosphine derivative of cyclopentadienylmanganese tricarbonyl CpMn(CO)(diphos) (I, diphos = $Ph_2PCH_2CH_2PPh_2$), since the presence of the bidentate diphosphine ligand considerably increases the basicity of the manganese atom [3]. This complex is therefore capable of inter-

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* For part IX, see ref. 1.

acting with a variety of different acceptors. Reactions of CpMn(CO)(diphos) in solution with CF_3COOH, Lewis acids and π-acids are described in this study.

Results and discussion

1. Reactions with π-acids

In the present work we have studied the interaction of I in solution with several π-acids: tetracyanoethylene (TCE), tetracyanoquinodimethane (TCQD) and chloranil (CA).

It is known that arenetricarbonyl chromium complexes, (π-Arene)$Cr(CO)_3$ form charge-transfer complexes with TCE and trinitrobenzene (TNB) [4,5]. Their formation in solution is accompanied by the appearance, in electron absorption spectra, of a charge-transfer band in the visible or near IR region. The fact that no changes are observed in the IR region of CO stretching modes makes it possible to assume that charge-transfer complexes are formed through the π-electron system of the arene ring. For complexes with TNB this conclusion is confirmed by X-ray structural data [6].

The behavior of complex I in reactions with π-acids differs sharply from the examples described above. Addition of a solution of I in methylene chloride or another solvent to a π-acid in the same solvent brings about a sharp change of colour from orange to bright-green (with TCE and TCQD) or to red-brown (with CA). This is accompanied by the appearance of a band in the region of CO stretching modes which is shifted by 100 cm^{-1} to higher frequencies, compared with the initial compound (Table 1). This indicates the participation of the central metal atom in the formation of the complex [1,2,7]. Considerable changes also occur in the IR spectra of the acceptors. Thus, for TCE and TCQD ν(CN) bands are shifted to lower frequencies by about 30—50 cm^{-1} (Fig. 1). The shift of the ν(CO) bands is practically the same for all π-acids studied, indicating the formation of the same product, namely the $[CpMn(CO)(diphos)]^{+\cdot}$ cation-radical. This assumption is confirmed by several facts.

In the first place the ν(CO) frequency coincides with the frequency of $[CpMn(CO)(diphos)]^{+\cdot}$, which is formed by oxidation of I with silver salts [8]. Secondly, in the ESR spectra of solutions of I in the presence of TCE, TCQD or CA, signals of π-acid anion-radicals are observed, indicating complete electron transfer from the donor to the acceptor. In the ESR spectrum of the frozen solution of the complex with TCQD at —150°C two signals are displayed that are superimposed on each other (Fig. 2): a narrow one corresponding to $TCQD^{\overline{\cdot}}$ and a wide one belonging to the cation radical. A dark, practically black, CpMn(CO)-(diphos)—TCQD complex is isolated from benzene solution, the ν(CO) band of which is also shifted to higher frequencies by 100 cm^{-1}. The ESR spectrum also displayes a signal with rather low intensity. This is not surprising since, for simple ion-radical salts (with 1 : 1 composition which follows from data of the electron spectra, see below) the concentration of free spins is usually low due to strong pairwise interaction [9].

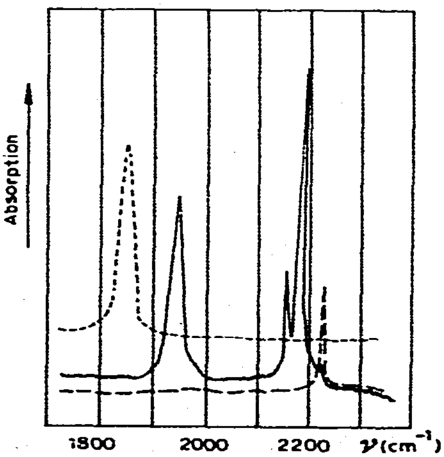
The third argument in favour of the oxidation of donor molecules in the presence of π-acids is derived from the appearance of new bands in the electron absorption spectra which correspond to the absorption of TCE (wide maximum at 350—500 nm) and TCQD (800—820 nm) anion-radicals [10—11]. The com-

TABLE 1

IR SPECTRA OF THE PRODUCTS OF THE REACTION OF CpMn(CO)(diphos) WITH VARIOUS ACCEPTORS IN THE REGION OF CO STRETCHING MODES

D + A	ν(CO) in CH_2Cl_2 solution (cm^{-1})		
	Initial complex	Reaction product	
CpMn(CO)(diphos)+$AgNO_3$	1835	1932	
CpMn(CO)(diphos)+TCQD [a]	1835	1935	
+TCE	—	1934 (2000)	
+CA	—	1931	
+TNB	1835		
CpMn(CO)(diphos)+$CpTiF_3$	1837	1932	
+$CpTiCl_3$	1836	1932	
+$CpTiBr_3$ [b]	1831	1928	
+$CpTiI_3$	—	1932	
+Et_5C_5TiBr	1836	1931	
+Cp_2TiCl_2	1835	1932	
+Cp_2ZrCl_2	1836	1931	
+Cp_2HfCl_2	1835	1931	
+Cp_2VCl_2	1835	1931	
CpMn(CO)(diphos)+$AlCl_3$	—	—	1964s
+$TiCl_4$	—	1935s	1962s
+$SnCl_2$ [c]	1834	1932s	1960sh
+$SnBr_4$ [c]	1836	1932s	
+$HgCl_2$ [b]	—	1932s	1962—65(sh)
CpMn(CO)(diphos)+CF_3COOH [c]	1836	1934	1963

[a] In CH_3NO_2. [b] In CH_2Cl_2 + THF. [c] Initial compound may be completely converted into the end product by addition of an excess of acceptor.



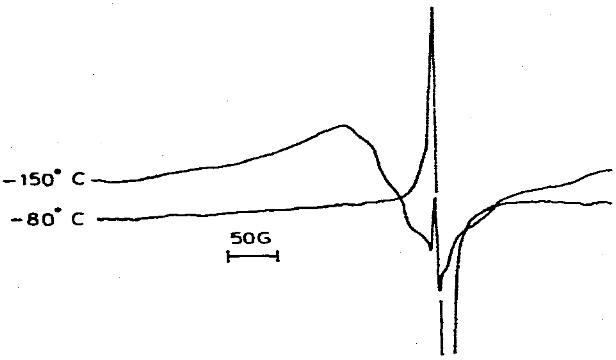


Fig. 1. IR spectra in the 2300—1700 cm^{-1} region of CH_2Cl_2 solutions of $C_5H_5Mn(CO)(Ph_2PCH_2CH_2PPh_2)$ (------), TCQD (— — —) and their mixture (———).

Fig. 2. ESR spectra of the product of the interaction of $C_5H_5Mn(CO)(Ph_2PCH_2CH_2PPh_2)$ with TCQD.

plex with CA is less stable and we were unable to obtain reliable data. In the case of TCQD the bands are displayed more distinctly as they are in the region in which donor absorption is absent and they coincide with the bands of ion-radical salts formed by interaction of TCQD with triethylamine and ferrocene (Table 2). The 1 : 1 composition of the I—TCQD complex was established by the method of isomolar series from the dependence of the band intensity near 810 nm upon the ratio of reagents in CH_2Cl_2. Similar investigation for ferrocene gave a 1 : 2 $Cp_2Fe \cdot 2TCQD$ composition, which is in agreement with published data [11].

Finally, we found that the solution of complex I and TCQD in CH_2Cl_2 is electroconductive. The value Λ_M 37 ohm^{-1} cm^2 mol^{-1} is close to the values of Λ_M for 1 : 1 electrolytes in CH_2Cl_2; for comparison we determined Λ_M for $CpMn(CO)(NO)^+PF_6^-$ in CH_2Cl_2 and obtained 30 ohm^{-1} cm^2 mol^{-1}. Thus, it follows from the data obtained that during interaction of complex I with π-acids in solutions, the donor molecule is oxidised with transfer of an electron to the acceptor and formation of a cation-radical. It should be noted that under the same conditions no interaction takes place with a weaker π-acid, TNB, and no changes are observed in the IR spectra.

π-Complexes, such as $CpMn(CO)_3$ (II), $Et_5C_5Mn(CO)_3$ (III) and $Et_5C_5Mn(CO)_2PPh_3$ (IV) in which the Mn atom is of lower basicity than in the diphosphine complex are not oxidised in the presence of π-acids. The IR spectra of mixtures of donor with acceptor in solutions are a superimposition of the spectra of the separate components and no signals appear in the ESR spectra. However, addition of TCE to CH_2Cl_2 solution leads to the appearance of new bands in the electron spectra of complexes II—IV, at 790, 750 and 740 nm respectively (Fig. 3). These bands are absent in the spectra of the initial II—IV complexes and do not belong to the anion-radical of TCE and can be assigned to charge transfer bands. Interaction of I with TCE does not give a band in this region.

Presumably, as for arenetricarbonyl chromium complexes [4,5], a charge transfer complex is formed in these cases. The case of complex I oxidation as compared with II—IV conforms with electrochemical data [8,12]. It has been shown that under electrochemical oxidation complex I can produce not only a monocation but also a dication [12]. Formation of the latter may be responsible for the appearance of a weak band at 2000 cm^{-1}, in addition to the band at 1934 cm^{-1}, in the IR spectrum of I on addition of TCE.

2. *Reactions with π-complexes*

Due to the high basicity of the Mn atom in I, this complex interacts with such

TABLE 2

ABSORPTION BANDS OF TCQD ANION-RADICAL APPEARING ON MIXING DONOR AND TCQD SOLUTIONS

D + A	New bands in the electron spectrum (nm)			
Et_3N + TCQD	410	421	435	810—820 (asym)
Cp_2Fe + TCQD	(440 wide band of Cp_2Fe)			810—820 (asym)
CpMn(CO)(diphos) + TCQD		421	435	800—810 (asym)

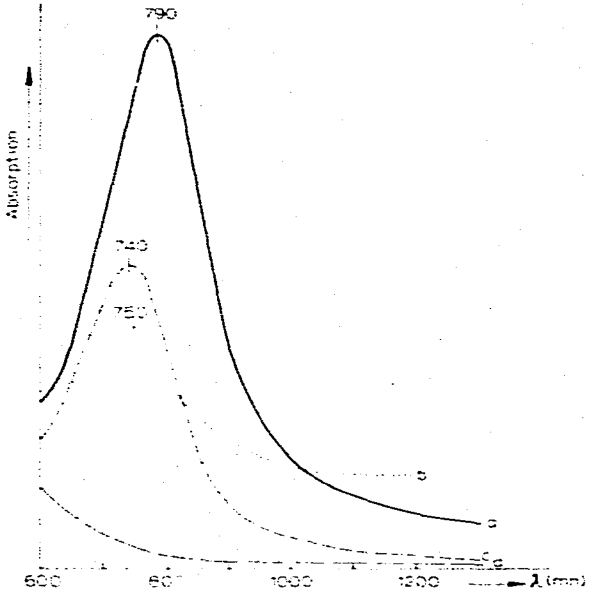


Fig. 3. Electron spectra in the 600—1200 nm region of the products of interaction of (a) $C_5H_5Mn(CO)_3$, (b) $Et_5C_5Mn(CO)_3$, (c) $Et_5C_5Mn(CO)_2PPh_3$ and (d) $C_5H_5Mn(CO)(Ph_2PCH_2CH_2PPh_2)$ with tetracyanoethylene in CH_2Cl_2 solution.

weak acceptors as π-complexes of the $CpTiX_3$ type (X = halogen) and with even weaker acceptors as Cp_2MCl_2 (M = V, Ti, Zr and Hf) (Table 1). It is interesting that π-complexes act here both as donors and as acceptors. Only a few examples of such behavior have been described. The interaction of Cp_2Fe and Cp_2Ni with Cb_2Ni (Cb = $(3)\text{-}1,2\text{-}B_9C_2H_{11}^{2-}$) have been reported in [13] and the interaction of several nitrosyl and carbonyl complexes with Cp_3Ln, where Ln is a lanthanide is described in [14].

Addition of the above mentioned π-complexes to a solution of I leads, in all cases, to the appearance of a band in the ν(CO) region of the IR spectrum, which is shifted to higher frequencies by 96—97 cm^{-1}. This shift corresponds to transition of the central metal atom to a higher oxidation state. The position of this band practically coincides with the position of the $CpMn(CO)(diphos)^{+}$ band which has been described above.

In this case the Mn atom is presumably oxidised with transfer of electron to the acceptor. The fact that this reaction is considerably solvent-dependent confirms this assumption.

Polar solvents promote this reaction. Thus, complex I does not react with Cp_2MCl_2 in benzene solutions, in CH_2Cl_2 solutions complex I predominates and in acetone and acetonitrile the oxidised form prevails. It has been shown for a CH_3NO_2 solution of I and Cp_2ZrCl_2 that interaction of donor with acceptor is accompanied by formation of ions in the solution leading to electroconductivity (Λ_M 30—50 ohm^{-1} cm^2 mol^{-1}). Monophosphine derivatives $CpM(CO)_2PPh_3$ (M = Mn, Re) in which the central atom is less basic than in I, do not interact with $CpTiX_3$ and Cp_2MCl_2 under the same conditions.

3. *Reactions with halides of mercury, tin, titanium, aluminum and protonation*

The data considered above shows that the diphosphine complex is readily oxidised to the cation even in the presence of such weak electron acceptors as π-acids and Lewis acids of the $CpTiX_3$ and Cp_2MCl_2 types. The interaction with stronger Lewis acids, such as metal halides leads to a more complex pattern in the CO stretching region than that observed in previous examples. In several cases two new bands are observed (for $TiCl_4$, $SnCl_4$ and $HgCl_2$) one of which practically coincides with the band of cation I and the second is shifted to higher frequencies, by about 30 cm^{-1}, in relation to the latter. Only a high-frequency band at 1964 cm^{-1} is observed for $AlCl_3$, while for $SnBr_4$ only a low-frequency band is displayed (Table 1). The positions of these bands are close to those of bands appearing as a result of protonation of I in acid media [3,15]. In this respect it is interesting to study the data on the protonation of diphosphine manganese complexes.

It has been shown by NMR spectroscopy [16,17] that a proton may attach to $CpMn(CO)L_2$ complexes in the *cis* or *trans* positions to the CO group, depending on the ligand structure. *Trans*-isomers are formed in the case of $L_2 = (PPh_3)_2$ or $Ph_2P(CH_2)_3PPh_2$ and *cis*-isomers in the case of $Ph_2P(CH_2)_nPPh_2$ ($n = 1, 2$). For $L_2 = (PPh_3)_2$ only one band of the protonated form is observed at 1937 cm^{-1} in the IR spectrum (Table 3). It is assigned, on the basis of comparison with NMR data, to the *trans*-isomer. For $L_2 = Ph_2PCH_2PPh_2$, the band is displayed at 1965 cm^{-1} (*cis*-isomer). In the case of $L_2 = Ph_2P(CH_2)_nPPh_2$ ($n = 2, 3$) the spectrum depends on the acidity of the medium.

In dilute CF_3COOH solutions in CH_2Cl_2 (1 : 100) or in mixtures of CF_3COOH, CH_3COOH and CH_2Cl_2 bands of both *cis*- and *trans*-isomers are observed, the intensity ratio of which changes with time (the intensity of the *trans*-isomer band increases) (Fig. 4). In more acid solutions of complex I the spectra indicate the predominance of the *cis*-isomer. This is in agreement with NMR data obtained at higher complex concentrations (0.3—0.5 mol/l) and higher acidity ($CF_3COOH/CH_2Cl_2 \approx 1:4$).

The appearance of two new bands in the IR spectrum of I after reactions with MX_n halides is probably connected with the geometrical isometry of the forming products. Their structures can not be determined precisely from the available data, so let us consider several possible structures:

1. Formation of an adduct with a metal—metal bond $Cp(CO)(diphos)Mn—MX_n$ (1).

TABLE 3

FREQUENCIES OF CO STRETCHING MODES OF THE PROTONATED FORMS OF $CpMn(CO)L_2$ COMPLEXES IN CF_3COOH CH_2Cl_2 MIXTURE

Protonated complex	$\nu(CO)$ (cm^{-1})	
	trans isomer	*cis* isomer
$CpMn(CO)(PPh_3)_2H^+$	1937	—
$CpMn(CO)(Ph_2PCH_2PPh_2)H^+$	—	1965
$CpMn(CO)(Ph_2PCH_2CH_2PPh_2)H^+$	1934	1963
$CpMn(CO)(Ph_2PCH_2CH_2CH_2PPh_2)H^+$	1920	1950

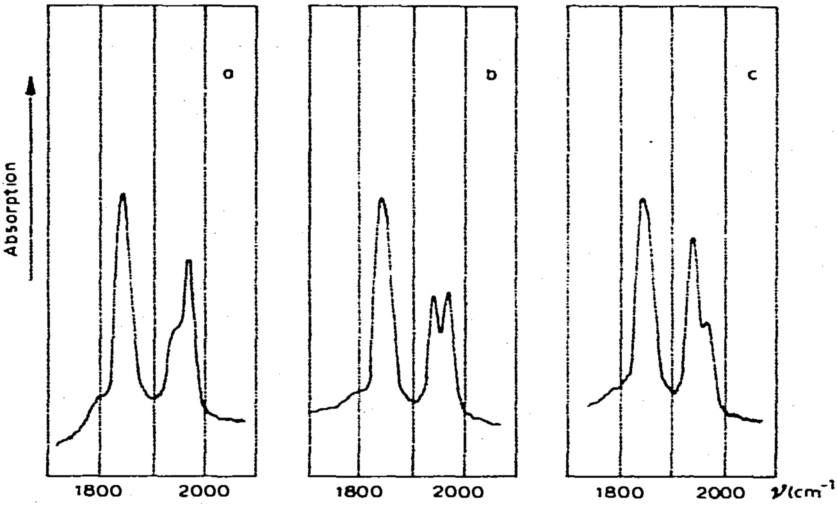


Fig. 4. IR spectra in the 1700—2100 cm^{-1} region of $C_5H_5Mn(CO)(Ph_2PCH_2CH_2PPh_2)$ in mild acid medium (dilute solution of CF_3COOH in CH_2Cl_2) at (a) the initial moment, (b) 30 min and (c) 50 min after preparation.

2. Formation of salt-like products $[Cp(CO)(diphos)MnX]^+ MX_{n-1}^-$ (2a), $[Cp(CO)(diphos)Mn - MX_{n-1}]^+ X^-$ (2b) or $[CpMn(CO)(diphos)—MX_{n-1}]^+ MX_{n+1}^-$ (2c).

3. Electron transfer with formation of $CpMn(CO)(diphos)^{\cdot+} \cdot MX_n^{\cdot-}$.

Due to the established electroconductivity of the products formed in CH_2Cl_2, structure 1 seems improbable. For instance, the value of Λ_M determined for CH_2Cl_2 solution of I in the presence of $SnBr_4$ is 35 ohm^{-1} cm^2 mol^{-1}. For structures 2 the formation of geometrical isomers is quite likely and in the case of 2a the near equality of the frequencies for interaction with different Lewis acids is understandable. Structure 3 explains the close value of one of the frequencies to the value of the ν(CO) cation frequency, the appearance of isomers in this case, however, is less understandable. Assuming formation of contact ionic pairs of the anion and cation in solution, the presence of two isomers may be connected with the different arrangement of the counterion in relation to the CO group of the cation. The presence of contact pairs may also explain the absence of signals in the ESR spectra of the solutions studied.

Our attempts to record the Raman spectra of solutions of I in the presence of Lewis acids, so as to obtain additional data on the structure of the forming products, failed due to decomposition of samples under the helium—neon laser beam. Therefore additional studies are required for the determination of the structure of compounds formed in solutions during interaction of CpMn(CO)(diphos) with Lewis acids.

Experimental

Diphosphine complexes $CpMn(CO)L_2$, where $L_2 = (PPh_3)_2$ or $Ph_2P(CH_2)_nPPh_2$ (n = 1—3) were synthesised and purified as described in [17]. Preparation of solutions and cells for spectra recording were carried out under a purified argon atmosphere. IR spectra were obtained on Zeiss UR-20 spectrometer in CaF_2 cells. The instrument was calibrated with gaseous DCI. Electron absorption spectra in the 200—2000 nm region were recorded on a Hitachi EPS-3T spectrometer in quartz cells. ESR spectra were obtained on a modified RE-1301 instrument with a reflecting resonator and on a Varian E-12A instrument. Electroconductivity measurements were carried out using the bridge scheme on a instrument described in [18], the cell constant was 0.6.

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References

1 B.V. Lokshin, E.B. Rusach, N.E. Kolobova, Yu.V. Makarov, N.A. Ustynyuk, V.I. Zdanovich, A.Zh. Zhakaeva and V.N. Setkina, J. Organometal. Chem., 108 (1976) 353.
2 B.V. Lokshin, E.B. Rusach, Z.P. Valueva, A.G. Ginzburg and N.E. Kolobova, J. Organometal. Chem., 102 (1975) 535.
3 B.V. Lokshin, A.G. Ginzburg, V.N. Setkina, D.N. Kursanov and I.B. Nemirovskaya, J. Organometal. Chem., 37 (1972) 347.
4 A.N. Egorochkin, V.A. Kuznetzov, A.N. Artiomov, N.I. Sirotkin, V.G. Kirilicheva and G.A. Razuvaev, Dokl. Akad. Nauk SSSR, 227 (1976) 878.
5 G. Hutner and E.O. Fischer, J. Organometal. Chem., 6 (1966) 288.
6 O.L. Carter, A.T. McPhail and G.A. Sim, J. Chem. Soc. A, (1966) 822.
7 A.G. Ginzburg, B.V. Lokshin, V.N. Setkina and D.N. Kursanov, J. Organometal. Chem., 55 (1973) 357.
8 P.M. Treichel, K.P. Wagner and H.J. Much, J. Organometal. Chem., 86 (1975) C13.
9 B.P. Bespalov and V.V. Titov, Usp. Chim., (1975) 2249.
10 O.W. Webster, W. Mahler and R.E. Benson, J. Amer. Chem. Soc., 84 (1962) 3678.
11 L.R. Melby, R.J. Harder, W.P. Hertler, W. Mahler, R.E. Benson and W.E. Mochel, J. Amer. Chem. Soc., 84 (1962) 3374.
12 L.I. Denisovich, S.P. Gubin, N.V. Zakurin and A.G. Ginzburg, J. Organometal. Chem., 101 (1975) C43.
13 I. Klikorka, J. Pavlik, E. Vecérnikova and M. Fojtkova, Proc. 3rd Conf. Coord. Chem., Bratislava-Smolenica, 1971, Bratislava (1971) 171.
14 A. Crease and P. Legzdins, J. Chem. Soc. Dalton Trans., (1973) 1501.
15 I.B. Nemirovskaya, V.N. Setkina, A.G. Ginzburg and D.N. Kursanov, Izv. Akad. Nauk SSSR, Ser. Khim., (1974) 762.
16 A.G. Ginzburg, L.A. Fedorov, P.V. Petrovsky, E.I. Fedin, V.N. Setkina and D.N. Kursanov, J. Organometal. Chem., 73 (1974) 201.
17 R.G. Hayter and L.F. Willams, J. Inorg. Nucl. Chem., 26 (1964) 1977.
18 E.S. Sevostianov, A.I. Gorbacbev and Yu.M. Kessler, Zh. Fiz. Khim., 36 (1962) 644.