Vibrational spectra and structure of zirconium and hafnium cyclopentadienyl hydrides

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Raman and IR spectra (4000—50 cm^{-1}) of solid cyclopentadienyl zirconium and hafnium hydrides Cp_2MH_2, Cp_2MD_2, $Cp_2Zr(H)X$, and $Cp_2Zr(D)X$ ($Cp = \eta^5$-C_5H_5; M = Zr, Hf; X = Cl, Br) have been studied. The vibrational modes of MH groups, Cp-rings, and metal—ligand bonds are discussed and the band assignments are proposed. In the solid state, these complexes form polymers with linear hydride bridges of the M—H—M type. The force constants of the M—H and M—Cp bonds increase on going from Zr to Hf.

Key words: vibrational spectra; zirconium, hafnium, hydrides, cyclopentadienyl complexes.

Hydride complexes attract the attention of chemists due to their catalytic activity and specific structure. Depending on the nature of the metal atom (M) and the ligands, they can be monomeric, dimeric, or polymeric. In the two latter cases they contain hydride bridges, whose existence in several compounds has been proved by X-ray analysis[1] and NMR spectroscopy.[2] Vibrational spectra also provide important information about the structure of hydrides, especially in those cases, when poor solubility makes it impossible to grow monocrystals or to use NMR spectroscopy. In particular, they allow one to distinguish terminal and bridged M—H bonds, because the formation of bridges causes a low-frequency shift and broadening of the bands of the stretching vibrations of M—H. The data of IR spectroscopy in the νMH frequency region have been presented in many works devoted to hydride complexes; however, in the majority of cases the authors considered only this IR spectral region, and the Raman spectra remained almost unstudied.

Previously we have studied the vibrational spectra of tris(cyclopentadienyl) zirconium and hafnium hydrides.[3,4] In the present work, complexes of the type Cp_2MH_2 (M = Zr, Hf; $Cp = \eta^5$-C_5H_5) and $Cp_2Zr(H)X$ (X = Cl, Br) have been studied using Raman and IR spectroscopy. These substances are almost insoluble in organic solvents, *i.e.*, they cannot be studied by X-ray analysis. On the basis of the IR spectra of the complexes studied and their alkyl-substituted at Cp-rings,[5—8] a bridged structure has been suggested for all of the dihydrides except $(\eta^5$-$Me_5C_5)_2ZrH_2$, which contains bulk pentamethylcyclopentadienyl rings that create steric hindrances to association. The NMR spectra of Cp_2ZrH_2 in the solid state[2] and in solution[9] also indicate the existence of bridged bonds. However, the available data do not allow us to make a choice between a dimeric and polymeric structure of the complexes.

Experimental

The synthesis of all of the complexes has been described previously.[5,10—14] IR spectra were obtained on a Bruker IFS-113v IR-Fourier spectrometer in the range of 4000—50 cm^{-1} with a resolution of 2 cm^{-1}. Raman spectra were recorded on a Ramanor HG-2S laser spectrometer (Jobin Ivon, France) with excitation at 514.5 nm from an Ar^+-laser. Normal vibrations were calculated by previously developed programs[15] on a personal computer. Samples for IR spectroscopy were prepared in an atmosphere of dry argon.

Results and Discussion

The properties of dihydride complexes of Zr and Hf are similar. This similarity is disturbed for halide hydride analogs. $Cp_2Zr(H)Cl$ can be prepared by several methods, while $Cp_2Zr(H)Br$ can only be prepared by reverse disproportionation:

$$Cp_2ZrH_2 + Cp_2ZrBr_2 \rightarrow 2\ Cp_2Zr(H)Br.$$

In this reaction, the bromide contains no traces of Cp_2ZrH_2, while in the case of the chloride it is very difficult to remove the admixture of the dihydride. The attempts to prepare mixed hafnium complexes failed.

The complex $Cp_2Hf(H)Cl$ has been previously described,[16] however, no elemental analysis data have been presented, and the IR spectrum of the compound coincides with that recorded by us for Cp_2HfH_2. It is

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Table 1. Parameters of vibrational spectra of Cp_2MH_2 and Cp_2MD_2 (M = Zr, Hf) in the region of 4000—50 cm^{-1}

Cp_2ZrH_2		Cp_2ZrD_2		Cp_2HfH_2		Cp_2HfD_2		Assignment
IR	Raman	IR	Raman	IR	Raman	IR	Raman	
3108 m—w		3108 v.w		3110 v.w		3108 v.w		νCH
3084 sh								
3070 m	3067 m	3071 w	3068 w	3065 m		3070 m		
				3059 m, sh		3062 m		
1528 m, br	1520 m	1093 s	1092 s—m, br	1572 m, br	1570 m, br	1127 s		νMH
						1122 m, sh		
1441 m	1444 w	1443 m	1444 w	1434 m	1443 v.w		1443 v.w	νCC
1371 m	1367 w	1370 m	1368 m	1361 m	1369 w		1369 w	νCC
1332 s, br		966 s		1382 m, br		995 s, br		ν_{as}(M—H—M)
				1270 w		1268 w		βCH
1125 w	1124 v.s		1126 v.s		1129 v.s		1124 v.s	νCC [a]
	1098 w				1100 w			
1072 w					1085 v.w		1088 v.w	βCH
1063 w	1062 v.w	1065 m	1065 w	1070 w	1063 v.w		1066 w	
1027 s		1032 v.w	1029 v.w	1028 m		1025 s		βCH
1016 s				1013 s		1016 s		
973 m								
896 w		896 w		900 w		899 w		
	848 w		850 v.w	852 m	854 m	853 m	851 w	ρCH
830 s	817 w			837 s	825 w	837 s		
						800 s		
803 v.s		800 v.s	807 w	810 v.s	810 w	811 v.s	817 w	
777 s		776 s		781 m		779 s		
737 m	727 w	520 w	521 w	749 w	749 w	534 s	532 w	βMH
693 v.w	697 w		502 v.w	725 w	732 sh			
637 w	649 m		459 m	664 w	660 m	473 s	463 m	
			446 w, sh	654 w		442 w		
	614 w	616 w	613 v.w	612 w	617 sh	619 w	620 w	χCCC
607 w	605 w				606 w			
589 w				589 w				
340 m	340 m	333 s	337 m	297 s	302 s	296 m	298 s	[b]
	306 m		303 m		318 m		318 m	
277 w	276 v.s	274 w	278 v.s	271 w	277 v.s	272 w	275 v.s	ν_sMCp
259 w	269 sh	253 m	266 m, sh	258 w	257 sh	256 w		ν_{as}MCp
	195 m		198 m		185 w		183 w	δ_{as}CpMCp
		170 w	175 w					
155 w	149 m	156 w	150 sh	145 w		144 w		
	135 m, br		140 m, br		123 m		122 m	
110 m		110 m		105 m		104 m		
	84 m		84 w		76 m		73 m	ν_s(M—H—M)
	80 m							
	52 m		52 w		49 s		47 s	
	42 m							
			19 w				30 m	

[a] Breathing vibrations. [b] Tilting vibrations.

likely that the authors of the work cited[16] have in fact prepared the dihydride, probably, with an admixture of the dichloride. The parameters of the IR and Raman spectra of the substances studied are listed in Tables 1 and 2.

Vibrations of M—H bonds. The assignment of the bands corresponding to the vibrations of the M—H bonds is unambiguous and is based on their shift upon deuteration (νMH/νMD ≈ 1.39 to 1.40). The bands of both the terminal and bridged M—H bonds are observed in the spectra of Cp_2MH_2 complexes. The bands of Zr—H—Zr bridge groups are only present in the spectra of $Cp_2Zr(H)X$ (see Tables 1 and 2). The vibrations of the M—H terminal bonds are highly characteristic because a light hydrogen atom is attached to a heavy metal, and thus the kinematic interaction of the M—H vibrations with the adjacent bonds is close to zero. The result of the "barrier effect" of a metal is that only one νMH band is observed in the frequency region of the stretching vibrations of M—H for MH_2 and MH_3 groups, because splitting of the symmetric and antisymmetric vibrations of M—H is very small. This can be seen from

Table 2. Parameters of vibrational spectra of $Cp_2Zr(H)X$ and $Cp_2Zr(D)X$ (X = Cl, Br) in the region of 4000—50 cm^{-1}

$Cp_2Zr(H)Cl$		$Cp_2Zr(D)Cl$,	$Cp_2Zr(H)Br$		$Cp_2Zr(D)Br$		Assignment
IR	Raman	IR	IR	Raman	IR	Raman	
3106 w	3108 v.w		3107 m		3105 w		νCH
		3100 w	3096 w		3095 w		
3082 w	3060 v.w	3085 w	3081 w		3077 w		
	1442 w		1433 m	1442 v.w	1441 m		νCC
1407 s, v.br		1004 m, br	1402 s, br		1000 m, br		ν_{as}(Zr—H—Zr)
	1367 m		1361 m	1371 w	1364 w	1367 w	νCC
			1272 w		1274 w		βCH
1125 v.w	1127 v.s		1126 v.w	1131 v.s		1124 m	[a]
1089 v.w	1094 w		1087 w		1088 w	1092 w	βCH
1065 w	1063 w		1068 w		1066 w		
1036 w			1033 m		1032 m		βCH
		1023 s	1017 m		1020 s		
1014 s		1013 s	1012 s		1014 s		
940 s, br		681 m	941 s, br		677 m		βZrH
		935 m			929 w		βCH
858 m			857 m		857 w		
836 s	847 w	843 m	840 s		838 m		
	817 m	814 v.s	818 v.s	825 w	818 s		
809 v.s					810 v.s		
791 w		772 sh	789 m		791 m		
610 v.w	612 w	616 w	610 w		611 w		χCC
	600 m						
342 m		342 m	346 m		344 m	344 m	[b]
334 m	336 s, br	331 m	332 m		332 s	333 m	
	298 s					296 m	
270 m	278 v.s	270 m	263 m	272 v.s	263 m	270 v.s	ν_sZrCp
249 s	255 m, sh	247 s	249 m		248 m		ν_{as}ZrCp + νZrCl
200 v.w	200 s	203 v.w		198 s	202 sh	197 s	δCpZrCp
			185 v.s		185 s		νZrBr
162 w	176 s	162 v.w	166 w	162 m	166 w	157 m	
	166 w						
	152 w						
140 w	145 m		143 m		145 m	138 m	
	123 w			116 m		126 w	
107 w	107 m					109 w	
99 w							
82 w	78 m		78 w	78 s		79 s	ν_s(Zr—H—Zr)
	52 w, br					38 w	

[a] Breathing vibrations. [b] Tilting vibrations.

the data for cyclopentadienyl hydride metallocomplexes presented in Table 3 (frequencies for group IV—VII metal derivatives are taken from the literature[17]). There is a tendency for νMH frequencies to increase both in the groups of the Periodic System as the atomic number of the metal increases and in the periods as the electrons fill the corresponding d-level. The force constants of the M—H bonds calculated in a simple two-atomic approximation change analogously. A similar increase in frequencies and force constants of M—H bonds on going down a group has been previously mentioned for Cp_3MH complexes (M = Zr, Hf).[3,4] The introduction of donor alkyl substituents into a Cp-ring, which increases the electron density at the metal, also causes an increase in the vibrational frequencies of the terminal MH groups. This is seen from the data pre-

Table 3. Frequencies of stretching vibrations (ν) and force constants (*K*) for terminal M—H bonds in cyclopentadienyl hydrides of group IV—VII transition metals

Complex	M	ν/cm^{-1}	$K/10^2$ N m^{-1}
Cp_2MH_2	Zr	1528	1.48
	Hf	1572	1.58
Cp_2MH_3	Nb	1710	1.85
	Ta	1735	1.92
Cp_2MH_2	Mo	1850	2.17
	W	1930	2.37
Cp_2MH	Tc	1984	2.49
	Re	2016	2.59

sented below[1,7,8] for complexes containing Cp-, Cp*-, and MeCp-rings (Cp* = η^5-Me_5C_5, MeCp = η^5-$CH_3C_5H_4$).

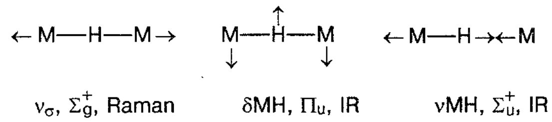
Complex	ν/cm^{-1}
Cp_2ZrH_2	1528
$CpCp^*ZrH_2$	1540
$(MeCp)_2ZrH_2$	1565
$(MeCp)Cp^*ZrH_2$	1585
$Cp^*_2ZrH_2$	1555

The latter compound deviates somewhat from the series, which may be caused by its monomeric structure.[6,8]

Two types of bridges: M—H—M and $\mathrm{M}{<}^{\mathrm{H}}_{\mathrm{H}}{>}\mathrm{M}$, can exist in the metal hydrides studied. The first can occur in polymers, while the second can exist in dimers. Monohydrides contain only bridged bonds and dihydrides contain both bridged and terminal M—H bonds. A polymeric structure with double hydride bridges without terminal M—H bonds would also be plausible, however, it is highly improbable because the metal atoms in the studied substances have only one vacant orbital. The bands of terminal M—H bonds in the spectra of the dihydrides Cp_2MH_2 also allow one to rule out this structure.

Taking into account the fact that the vibrations of M—H are highly characteristic, the vibrations of the linear and double hydride bridges may be considered on the basis of the local symmetry of the M—H—M and $\mathrm{M}{<}^{\mathrm{H}}_{\mathrm{H}}{>}\mathrm{M}$ fragments (D_h and D_{2h}, respectively). The types of vibrations for bridges with linear geometry are presented in Scheme 1 (their designations, symmetry, and activity in the spectra are indicated).

Scheme 1



ν_σ, Σ_g^+, Raman

δMH, Π_u, IR

νMH, Σ_u^+, IR

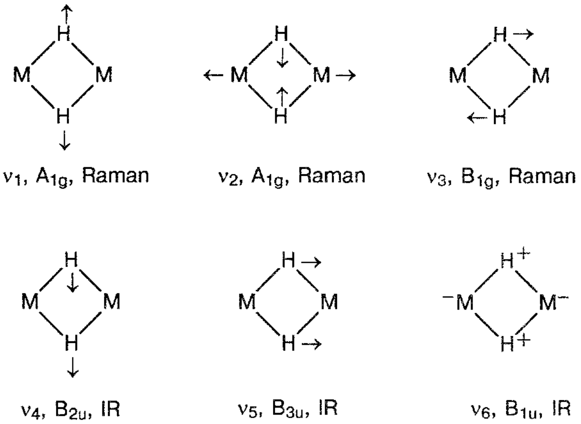
The ν_σ vibration, in which only heavy metal atoms participate, must be low-frequency and should appear only in the Raman spectra. The νMH and δMH vibrations are active in IR spectra and forbidden in Raman spectra.

The symmetry of the vibrations and the selection rules for double hydride bridges are presented in Scheme 2.

The ν_1—ν_5 vibrations occur in the plane of the cycle and the ν_6 vibration occurs out of the plane.

In order to perform a more detailed analysis of the vibrations of a double bridge we performed a model calculation of the frequencies and eigenvectors of its planar vibrations. The cycle was assumed to be planar and quadratic with M—H bond lengths of 2 Å and an effective atomic mass (*M*) of 200, *i.e.*, close to the mass of the Cp_2Zr fragment. It should be mentioned that calculations with changed bond lengths, angles, and *M* resulted in parameters that were not particularly different from those obtained for the presented variant where the following force constants for the bonds and their interaction were used (10^2 N m^{-1}): $K_q = 1.1$, $H_{qq} = 0.03$; for angles and their interaction (10^{-18} N m rad^{-2}): $K_\alpha = 0.16$, $K_\beta = 0.64$, $H_{\alpha\beta} = 0.13$; for the interaction of bonds and angles (10^{-8} N rad^{-1}): $H_{q\alpha} = 0.05$, $H_{q\beta} = 0.19$ (*q* is a stretching of the M—H bond, α and β are variations in the H—Zr—H and Zr—H—Zr angles).

Scheme 2



ν_1, A_{1g}, Raman

ν_2, A_{1g}, Raman

ν_3, B_{1g}, Raman

ν_4, B_{2u}, IR

ν_5, B_{3u}, IR

ν_6, B_{1u}, IR

It can be seen from the data of Table 4 that stretching of the M—H bond makes the main contribution to the energy of all of the vibrations, except that at the lowest-frequency. Therefore, they may be considered as stretching vibrations of the M—H bonds, although the contributions to the energy due to changes in the angles (α and β) are fairly large in some cases. The low-frequency vibration is an analog of the ν_σ vibration of the linear M—H—M bridge and can be designated as a metal—metal vibration. It is most important that all four νMH vibrations are in the same range and should be observed in both the IR and Raman spectra. Bridges of different types can be distinguished by this property: the stretching vibration of a linear bridge has no lines in the Raman spectra and should appear only in the IR spectra, whereas the vibrations of a double bridge are observed in both the IR and Raman spectra.

According to the data in Table 1, the vibrations of the M—H and M—D bridge bonds for Cp_2MH_2 and Cp_2MD_2 complexes appear only in the IR spectra and are absent in the Raman spectra. This allows one to unambiguously exclude a dimeric structure and to suggest that polymers of the $[Cp_2M(H)(\mu\text{-}H)]_n$ type exist in the solid substance. A polymeric structure explains, in particular, the very low solubility of the Cp_2MH_2 compounds. The presence of terminal and bridged Zr—H bonds in Cp_2ZrH_2 in the solid state is confirmed by NMR spectra, however, this is insufficient evidence for choosing between the dimeric and polymeric forms.

Table 4. Frequencies (ν) and potential energy distribution (PED) of planar vibrations of double M_2H_2 bridges

Symmetry	M_2H_2		M_2D_2		Approximate assignment, selection rules
	ν/cm^{-1}	PED	ν/cm^{-1}	PED	
B_{1g}	1350	$100q$	957	$100q$	νMH, Raman
A_{1g}	1344	$74q + 5\alpha + 21\beta$	953	$74q + 5\alpha + 21\beta$	νMH, Raman
B_{3u}	1330	$93q + 7\alpha$	943	$93q + 7\alpha$	νMH, IR
B_{2u}	1313	$77q + 23\beta$	931	$77q + 23\beta$	νMH, IR
A_{1g}	67	$20\alpha + 80\beta$	67	$20\alpha + 80\beta$	νMM, Raman

As follows from the data in Table 2, mixed halide hydride $Cp_2Zr(H)X$ complexes also have a polymeric structure. They have no terminal Zr—H bonds and the vibrations of the Zr—H—Zr bridges appear only in the IR spectra, which agrees well with a $[Cp_2Zr(X)(\mu\text{-}H)]_n$ type structure.

The appearance of the spectra of the hydride bridges (a low-frequency shift and band broadening) is similar to that observed in the formation of hydrogen bonds A—H—B, when a labile H atom is partially positive and the B atom acts as a base. However, the situation is quite the opposite for hydride bridges, because the charge at the H atom is negative and B possesses Lewis acid properties. Perhaps the fact that the $Cp^*{}_2ZrH_2$ complex is monomeric is explained not only by steric factors but also by the reduced Lewis acidity of the metal atom due to the presence of 10 donor methyl groups. The fact that the indenyl analog $(\eta^5\text{-}C_9H_7)_2ZrH_2$ is dimeric, according to the data of NMR spectroscopy,[18] despite the fact that its π-ligand is larger than that of Cp, also favors this supposition.

For the polymeric form $[Cp_2M(H)(\mu\text{-}H)]_n$ with a linear hydride bridges, one may expect three or four bands of bending vibrations of M—H: two bands for the vibrations of the terminal M—H bonds and one band for the degenerate vibration of the hydride bridge, which may be split due to the low symmetry of the immediate environment. In the spectra of Cp_2ZrH_2, several bands are observed at 630—740 cm^{-1}, which shift after deuteration to the 440—520 cm^{-1} region (νH/νD = 1.39 to 1.41). For Cp_2HfH_2 and Cp_2HfD_2, these bands are at 650—700 and 440—535 cm^{-1}, respectively. Although an unambiguous assignment of each of them is difficult, it is clear that they belong to bending δMH vibrations. It may be indicated for comparison that these bands are at 753 and 538 cm^{-1} (M = Zr) and 765 and 531 cm^{-1} (M = Hf) in the spectra of Cp_3MH and Cp_3MD (M = Zr, Hf).

Only one degenerate δMH vibration, which is active in the IR spectra and forbidden in the Raman spectra (see above), is expected for the polymeric compounds $Cp_2Zr(H)X$ (X = Cl, Br). Only bands at 940 and 941 cm^{-1}, which are active only in the IR spectra and shift after deuteration to 681 and 677 cm^{-1} (νH/νD = 1.38 to 1.39), agree with this rule for $Cp_2Zr(H)Cl$ and $Cp_2Zr(H)Br$, respectively. The fact that the frequencies are higher than those typical of vibrations of bridged bonds in dihydrides is likely caused by the presence of acceptor halogen atoms, which enhance the Lewis acidity of the central metal atom and result in strengthening of the hydride bridge. The fact that the frequency of the Zr—H—Zr stretching vibration in mixed complexes is higher (1407—1402 cm^{-1}) than in the dihydride (1332 cm^{-1}) is in keeping with this notion.

Vibrations of cyclopentadienyl rings. The frequencies of the internal vibrations of the Cp-rings are higher than 600 cm^{-1} and lie in ranges typical of all of the $\eta^5\text{-}C_5H_5$-complexes[19] (see Tables 1 and 2). Comparison with the spectra of other Cp-compounds allows one to note several specific features characteristic of η^5-Cp-complexes with a relatively weak metal—ligand covalent bond: the frequencies of the breathing and degenerate vibrations of the ring are shifted up to 1125—1130 cm^{-1} compared with those observed for ferrocene (1105 cm^{-1}) and other typical π-complexes containing the Cp-ligand; the intensity of the band of the breathing vibration in the IR spectrum is very low, although this band is one of the most intensive in the Raman spectrum.

These spectral properties are characteristic of structures in which the Cp—M bond is highly ionic. However, unlike ionic complexes, the bands of the nonplanar vibrations of CH (ρCH) for the studied compounds lie in the 800—850 cm^{-1} range, which corresponds to covalent structures, and only one of the ρCH vibrations has a lower frequency of 776—779 cm^{-1} close to the values typical of ionic complexes (700—750 cm^{-1}). Similar specific features have been previously noted[3,4] for the spectra of tris(cyclopentadienyl) zirconium and hafnium hydrides Cp_3MH.

Framework metal—ligand vibrations. The vibrational frequencies of the Cp_2M framework are below 500 cm^{-1}. Assuming local C_{2v} symmetry, the bands of two stretching and four tilting vibrations of M—Cp are expected in the spectrum. Since we could not record the Raman spectra of the solutions and measure the polarization of lines due to the poor solubility of the complexes, exact assignment of the bands according to symmetry is impossible. Based on the previously obtained results[3] and comparison with the spectra of Cp_2MX_2 (M = Ti, Zr, Hf; X = Cl, Br) complexes,[20—23] we may assign the most intensive (in the low-frequency range of the Raman spectra) band at 270—278 cm^{-1} to the symmetrical stretching vibrations of M—Cp (ν_sMCp). The assignment of the bands of the antisymmetrical stretching (ν_{as}MCp) and tilting vibrations based on comparison with other compounds containing the Cp_2M fragment, including $(Cp_2MX)_2O$ (M = Zr, Hf)[24] and $Cp_2ZrX(NO_3)$,[25] for which the assignment took into account the polarization of lines in the Raman spectra. The νMCp and νMX vibrations interact when X = Cl, which appears as a shift in their bands. However, this interaction is weaker for X = Br and F due to the differences in masses, and the spectra in the frequency range of vibrations of the Cp_2M fragment are more characteristic and resemble the corresponding spectra of the hydride complexes studied in the present work. The rather intensive bands at 300—350 cm^{-1} (often as doublets) both in the IR and Raman spectra are assigned to tilting vibrations. It is interesting that the spectra of the zirconium and hafnium hydride complexes are similar in this range, while for oxane derivatives $(Cp_2MX)_2O$ the bands of tilting vibrations are intensive when M = Zr and are almost absent for M = Hf due to low intensity.

The bands at 245—270 cm^{-1} are assigned to the antisymmetrical vibrations ν_{as}MCp. When the tilting modes are at a higher frequency than νMCp this usually indicates covalent binding between the metal atom and the ligand.[19]

References

1. S. B. Jones and J. L. Petersen, *Inorg. Chem.*, 1981, **20**, 2889.
2. W. L. Jarrett, R. D. Farlee, and L. G. Butler, *Inorg. Chem.*, 1987, **26**, 1381.
3. B. V. Lokshin, Z. S. Klemenkova, M. G. Ezernitzkaya, L. I. Strunkina, and E. M. Brainina, *J. Organomet. Chem.*, 1982, **235**, 69.
4. E. M. Brainina, L. I. Strunkina, B. V. Lokshin, and M. G. Ezernitzkaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 447 (in Russian).
5. P. S. Wailes and H. Weigold, *J. Organomet. Chem.*, 1970, **24**, 405.
6. J. E. Bercaw, *Adv. Chem. Ser.*, 1978, **167**, 136.
7. P. T. Wolczanski and J. E. Bercaw, *Organometallics*, 1982, **1**, 793.
8. J. M. Manriquez, D. R. Mc Allister, R. D. Sanner, and J. E. Bercaw, *J. Am. Chem. Soc.*, 1978, **100**, 2716.
9. D. G. Bickley, N. Hao, P. Bougeard, B. G. Sayer, R. C. Burns, and M. J. Mc Glinchey, *J. Organomet. Chem.*, 1983, **246**, 257.
10. L. I. Strunkina, M. Kh. Minacheva, Z. S. Klemenkova, and B. V. Lokshin, *Metalloorg. Khim.*, 1991, **4**, 819 [*Organomet. Chem. USSR*, 1991, **4**, 398 (Engl. Transl.)].
11. L. I. Strunkina, M. Kh. Minacheva, Z. S. Klemenkova, L. V. Vinogradova, and B. V. Lokshin, *Metalloorg. Khim.*, 1989, **2**, 1054 [*Organomet. Chem. USSR*, 1989, **2** (Engl. Transl.)].
12. L. I. Strunkina, Z. S. Klemenkova, B. V. Lokshin, and E. M. Brainina, *Metalloorg. Khim.*, 1988, **1**, 389 [*Organomet. Chem. USSR*, 1988, **1** (Engl. Transl.)].
13. L. I. Strunkina, M. Kh. Minacheva, Z. S. Klemenkova, and B. V. Lokshin, *Metalloorg. Khim.*, 1989, **2**, 1196 [*Organomet. Chem. USSR*, 1989, **2**, 635 (Engl. Transl.)].
14. E. M. Brainina, L. I. Strunkina, N. A. Kuz'mina, and E. M. Grechkina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 228 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1985, **34**, 216 (Engl. Transl.)].
15. S. V. Trepalin and B. P. Novikov, *Zh. Prikl. Spektrosc.*, 1980, **33**, 545 [(*J. Appl. Spectrosc. USSR*, 1980, **33** (Engl. Transl.)].
16. G. A. Tolstikov, M. S. Mishtakov, and F. A. Valeev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 2576 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1979, **28**, 2392 (Engl. Transl.)].
17. E. Maslovsky, Jr., *Vibrational Spectra of Organometallic Compounds*, J. Wiley, New York, 1977.
18. H. Weigold, A. P. Bell, and R. I. Willing, *J. Organomet. Chem.*, 1974, **73**, C23.
19. V. T. Aleksanyan and B. V. Lokshin, *Kolebatel'nye spektry π-kompleksov perekhodnykh metallov, Ser. Usp. nauki i tekhniki* [*Vibrational Spectra of Transition Metal π-Complexes, Div. Adv. Sci. Techn.*], VINITI, Moscow, 1976 (in Russian).
20. E. Maslovsky and K. Nakamoto, *Appl. Spectrosc.*, 1981, **25**, 187.
21. E. Samuel, R. Ferner, and M. Bigorgne, *Inorg. Chem.*, 1973, **12**, 881.
22. P. M. Duce, B. M. Kingston, M. F. Lappert, R. C. Srivastava, M. J. Frazer, and W. E. Newton, *J. Chem. Soc. A.*, 1969, 2814.
23. H. A. Martin, M. van Gorkom, and R. O. De Jongh, *J. Organomet. Chem.*, 1972, **36**, 93.
24. Z. S. Klemenkova, B. V. Lokshin, M. Kh. Minacheva, and O. A. Mikhailova, *Metalloorg. Khim.*, 1990, **3**, 144 [*Organomet. Chem. USSR*, 1990, **3**, 78 (Engl. Transl.)].
25. B. V. Lokshin, Z. S. Klemenkova, M. Kh. Minacheva, G. I. Timofeeva, and E. M. Brainina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 2599 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1985, **34**, 2409 (Engl. Transl.)].

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