IR spectroscopic study of hydrogen bonds in permethylated α-metallocenylcarbinols in the solid state (M = Fe, Ru, Os)

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Abstract

Reliable spectroscopic criteria are suggested which permit an assignment of the $\nu(OH)$ bands in the IR spectra of α-metallocenylcarbinols (M = Fe, Ru, Os) to intermolecular hydrogen bonds of the OH $\cdots$ O and OH $\cdots$ π types or to intramolecular hydrogen bonds of the OH $\cdots$ M type in the crystal and the melt. The effect of metal atom basicity, and of substituents in the carbinol group (R = H, Me, Ph, C_6F_5, Mes) and in the Cp rings on the ratio between associates and chelates is analyzed. The influence of the above factors on the character and stability of intermolecular hydrogen bonds in associates is established.

Introduction

We have recently examined the character and relative stability of intermolecular hydrogen bonds in α-ferrocenylcarbinols and their permethylated analogues [1]. It was found that, instead of the expected associates involving OH $\cdots$ O intermolecular H-bonds, [9]FcCHMesOH undergoes an unusual type of association with OH $\cdots$ π (Mes) intermolecular H-bonds. The stability of these intermolecular hydrogen bonds was shown to be mainly controlled by steric factors rather than electronic effects of the substituents.

The purpose of the present work was to study the influence of changing the metal atom on the character and stability of H-bonds in permethylated and some non-methylated α-metallocenylcarbinols.

As model compounds, the following carbinols were chosen: [9]McCHROH *, where R = H (I), Me (II), Ph (III), C_6F_5 (IV), Mes (V) McCHPhOH (VI) and McCPh$_2$OH (VII); M = Os (a), Ru (b), Fe (c).

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* Mc = $C_5H_5MC_5H_4$; [9]Mc = $C_5Me_5MC_5Me_4$.

We now report the results of a study of the IR spectra of these compounds in the crystal and the melt in the ν(OH) range (3000–3700 cm^{-1}); a comparison with the spectra of dilute CCl$_4$ solutions ($c = 10^{-3}$ mol/l) is also presented [2].

Results and discussion

As can be seen from Table 1, the spectra of all the studied carbinols in the crystal state do not show the ν(free OH) bands which are observed in solution in the range 3615–3620 cm^{-1}. There can be no question as to the assignment of the ν(bonded OH) bands of the primary ruthenium and osmium nonamethylmetallocenyl-carbinols. Here again, as in the case of ^{9}FcCH$_2$OH [1], in th e lowest-frequency region one can observe very broad absorption bands (3200–3150 cm^{-1}), whose positions are independent of the choice of metal atom. This means that compounds Ia-c in the crystal state involve the most stable intermolecular hydrogen bonds of the OH $\cdots$ O type.

As far as the secondary and tertiary carbinols of Ru and Os are concerned, the assignment of the ν(bonded OH) bands presents a problem. The spectra of these compounds exhibit one or two absorption bands ν(OH) in almost the same region as the bands of OH $\cdots$ O intermolecular hydrogen bonds were observed for ferrocenylcarbinols, namely 3500–3300 cm^{-1} [1]. However, in contrast to the latter case, this region also exhibits bands of sufficiently stable intramolecular hydrogen bonds of the type OH $\cdots$ M (M = Ru, Os) which are seen in the spectra of dilute CCl$_4$ solutions [2]. The possible competition between the formation of chelate cycles and associates require reliable criteria to be derived which allow one to assign the ν(OH) vibrations to either intramolecular or intermolecular hydrogen bonds in the crystal spectra.

First, for the spectra of solid samples, a comparison between the half-width of the bands, $\Delta\nu(1/2)$, and the shift values, $\Delta\nu$(OH) = ν(free OH) − ν(bonded OH), was undertaken. For ferrocenylcarbinols, which form intermolecular hydrogen bonds of the OH $\cdots$ O type [1], the above mentioned parameters were found to obey a linear relationship (Fig. 1). The values of $\Delta\nu(1/2)$ for the bands in the spectra of the primary Ru and Os nonamethylmetallocenylcarbinols (1a,b) and those of Mc-CHPhOH (VIa–c) lie on the same straight line. At the same time, the points corresponding to $\Delta\nu(1/2)$ for the bands of compounds, Va,b and VIIa,b are located below this line. In the case of bulky tertiary carbinols VIIa,b, the half-widths of the bands appear to be abnormally low ($\Delta\nu(1/2)$ = 16–26 cm^{-1}). For ^{9}McCHMesOH containing a bulky substituent, on replacing Ru (Vb) by Os (Va), an increase in the $\Delta\nu$(OH) value is accompanied by a substantial decrease in the value of the ν(OH) half-width (30 and 58 cm^{-1}, respectively), but not by its growth. The $\Delta\nu(1/2)$ values for the bands of carbinols IIIa,b, including the smaller substituent (Ph), are far more pronounced (118 and 100 cm^{-1}, respectively), with the points lying above the line. Note that the value of the shift remains practically the same, whereas the half-width increases on going from IIIa to IIIb; the spectrum of the latter compound, in addition to the above band, also showed a wide low-frequency shoulder. These data led us to conclude that, in the case of compounds IIIa,b, the bands do not arise from OH $\cdots$ O intermolecular hydrogen bonds.

Thus, the establishment of a linear dependence between the half-width and the shift values for intermolecular H-bonds of the OH $\cdots$ O type enable one to

Table 1

IR spectra of ⁹McCHROH (I–V), McCHROH (VI) and McCR$_2$OH(VII) in the ν(OH) region in the solid state (in Nujol) [a]

N	M / R	Os (a) νOH (cm⁻¹)	$\Delta\nu$ (cm⁻¹)	$\Delta\nu1/2$ (cm⁻¹)	Ru (b) νOH (cm⁻¹)	$\Delta\nu$ (cm⁻¹)	$\Delta\nu1/2$ (cm⁻¹)	Fe (c) νOH (cm⁻¹)	$\Delta\nu$ (cm⁻¹)	$\Delta\nu1/2$ (cm⁻¹)	Assignment	
I	H	3200	420	270	3180	440	270	3190	430	270	ν(OH ⋯ O)	inter
II	CH_3	–	–	–	3500	115		3555	60	20	ν(OH ⋯ M)	intra
					3460	155		3460	155	60	ν(OH ⋯ O)	inter
III	C_6H_5	3442	173	118	3444 shoulder	171	100	3545 w	68	–	ν(OH ⋯ M)	intra
					3300			3450 s	163		ν(OH ⋯ O)	inter
IV	C_6F_5	3408 s	208	100	–	–	–	3550 w	60	20	ν(OH ⋯ M)	intra
		3300 s	316	180				3420 s	190	80	ν(OH ⋯ O)	inter
V	Mes	3360	255	30	3568	50	16	3550	65	16	ν(OH ⋯ π(Mes))	inter
					3438	180	58				ν(OH ⋯ M)	intra
VI	C_6H_5	3390	225	130	3415	200	110	3460	162	70	ν(OH ⋯ O)	inter
VII	$(C_6H_5)_2$	3447	168	26	3500	115	16	3540	75	18	ν(OH ⋯ M)	intra

[a] Abbreviations: s, strong; w, weak; inter, intermolecular hydrogen bond; intra, intramolecular hydrogen bond.
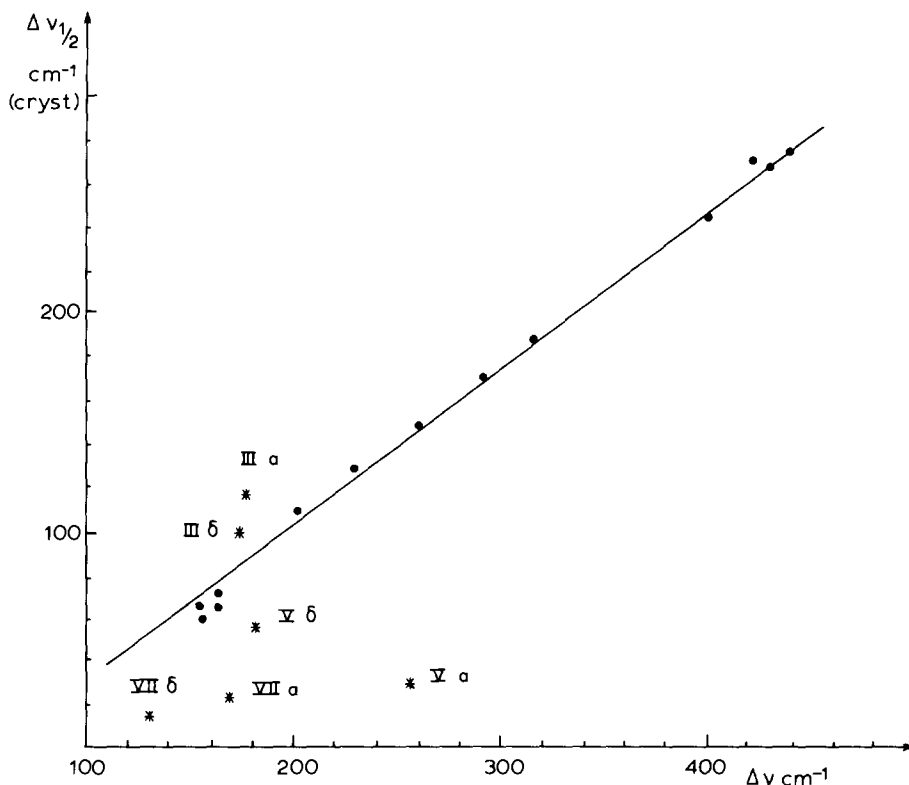
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Fig. 1. Linear relationship between $\Delta\nu(1/2)$ and $\Delta\nu$ in crystals, $\Delta\nu(1/2) = (0.74 \pm 0.02)\,\Delta\nu - (47 \pm 4)$, $r = 0.995$, $S_0^2 = 39.77$, $n = 13$.

distinguish the bands which do not obey this dependence and are likely indicative of $\nu(\text{OH} \cdots \text{M})$ vibrations in the chelate cycles.

Such an assignment is supported by another approach, namely an analysis of the changes in the band halfwidths on going from the solid state to a dilute solution (in CCl_4). The $\Delta\nu(1/2)$ values of the bands for associates, which in the crystal vary from 70 to 270 cm^{-1} (Tab. 1), are replaced in dilute solution by lower-frequency chelate bands ($\Delta\nu(1/2) = 50\text{--}120$ cm^{-1} [2]). With reference to Fig. 2, which illustrates the ratio between the $\Delta\nu(1/2)$ values for crystal and solution, it is seen that the points obeying the linear relationship for intermolecular H-bonds (Fig. 1) lie below the dotted line with a slope equal to unity. On the other hand, the points corresponding to the bands which were tentatively attributed to intramolecular hydrogen bonds in the crystal can be seen above the dotted line. The $\Delta\nu(1/2)$ values are 16–118 cm^{-1} for the crystal (Tab. 1), whereas for solution these vary in the 66–164 cm^{-1} range depending on the substituent R and the metal. As one goes from crystal to solution, the broadening of the $\nu(\text{OH})$ bands related to the $\nu(\text{OH} \cdots \text{M})$ vibrations in chelates is in accord with the usual change in halfwidths of these bands under less ordered conditions [3].

Of particular interest are the spectroscopic features of the secondary carbinols when the temperature of crystal samples is raised to the melting point. It turned out that the spectra of molten compounds show bands whose positions coincide with
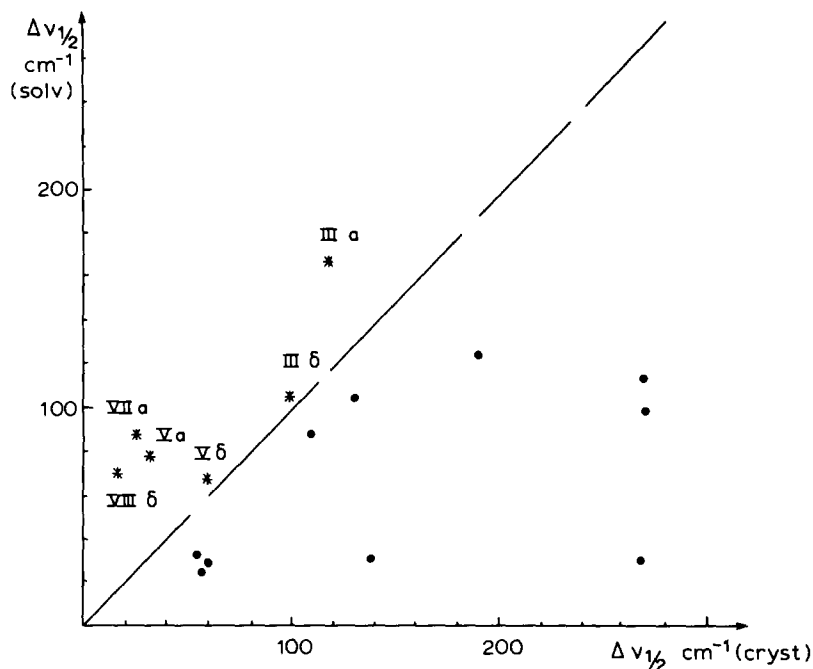
Fig. 2. Relationship between the ν(OH) band halfwidths in solution (CCl$_4$) and the crystal.

those of the bands for OH $\cdot \cdot \cdot$ M intramolecular hydrogen bonds observed in dilute CCl$_4$ solutions (e.g., Fig. 3). Note that compounds VIa–c, which are associated in the crystal owing to OH $\cdot \cdot \cdot$ O bonds, exhibit new bands whose frequencies are higher by 70–100 cm^{-1} * (Table 2). As follows from Table 2, quite different changes occur in the spectra of molten compounds whose bands were assigned to intramolecular hydrogen bonds (OH $\cdot \cdot \cdot$ M) on the basis of the abovementioned criteria. Here, either far smaller shifts towards high frequencies (5–36 cm^{-1} for IIIa–c, IVa and Va,b) or even low-frequency shifts, are observed. A low-frequency shift of the ν(OH) vibrations takes place upon heating and melting carbinols with a tertiary carbinol group CPh$_2$ (the ν(OH) frequencies decrease by 7 and 30 cm^{-1} for VIIa and VIIb, respectively). An abnormal increase in the stability of intramolecular H-bonds with an increase in temperature up to the melting point suggests that the packing of such sterically hindered molecules in the crystal is accompanied by a weakening of the H-bonds in the cyclic chelates.

The changes observed in the spectra of [9]FcCHROH (IIIc,IVb) allow the assignment of the weak low frequency bands at 3545 cm^{-1} to be revised. Previously, these bands were attributed to intermolecular hydrogen bonds of the OH $\cdot \cdot \cdot$ π type (Cp) owing to their occurence at high frequency typical of ν(OH $\cdot \cdot \cdot$ π) vibrations [1]. However, on heating to the melting point, these bands behave like those for

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* In primary nonamethylmetallocenylcarbinols heating results in a weakening of the intermolecular hydrogen bonds, which is manifested by a high-frequency shift of the broad band by ca. 150 cm^{-1}; the bands for chelates, however, do not appear (the ν(OH) frequencies [2] are higher by ca. 100 cm^{-1} than those for the molten compounds).

Table 2

IR spectra of ^{9}McCHROH (I–V), McCHROH (VI) and McCR$_2$OH (VII) in the ν(OH) region in the melt

N	R	Os(a) ν (cm⁻¹)	Δν (cm⁻¹)	ΔΔν[a] (cm⁻¹)	Ru(b) ν (cm⁻²)	Δν (cm⁻¹)	ΔΔν[a] (cm⁻¹)	Fe(c) ν (cm⁻¹)	Δν (cm⁻¹)	ΔΔν[a] (cm⁻¹)	Assignment
	2	3	4	5	6	7	8	9	10	11	12
I	H	3350	270	150	3330	290	150	3350	270	260	ν(OH · · · O) inter
III	C_6H_5	3447	168	5	3480	135	40	3575	38	25	ν(OH · · · M) intra
IV	C_6F_5	3405	211	3	–	–	–	–	–	–	ν(OH · · · M) intra
V	Mes	3618			3618			3615			ν(free OH)
								3550	65		ν(OH · · · π (Mes)) inter
		3390	225	30	3438	180	0				ν(OH · · · M) intra
VI	C_6H_5				3490	125	75	3560	62	100	ν(OH · · · M) intra
								3480 (shoulder)	142		ν(OH · · · O) inter
VII	$(C_6H_5)_2$	3440	175	–7	3470	145	–30	–	–	–	ν(OH · · · M) intra

^{a} $\Delta\Delta\nu = \nu$(OH) for melt − ν(OH) for crystal.

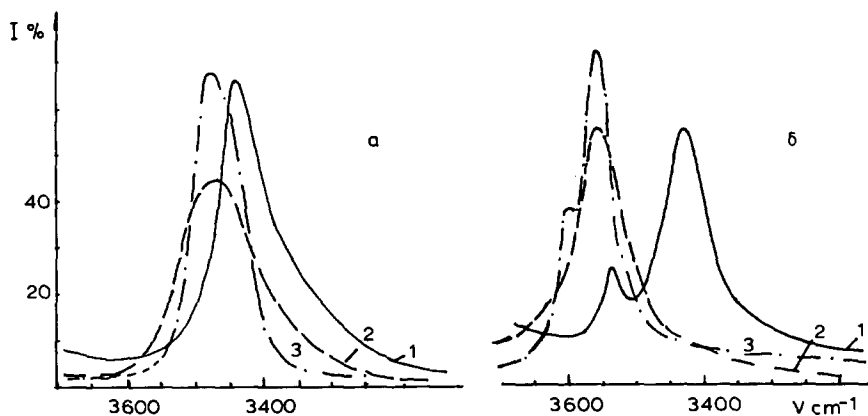Abbreviations: inter, intermolecular hydrogen bond; intra, intramolecular hydrogen bond.

Fig. 3. IR spectra of the compounds ^{9}RcCHPhOH (a) and ^{9}FcCHROH (b): 1, in Nujol; 2, in the melt; 3. in solution (CCl_4) ($c = 2 \times 10^{-3}$ mol/l, $d = 2$ cm).

$\nu(OH \cdots M)$ of chelates. Namely, they undergo a high-frequency shift of 35–40 cm^{-1} such that the occurrence of the bands in the melt coincides with the $\nu(OH \cdots Fe)$ frequency in CCl_4. The $OH \cdots \pi$ (Mes) bands, corresponding to intermolecular hydrogen bonds, behave in a different way. As the temperature increases, the intensity of these bands in Vb,c decreases, while the newly apparent ν(free OH) vibrations (3615 cm^{-1}) gain strength, i.e. weak bonds undergo ruptur (Fig. 4).

Thus, the three approaches to band assignment, namely, a consideration of (i) the $\nu(1/2)$ to $\Delta\nu$ ratio in the crystal, (ii) the ratio between $\Delta\nu(1/2)$ obtained for the crystal and in solution and (iii) a comparison of the band shifts upon melting, are found to give agreed results. Therefore, the assignment of the bands presented in Table 1 seems to be reliable.

It is interesting to examine the influence of the nature of the metal atom, and of substituents in the Cp rings and the carbinol group, upon the ratio in the crystal
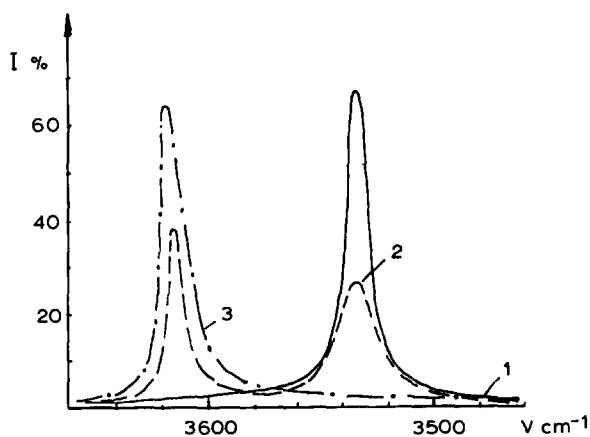

Fig. 4. IR spectra of ^{9}FcCHMesOH: 1, in Nujol; 2, in the melt; 3, in solution (CCl_4) ($c = 5 \times 10^{-3}$ mol/l, $d = 2$ cm).

between associates and molecules with OH · · · M intramolecular hydrogen bonds as well as on the character and stability of intermolecular H-bonds.

From the data shown in Table 1 it follows that an increase in the metal atom basicity hinders self-association by increasing the number of molecules with intramolecular hydrogen bonds; eventually, intermolecular hydrogen bonds may be totally excluded.

Thus, the carbinols of osmium, which has the greatest basicity [4], show the maximum stability of intramolecular hydrogen bonds of the OH · · · M type [2]. As a result, in the spectra of compounds IIIa, Va and VIIa, no bands typical of intermolecular hydrogen bonds can be seen. Vibrations of only one type, namely ν(OH · · · M), are observed in these spectra. Of the analogous ruthenium derivatives, only the bulky tertiary carbinol VIIb gives such a picture. The spectra of IIIb and Vb demonstrate the occurence of two types of molecules with inter- and intramolecular hydrogen bonds. Thus, the spectrum of IIIb shows the band for the OH · · · O hydrogen bond as a low-frequency shoulder on the band for intramolecular H-bonds (3444 cm^{-1}). The spectrum of Vb presents, in addition to ν(OH) of chelates, a band for self-associated bonds of the type OH · · · π (Mes) (at 3438 and 3568 cm^{-1}, respectively).

Owing to the far lower basicity of the iron atom [4], the cyclic chelates IIIc and IVc are completely or almost completely broken in the solid state.

The effect of steric hindrance, arising from methylation of the Cp rings, on self-association becomes clear upon a comparison between [9]McCHPhOH (IIIa–c) and McCHPhOH (VIa–c). For the latter compounds, whatever the choice of metal, one observes intermolecular hydrogen bonds of the OH · · · O type and there are no isolated molecules with chelate cycles. Note that the associates in compounds VIa–c have different stabilities decreasing in the series Os (4.4) > Ru (3.8) > Fe (3.3. kcal/mol), whereas the proton-donating abilities of these carbinols are similar [2]. Depletion of the enthalpies for intermolecular hydrogen bands may be due to an increase in the steric hindrances with decreasing metal atom size.

The carbinol substituents exert a substantial influence on the ratio between associates and chelates, as well as on the character and stability of H-bonds in self-associates. In this case, steric effects are of more importance than electronic ones.

The greatest stability of intermolecular hydrogen bonds and the absence of the metal effect ($-\Delta H = 6.6$. kcal/mol) are typical of the primary nonamethylmetallocenylcarbinols (Ia–c). Substitution of a methyl group for a hydrogen atom (IIb,c) leads to a substantial decrease in the stability of the OH · · · O intermolecular hydrogen bonds, but again the stability is the same for Ru and Fe derivatives in IIb,c ($-\Delta H = 3.3$ kcal/mol). The spectrum of IIb is also indicative of chelates with intramolecular hydrogen bonds of the OH · · · Ru type. As mentioned above, the substituent causing the greatest steric hindrance, Mes (V), changes the character of the H-bond in the associates of carbinols Vb,c. The stability of intermolecular hydrogen bonds of the type OH · · · π (Mes) is rather small, being the same for Ru and Fe derivatives ($-\Delta H = 1.4$–1.5 kcal/mol).

The influence of electron-accepting properties of substituents is seen upon substitution of C_6H_5 (III) by C_6F_5 (IV). In the case of M = Os, besides intramolecular hydrogen bonds typical of IIIa, compound IVa involves substantially stable associates with intermolecular hydrogen bonds of the OH · · · O type ($-\Delta H = 5.0$

kcal/mol). In the relevant iron derivatives, the electron-accepting properties of R are responsible for an increase in the stability of intermolecular H-bonds from 3.3 (IIIc) to 3.6 (IVc) kcal/mol [1].

Conclusion

Reliable spectroscopic criteria which allow an assignment of the ν(OH) bands in permethylated α-metallocenylcarbinols have been derived. The factors unfavourable for self-association with intermolecular H-bonds of the OH $\cdots$ O type, which is typical for alcohols, are revealed. The steric hindrance arising from methylation of the Cp-rings, as well as an increase in the size and number of substituents on the carbinol group, weakens the stability of intermolecular hydrogen bonds. In the case of R = Mes, the character of H-bonds in associates undergoes a change.

Moreover, the above factors favour the replacement of associates by chelates; of great importance here is an increase in the size and basicity of the metal atom, which results in the increased stability of intramolecular H-bonds of the type OH $\cdots$ M. In most of the osmium carbinols studied and in the bulky tertiary ruthenium carbinol no self-association can be seen.

Experimental

The compounds studied were synthesized according to published procedures [4]. The spectra were recorded with "Specord M-80" and "IR-75" instruments in Nujol. The $-\Delta H$ values were determined from the following relationship [6].

$$-\Delta H = \frac{18 \,\Delta \nu}{(\Delta \nu + 720)}$$

The ν(OH) values for the broad bands were obtained by determining the bands' centres of gravity.

The spectra of molten compounds were measured by heating the powders and suspensions in Nujol in a temperature-controlled cell.

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