THE VIBRATIONAL SPECTRA OF COMPLEXES OF NORBORNADIENE WITH SOME GROUP VIII METALS

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Summary

The infrared and Raman spectra of norbornadiene complexes of Pd, Pt, Rh and Fe have been studied. An assignment of the normal modes is given and the ligand vibrations in the complex are compared with those for "free" norbornadiene. The $\nu(C=C)$ stretching frequency of coordinated norbornadiene is shifted from 1575 cm^{-1} to over 1400 cm^{-1}.

The strength of the metal—ligand bond, increases in the series Pd < Pt < Rh and for halogen complexes in the series chloride < bromide < iodide. ESCA spectroscopy data obtained are in agreement with these conclusions.

Introduction

In recent years the interest in the spectroscopic properties of the olefinic transition metal π-complexes has increased considerably. The vibrational spectra of some typical compounds of this type, e.g. complexes of ethylene and its homologs [1,2], butadiene [3], 1,5-cyclooctadiene [4,5], 1,5-hexadiene [6], cyclopentene [7], etc. have been studied in detail. These papers discuss the behaviour of the ligand vibrational frequencies in the course of complex formation as well as the frequencies of metal—ligand vibrations. Special attention has been paid to the assignment of the coordinated double bond frequency $\nu(C=C)$ in the spectra of π-complexes. To explain the behaviour of the $\nu(C=C)$ vibration, a concept has been proposed that takes into account the complex nature of this mode [8]. This vibration is coupled with other modes, in particular with the bending vibration of the $=C-H$ bond [$\beta(=C-H)$]. The sum of relative shifts of $\nu(C=C)$ and $\beta(=C-H)$ frequencies upon coordination has been proposed as a measure of the strength of the coordination bond [8]. To investigate this problem in more detail it is reasonable to expand the range of compounds and

include complexes with widely employed cyclic olefinic ligands such as norbornadiene. Until recently the spectra of norbornadiene and its complexes have been practically unknown.

In a previous paper we reported the analysis of vibrational spectra of "free" norbornadiene [9] and its complexes with Cr and Mo [10]. Simultaneously, the spectra of norbornadiene [11] and its complexes with chromium, molybdenum and tungsten tetracarbonyls [12] and palladium halides [13] have been described. We extended the list of investigated norbornadiene complexes by passing from Group VI to Group VIII metals. Now we present the IR and Raman spectra of the following norbornadiene complexes: $C_7H_8PtCl_2$, $C_7H_8PtBr_2$, $C_7H_8PtI_2$, $C_7H_8PdCl_2$, $C_7H_8PdBr_2$, $(C_7H_8RhCl)_2$, $C_7H_8Fe(CO)_3$. We also measured ESCA spectra and the thermal stability of some of these complexes.

Results and discussion

The IR and Raman data are summarized in Tables 1-4 for $C_7H_8Fe(CO)_3$, $(C_7H_8RhCl)_2$, the Pd and the Pt complexes, respectively.

According to the X-ray data for $C_7H_8PdCl_2$ complexes [14] the change of

TABLE 1

INFRARED AND RAMAN SPECTRA OF $C_7H_8Fe(CO)_3$

IR		Raman	IR		Raman
Liquid	Soln. in CS_2	Liquid	Liquid	Soln. in CS_2	Liquid
		100 vs, dp			
250 w		250 ms, dp	1225 w		1228 ms, p
283 mw			1232 vw	1232 vw	
304 mw		301 vs, p	1250 vw		
		385 vw	1305 s	1303 s	1309 w, dp
400 w			1374 w	1370 w	1372 w, dp
453 ms	453 m	450 (sh)	1401 m	1400 w	1401 mw, p
470 m	470 w	468 vs, p	1438 m		1438 mw, p
492 ms	491 m	500 (sh)			
540 m	540 w	539 mw, p		1952 vs	1947 s, dp
564 vs	564 s			2023 vs	2021 m, p
		582 w, dp			
598 vs	597 s				
614 vs	614 s	611 w, p	2840 w		
630 vs	628 s		2858 m		2855 w, p
765 m(sh)	765 m(sh)	768 w, p	2915 m(sh)		2915 m, p
784 ms	784 m				
866 m	865 mw		2928 s		2928 m, p
893 m	893 mw	891 m, p	2960 s		2960 w, dp
902 m	902 m		3007 s		3010 m, p
918 m	918 m				
935 w		933 s, p	3070 vw		3070 w, dp
955 w		953 w, dp			3090 s, p
997 m	995 m				
1033 m	1032 w	1032 m, dp			
1077 m	1076 m	1078 s, p			
1105 w	1105 vw	1108 w, dp			
1162 m	1160 m				
1178 s	1178 ms	1180 w, dp			

TABLE 2

INFRARED AND RAMAN SPECTRA OF $(C_7H_8RhCl)_2$

IR		Raman		IR		Raman	
Solid	Soln. in CS$_2$	Solid	Soln. in CH$_2$Cl$_2$	Solid	Soln. in CS$_2$	Solid	Soln. in CH$_2$Cl$_2$
247 vs 244 vs		250 m	264 w	1391 m	1391 m	1395 m	1400 m, p
296 vw		298 vw		1432 m	1440 m	1430 vw	
358 w		360 s	358 s, p				
373 m		376 m		2825 vw	2825 vw		
				2847 m	2851 m		
495 ms	501 ms	495 w	501 w, dp	2900 s	2911 s	2890 m	
563 w	563 w	555 s	562 s, p	2926 s	2926 ms		
610 vw	614 w	614 w	617 w, dp	2955 s	2953 s	2951 w	
766 m	771 m	767 w		2998 s	3035 s	2996 w	
778 m	780 w						
794 ms	794 ms			3013 s		3014 w	
807 vw							
853 vw							
879 m	881 m	884 w		3036 w	3048 w	3035 m	
896 w	894 vw	892 w	892 m, p	3055 w	3060 w	3063 m	
930 s	930 s	924 m	925 m, p				
937 s	940 (sh)	937 w	937 (sh)				
957 vw		955 w	953 w, dp				
995 w	991 w						
1025 w	1026 m	1022 w					
1032 w		1033 w					
1067 w	1065 w	1063 s	1063 s, p				
1099 w	1100 vw	1102 m	1102 w, dp				
1153 m	1154 m						
1168 s	1169 s						
1220 vw		1220 m	1225 m, p				
1232 w							
1252 w							
1304 s	1302 s	1304 w	1305 w, dp				
1375 mw	1374 w	1380 w	1380 w, dp				

molecular geometry of norbornadiene upon coordination is minor: the double bond is somewhat elongated (1.33—1.36 Å) and the dihedral angle between the double bond planes is smaller (115°—110°). The coordinated molecule retains C_{2v} symmetry.

The vibrational spectrum of norbornadiene also does not change significantly after coordination: the frequencies of most ligand vibrations remain constant within 20 cm^{-1}. Therefore in most cases the assignment for coordinated norbornadiene could be done by direct comparison with the spectrum of the "free" ligand [9]. Additional evidence for the assignment given is obtained from polarization data in the Raman spectrum of $(C_7H_8RhCl)_2$ (solution) and $C_7H_8Fe(CO)_3$ (liquid) complexes (Table 5). The greatest changes are observed for the C=C stretching modes and some skeletal vibrations alter to a lesser extent. Interesting changes occur as well in the region of out-of-plane bending $\rho(=C-H)$ modes. The low frequency part of the spectrum contains also most

TABLE 3

INFRARED AND RAMAN SPECTRA OF Pd^{II} COMPLEXES

C$_7$H$_8$PdCl$_2$		C$_7$H$_8$PdBr$_2$	
IR solid	Raman solid	IR solid	Raman solid
106 m			
115 m		103 w	
150 w			
		208 s	208 vs
		225 s	228 s
235 m	234 w	230 m	
268 s	264 vs		
	289 (sh)		
302 s	300 ms	302 m	303 ms
333 s	339 w	324 m	
488 m	488 m	488 w	488 m
517 vw	517 s	511 vw	513 s
	597 m	592 vw	590 m
668 vw			
687 vw			
735 w			
770 s	773 w	768 s	
791 s	790 w	781 s	792 w
		806 s	
799 ms		811 s	817 w
821 w			
830 m	830 vw	834 vw	
880 m	883 w	876 m	883 w
899 s	902 w	892 m	899 w
		935 m	
940 s	941 m	937 m	943 w
960 m			
968 m	954 w	956 ms	950 (sh)
1006 w		1000 w	
1049 w		1040 w	
1086 w	1087 s	1084 w	1084 s
	1124 w		1129 w
1160 m		1164 m	
1182 s		1178 ms	
1227 s	1229 m	1228 m	1228 m
1245 vw		1244 w	
1260 w		1259 vw	
1307 s		1310 s	
1410 s	1409 m	1407 m	1409 m
1425 m	1429 w	1421 m	1422 m
1453 m	1452 m	1442 m	1444 m
2849 w		2832 vw	
2861 w		2860 vw	
2920 w			
2930 w		2927 m	2925 w
2970 w	2970 vw	2968 w	2968 w
3041 s		3036 m	
3050 s	3041 m	3048 m	3037 m
3060 s	3060 w	3060 m	3058 w
3090 m	3089 m	3088 w	
3101 w	3100 m	3100 w	3100 m

TABLE 4

THE INFRARED AND RAMAN SPECTRA OF Pt^{II} COMPLEXES

C$_7$H$_8$PtCl$_2$		C$_7$H$_8$PtBr$_2$		C$_7$H$_8$PtI$_2$	
IR solid	Raman solid	IR solid	Raman solid	IR solid	Raman solid
105 w		105 m		86 w	
115 vw				96 w	
150 w					
				176 s	176 s, p^a
				180 ms	183 s, dp^a
		220 s			
		225 s	222 vs		
265 m		260 s		258 s	255 w
				288 mw	289 s, p^a
291 s	295 vs				
318 s		295 s	296 (sh)	301 w	
320 s	323 s	301 m(sh)	304 s		
340 s	340 ms	331 s		318 w	
345 s	348 ms	339 s	340 m	325 w	324 m
489 m	492 ms	488 ms	488 m	481 w	480 mw
550 vw	550 w	545 vw	544 w		
562 vw	567 s	560 vw	562 ms		550 m
612 w	618 m	609 ms	611 m		600 m
678 vw		678 w			
				721 w	
776 s	778 mw	776 s	776 w	770 s	
801 s		800 s		801 s	
831 m		828 ms		819 m	
849 s					
852 s		844 s			
882 m		882 m		887 w	
891 m	882 vw	890 m	880 vw	889 w	889 w
905 m	908 m	903 w	906 w	897 w	898 w
937 m	941 ms	932 m	936 m	930 w	934 mw
951 m	956 mw	950 m	955 w	948 ms	
				953 m(sh)	
979 s					
981 s		976 s			
992 m		992 m		996 m	
1032 w	1040 w	1030 m	1038 w	1030 w	
				1060 (br)	
1082 w	1085 s	1081 w	1082 s		1077 s
1116 ms	1116 mw	1113 m	1112 w		
1162 m		1161 m		1160 w	
1180 s	1185 w	1180 s	1181 w	1173 ms	1177 w
1229 m	1232 m	1229 m	1230 m	1223 w	1222 m
1242 w		1241 m		1241 vw	
1253 w		1251 w		1256 vw	
1310 vs		1309 vs		1308 vs	
1392 s	1394 w	1393 w	1395 m	1389 m	1389 mw
1410 w	1414 m	1410 w	1412 m	1407 w	1407 m
1440 ms	1440 m	1439 s	1440 m	1434 m	1434 m
2838 vw		2839 w		2831 w	
2863 vw		2862 w		2855 w	
		2912 vw			
2930 m	2930 w	2928 m	2928 m	2922 m	2921 w
2961 m	2965 w	2960 w	2960 w	2961 w	2960 w
			3029 w	3030 m	3031 m
3056 s	3055 m	3053 s	3049 m	3050 m	
3070 s	3069 m	3068 s	3066 m		

^{a}Solution in CH$_3$I.

TABLE 5

THE OLEFIN FREQUENCIES OF NORMAL VIBRATIONS IN "FREE" NORBORNADIENE AND IN ITS COMPLEXES

No.	Assignment	Norbornadiene [9] (liq.)		(C$_7$H$_8$RhCl)$_2$ (soln.)		C$_7$H$_8$Fe(CO)$_3$ (liq.)	
		IR	Raman	IR	Raman	IR	Raman
ν_4	ν(C=C) a$_1$		1575 s, p	1391 m	1400 m, p	1400 m	1401 m, p
ν_{23}	ν(C=C) b$_1$	1543 s	1549 w	1374 w	1380 w, dp	1374 w	1372 w, dp
ν_5	β_s(CH$_2$) a$_1$	1449 m	1451 m, dp	1440 m		1438 m	1438 m, p
ν_{14}	β(=C—H) a$_2$	1388 w					
ν_{24}	β(C—H) b$_1$	1334 m					
ν_{32}	β(C—H) b$_2$	1310 vs		1302 s	1305 w, dp	1303 s	1309 w, dp
ν_{33}	Skel. b$_2$	1266 w	1271 m, dp	1252 w		1250 vw	
ν_{15}	Skel. a$_2$	1245 vw	1241 m, dp	1232 w		1232 vw	
ν_6	β(C—H) a$_1$	1226 s	1229 m, p	1222 vw	1225 m, p	1225 vw	1228 m, p
ν_{34}	β_w(CH$_2$) b$_2$	1203 s	1204 w	1168 s		1178 s	1180 w, dp
ν_{16}	β(C—H) a$_2$	1180 vw	1188 vw				
ν_{35}	Skel. b$_2$	1149 m	1153 w, dp	1154 m		1162 m	
ν_{36}	β(C—H) b$_2$	1113 m		1100 w	1101 w, dp	1105 w	1108 w, dp
ν_7	Skel. a$_1$	1105 w	1108 s, p	1065 w	1063 s, p	1073 m	1078 s, p
ν_{17}	β_t(CH$_2$) a$_2$	1060 w	1068 w	1032 w	1033 w	1036 m	1032 m, dp
ν_{25}	β(C—H) b$_1$	1015 w	1017 w, dp	991 w		995 m	
ν_{18}	Skel. a$_2$		952 m, dp		955 m, dp	955 vw	953 w, dp
ν_8	Skel. a$_1$	937 m	938 s, p	930 s	925 m, p	935 w	933 s, p
ν_{37}	Skel. b$_2$	914 w	914 w, dp			918 w	
ν_{26}	Skel. b$_1$	894 w	893 m, dp	881 m	884 w	902 m	
ν_9	β(C—H) a$_1$	876 s	878 m, p	894 vw	892 w, p	893 m	891 m, p
ν_{19}	ρ(CH) a$_2$		857 m	853 vw		866 m	
ν_{27}	β_τ(CH$_2$) b$_1$	800 s	800 w	794 ms		784 ms	
ν_{10}	Skel. a$_1$	775 w	775 m, p	780 w		765 m	
ν_{11}	ρ(CH) a$_1$	728 vs	731 w	768 w	771 m		
ν_{28}	ρ(CH) b$_1$	660 vs					
ν_{39}	Skel. b$_2$	544 m	541 m	614 w	617 w, dp		
ν_{29}	Skel. b$_1$	504 s		501 ms	501 w, dp	492 ms	500 w, dp
ν_{20}	Skel. a$_2$		445 m, dp			453 m	450 (sh)
ν_{12}	Skel. a$_1$	421 m	423 m, p	563 w	555 s, p	540 m	539 m, p

information on the characteristics of the coordination bond in the compounds investigated.

The region of ν(C=C) and β(=C—H) frequencies

In the spectra of the compounds investigated the shift of the β(=C—H) frequency upon coordination is negligible ($\leqslant 0.8\%$) and it is smaller than in Pt^{II}, Pd^{II} and Rh^I complexes with 1,5-cyclooctadiene [4] and 1,5-hexadiene [6] where the maximum shifts for Rh^I complexes are 3 and 1% respectively.

Thus a big β(=C—H) shift in Zeise's salt (7.5%) is an exception rather than the rule. Therefore in order to specify the strength of the coordination bond in the norbornadiene complexes one need only take into account the shift of ν(C=C).

When the norbornadiene molecule is coordinated to a transition metal the frequencies of its symmetric and antisymmetric ν(C=C) modes shift generally over 170 cm^{-1} to the region of 1370-1450 cm^{-1}, where the ligand should have one extra vibrational transition due to the methylenic scissoring mode, β_s(CH$_2$). Actually the spectra of the norbornadiene complexes investigated display three

TABLE 6

THE ASSIGNMENTS FOR ν(C=C) AND β_s(CH$_2$) FREQUENCIES IN THE SPECTRA OF NORBORNA-DIENE COMPLEXES

Compound	Frequency (cm^{-1})			% $\Delta\nu_s$(C=C)/ν_s(C=C)
	ν_s(C=C)	ν_{as}(C=C)	β_s(CH$_2$)	
C$_7$H$_8$(L)	1579	1547	1455	
LCr(CO)$_4$[a]	1457	1427	1432	8.1
LMo(CO)$_4$[a]	1456	1423	1431	8.2
LFe(CO)$_3$	1400	1371	1438	11.5
(LRhCl)$_2$	1395	1380	1430	13.2
LPtCl$_2$	1414	1394	1440	11.9
LPtBr$_2$	1412	1395	1440	11.9
LPtI$_2$	1407	1389	1434	12.2
LPdCl$_2$	1429	1409	1452	10.5
LPdBr$_2$	1422	1409	1444	11.0

[a]See the assignment proposed for C$_7$H$_8$Cr(CO)$_4$ and C$_7$H$_8$Mo(CO)$_4$ complexes in ref. 10. We note that Butler and Barna [12] and then Adams and Fernando [13] gave other assignments of the vibrational frequencies in this region: they have assigned to the β_s(CH$_2$) mode the 1450 cm^{-1} Raman line having a low degree of depolarization not specific of such vibrations.

bands in this region which could be assigned according to the depolarization degree data in the Raman spectra of (C$_7$H$_8$RhCl)$_2$ (in solution) and liquid C$_7$H$_8$Fe-(CO)$_3$. The high frequency line which is almost depolarized was assigned to β_s(CH$_2$) (in the Raman spectrum of norbornadiene the corresponding line is practically depolarized (ρ = 0.73) [9]). The second polarized line is due to the ν_s(C=C) mode (and the low frequency depolarized line is assigned to ν_{as}(C=C)). The bands at 1450-1370 cm^{-1} in the spectra of Pt^{II} and Pd^{II} complexes are also assigned in the same way (see Table 6).

Analyzing the data of Table 6 it should be pointed out that the nature of the second ligand in the norbornadiene complexes certainly affects the electronic density distribution. Thus in order to reveal the regularities in ν(C=C) shift depending on the metal one should discuss the carbonyl and halogen complexes separately.

In the carbonyl complexes the value of the shift of ν(C=C) changes in the series Fe^0 > Cr^0 ≈ Mo^0, that is on going from Group VI to Group VIII elements the value of $\Delta\nu$(C=C) increases, in agreement with common concepts on the greater contribution of back donation to the coordination bond with an occupation of d-shell in transition metal.

The well known regularity is observed in the spectra of halogen complexes: the lowering of the ν(C=C) frequency upon complexation decreases in the order Rh^I > Pt^{II} > Pd^{II}. In general the ESCA spectra of Pt^{II} and Pd^{II} complexes and the data on thermal stabilities of the complexes agree with the IR and Raman spectral data (Table 7).

It can be seen from Table 7 that a replacement of the respective acido ligands by norbornadiene results in an electron density shift from the metal to the π-ligand, and the shift is greater on going from palladium to the corresponding platinum complexes. The thermal stabilities of platinum complexes exceed those of palladium compounds.

TABLE 7

THE CHANGES OF THE ELECTRONIC DENSITY ON THE METAL AND HALOGEN (ESCA DATA) AND THE DECOMPOSITION TEMPERATURES OF THE NORBORNADIENE COMPLEXES

Compound	Bonding energy E(eV)	ΔE(eV)	Bonding energy E(eV)	ΔE(eV)	Decomposition temperature (°C)
	Pt 4f		*Cl 2p*		
K_2PtCl_4	73.1		198.9		
		1.5		0.4	
$C_7H_8PtCl_2$	74.6		199.3		310
			Br 3d		
K_2PtBr_4	72.7		69.5		
		1.9		0.2	
$C_7H_8PtBr_2$	74.6		69.7		290
$C_7H_8PtI_2$	73.8	2.2[a]			260
	Pd 3d		*Cl 2p*		
K_2PdCl_4	338.4		199.0		
		0.6		—0.5	
$C_7H_8PdCl_2$	339.0		198.5		220
			Br 3d		
K_2PdBr_4	337.9		69.6		
		1.5		—0.2	
$C_7H_8PdBr_2$	339.4		69.4		220
	Rh 3d		*Cl 2p*		
$(C_7H_8RhCl)_2$	308.5		198.9		

[a] Datum obtained indirectly.

It is evident from Table 7 that the change of electron density at the metal depends on the nature of halogen: it is somewhat higher on going from chloride to bromide and iodide analogs, which is most clearly expressed in the case of palladium complexes.

A comparison of the spectra of platinum and palladium complexes with various halogen ligands shows that the double bond frequency shift differs negligibly upon replacement of halogen. However, there is a tendency towards an increase of relative shift of $\nu(C=C)$ in the series Cl < Br < I, which along with ESCA data demonstrates an increase of coordination bond strength in this series.

However, the thermal stability of platinum complexes decreases upon replacement of halogen in the series Cl > Br > I, while for palladium complexes it is independent of the nature of the halogen.

It should be noted that decomposition of the norbornadiene chloride complexes occurs step by step, by elimination first of norbornadiene, then of acido ligand. In all other cases, the complexes decompose with the simultaneous loss of halogen and norbornadiene.

The region of $\rho(=C—H)$ frequencies

Another interesting change in the spectrum of olefinic ligand upon coordination reported earlier [10,15] is the decrease of the IR intensities of out-of-plane CH bonds with their simultaneous shift towards the higher frequencies. The effect of decreasing intensity is observed most clearly for the halogen complexes, which display no strong $\beta(M—C—O)$ vibration bands in the IR spectrum, as do carbonyl complexes. The $\rho(=C—H)$ bands at 660 and 728 cm^{-1} in the

spectrum of "free" ligand are readily identified because of their high intensity. We failed to identify the $\rho(=C—H)$ bands in the spectra of complexes because of the complex pattern of spectrum in the region 600-1000 cm^{-1}. Meanwhile, using the most intense IR band in this region one may estimate the upper limit of the integrated intensity of $\rho(=C—H)$ in the coordinated norbornadiene for the soluble complexes. It is at least as much as 2.5-3 times lower than in the "free" ligand. The $\rho(=C—H)$ modes are very characteristic [16] and roughly speaking their intensities could be associated with the C—H bond polarity. Since the hydrogen atom shifts in these vibrations are as much as several times greater than the corresponding value for carbon atoms, the change of dipole moment at $\rho(=C—H)$ vibrations may be associated qualitatively with the effective charge on the hydrogen atom of the $=C—H$ bond. ^{1}H NMR spectra show that the olefin coordination results in a shift of olefin proton signals over 2-3 ppm upfield [17], i.e. the density of electronic cloud in the space of olefinic protons increases with coordination. This fact, and the IR spectral data lead to a qualitative conclusion that the $=C—H$ bond hydrogen in "free" olefin is a positive pole of the dipole which agrees with the common concepts on the electron density distribution in the olefinic systems.

Metal—olefin and metal—halogen frequencies

Unlike the spectra of other diolefinic complexes (e.g. complexes of 1,5-hexadiene or 1,5-cyclooctadiene with Pt^{II}, Pd^{II} and Rh^I, the norbornadiene complexes display no bands with noticeable intensity in the region of 370-470 cm^{-1} specific for the frequencies of metal—olefin vibrations [4,8]. The bending skeletal ligand modes are observed in the higher frequency region. Among these one may outline the 510 cm^{-1} mode in the spectra of Pd^{II} complexes and 550 cm^{-1} vibration in the spectra of Rh^I and Pd^{II} complexes. Unlike other ligand vibrations, the frequency of this mode depends considerably on the nature of the metal and appears in the Raman spectrum as a strong and polarized line. The Raman line at 500-550 cm^{-1} has rather high frequency for its assignment to ν(metal—ligand) vibration. Most probably this line is due to a symmetrical skeletal bending vibration (in the spectrum of "free" ligand its frequency is 423 cm^{-1})* Such an increase in the frequency of a symmetrical skeletal bending vibration has been observed as well for cyclopentene-platinum(II) and -palladium(II) complexes [7].

The ν_s(M—L) vibrations in the spectra of C$_7$H$_8$Cr(CO)$_4$ and C$_7$H$_8$Mo(CO)$_4$ complexes have been observed at unusually low frequencies: at 249 and 224 cm^{-1} respectively [10,12]. One may assume that in the norbornadiene complexes investigated the ν(M—L) modes will be also observed at sufficiently low frequencies. Actually in the Raman spectrum of C$_7$H$_8$Fe(CO)$_3$ complex a strong and polarized line at 301 cm^{-1} corresponds to the ν_s(M—L) vibration [the second strong, polarized line at 468 cm^{-1} is assigned to ν_s(Fe—CO)].

In the spectra of halogen complexes one should first eliminate the frequencies of metal—halogen modes. Usually these are the most prominent lines in the vibrational spectra of olefinic complexes [1,2]. The IR and Raman spectra of

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* Adams and Fernando [13] have also assigned this line to a symmetrical "butterfly" type skeletal vibration of norbornadiene.
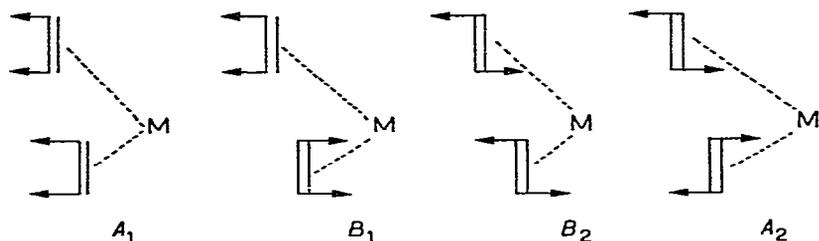
Fig. 1. Metal—ligand vibrations.

norbornadiene-platinum(II), -palladium(II) and -rhodium(I) complexes exhibit one or two closely located bands shifting regularly upon replacement of halogen, and therefore assigned to ν(M—Hal)*:

ν(Pt—Cl)	ν(Pt—Br)	ν(Pt—I)	ν(Pd—Cl)	ν(Pd—Br)	ν(Rh—Cl)
295 cm^{-1}	222 cm^{-1}	176 cm^{-1}	268 cm^{-1}	208 cm^{-1}	244 cm^{-1}
	225 cm^{-1}	180 cm^{-1}		225 cm^{-1}	247 cm^{-1}

The 247 cm^{-1} frequency was assigned to ν(Rh—Cl) in ref. 18. In addition to the bands corresponding to ν(M—Hal) vibrations, the spectra of halogen complexes in the region 200-370 cm^{-1} show at least 3 bands which in some cases are split due to crystal field effects. These bands were assigned to ν(M—L) modes. On the basis of model shown in Fig. 1 one can anticipate four such vibrations in the case of diolefinic complexes, which belong to A_1, A_2, B_1 and B_2 symmetry species in the case of C_{2v} symmetry of the complex (see Fig. 1).

It can be seen from Fig. 1 that the A_2 type mode should differ from other M—L stretching vibrations since it is associated with a considerable deformation of the ligand molecule skeleton, thus it should be observed in the higher frequency region. The interaction of M—C bonds which leads to the split of the M—L modes into symmetric A_1 and antisymmetric B_2 should be significantly greater than the interaction leading to splitting into symmetric A_1 and antisymmetric B_1 modes. Thus the frequencies of A_1 and B_1 species should be closer than A_1 and B_2 species.

Taking into account these concepts, and keeping in mind that the line corresponding to A_1 species should be strong and polarized in the Raman spectrum, one may propose the ν(M—L) frequency assignment given in Table 8. The A_2 type vibrations were not identified in the spectra of complexes. Upon replacement of metal the frequencies ν_s(M—L) in the chloride complexes change in the series $Rh^I > Pt^{II} > Pd^{II}$, i.e. in the same order as a decrease of ν(C=C) shift upon coordination with various metals.

A decrease of ν(M—L) frequency on going from platinum(II) chloride to bromide and iodide analogs may be explained by kinematic interaction of vibrations in the olefin—metal—halogen system. However, the ν^{A_1}(M—L) frequency in the Pd^{II} complexes does not change on going from chlorides to bromides, which is probably due to the higher strength of the palladium—olefin bond, which agrees with ESCA data.

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* In ref. 13 the 268 cm^{-1} line in the Raman spectrum of $C_7H_8PdCl_2$ shifted to 208 cm^{-1} in the spectrum of $C_7H_8PdBr_2$ has been assigned erroneously to ν_s(M—L).

TABLE 8

ASSIGNMENT OF METAL—OLEFIN VIBRATIONS

Vibration		$C_7H_8Fe(CO)_3$	$C_7H_8PtCl_2$	$C_7H_8PtBr_2$	$C_7H_8PtI_2$	$C_7H_8PdCl_2$	$C_7H_8PdBr_2$	$(C_7H_8RhCl)_2$
Stretch B_2	IR	250 w	265 m	260 s	258 s	235 m	230 m	296 vw
	R	250 ms, dp			255 w	234 w		298 vw
Stretch A_1	IR	304 mw	319 s	298 s	288 mw	302 s	302 m	358 w
	R	301 vs, p	323 s	300 s	289 s, p	300 ms	303 ms	358 s, p
Stretch B_1	IR		342 s	335 s	322 w	333 s	324 m	373 m
	R		344 ms	340 m	324 m	339 w		376 m

Experimental

The complexes $C_7H_8PtHal_2$, $C_7H_8PdHal_2$ and $(C_7H_8RhCl)_2$ are stable crystalline solids. They were prepared using the procedures described in ref. 19. The complex $C_7H_8Fe(CO)_3$ was obtained according to ref. 20 followed by multiple purification on a chromatographic column until the IR spectrum of the specimen showed no impurities of ketones generated as by-products. Composition of all the complexes obtained was confirmed by microanalysis.

The IR spectra of complexes $C_7H_8MHal_2$ (M = Pt and Pd, Hal = Cl, Br and I) and $(C_7H_8RhCl)_2$ in the region of 4000-60 cm^{-1} were obtained on Zeiss UR-20, Perkin—Elmer 457 and Fis-1 spectrophotometers (KBr pellets, nujol mulls).

The IR spectra of liquid $C_7H_8Fe(CO)_3$ in the region of 4000-250 cm^{-1} were recorded on Zeiss UR-20 and Perkin—Elmer 457 spectrophotometers.

The Raman spectra of crystalline Pt^{II}, Pd^{II} and Rh^I complexes, solution of $(C_7H_8RhCl)_2$ in CH_2Cl_2 and liquid $C_7H_8Fe(CO)_3$ were recorded on Codberg PHO and modified DFS-12 spectrometers equipped with a He—Ne (6328 Å) laser. The laser output power varied from 50 to 15 mW. The ESCA spectra of Pt^{II}, Pd^{II} and Rh^I complexes were measured on Varian VIEE-15 instrument using a technique previously described [21,22]. The reproducibility of the positions of the energy maxima was estimated as 0.1 to 0.2 eV.

The experimental data are summarized in Tables 1-4. In discussion, the results of an analysis of the vibrational spectrum of norbornadiene [9] are also included.

Acknowledgements

References

1 J. Hiraishi, Spectrochim. Acta, Part A, 25 (1969) 749.
2 J. Hiraishi, D. Finseth and F.A. Miller, Spectrochim. Acta, Part A, 25 (1969) 1657.
3 G. Davidson and D.A. Duce, J. Organometal. Chem., 44 (1972) 365.
4 D.B. Powell and T.J. Leedham, Spectrochim. Acta, Part A, 28 (1972) 337.
5 T.J. Leedham, D.B. Powell and J.G.V. Scott, Spectrochim. Acta, Part A, 29 (1973) 559.
6 I.A. Zakharova, L.A. Leites and V.T. Aleksanyan, J. Organometal. Chem., 72 (1974) 283.
7 D.W. Wertz, D.F. Bocian and M.J. Hazouri, Spectrochim. Acta, Part A, 29 (1973) 1439.
8 D.B. Powell, J.G.V. Scott and N. Sheppard, Spectrochim. Acta, Part A, 28 (1972) 327.

9 V.T. Aleksanyan, I.A. Garbouzova, M.A. Prianichnikova and I.N. Patourian, Izv. Akad. Nauk SSSR, Ser. Khim., 4 (1973) 777.
10 I.A. Garbouzova, V.T. Aleksanyan and M.A. Prianichnikova, Izv. Akad. Nauk SSSR, Ser. Khim., 8 (1973) 1722.
11 I.W. Levin and W.C. Harris, Spectrochim. Acta, Part A, 29 (1973) 1815.
12 I.S. Butler and G.G. Barna, J. Raman Spectrosc., 1 (1973) 141.
13 D.M. Adams and W.S. Fernando, Inorg. Chim. Acta, 7 (1973) 277.
14 N.C. Baenziger, G.F. Richards and I.R. Doyle, Acta Crystallogr., 18 (1965) 924.
15 B.V. Lokshin, V.T. Aleksanyan, Z.S. Klemenkova and L.V. Rybin, J. Organometal. Chem., 74 (1974) 97.
16 L.M. Sverdlov, M.A. Kovner and E.L. Krainov, Vibrational Spectra of Polyatomic Molecules, Nauka, Moscow, 1970, p. 245.
17 E.O. Fisher and H. Werner, Metal π-complexes, Elsevier, Amsterdam, 1966, p. 94.
18 M.A. Bennet, R.I.H. Clark and D.L. Milner, Inorg. Chem., 6 (1967) 1647.
19 E.W. Abel, M.A. Bennet and G.J. Wilkinson, J. Chem. Soc., (1959) 3178.
20 R. Pettit, J. Amer. Chem. Soc., 81 (1959) 1266.
21 V.I. Nefedov, M.A. Porai-Koshitz, I.A. Zakharova et al., Izv. Akad. Nauk SSSR, Ser. Fiz., 2 (1972) 381.
22 V.I. Nefedov, M.A. Porai-Koshitz, I.A. Zakharova and M.E. Djatkina, Dokl. Akad. Nauk SSSR, 202 (1972) 3, 605.