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Hydrogen bonds and conformations of permethylated α -metallocenylcarbinols (M = Os, Ru, Fe)

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Abstract

IR spectral data show that, in contrast to α -ferrocenylcarbinols which form $\text{OH} \cdots \pi$ and $\text{OH} \cdots \text{M}$ intramolecular hydrogen bonds, α -ruthenocenyl- and α -osmocenylcarbinols, as well as their permethylated analogues, involve hydrogen bonds of only one type, $\text{OH} \cdots \text{M}$. The relative stabilities of the cyclic chelates closed by the $\text{OH} \cdots \text{M}$ hydrogen bonds are consistent with the sequence of metal basicities ($\text{Fe} < \text{Ru} < \text{Os}$). The variations in influence of the carbinol group substituents on the stability of $\text{OH} \cdots \text{Ru}(\text{Os})$ and $\text{OH} \cdots \text{Fe}$ bonds are interpreted in terms of the results of conformational calculations. The absence of a correlation between the stability of cyclic chelates and the proton-donating ability of the OH group is explained by the predominance of steric effects.

Introduction

Recently we communicated the results of a study of intramolecular hydrogen bonds in α -nonamethylferrocenylcarbinols, ${}^9\text{FeCHROH}$, and their non-methylated analogues, FeCHROH [1]. The influence of substituents R at the carbinol C atom and Cp ligands on the character and stability of intramolecular hydrogen bonds has been established. The combination of spectral methods and conformational calculations made it possible to prove that the permethylated iron complexes studied involve hydrogen bonds of only one type, namely $\text{OH} \cdots \text{M}$ bonds.

The object of this study was to examine intramolecular hydrogen bonds and conformations of α -osmocenyl- and α -ruthenocenylcarbinols of the type ${}^9\text{McCHROH}$, where R = H (I), Me (II), Ph (III), C_6F_5 (IV), $\text{C}_6\text{H}_2\text{Me}_3 = \text{Mes}$ (V), McCHPhOH (VI) and McPh_2OH (VII), and M = Os (a) and Ru (b); $\text{Mc} = \text{C}_5\text{H}_4\text{MC}_5\text{H}_5$ and ${}^9\text{Mc} = \text{C}_5\text{Me}_4\text{C}_5\text{Me}_5$. These compounds were compared with the analogous ferrocenylcarbinols (c).

IR spectra were measured in CCl_4 in the $\nu(\text{OH})$ range under conditions which excluded self-association. To estimate the proton-donating ability of the carbinols

their spectra were measured in a CCl_4/DMSO mixture as a standard proton-accepting solvent. The molecular mechanics method was used for conformational calculations for the carbinols $^9\text{RcCHROH}(\text{OcCHROH})$ (I–VI), $^9\text{FcCHROH}$ (III, IV) and their non-methylated counterparts.

Results and discussion

1. Intramolecular hydrogen bonds in α -metallocenylcarbinols

As can be inferred from Tab. 1, the spectra of dilute CCl_4 solutions show bands due to intramolecular hydrogen bonds of the $\text{OH} \cdots \text{M}$ type. There is no doubt as to the assignment of these bands, which occur in a far lower frequency region than do $\text{OH} \cdots \pi$ hydrogen bonds [1], namely in the range $3515\text{--}3390\text{ cm}^{-1}$ (Fig. 1).

The spectra of carbinols IVa,b exhibit, in addition to the fundamental band ($3400\text{--}3440\text{ cm}^{-1}$), high-frequency shoulders at $3520\text{--}3540\text{ cm}^{-1}$ (Fig. 1, curve 3) which can be attributed on the basis of conformational calculation analysis.

The values of the OH band shifts, $\Delta\nu(\text{OH}) = \nu(\text{free OH}) - \nu(\text{bonded OH})$, were chosen as a measure of the relative stabilities of intramolecular hydrogen bonds; for a number of compounds, the values of integral intensities (A) were also used. The data obtained led to the conclusion that for the osmium carbinols under investigation, the stability of the resulting cyclic chelates is greater than that for the corresponding ruthenium derivatives ($\Delta\nu = 154\text{--}227\text{ cm}^{-1}$ and $104\text{--}185\text{ cm}^{-1}$, respectively). The lowest stability of intramolecular hydrogen bonds among the compounds considered is shown by ferrocenylcarbinols, $\Delta\nu = 27\text{--}67\text{ cm}^{-1}$ [1]. The sequence of the values of cyclic stabilities:

$$\text{Os} > \text{Ru} > \text{Fe} \quad (1)$$

corresponds to a decrease in the metal atom basicity [2].

It has been found that in $^9\text{McCHROH}$, with $\text{M} = \text{Ru}$ and Os , the influence of the substituents R on the stability of the hydrogen bonds is the same in both cases. A good linear correlation has been established between the $\nu(\text{OH})$ vibrations for ruthenium and osmium carbinols, with a slope close to unity (1.24) (Fig. 2). However, the variation in intramolecular hydrogen bond stability is not fully consistent with electronic effect of the substituent R. Thus, the values of $\Delta\nu$ increase in the series:

$$\text{Me} < \text{Ph} < \text{H} < \text{C}_6\text{F}_5 < \text{Mes} \quad (2)$$

Hence, with substituents such as H and Mes, the intramolecular hydrogen bond stability is greater than one would expect taking into account the widely held views on their electronic effects. This sequence does not fall into line with that obtained earlier for $^9\text{FcCHROH}$, the latter series of R (H, Mes $<$ Me $<$ C_6F_5 $<$ Ph) [1]. On the other hand, the values of K_f , characterising an ability to form hydrogen bonds grow in the order:

$$\text{H} \leq \text{Mes} < \text{C}_6\text{F}_5 < \text{Ph} < \text{Me} \quad (3)$$

which is different from Eq. 2 but closely resembles that obtained earlier for $^9\text{FcCHROH}$ [1]. The rationale for these discrepancies, which is based on conformational calculation results, is given below. As expected, the substitution of the hydrogen atom in McCHPhOH by the second electron-deficient moiety (VIIa, VIIb)

Table 1
IR spectral data for McCHROH and ${}^9\text{McCHROH}$ in the $\nu(\text{OH})$ region and the formation constants (K_f) for intramolecular hydrogen bonds in CCl_4

Carbinol	Os (a)				Ru (b)				Assignment
	ν cm^{-1}	$\Delta\nu$ $1/2$ cm^{-1}	$\Delta\nu$ cm^{-1}	$A \cdot 10^{-4}$	K_f	ν cm^{-1}	$\Delta\nu$ $1/2$ cm^{-1}	$\Delta\nu$ cm^{-1}	
${}^9\text{McCH}_2\text{OH}$ (I)	3620	16				3620			$\nu(\text{free OH})$
	3438	114	182		1.3	3460	100	160	$\nu(\text{OH} \cdots \text{M})$
${}^9\text{McCHCH}_3\text{OH}$ (II)	-	-	-	-	-	3618	80	104	$\nu(\text{free OH})$
						3514			$\nu(\text{OH} \cdots \text{M})$
${}^9\text{McCHC}_6\text{H}_5\text{OH}$ (III)	3615				20	3615	16		$\nu(\text{free OH})$
	3442	135	173			3480	110	135	$\nu(\text{OH} \cdots \text{M})$
${}^9\text{McCHC}_6\text{F}_5\text{OH}$ (IV)	3617					3614			$\nu(\text{free OH})$
	{ 3520 3400	128	216		11.3	{ 3540 3440	100	174	$\nu(\text{OH} \cdots \text{M})$
${}^9\text{McCHMesOH}$ (V)	3617	16			3.1	3618	14		$\nu(\text{free OH})$
	3390	80	227	3.98		3433	66	185	$\nu(\text{OH} \cdots \text{M})$
$\text{McCHC}_6\text{H}_5\text{OH}$ (VI)	3615	16			8.1	3615	90	124	$\nu(\text{free OH})$
	3461	108	154	1.78		3491	72	143	$\nu(\text{OH} \cdots \text{M})$
$\text{McC}(\text{C}_6\text{H}_5)_2\text{OH}$ (VII)	3615	16			20.6	3615	16		$\nu(\text{free OH})$
	3440	88	175	2.11		3472	72	143	$\nu(\text{OH} \cdots \text{M})$

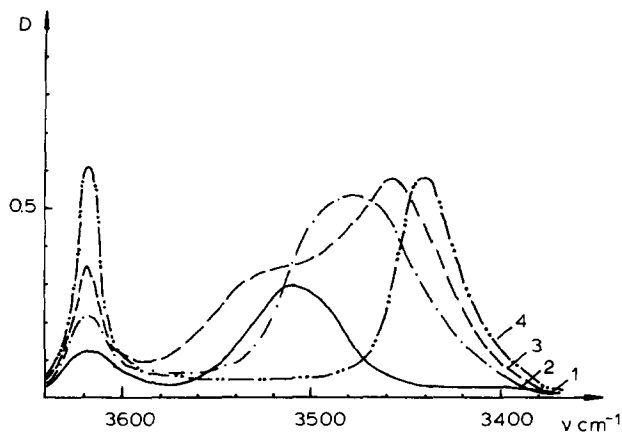


Fig. 1. IR spectra of ${}^9\text{RcCHROH}$ solutions in CCl_4 ($c = 2.5 \times 10^{-3}$ mol/l, $d = 2$ cm): 1, R = Me (IIb); 2, R = Ph (IIIb); 3, R = C_6H_5 (IVb); 4, R = Mes (Vb).

leads to an increase in the stability of the intramolecular hydrogen bonds ($\Delta\nu$, A) as well as in the K_f values.

Using the carbinols with R = Ph as a model, we examined the influence of methyl group introduced into the Cp rings. The values of $\Delta\nu$ and integral intensities (A) of the bands for ${}^9\text{McCHPhOH}$ (M = Ru and Os) are somewhat greater than those for

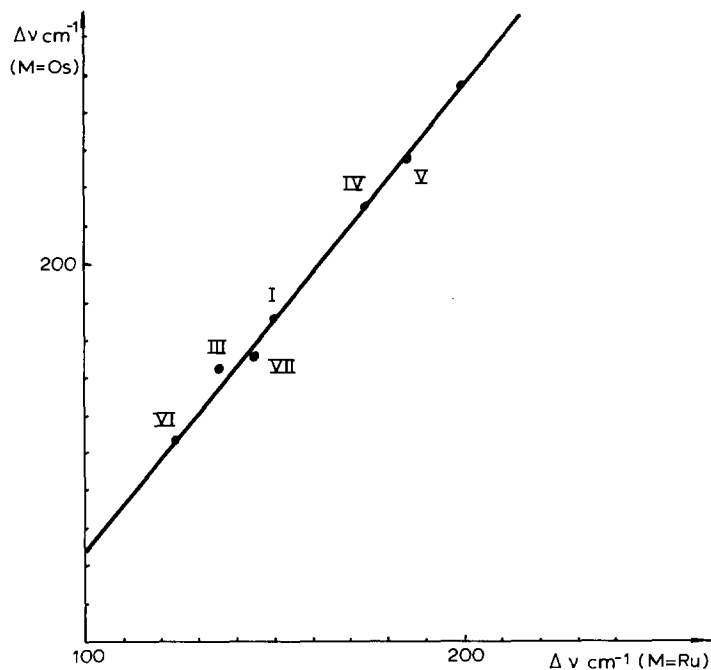


Fig. 2. Linear relation between the $\Delta\nu$, cm^{-1} values for ruthenium and osmium carbinols, $\Delta\nu_{\text{Os}} = (1.242 \pm 0.01) \Delta\nu_{\text{Ru}}$, $r = 0.996$; $S^2 = 11.9$

McCHPhOH, suggesting that an increased stability of the cyclic chelates arises from methylation of the Cp rings. In the case of the corresponding iron carbinols, the opposite effect was observed [1].

2. Proton-donating properties

In order to define the sensitivity of the chelate cycle stability to the influence of the proton-donating properties of the OH group, the interaction of metallocenyl-carbinols with DMSO as a standard proton-accepting solvent was examined (Tab. 2). It turned out that the proton-donating properties of the OH groups are not a decisive factor controlling the ability to form intramolecular hydrogen bonds and the relative stability of the resulting cycles. The *R*-dependent variations in the stability of the intermolecular hydrogen bonds with DMSO are in accord with the electronic effects of substituents. For the compounds McCHROH, the sequence



which differs from the series (Eq. 2) given above, was obtained. A comparison between $^9\text{McCHPhOH}$ and McCHPhOH (Tab. 2) reveals that the proton-donating ability of carbinols with permethylated Cp rings is somewhat lower than that of their non-methylated analogous. At the same time, as already noted, the stability of intramolecular hydrogen bonds gains strength with methylation of the Ru and Os carbinols, the values of $\Delta\nu$, A and K_f being greater for $^9\text{McCHROH}$. This means that the effect of the methyl group in the Cp rings on an increase in the proton-accepting ability of the metal atom prevails over a weakening of the proton-donating properties of the OH group. On the other hand, on going from ferrocenyl- to nonamethylferrocenylcarbinols, the weakening of OH proton-donating properties (intermolecular hydrogen bonds with DMSO) in the latter compounds is consistent with the reduced stability of intramolecular hydrogen bonds [1].

Structural analogues, ruthenocenyl- and osmocenylcarbinols, are similar in terms of proton-donating properties and display almost no difference from the relevant ferrocenylcarbinols. Under identical experimental conditions in ferrocenylcarbinols, the chelate cycles are completely broken, whereas in the ruthenium and osmium analogues these can successfully compete with intermolecular hydrogen bonds owing to the comparable stabilities of both types of H-bonds mentioned. This is true for the compounds IIb, IIIa, IIIb, VIIa and VIIb, which exhibit substantial constants for intramolecular hydrogen-bond formation, $K_f = 25\text{--}12$. The difficulty in evaluating $-\Delta H$ is connected with the necessity of separating the bands (see Experimental section).

Thus, concluding the comparison one may say that the proton-donating ability of the carbinols studied appears to be controlled by the electronic influence of the carbinol substituent and is practically independent of the nature of the metal atom.

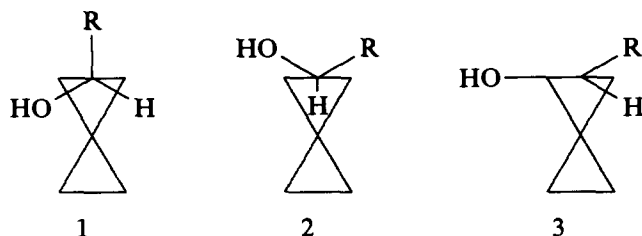
3. Conformational calculations and spectral data

In order to understand better how the specificity of hydrogen bonds is affected by molecular conformations, let us consider the results of conformational calculations for a series of carbinols. Since the values of Ru and Os atomic radii are close, the conformational features for the carbinols of these metals are identical. The calculations reveal the steric effects that depend on the size of the metal atom

Table 2

Spectral characteristics and enthalpies ($-\Delta H$, kcal/mol) for the intermolecular hydrogen bonds of ⁹McCHROH (I-V), McCHPhOH (VI), McCHPh₂OH (VII) with DMSO

M	Os(a)		Ru(b)		Fe(c)	
	ν cm ⁻¹	$\Delta\nu$ cm ⁻¹	ν cm ⁻¹	$\Delta\nu$ cm ⁻¹	ν cm ⁻¹	$\Delta\nu$ cm ⁻¹
Carbinol						
I	3390	233	3390	230	3382	238
II	-	-	3410	208	3400	219
III	3355	260	3352	267	3350	263
IV	3295	322	3295	322	-	-
V	3360	257	3362	256	3360	255
VI	3335	280	3335	280	3340	272
VII	3316	299	3318	297	-	-
		$-\Delta H$		$-\Delta H$		$-\Delta H$
		4.4		4.4		4.5
		-		4.1		4.2
		4.8		4.9		4.8
		5.6		5.6		-
		4.7		4.7		4.7
		5.0		5.0		5.0
		5.3		5.3		-



Scheme 1.

(Os \approx Ru $>$ Fe) or carbinol substituent and those induced by the introduction of methyl groups to the Cp rings.

A similarity has been established between conformational features for the primary metalocenylcarbinols of ruthenium (osmium) and iron [1]. For all these carbinols, as well as for their permethylated analogues, the steric hindrances are minimal, the differences in the conformational energy U_{conf} for various angles of rotation by the carbinol group around the C–C bond (ϕ) being less than 0.5 kcal/mol.

The character of the conformational curves for the secondary carbinols points to an increased steric influence, the curves U_{conf} for $\text{RcCHROH}(\text{OcCHROH})$ and FcCHROH with R = Me, Ph being similar in all cases. These compounds take up conformations with the OH group situated either under the Cp ring, i.e. rotated towards the metal atom ($\phi < 0$), or above the Cp ring ($\phi > 0$) (see conformations 1 and 2 in Scheme 1). At the same time, as can be seen from Fig. 3, the differences in the stabilities of the conformations are small (≤ 1.5 kcal/mol), suggesting that steric factors do not impose limitations on the formation of hydrogen bonds with the metal atom or Cp ring.

Comparing the conformational calculation results (Fig. 3) and the spectral data (Table 1) for McCHPhOH , one finds that, contrary to FcCHPhOH , which involves both $\text{OH} \cdots \pi$ and $\text{OH} \cdots \text{Fe}$ intramolecular hydrogen bonds [1], the ruthenium and osmium analogues (VIa, VIb, Tab. 1) show only an $\text{OH} \cdots \text{M}$ type bond.

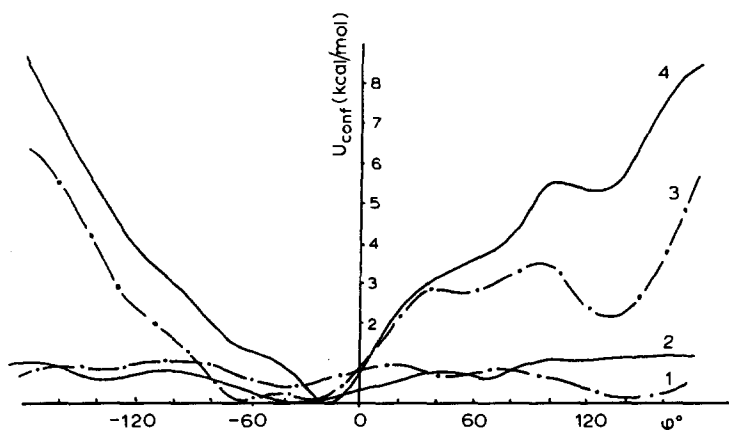


Fig. 3. Plot of U_{conf} (kcal/mol) vs. ϕ (the angle of rotation of the carbinol group around the C–C bond) in metalocenyl carbinols: 1, RcCHPhOH (VIb); 2, FcCHPhOH (VIc); 3, $^9\text{RcCHPhOH}$ (IIIb); 4, $^9\text{FcCHPhOH}$ (IIIc).

Hence, hydrogen-bond formation with the metal must be controlled by the greater basicity of Ru and Os atoms, rather than by a conformational preference.

The plot of U_{conf} vs. ϕ undergoes a great change upon methylation of the Cp rings of the secondary α -metallocenylcarbinols. With increasing steric hindrance, the number of energetically preferable conformations diminishes. Thus, conformations with the OH group located above the Cp rings (i.e. conformation 2 in Scheme 1) become unfavourable. As expected, in the Ru and Os derivatives the steric influence is weaker than in isostructural iron complexes. For ${}^9\text{RcCHROH}$ and ${}^9\text{OcCHROH}$, the energetic differences (Fig. 3) between the minima, corresponding to conformations 1 and 2, are not so pronounced as in the case of ${}^9\text{FcCHPhOH}$. On the other hand, the intramolecular $\text{OH} \cdots \text{Ru}(\text{Os})$ hydrogen bond appears from IR data to have a far greater stability and, as a result, the $\text{OH} \cdots \pi$ type bond is not able to compete (compounds IIa, IIb, IIIa, IIIb in Tab. 1). The influence of the metal atom size on the character of the conformational curve becomes more pronounced with increasing substituent size; the Ru(Os) and Fe carbinols show different values of ϕ , which indicate the position and shape of the minima for U_{conf} in the stable conformations ($\phi \leq 0$) (see Figs. 3 and 4). These differences are of importance, since the value of ϕ fixes the distance between the oxygen and metal atoms and is consequently responsible for the stability of the $\text{OH} \cdots \text{M}$ intramolecular hydrogen bonds*.

Thus with $\text{R} = \text{Me}$, the position of the most pronounced minimum is the same for all nonamethylmetallocenylcarbinols under investigation ($\phi = -45^\circ$). An increase in the size of the substituent R causes a decrease in the value of ϕ to -20° in the case of $\text{R} = \text{Ph}$; with $\text{R} = \text{C}_6\text{F}_5$ and Me s ϕ is -10 and 0° respectively. Taking into account that as the angle decreases, the $\text{O} \cdots \text{Fe}$ distance increases, one can reasonably explain an abnormal weakening of the $\text{OH} \cdots \text{Fe}$ intramolecular hydrogen bond in IVc as compared to that in IIIc, which does not correspond to a reinforcement of the electron-accepting properties of the C_6F_5 substituent. As noted in [1], a coplanar arrangement of the OH group and the Cp ring ($\phi = 0^\circ$) excludes the formation of an intramolecular hydrogen bond in Vc (conformation 3 in Scheme 1).

For the nonamethylmetallocenylcarbinols of ruthenium and osmium, an increase in the substituent size leads to an increased conformational mobility. Thus if $\text{R} = \text{Ph}$, the energetic minimum appears to be wider ($\phi = -20 - 60^\circ$) than that for ${}^9\text{FcCHPhOH}$ ($\phi = -20^\circ$) (Fig. 3).

In such a case, the formation of cyclic chelates involving more favourable ϕ angles becomes possible. For this reason, perhaps, methylation of the Cp ring in McCHPhOH results in different effects for $\text{M} = \text{Ru}(\text{Os})$ and $\text{M} = \text{Fe}$.

The weakening of the proton-donating abilities of the OH group does not lead to a weakening of the intramolecular hydrogen bonds in IIIa,b as compared to VIa,b, whereas upon methylation of ferrocenylcarbinols the effect is observed for all the substituents [1].

The carbinols with $\text{R} = \text{C}_6\text{F}_5$ (IVa,b) show two minima close in energy corresponding to $\phi_1 = -10^\circ$ (as in IVc) and to $\phi_2 = -70^\circ$ (Fig. 4). Theoretically, an

* The $\text{Fe} \cdots \text{O}$ distance (3.2–3.7 Å) corresponds to that found experimentally for the crystal, where an $\text{Fe} \cdots \text{H}-\text{O}$ bond (3.57 Å) has been established [3].

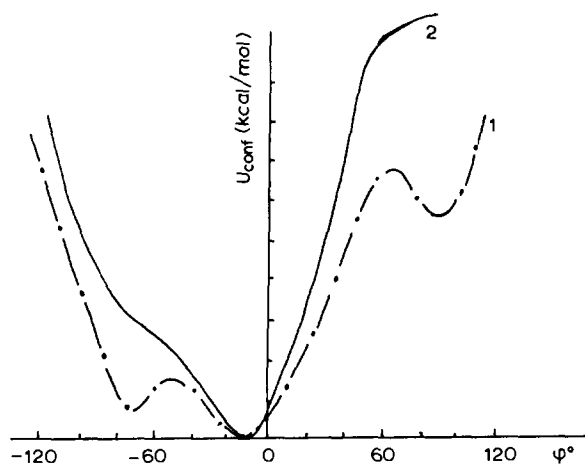


Fig. 4. Plot of U_{conf} (kcal/mol) vs. the angle of rotation ϕ in metalocenylcarbinols: 1, ${}^9\text{RcCHC}_6\text{F}_5\text{OH}$ (IVb); 2, $\text{FeCHC}_6\text{F}_5\text{OH}$ (IVc).

intramolecular hydrogen bond of the $\text{OH} \cdots \text{M}$ type may involve two stable conformations. As follows from Table 1, the spectra of these compounds, along with the bands at 3400 and 3440 cm^{-1} for IVa and IVb, respectively, exhibit high-frequency shoulders at 3520 and 3540 cm^{-1} . In other words, the spectral pattern gives evidence for the presence of chelate cycles which are substantially different in stability.

The high-frequency shoulders are likely to be conformations with a weak intramolecular hydrogen bond of the type $\text{M} \cdots \text{HO}$ (conformation 2) formed with the OH group rotating towards the metal by 10° . Figure 5 clearly indicates that for $\text{R} = \text{Mes}$ (Va, Vb), in addition to the stable conformation 3 (in which, like the

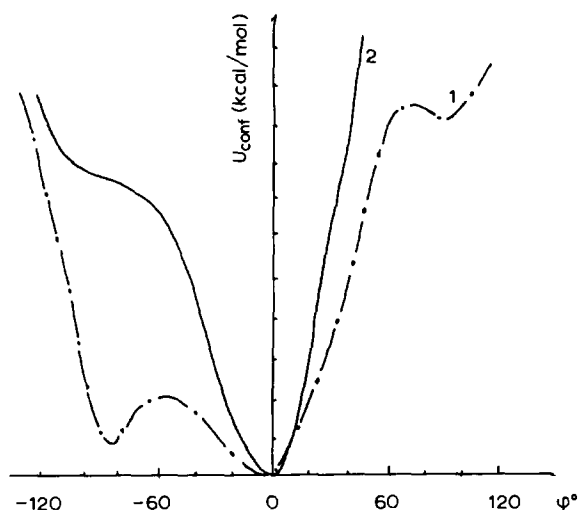


Fig. 5. Plot of U_{conf} (kcal/mol) vs. the angle of rotation ϕ in metalocenylcarbinols: 1, ${}^9\text{RcCHMesOH}$ (Vb); 2, ${}^9\text{FcCHMesOH}$ (Vc).

relevant iron carbinol [1], the OH group and Cp ring are coplanar), a second minimum with the OH group rotated towards the metal atom ($\phi_2 = -85^\circ$) is observed. These conformations show only a slight difference in energy, ~ 1.5 kcal/mol, i.e., in contrast to ${}^9\text{FcCHMesOH}$, there are no steric limits imposed on the formation of the $\text{OH} \cdots \text{M}$ intramolecular hydrogen bond. In fact, as mentioned above, the spectra of Va and Vb show $\nu(\text{OH} \cdots \text{M})$ bands with the greatest shifts, $\Delta\nu$. Thus, it is easy to explain the abnormally high stability of the intramolecular hydrogen bond in compounds Va and Vb as being determined by the maximum OH group rotation towards the metal atom.

Noteworthy are the formation constant values for intramolecular hydrogen bonds. The variations in these values induced by changing the metal atom run parallel with the basicity of the metal and the hydrogen bond stability, namely $\text{Os} > \text{Ru} > \text{Fe}$ (Tab. 1). As already noted, the *R*-dependent sequence of formation constants is different from that of $\Delta\nu$ (see series 3 and 2, respectively), the series being the same for the Ru, Os and Fe derivatives.

The fact that the constants K_f increase along the series shown in Eq. 3 is not surprising in view of the results of conformational calculations. The minimal formation constant for the primary carbinols reflects the lack of energetically favourable conformations. As far as the secondary nonamethylferrocenylcarbinols are concerned, the sequence of constants is in accord with the increased ϕ angle corresponding to the most stable conformation:



A more complicated picture is observed for ${}^9\text{RcCHROH}$ and ${}^9\text{OcCHROH}$. In the instances where there are two minima in U_{conf} , namely for $\text{R} = \text{C}_6\text{F}_5$ and Mes, the constant values decrease owing to the population of conformations unfavourable for intramolecular hydrogen bond formation ($\phi_1 = -10$ and 0° , respectively).

Conclusion

Thus in contrast to ferrocenylcarbinols, which involve both $\text{OH} \cdots \pi$ and $\text{OH} \cdots \text{M}$ intramolecular hydrogen bonds, all α -ruthenocenyl- and α -osmocenylcarbinols under investigation exhibit hydrogen bonds of only one type, $\text{OH} \cdots \text{M}$. The relative stability of the cyclic chelates increases along the series $\text{Fe} < \text{Ru} < \text{Os}$, i.e. consistent with an increase in the metal basicity.

Methylation of the Cp rings in ruthenium and osmium carbinols, in contrast to the iron analogue, causes a small increase in the stability of the cyclic chelates.

The *R*-dependent sequence of chelate cycle stability is the same for $\text{OH} \cdots \text{Ru}$ and $\text{OH} \cdots \text{Os}$ intramolecular hydrogen bonds, but is different from that for the $\text{OH} \cdots \text{Fe}$ hydrogen bond. In accordance with the results of conformational calculations, it reflects the influence of metal atom size on the conformational mobility of the OH group in metallocenylcarbinols.

In the case of ${}^9\text{RcCHROH}$ and ${}^9\text{OcCHROH}$, an increase in substituent size gives rise to a second conformation with a greater angle of rotation of the OH group towards the metal atom ($\phi = 60$ – 85°); as a consequence, the stability of the intramolecular hydrogen bond increases. In ${}^9\text{FcCHROH}$, owing to the smaller size of the metal atom, conformations with such great angles are unrealistic. Here, an increase in the substituent size brings about an elongation of the $\text{OH} \cdots \text{M}$ distance

and a weakening of intramolecular hydrogen bonds; thus for R = Mes there is no conformation involving these bonds.

For all carbinols under investigation, the prevailing importance of steric factors upon cyclic chelate formation is manifested in the absence of a correlation between the changes in the stability of intramolecular hydrogen bonds and the proton-donating ability of carbinols, which is determined by the electronic effect of the R substituent.

Experimental

The compounds studied were prepared by published procedures [4].

IR spectra were recorded with IR-75 and M-80 Specord spectrophotometers, in 5×10^{-3} mol/l CCl_4 solutions, $d = 2$ cm. The integral intensities were calculated as described previously [5]. The concentration of DMSO in CCl_4 was 7 mol/l ($d = 0.2$, carbinol concentration 2×10^{-1} mol/l). In the case of compounds IIb, IIIa, IIIb, VIIa and VIIb, which have large constants for $\text{OH} \cdots \text{M}$ intramolecular hydrogen-bond formation, the positions of maxima under conditions producing a strong overlap of bands were determined by the use of graphic separation. The enthalpies of the hydrogen bonds, $-\Delta H$, were evaluated using Eq. 6 [6].

$$-\Delta H = \frac{18 \Delta \nu}{(\Delta \nu + 720)} \quad (6)$$

Conformational calculations were carried out using a mechanical molecular model with a MOLBD3 program [7] on an EC 1061 computer.

The detailed procedure for conformational molecular calculations for π -complexes is reported in [8,9]. In evaluating the relative conformational energy, the rotation angle C-C-O (ϕ), which is indicative of the carbinol group orientation with respect to the Cp ring, was changed in increments of 20° .

The angle ϕ was taken to be 0° if the oxygen atom of the OH group was located in the Cp ring plane; ϕ was regarded as positive when this group was situated above the ring and negative with the OH group under the ring, i.e. oriented towards the metal atom. For ferrocene derivatives, the Fe-Cp (centroid) distance was taken to be 1.605 Å and for ruthenocene compounds, whose geometric characteristics are identical with those of osmocene, it was taken as 1.808 Å.

References

- 1 E.S. Shubina, L.M. Epstein, T.V. Timofeeva, Yu.T. Struchkov, A.Z. Kreindlin, S.S. Fadeeva and M.I. Rybinskaya, *J. Organomet. Chem.*, 346 (1988) 59.
- 2 B.V. Lokshin, A.G. Ginzburg, Ye.B. Nazarova, *Usp. Khimii*, 49 (1980) 223
- 3 Yu.T. Struchkov, A.S. Batsanov, S. Toma, M. Salisova, *J. Organomet. Chem.*, 329 (1987) 373.
- 4 M.I. Rybinskaya, A.Z. Kreindlin, S.S. Fadeeva, P.V. Petrovskii, *J. Organomet. Chem.*, 345 (1988) 341.
- 5 A. Cabana, C. Sandorfy, *Spectrochem. Acta*, 16 (1960) 335.
- 6 A.V. Iogansen, in *The hydrogen bond*, Nauka, Moscow, 1981, p. 134.
- 7 R.H. Boyd, *J. Chem. Phys.* 49 (1968) 2579.
- 8 T.V. Timofeeva, Yu.L. Slovokhotov, Yu.T. Struchkov, *Dokl. Akad. Nauk SSSR*, 294 (1987) 1173.
- 9 Yu.L. Slovokhotov, T.V. Timofeeva, Yu.T. Struchkov, *Zh. Strukt. Khim.*, 28 (1987) N 4, 3.