Bull Soc Chim Fr (1995) 132, 1073-1082

A study of π-complexation of phenol and β-estradiol by 'Cp*M' M = Rh, Ir moieties: syntheses, solution behavior and reactivity; X-ray molecular structure of $[Cp^*Rh(\eta^5\text{-}C_6H_5O\cdot H_2O)][BF_4]$, $Cp^* = \text{-}C_5Me_5$

Jean Le Bras[1], Hani El Amouri[1*], Yvon Besace[1], Jacqueline Vaissermann[2], Gérard Jaouen[1*]

[1] *Ecole nationale supérieure de chimie de Paris, URA CNRS 403, 11, rue Pierre-et-Marie-Curie, 75231 Paris Cedex 05*
[2] *Université Pierre-et-Marie-Curie, place Jussieu, 75231 Paris Cedex 05, France*

(received 2 March 1995, accepted 19 September 1995)

Summary – Treatment of $[Cp^*Rh(CH_3CN)_3][BF_4]_2$ **1a** with PhOH at room temperature in dichloroethane afforded the asymmetric trimer $[\{Cp^*Rh(\eta^6\text{-PhOH}\cdots)\}_2(\eta^5\text{-PhO}\cdots)RhCp^*][BF_4]_5$ **2a** in 87% yield, where the η-phenoxo species is hydrogen-bonded to the corresponding η-phenolic forms. The analogous iridium complex **2b** was obtained from acetone/dichloroethane mixture in 80% yield. These species **2a** and **2b** were found to be fluxional in solution, for instance, the variable temperature ^1H NMR spectra for the rhodium species **2a** show that the η-Cp* signals coalesce at $T = 354$ K with $\Delta G^{\#} = 18\pm0.5$ kcal/mol. A mechanism of exchange in accord with the experimental data is proposed. Protonation of **2a** by $HBF_4 \cdot Et_2O$ in acetone gave the unstable phenolic compound $[Cp^*Rh(\eta^6\text{-PhOH})][BF_4]_2$ **3a** in 50% yield. On the other hand, **2a** can be deprotonated by NEt_3 to give quantitatively the phenoxo derivative $[Cp^*Rh(\eta^5\text{-PhO}\cdot H_2O)][BF_4]$ **4a**. Compound **4a** crystallizes in the orthorhombic space group $Ccm2_1$, $a = 17.469(3)$ Å, $b = 28.845(4)$ Å, $c = 14.115(2)$ Å, $V = 7\,112(2)$ Å^3, $Z = 16$. The structure of **4a** shows that the -C=O group of the phenyl ring is bent upward with $\theta = 14°$, and different from the structure of the ruthenium analog. The iridium species **2b** behaved similarly when treated with NEt_3 to give an off-white compound $[Cp^*Ir(\eta^5\text{-PhO}\cdot H_2O)][BF_4]$ **4b**. When a yellow solution of $[Cp^*Rh(S)_3][BF_4]_2$ (S = coordinated solvent) was treated with 17β-estradiol in acetone/THF, a mixture of four products (α,β)-$[Cp^*Rh(\eta^6\text{-estradiol})][BF_4]_2$ **13ab** and (α,β)-$[Cp^*Rh(\eta^5\text{-estradienonyl})][BF_4]$ **14ab** was obtained with α/β ratio 9:1. In general the phenoxo form was more stable than the phenolic one for both π-bonded systems (phenol, 17β-estradiol). The effect of the counterion (BF_4 and/or CF_3SO_3) on the stability of the π-bonded phenolic forms (both systems) as well as the reactivity of the π-bonded phenoxo forms (both systems) towards electrophiles (MeI, CF_3SO_3Me) are compared and discussed.

phenol / phenoxo / π-complexation / electrophile / estradiol / estradienonyl

Introduction

The π-complexation of arenes by organometallic moieties is a well-documented area [1]; the introduction of organometallic fragments such as $Mn(CO)_3^{+1}$ or $Cr(CO)_3$ enhance the reactivity of the bonded arene towards nucleophilic attack [2]. The use of organometallic synthons in organic synthesis has proved to be of great utility, thus allowing specific reactions to occur, which are not possible *via* the usual organic procedures [2bc].

Phenols form an interesting class of arenes. They are unusual because of their enolic structure, since enols are usually unstable and tautomerize easily into the corresponding ketones, but this is not true for phenols due to the aromatic character of the benzene ring. Hence phenols are attractive for coordination chemistry. Recently it has been shown that the 'Cp^*Ru^{+1}' unit, forms stable adduct with phenol [3], perhaps owing to its electron-releasing nature compared with metallocarbonyl fragments. Interestingly, the introduction of the ruthenium fragment stabilizes the ketonic form of the bonded arene [3]. Although the complexation of phenol has been reported, less is known about the reactivity of the complexed arene.

In light of the previous reports, we examined the complexation of phenol and β-estradiol by $[Cp^*M][X]_2$ (X = BF_4, CF_3SO_3 M = Rh, Ir) and the reactivity of the complexed arenes. It is worth mentioning that in these studies we considered phenol as a model system for the 'A' ring of the 17β-estradiol. The introduction of organometallic moieties to the A-ring of hormones has already been investigated by us and other groups [4]. A brief communication on the estradiol A-ring complexation by "Cp^*Rh^{2+}" has been reported [5].

In this paper, we report a detailed investigation into the synthesis and spectroscopic characterization

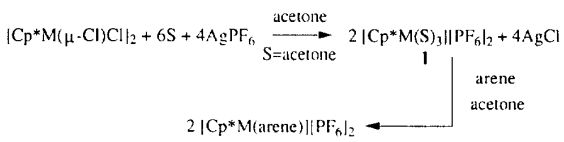
* Correspondence and reprints

of π-complexed phenol and 17β-estradiol. The solution behavior, the effect of counterion and the reactivity of the complexed arenes (both systems) towards MeI and CF_3SO_3Me are also presented.

Results and discussion

Synthesis and NMR characterization

The coordination of arenes by 'Cp*M' (M = Rh, Ir) has been well investigated [6]. Scheme 1 shows the general procedure for the preparation of such complexes.



Scheme 1

We have found that complexation of phenol by $[Cp^*Rh(CH_3CN)_3][BF_4]_2$ **1a** in a non-coordinating solvent such as dichloroethane affords reproducibly a white precipitate in 87% yield. This material was characterized by spectroscopic methods (^{13}C and ^1H NMR) at low temperature as the asymmetric trimer $[\{Cp^*Rh(\eta^6\text{-PhOH}\cdots)\}_2(\eta^5\text{-PhO}\cdots)RhCp^*][BF_4]_5$ **2a**. The analogous iridium species **2b** was obtained in 80% yield by refluxing a dichloroethane solution of $[Cp^*Ir(CH_3CN)_3][BF_4]_2$ **1b** with phenol; this reaction did not proceed at room temperature. Another synthetic procedure for **2b** involves the treatment of $[Cp^*Ir(CH_3)_2CO)_3][BF_4]_2$ with phenol in acetone/dichloroethane mixture for 1 h at room temperature. It is worth emphasizing that we did not detect the presence of any uncomplexed hydrogen-bonded phenol ring by ^1H NMR. Our results differ from those reported for the analogous ruthenium system, where treatment of 'Cp^*Ru^{+1}' by phenol afforded the complex $[Cp*Ru(PhO)\cdot 2PhOH]$ **7** in which two molecules of phenol are hydrogen bonded to the complexed oxocyclohexadienyl unit (fig 1) [3ab].

The hexafluorophosphate rhodium and iridium dimers $[\{Cp^*M(PhO)\}_2H][PF_6]_3$, M = Rh, Ir, have been reported and a symmetric structure was proposed [7]. We note that the ^1H NMR data for these complexes do not correspond to any of our compounds **2a** or **2b**.

The IR spectrum of **2a** recorded in a KBr disc shows a large band at 3 400 cm^{-1} attributed to the unsymmetrical hydrogen bonds (-OH$\cdots$O=) between the η^5-phenoxo and η^6-phenol rings [3, 8]. The ^1H NMR spectrum of **2a** recorded in $(CD_3)_2CO$ at T = 297 K exhibits two set of multiplets in the aromatic region between 6.0 and 7.5 ppm (table I), attributed to the hydrogen-bonded η^5-phenoxo and η^6-phenol rings with 1.1:2 ratio by integration; this was also assigned by ^1H-^1H COSY experiments. In addition we note the presence of two singlets at 2.24 and 2.31 ppm assigned to the π-bonded Cp* rings. Upon warming the sample tube to 354 K, these signals coalesce into one, suggesting a fluxional behavior is taking place (see below).

The ^{13}C NMR spectrum of **2a** recorded at T = 233 K shows eight peaks (table II), each of which appears as a doublet (located between 90 and 113 ppm). These are assigned to the *ortho*, *meta* and *para* carbons of the two different bonded arenes as well as to the unsaturated carbons of the two distinguishable Cp* rings. Furthermore, we note the presence of two signals at 147 and 150 ppm attributed to the carbons bearing the oxygen and the hydroxyl function of the bonded arenes. These results are in accord with an absence of symmetry in the trimer $[\{Cp^*Rh(\eta^6\text{-PhOH}\cdots)\}_2(\eta^5\text{-PhO}\cdots)RhCp^*][BF_4]_5$ **2a** (see fig 1).

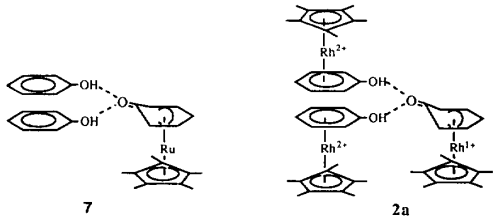


Fig 1

Fluxional behavior of **2a**

The behavior of **2a** in solution was monitored by recording its ^1H NMR spectrum at various temperatures. At T = 297 K two singlets are observed at 2.24 and 2.31 ppm attributed to the bonded Cp* rings with multiplet signals in the aromatic region between 6.0 and 7.5 ppm attributed to the phenolic and the oxocyclohexadienyl forms of the hydrogen-bonded arenes in **2a**. Upon warming the NMR sample tube the two singlets attributed to the Cp* rings coalesce into one peak at T = 354 K centered at 2.27 ppm with $\Delta G^{\#}$ = 18 $\pm$ 0.5 kcal/mol. This behavior was found to be reversible and reproducible.

The temperature dependence of the spectra suggests that a fluxional process is occurring. Two possible mechanisms of exchange are advanced. Firstly, the two bonded phenyl rings in **2a** exchange their forms as if the hydrogen atom were moving from one oxygen to the other concomitant with this motion; we assume that at high temperature the hydrogen bond would break to give the two monomers $[Cp^*Rh(\eta^6\text{-PhOH})][BF_4]_2$ **3a** and $[Cp^*Rh(\eta^5\text{-PhO})][BF_4]$ **4a** which would subsequently exchange their forms. Thus the energy of activation $\Delta G^{\#}$ = 18 $\pm$ 0.5 kcal/mol corresponds: (a) to the barrier required for the bent form of $[Cp^*Rh(\eta^5\text{-PhO})][BF_4]$ **4a** (see below) to presumably exchange with the flat form of $[Cp^*Rh(\eta^6\text{-PhOH})][BF_4]_2$ **3a**; and (b) to the energy required for the hydrogen transfer.

Another exchange scenario would be that the fluxionality arises from vibrations of the hydrogen atom so that it moves closer to the different oxygen atoms without splitting the super-structure **2a** into monomers. Since this also requires changes in the shape of the phenoxy groups (flat $\leftrightarrow$ bent) the activation energy for this process might be relatively high [9].

At this stage it is worth comparing our results with those reported for the analogous ruthenium system by

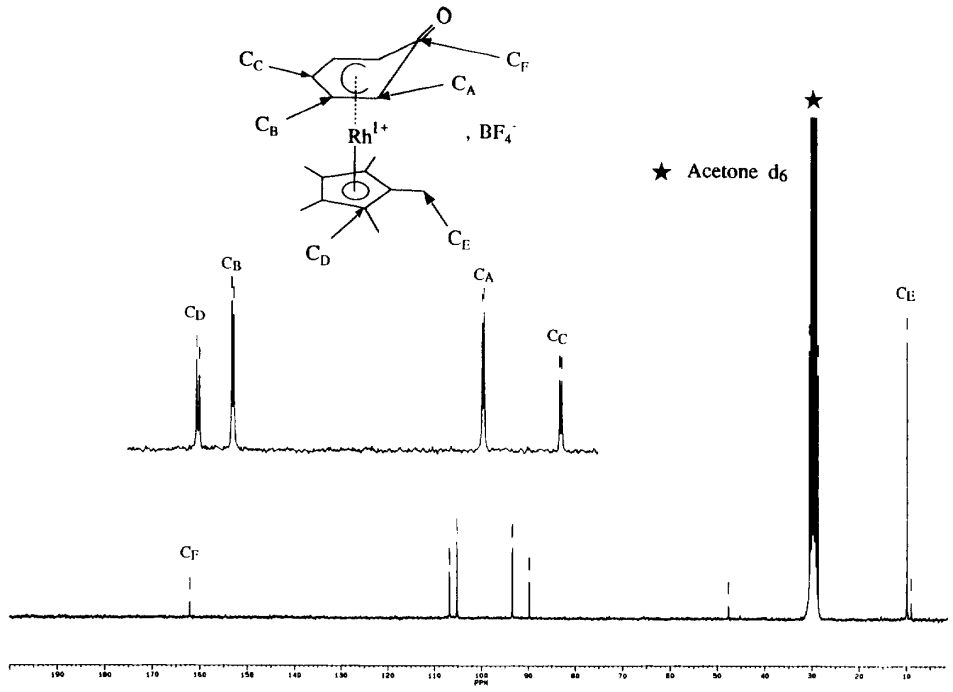


Fig 2. ^{13}C NMR spectrum of **4a** recorded in acetone-d_6. Note that the metal-bonded arene carbons appear as doublets (J_{Rh-C} = 6 Hz), while the free carbonyl carbon $\mathbf{C_F}$ is a singlet.

Chaudret *et al*, who observed a rapid exchange process even at 183 K [3a], between the phenolic species [Cp*Ru(η^6-PhOH)][CF_3SO_3] and its corresponding oxocyclohexadienyl derivative [Cp*Ru(PhO)] which possesses almost a planar structure [3b]. They attributed this result to the ease of deformation of the phenyl ring in the ruthenium system.

This stark contrast observed between the rhodium system and that of ruthenium is most likely attributed to the protonation process, since the deformation of the phenyl ring should not require a high barrier of activation. Thus, addition of $HBF_4 \cdot Et_2O$ to a solution of **2a** in acetone afforded the unstable phenol monomer [Cp*Rh(η^6-PhOH)][BF_4]$_2$ **3a** as a light yellow microcrystalline solid in 50% yield. This was found to transform slowly in acetone to give the starting material **2a**.

When an acetone solution of **2a** was treated with NEt_3 the reaction mixture became yellow; addition of diethyl ether gave a yellow microcrystalline solid. This complex was identified by spectroscopic methods and by elemental and X-ray analysis as [Cp*Rh(η^5-PhO · H_2O)][BF_4] **4a**. In a similar way the iridium species **2b** reacts with NEt_3 in acetone to give quantitatively an off-white product identified as [Cp*Ir(η^5-PhO · H_2O)][BF_4] **4b**. The IR spectra recorded separately for **4a** and **4b** in CH_2Cl_2 show strong peaks at 1 630 and 1 635 cm^{-1}, respectively. These bands are attributed to the ν(-C=O) of the bonded arenes; similar results were obtained for the analogous hexafluorophosphate salt derivatives [Cp*M(η^5-PhO)][PF_6], M = Rh, Ir, **5ab**, which have not been fully characterized [7]. The infrared spectra also show the presence of medium broad bands at 3 300 and 3 400 cm^{-1} for the Rh and Ir complexes, respectively. These bands are attributed to the hydrogen bonding formed with the H_2O molecules. The ^1H NMR spectrum of **4a** recorded in acetone-d_6 shows the *ortho* protons at 5.66 ppm at high field compared to the phenolic derivative **3a**. This is an indication of loss of the aromatic form in favor of the oxocyclohexadienyl structure. It is worth mentioning that the *ortho* protons of the η^5-phenoxo form in **2a** appear as a doublet at 6.05 ppm and downfield compared to those in **4a** ($\Delta\delta$ = 0.4 ppm). This reinforces the hypothesis of a hydrogen bond linkage with η^6-phenolic unit in **2a**. Similar results were obtained for the iridium derivative **4b**.

The ^{13}C NMR of **4a** shows interesting features. There are four signals located between 89 and 107 ppm; each peak appears as a doublet with J_{Rh-C} = 5.6 and 7.8 Hz (Rh, spin = 1/2). These signals are attributed to the *ortho*, *para* and *meta* carbons of the phenyl ring as well as the unsaturated carbon of the coordinated -Cp* ring. It is worth emphasizing that the signal appearing at 161.95 ppm, assigned to the (C-O) of the π-bonded phenoxide is a singlet (see fig 2). This precludes a direct interaction between the rhodium and the carbonyl carbon of the bonded arene. This result has been confirmed by an X-ray structural determination of **4a** (see below).

*X-ray molecular structure of [Cp*Rh(η^5-PhO · H_2O)][BF_4]* **4a**

Recrystallization of [Cp*Rh(η^5-PhO · H_2O)][BF_4] **4a** from acetone/hexane gave a sample suitable for X-ray crystallography. Compound **4a** crystallizes in the

Table I. ^{1}H NMR data for complexes **2–4** in $(CD_3)_2CO$ at 250 MHz.

Compound	η^6-phenol	η^5-phenoxo	Cp^*_{phenol}	$Cp^*_{phenoxo}$
2a	7.35 m, 4H	6.85 m, 2H	2.31 s, 30H	2.24 s, 15H
	7.15 m, 2H	6,0 d, 2H		
	6.90 d, 4H	6,70 m, 1H		
2b	7.40 m, 4H	6.80 m, 2H	2.40 s, 30H	2.35 s, 15H
	7.30 m, 2H	6.70 m, 1H		
	7.05 d, 4H	5.90 m, 2H		
3a	7.35 dd[a], 2H		2.30 s, 15H	
	7.15 t[b], 1H			
	6.91 d, 2H			
4a	6.70 dd, 2H		2.22 s, 15H	
		6.55 t, 1H		
		5.66 d, 2H		
4b		6.75 t, 1H		2.35 s, 15H
		6.60 t, 2H		
		5.70 d, 2H		

[a] $J_{HH'} = 8.5$ Hz; [b] $J_{HH'} = 7.5$ Hz.

orthorhombic space group $Ccm2_1$. There are three independent molecules in the unit cell whereby the asymmetric unit consists of one complex cation (I) in a general position, two half complex cations (II and III) in $y = 0$ and $y = 1/2$ (which are totally generated by crystallographic mirror planes), two BF_4^- anions and two molecules of H_2O undergoing hydrogen bonding with the cation complexes (see fig 3). One of the water molecules is hydrogen bonded to cation I and to a fluorine atom of BF_4^- with O(4)–H···O(I) = 2.69 Å and O(4)–H···F(14) = 2.83 Å. The second water molecule forms weaker hydrogen bonds with the cations II and III where O(5′)–H···O(II) = 2.99 Å and O(5)–H···O(III) = 2.83 Å. At this point a brief discussion on the capacity of these π-coordinated phenoxo to form hydrogen bonding is required; in this regard we note that the analogous rhodium and ruthenium complexes $[(PPh_3)_2Rh(PhO)\cdot 2PhOH]$ [3] **6** and $[Cp^*Ru(PhO)\cdot 2PhOH]$ [8] **7** have been reported, where the π-coordinated phenoxo forms hydrogen bonds with two free phenol molecules. Complex **7** has been identified by X-ray analysis (see below). This also confirms the asymmetric structure proposed for $[\{Cp^*Rh(\eta^6\text{-}PhOH\cdots)\}_2(\eta^5\text{-}PhO\cdots)RhCp^*][BF_4]_5$ **2a** in which the π-coordinated phenoxo unit acts as a hydrogen acceptor while the π-coordinated phenol moiety behaves as a hydrogen donor.

Figure 4 shows a view of cation $[Cp^*Rh(\eta^5\text{-}PhO)]^+$; crystallographic data collection parameters and selected bond lengths and angles are listed in tables III–VI. The structure shows that the 'Cp*Rh' unit is coordinated to only five carbons of the phenyl ring with dRh-C_{12-16} = 2.24, 2.23 and 2.22 Å in cations I, II and III, while the bond distance dRh-C_{11} is 2.48, 2.43 and 2.43 Å, respectively; loss of aromaticity in the bonded phenoxo unit is indicated by the irregularity of the arene C-C bond lengths. Another important feature of this structure is described by the short bond distance for C11-O1 = 1.24, 1.24 and 1.28 Å in cations I, II and III characteristic of a double bond, which on average is about 1.25 Å. This bond distance is shorter than that reported for the analogous ruthenium derivative $[Cp^*Ru(PhO)\cdot 2PhOH]$ **7** with dC-O = 1.28 Å [3b], but longer than the rhodium-hormone complex $[Cp^*Rh(\eta^5\text{-}$estradienonyl$][BF_4]$ **13a** with dC-O = 1.20 Å [5]. The dihedral angle θ between the plane C12-C11-C16 and the rest of the ring in **4a** is 14°, which is also the case for the other two cations. This angle θ is greater than that reported for **7** ($\theta = 4°$) but slightly smaller than that of $[Cp^*Rh(\eta^5\text{-}$estradienonyl$][BF_4]$ **13a** with ($\theta = 16°$) [5].

Reactivity of $[Cp^*M(\eta^5\text{-}PhO\cdot H_2O)][BF_4]$, M = Rh, Ir, **4ab** *with electrophiles (MeI, CF_3SO_3Me)*

Treatment of $[Cp^*Rh(\eta^5\text{-}PhO\cdot H_2O)][BF_4]$ **4a** with MeI in CH_2Cl_2 for 2 h failed to give any reaction, and the starting material **4a** was recovered. This reaction was performed in acetone but using a stronger methylating agent CF_3SO_3Me. After 10 min the reaction was stopped and an off-white product was isolated and identified as $[Cp^*Rh(\eta^6\text{-}PhOH)][BF_4][CF_3SO_3]$ **8a** and not the expected anisole derivative $[Cp^*Rh(\eta^6\text{-}PhOMe)][BF_4][CF_3SO_3]$ (see scheme 2). Methylation of the analogous ruthenium derivative $[Cp^*Ru(PhO)]$ **9** with MeI was reported [10] to give the anisole derivative $[Cp^*Ru(\eta^6\text{-}PhOMe)][I]$ **10**. We believe that the deactivation of the phenoxo derivative **4a** towards protonation and methylation could be related to the cationic

Table II. ^{13}C NMR data for complexes **2–4** in $(CD_3)_2CO$ at 62 MHz.

Compound	η^6-phenol	η^5-phenoxo	Cp^*_{phenol}	$Cp^*_{phenoxo}$
2a	149.8 s, C=O	147.14 s, C=O	111.49 d, -C=C-	110.70 -C=C-
	107.04 d, 99.93 d,	106.94 d, 98.24 d,	J_{Rh-C} = 8 Hz	J_{Rh-C} = 8 Hz
	J_{Rh-C} = 5 Hz	97.67 d	10.00 s, Me-Cp	9.89 s, Me-Cp
2b	not observed C=O	not observed C=O	104.5 s, -C=C-	97.5 s, -C=C-
	101.0, 92.00, 85.20	96.0, 86.50, 84.00	10.00 s, Me-Cp	9.89 s, Me-Cp
	(C*meta, para, ortho*)	(C*meta, para, ortho*)		
4a		161.95 s, C=O		106.72 d, -C=C-
		105.12 d, 93.39 d,		J_{Rh-C} = 7.8 Hz
		89.76 d, J_{Rh-C} = 5.6 Hz		9.98 s, Me-Cp
4b		not observed -C=O		100.35 s, -C=C-
		95.97, 81.80, 84.68,		9.76 s, Me-Cp
		(C*meta, para, ortho*)		

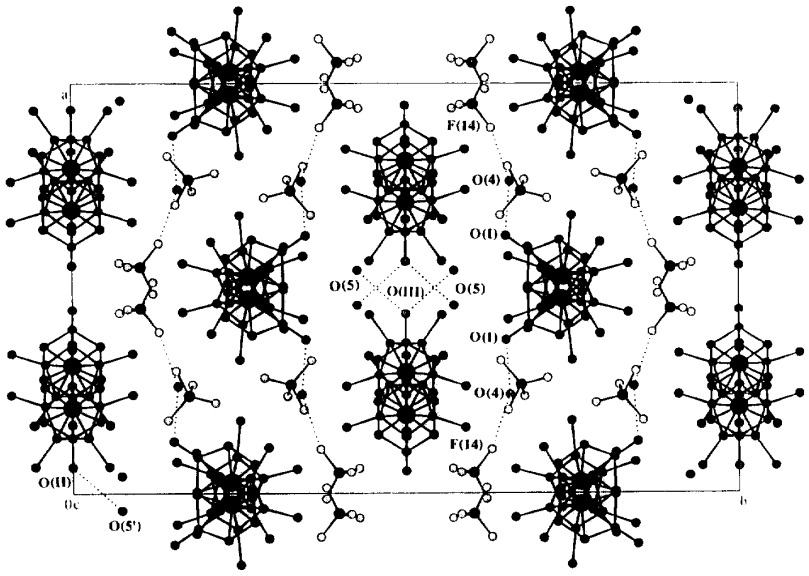


Fig 3. Unit cell of **4a** showing hydrogen bonding network between cations I, II and III with water molecule and BF_4^- free anion.

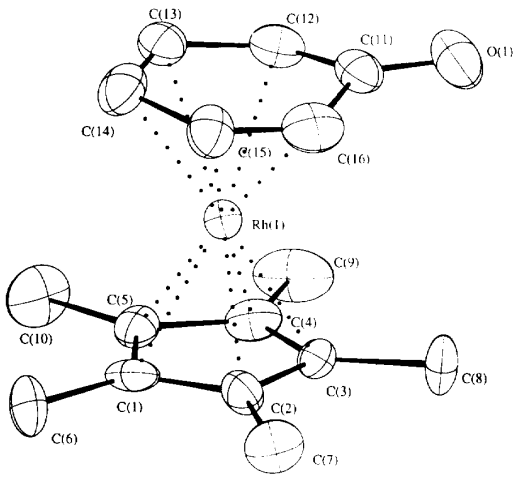


Fig 4. X-ray molecular structure of [Cp*Rh(η^5-PhO)] showing the atom numbering.

nature of this species, which is different from the neutral ruthenium complex [Cp*Ru(PhO)] **9** and hence it impedes the reactions with electrophiles.

The iridium derivative [Cp*Ir(η^5-PhO · H_2O)][BF_4] **4b** behaved similarly to the rhodium complex **4a** with respect to methylation. It is worth mentioning that the phenolic derivative [Cp*Ir(η^6-PhOH)][BF_4]$_2$ **3b** is unstable and could not be isolated. In contrast, the triflate derivative [Cp*Ir(η^6-PhOH)][BF_4][CF_3SO_3] **8b** was very stable. We believe that the counter anion $CF_3SO_3^-$ stabilizes these phenolic derivatives (M = Rh, Ir). The effect of triflate anion to stabilize the phenolic form of π-bonded arenes has already been reported. For instance, the estradiol complex

Table III. Crystallographic data for [Cp*Rh(η^5-PhO) · H_2O][BF_4] **4a**.

Chemical formula	$C_{16}H_{20}ORhBF_4 \cdot H_2O$
fw	435.9
crystal system	orthorhombic
space group	$Ccm2_1$
Z	16
a, Å	17.469(3)
b, Å	28.845(4)
c, Å	14.115(2)
V, Å^3	7 112(2)
ρ (calcd), g cm^{-3}	1.63
μ (Mo$K\alpha$) cm^{-1}	9.9
F(000)	3 520
diffractometer	Nonius CAD4
monochromator	graphite
radiation	Mo$K\alpha$ (0.71070)
temperature °C	20
scan type	$\omega/2\theta$
scan range θ, deg	1.2 + 0.34 tan θ
2θ range, deg	2 - 50
reflection collected	3 318
reflection used (criteria)	2 642 ($I > 3\sigma(I)$)
R	0.0358
R_w^*	0.0385
absorption correction**	min 0.82 max 1.17
secondary ext	41 10^{-6}
weighting scheme	unit weights
rms (shift/esd) (last ref)	0.37
ls parameters	470

* $R_w = [\Sigma_i W_i(F_o F_c)^2/\Sigma_i W_i F_o^2]^{1/2}$
** Difabs: Walker N, Stuart D, *Acta Cryst*, 1983, A 39, 159.

α-[Cp*Ru(estradiol)][CF_3SO_3] **11** was identified spectroscopically and by X-ray analysis [4b]. In particular the $CF_3SO_3^-$ anion forms a hydrogen bond with the phenolic (-OH) group of the A-ring, and thus stabilizes this π-bonded phenol form.

Table IV. Collection parameters for [Cp*Rh(η^5-PhO) · H_2O][BF_4] **4a**.

Atom	x/a	y/b	z/c	U (eq)
Rh(1)	0.02773(4)	0.23699(2)	0.7762(2)	0.0373
Rh(2)	0.19000(6)	0.5000	0.9515(2)	0.0364
Rh(3)	0.20733(6)	0.0000	0.9317(2)	0.0396
O(1)	0.1290(6)	0.1505(3)	0.8941(8)	0.0805
O(2)	0.3335(6)	0.5000	0.784(1)	0.0771
O(3)	0.0651(7)	0.0000	0.757(1)	0.0776
O(4)	0.262(1)	0.1551(6)	0.798(1)	0.1971
O(5)	−0.0424(6)	0.0714(4)	0.791(1)	0.1183
C(1)	−0.0368(6)	0.2649(4)	0.6590(7)	0.0425
C(2)	−0.0324(6)	0.2159(4)	0.6552(8)	0.0458
C(3)	0.0481(6)	0.2045(4)	0.6429(8)	0.0448
C(4)	0.0897(6)	0.2462(5)	0.6451(8)	0.0505
C(5)	0.0377(6)	0.2834(4)	0.6579(7)	0.0441
C(6)	−0.1107(8)	0.2925(5)	0.668(1)	0.0732
C(7)	−0.0983(7)	0.1835(5)	0.6522(9)	0.0685
C(8)	0.0776(9)	0.1560(4)	0.633(1)	0.0722
C(9)	0.1754(7)	0.2508(6)	0.637(1)	0.0795
C(10)	0.059(1)	0.3346(4)	0.661(1)	0.0735
C(11)	0.0871(8)	0.1850(4)	0.8956(9)	0.0582
C(12)	0.1149(7)	0.2325(4)	0.8928(9)	0.0578
C(13)	0.0701(8)	0.2706(4)	0.9075(8)	0.0577
C(14)	−0.0116(7)	0.2660(4)	0.9142(8)	0.0588
C(15)	−0.0415(7)	0.2206(5)	0.9052(9)	0.0588
C(16)	0.0041(8)	0.1840(4)	0.8889(8)	0.0564
C(21)	0.1375(9)	0.5000	1.094(1)	0.0489
C(22)	0.1872(7)	0.5404(4)	1.0822(7)	0.0409
C(23)	0.2618(6)	0.5248(3)	1.0659(7)	0.0399
C(24)	0.054(1)	0.5000	1.118(2)	0.0838
C(25)	0.161(1)	0.5892(5)	1.092(1)	0.0733
C(26)	0.3324(9)	0.5548(6)	1.050(1)	0.0844
C(27)	0.2646(8)	0.5000	0.806(1)	0.0372
C(28)	0.2208(7)	0.4589(5)	0.8246(8)	0.0481
C(29)	0.1431(6)	0.4583(4)	0.8362(8)	0.0471
C(30)	0.1002(9)	0.5000	0.844(1)	0.0543
C(31)	0.2616(9)	0.0000	1.069(1)	0.0438
C(32)	0.2130(7)	−0.0406(4)	1.0621(8)	0.0457
C(33)	0.1370(6)	−0.0242(4)	1.0488(7)	0.0473
C(34)	0.348(1)	0.0000	1.087(1)	0.0672
C(35)	0.2400(8)	−0.0903(4)	1.0693(9)	0.0643
C(36)	0.0663(7)	−0.0541(5)	1.037(1)	0.0656
C(37)	0.1346(8)	0.0000	0.785(1)	0.0485
C(38)	0.1766(8)	0.0408(5)	0.8060(9)	0.0672
C(39)	0.2571(8)	−0.0406(5)	0.817(1)	0.0705
C(40)	0.299(1)	0.0000	0.827(1)	0.0833
B(1)	0.4491(9)	0.1017(6)	0.896(1)	0.0708
B(2)	0.2378(9)	0.1718(6)	0.372(1)	0.0636
F(11)	0.4479(9)	0.0818(7)	0.813(1)	0.1886
F(12)	0.5140(5)	0.1216(3)	0.906(1)	0.1256
F(13)	0.441(1)	0.0667(6)	0.941(2)	0.2161
F(14)	0.3912(5)	0.1301(5)	0.907(1)	0.1627
F(21)	0.1783(5)	0.1432(3)	0.3816(9)	0.1052
F(22)	0.2967(7)	0.1535(4)	0.335(1)	0.1555
F(23)	0.2205(5)	0.2140(3)	0.346(1)	0.1101
F(24)	0.263(1)	0.1775(6)	0.461(1)	0.1977

*π-Complexation of β-estradiol by [Cp*Rh(S)$_3$][X]$_2$, X = BF_4, CF_3SO_3*

When a THF solution of β-estradiol was treated with one equivalent of [Cp*Rh(S)$_3$][BF_4]$_2$ in acetone at room temperature for 2 h, the initial yellow solution decolorized and a white precipitate was formed.

Table V. Selected bond lengths (Å) for [Cp*Rh(η^5-PhO) · H_2O][BF_4] **4a**.

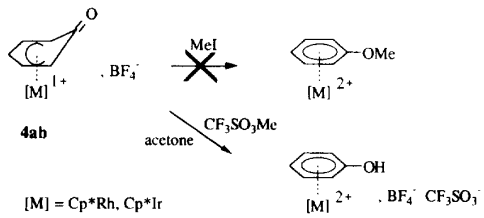
	Cation I		
Rh(1)-C(1)	2.16(1)	Rh(1)-C(2)	2.09(1)
Rh(1)-C(3)	2.13(1)	Rh(1)-C(4)	2.16(1)
Rh(1)-C(5)	2.15(1)	Rh(1)-C(11)	2.48(1)
Rh(1)-C(12)	2.25(1)	Rh(1)-C(13)	2.22(1)
Rh(1)-C(14)	2.23(1)	Rh(1)-C(15)	2.24(1)
Rh(1)-C(16)	2.25(1)	O(1)-C(11)	1.24(1)
C(1)-C(2)	1.41(2)	C(1)-C(5)	1.41(1)
C(1)-C(6)	1.52(2)	C(2)-C(3)	1.45(1)
C(2)-C(7)	1.48(2)	C(3)-C(4)	1.40(2)
C(3)-C(8)	1.50(1)	C(4)-C(5)	1.42(2)
C(4)-C(9)	1.51(2)	C(5)-C(10)	1.52(2)
C(11)-C(12)	1.45(2)	C(11)-C(16)	1.45(2)
C(12)-C(13)	1.37(2)	C(13)-C(14)	1.44(2)
C(14)-C(15)	1.42(2)	C(15)-C(16)	1.34(2)
	Cation II		
Rh(2)-C(21)	2.21(2)	Rh(2)-C(22)	2.18(1)
Rh(2)-C(23)	2.17(1)	Rh(2)-C(27)	2.43(1)
Rh(2)-C(28)	2.21(1)	Rh(2)-C(29)	2.18(1)
Rh(2)-C(30)	2.18(2)	O(2)-C(27)	1.24(2)
C(21)-C(22)	1.46(1)	C(21)-C(24)	1.49(2)
C(22)-C(23)	1.40(1)	C(22)-C(25)	1.49(2)
C(23)-C(23)′	1.43(2)	C(23)-C(26)	1.52(2)
C(27)-C(28)	1.43(1)	C(28)-C(29)	1.37(2)
C(29)-C(30)	1.42(1)		
	Cation III		
Rh(3)-C(31)	2.15(2)	Rh(3)-C(32)	2.18(1)
Rh(3)-C(33)	2.17(1)	Rh(3)-C(37)	2.43(2)
Rh(3)-C(38)	2.20(1)	Rh(3)-C(39)	2.18(1)
Rh(3)-C(40)	2.18(2)	O(3)-C(37)	1.28(2)
C(31)-C(32)	1.45(1)	C(31)-C(34)	1.54(2)
C(32)-C(33)	1.42(2)	C(32)-C(35)	1.51(2)
C(33)-C(33)′	1.40(2)	C(33)-C(36)	1.52(2)
C(37)-C(38)	1.42(2)	C(38)-C(39)	1.42(2)
C(39)-C(40)	1.39(2)		

Analysis of the two phases by ^{1}H NMR showed by integration the presence of four complexes (α,β)-[Cp*Rh(η^6-estradiol)][BF_4]$_2$ **12ab** (54%/10%) and (α,β)-[Cp*Rh(η^5-estradienonyl)][BF_4] **13ab** (30%/5%) (estradienonyl is a simple term employed to define the corresponding dienonyl form of estradiol) (see scheme 3). The symbols α and β are used to define the selective complexation of the two faces of the estradiol A-ring. These species were identified by spectroscopic analysis, and the X-ray structure of **13a** was reported in a previous communication [5].

In comparison with π-complexation of PhOH, we note the absence of dimeric species in the case of estradiol, which is the reason for the absence or the weakness of hydrogen bonding between the π-phenoxo form and its corresponding phenolic species. Further the phenolic form of the A-ring appears to be unstable in solution and it transforms slowly in acetone to give the corresponding dienonylic complex. Such behavior also seems to occur within the PhOH system (see above). Once again the role of the counterion seems to be essential in stabilizing the phenolic form of the A-ring. Thus when [Cp*Rh(S)$_3$][CF_3SO_3]$_2$ was treated with estradiol in acetone solution for 2 h only two compounds were isolated (α,β)-[Cp*Rh(η^6-estradiol)][CF_3SO_3]$_2$ **14ab** with

Table VI. Selected angles (deg) for [Cp*Rh(η^5-PhO) · H_2O][BF_4] **4a**.

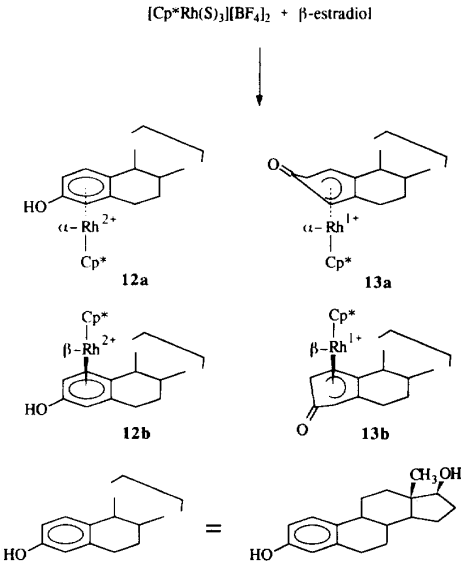
		Cation I	
C(5)-C(1)-C(2)	109.1(9)	C(3)-C(2)-C(1)	106.5(10)
C(7)-C(2)-C(1)	126.0(10)	C(7)-C(2)-C(3)	127.2(11)
C(4)-C(3)-C(2)	107.7(9)	C(8)-C(3)-C(2)	123.7(11)
C(8)-C(3)-C(4)	128.6(11)	C(5)-C(4)-C(3)	108.6(9)
C(9)-C(4)-C(3)	125.9(12)	C(9)-C(4)-C(5)	125.5(12)
C(4)-C(5)-C(1)	107.9(9)	C(10)-C(5)-C(1)	126.2(11)
C(10)-C(5)-C(4)	125.7(11)	C(12)-C(11)-O(1)	124.2(12)
C(16)-C(11)-O(1)	124.9(12)	C(16)-C(11)-C(12)	110.5(11)
C(13)-C(12)-C(11)	124.3(12)	C(14)-C(13)-C(12)	120.3(11)
C(15)-C(14)-C(13)	116.5(11)	C(16)-C(15)-C(14)	121.7(12)
C(15)-C(16)-C(11)	124.3(12)		
		Cation II	
C(22)-C(21)-C(22)′	105.8(13)	C(24)-C(21)-C(22)	127.1(6)
C(23)-C(22)-C(21)	108.3(10)	C(25)-C(22)-C(21)	124.1(12)
C(25)-C(22)-C(23)	127.5(12)	C(23)′-C(23)-C(22)	108.8(6)
C(26)-C(23)-C(22)	126.7(11)	C(26)-C(23)-C(23)′	124.5(8)
C(28)-C(27)-O(2)	124.1(7)	C(28)-C(27)-C(28)′	111.5(13)
C(29)-C(28)-C(27)	124.1(12)	C(30)-C(29)-C(28)	121.6(12)
C(29)-C(30)-C(29)′	115.5(14)		
		Cation III	
C(32)-C(31)-C(32)′	107.8(14)	C(34)-C(31)-C(32)	126.0(7)
C(33)-C(32)-C(31)	106.6(10)	C(35)-C(32)-C(31)	125.3(11)
C(35)-C(32)-C(33)	128.1(11)	C(33)′-C(33)-C(32)	109.5(7)
C(36)-C(33)-C(32)	125.8(11)	C(36)-C(33)-C(33)′	124.7(7)
C(38)-C(37)-O(3)	123.8(8)	C(38)-C(37)-C(38)′	112.2(15)
C(39)-C(38)-C(37)	122.2(13)	C(40)-C(39)-C(38)	122.8(15)
C(39)-C(40)-C(39)′	114.4(20)		



Scheme 2. Reactivity of **4ab** with MeI and $MeCF_3SO_3$.

(α/β 9:1). This result suggests that the triflate ions helps in stabilizing the phenolic form as observed in the π-complexation of phenol.

The reactivity of α-[Cp*Rh(η^5-estradienonyl)][BF_4] **13a** with electrophiles (MeI and $MeCF_3SO_3$) was found to be similar to those observed for [Cp*M(η^5-PhO) · H_2O][BF_4] **4ab** M = Rh, Ir. Thus when an acetone solution α-[Cp*Rh(η^5-estradienonyl)][BF_4] **13a** was treated with MeI at room temperature for 2 h or under reflux, the initial compound was recovered. Methyl alkylation of α-[Cp*Rh(η^5-estradienonyl)][BF_4] by $MeCF_3SO_3$ in acetone solution was not observed either, but a new compound was obtained and was identified by spectroscopic methods as α-[Cp*Rh(η^6-estradiol)][CF_3SO_3][BF_4] **15a**. These results confirm the passive nature of these phenoxide complexes towards methyl alkylation. We can therefore exclude any assumption that consider the presence of one equivalent of H_2O in the derivatives **4ab** as an obstacle for these reactions to occur.

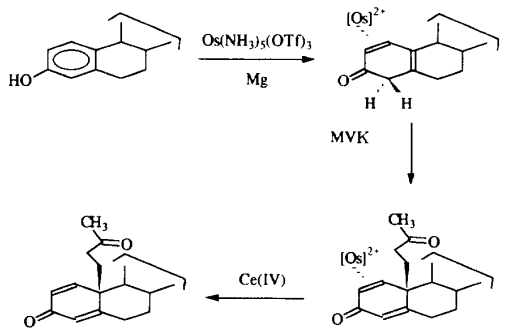


Scheme 3. Synthetic route to (α,β)-[Cp*Rh(η^6-estradiol)]$^{2+}$ **12ab** and (α,β)-[Cp*Rh(η^5-estradienonyl)]$^{+1}$ **13ab**.

Concluding remarks

This paper deals with the π-complexation of phenol and β-estradiol by $[Cp^*M]^{2+}$, M = Rh, Ir. The trimeric species [{Cp*M(η^6-PhOH···)}$_2$(η^5-PhO···)MCp*][BF_4]$_5$ **2ab** were obtained in which the π-coordinated phenoxo unit is hydrogen-bonded to the π-coordinated phenol moiety, while only monomer species (α,β)-[Cp*Rh(η^6-estradiol)][BF_4]$_2$ and/or (α,β)-[Cp*Rh(η^5-estradienonyl)][BF_4] were formed, suggesting that the formation of hydrogen bonds between a phenoxo and phenol form of the estradiol A-ring is difficult, perhaps due to steric factors. The effect of the triflate anion to stabilize the phenolic form seems to operate in both systems (PhOH, β-estradiol). The reactivities of α-[Cp*Rh(η^5-estradienonyl)][BF_4] and [Cp*M(η^5-PhO · H_2O)][BF_4] **4ab** with MeI and $MeCF_3SO_3$ were found to be similar; no methylation occurred, in contrast to what was reported for the ruthenium analog [Cp*Ru(PhO)].

The X-ray molecular structure of [Cp*Rh(η^5-PhO · H_2O)][BF_4] **4a** in the solid state seems to be very similar to that of the estradiol A-ring of α-[Cp*Rh(η^5-estradienonyl)][BF_4], where the arene is only coordinated by five carbons to the Cp*Rh unit; the ketonic carbonyls in these complexes are bent upward by $\theta = 14°$ and $\theta = 16°$, respectively. This differs completely from what was observed in the solid state for the analogous ruthenium derivative [Cp*Ru(PhO)·2PhOH] **7**, in which the arene ring is almost flat (the bending angle $\theta = 4°$). Furthermore their behavior (Rh and Ru systems) in solution appear to be completely different. For example, the exchange phenomenon in the ruthenium derivatives is rapid even at 183 K while the same process in the rhodium series requires 18 kcal/mol.



Scheme 4

As an aside we note that Harman *et al* have recently reported an elegant synthetic procedure of Δ^1-testosterones from β-estradiol *via* η^2-coordination of the A-ring with $Os(NH_3)_5^{2+}$. This η^2-π-coordination partially dearomatizes the A-ring and activates it towards electrophilic addition, *eg*, methylvinylketone (MVK) [11] (scheme 4). This example represents our future objective; we are currently studying the possibility of carrying out such a transformation using the $[Cp^*M][BF_4]_2$ moieties.

Experimental section

General procedures

All manipulations were carried out under argon atmosphere using Schlenk techniques. Solvents were purified and dried prior to use by conventional distillation techniques. All reagents obtained from commercial sources were used without further purification. ^1H and ^{13}C NMR were recorded on Bruker AM 250 MHz instrument. ^1H NMR chemical shifts are reported in parts per million referenced to residual solvent proton resonance. Infrared spectra were obtained on a Bruker IFS48 infrared FT instrument and all absorptions are expressed in wave numbers (cm^{-1}). Elemental analyses were performed by the Microanalytical Laboratory of Université Paris VI.

Synthesis of $[Cp^*Rh(CH_3CN)_3][BF_4]_2$ **1a**

This compound was prepared in a similar fashion to that of the analagous hexafluorophosphate salt $[Cp^*Rh(CH_3CN)_3][PF_6]_2$ reported by Maitlis *et al.* A solution of $AgBF_4$ (630 mg, 3.23 mmol) in 5 mL THF was added to a solution of $[Cp^*RhCl_2]_2$ (550 mg, 0.81 mmol) in 50 mL CH_3CN, to provoke rapid precipitation of AgCl, the mixture was stirred for 10 min and then filtered. The yellow solution was stirred for further 2 h and then concentrated under vacuum, addition of diethyl ether gave an yellow oil-like product, which upon cooling solidified. The yellow microcrystalline product was separated and dried under vacuum (yield 830 mg, 96%). Compound **1a** should be kept under argon, it hydrolyzes rapidly in air.

^1H NMR (250 MHz, (CD_3CN)) δ 1.75 (s, 15H, Cp-Me), 2.00 (s, 9H, bonded-CH_3CN).

Synthesis of $[Cp^*Ir(CH_3CN)_3][BF_4]_2$ **1b**

This compound was prepared in a similar way to that of **1a** and isolated as a white microcrystalline solid (yield 80%).

^1H NMR (250 MHz, (CD_3CN)) δ 1.75 (s, 15H, Cp-Me), 2.00 (s, 9H, bonded-CH_3CN).

Synthesis of $[\{Cp^*Rh(\eta^6\text{-}PhOH\cdots)\}_2(\eta^5\text{-}PhO\cdots)RhCp^*][BF_4]_5$ **2a**

A solution of phenol (141 mg, 1.5 mmol) in 10 mL $C_2H_4Cl_2$ was added to a yellow solution of $[Cp^*Rh(CH_3CN)_3][BF_4]_2$ (267 mg, 0.5 mmol) in 10 mL $C_2H_4Cl_2$ and the mixture was stirred for 12 h. The reaction mixture became light yellow and a white precipitate was formed. The product was filtered and washed twice with CH_2Cl_2 then dried under vacuum. Recrystallized from acetone/ether (yield 220 mg, 87%).

^1H NMR (250 MHz, $(CD_3)_2CO$) T = 297 K δ, 7.35 (m, 4H, phenol Hs), 7.15 (m, 2H, phenol Hs), 6.90 (m, 4H, phenol Hs), 6.85 (m, 2H, phenoxo Hs), 6.70 (m, 1H, phenoxo H), 6.00 (d, 2H, phenoxo Hs), 2.31 (s, 30H, Cp-Me), 2.24 (s, 15H, Cp-Me).

^{13}C NMR (62.86 MHz, $(CD_3)_2CO$) T = 240 K δ, 149.08 (s, -CO-phenyl), 147.14 (s, -CO-phenyl), 111.49 (C=C, -Cp*, d, J_{Rh-C} = 8 Hz), 110.71 (C=C, -Cp*, d, J_{Rh-C} = 8 Hz), 107.04, 99.93, 95.13 (C_{meta}, C_{para} and C_{ortho}-phenyl, each d, J_{Rh-C} = 5 Hz), 106.94, 98.29, 94.67 (C_{meta}, C_{para} and C_{ortho}-phenyl, each d, J_{Rh-C} = 5 Hz), 10.00 (s, Me-Cp), 9.89 (s, Me-Cp).

IR (KBr disk) ν(O···H-O-), 3 426, ν(C=O···H), 1 469.

Anal calc for $C_{48}H_{62}O_3B_5F_{20}Rh_3 \cdot 2CH_2Cl_2$: C, 37.50; H, 4.12. Found: C, 37.51; H, 4.12.

Synthesis of $[\{Cp^*Ir(\eta^6\text{-}PhOH\cdots)\}_2(\eta^5\text{-}PhO\cdots)IrCp^*][BF_4]_5$ **2b**

The complex **2b** was prepared in two ways. *Method A*: the reaction mixture of $[Cp^*Ir(CH_3CN)_3][BF_4]_2$ **1b** and phenol was refluxed in $C_2H_4Cl_2$ for 12 h to give an off-white precipitate. The compound was filtered and washed with $C_2H_4Cl_2$ then dried under vacuum (yield 80%). *Method B*: to a solution of $[Cp^*Ir(CH_3)_2CO)_3][BF_4]_2$ prepared *in situ* was added 3 equiv of PhOH in dichloroethane and the mixture was stirred for 1 h. The reaction mixture was reduced under vacuum then diethyl ether was added to give an off-white precipitate. This material was separated and washed with diethylether then dried under vacuum. Recrystallized from acetone/ether (yield 80%).

^1H NMR (250 MHz, $(CD_3)_2CO$) T = 297 K δ, 7.40 (m, 4H, phenol Hs), 7.30 (m, 2H, phenol Hs), 7.05 (m, 4H, phenol Hs), 6.80 (m, 2H, phenoxo Hs), 6.70 (m, 1H, phenoxo H), 5.90 (m, 2H, phenoxo Hs), 2.40 (s, 30H, Cp-Me), 2.35 (s, 15H, Cp-Me).

^{13}C NMR (62.86 MHz, $(CD_3)_2CO$) δ, not observed (-CO-phenyl), not observed (s, -CO-phenyl), 104.50 (C=C, -Cp*), 97.50 (C=C, -Cp*), 101.0, 92.00, 85.50 (C_{meta}, C_{para} and C_{ortho}-phenyl), 96.0, 86.50, 84.0 (C_{meta}, C_{para} and C_{ortho}-phenyl), 10.00 (s, Me-Cp), 9.89 (s, Me-Cp).

IR (KBr disk) ν(O···H-O-), 3 426, ν(C=O···H), 1 469.

Anal calc for $C_{48}H_{62}O_3B_5F_{20}Ir_3$. C, 33.88; H, 3.64. Found: C, 34.72; H, 3.70.

Synthesis of $[Cp^*Rh(\eta^6\text{-}PhOH)][BF_4]_2$ **3a**

$HBF_4 \cdot Et_2O$ (100 μL) in diethylether solution was added to a colorless solution of **2a** (50 mg). The mixture was stirred for 30 min then the solution was concentrated under vacuum. Addition of diethyl ether gave a yellow unstable microcrystalline solid, which was separated, washed once and rapidly with ether and dried under vacuum. It is worth mentioning that upon washing for longer period of time, this compound transforms into the starting material **2a** (yield 28 mg, 50%).

^{1}H NMR (250 MHz, $(CD_3)_2CO$) δ, 7.35 (dd, 2H, H_{meta}), 7.15 (t, 1H, H_{para}), 6.91 (d, 2H, H_{ortho}, J_{H-H} = 7.5 Hz, J_{H-H} = 8.5 Hz), 2.30 (s, 15H, Cp-Me).

*Synthesis of [Cp*Rh(η^5-PhO · H_2O)][BF_4]* **4a**

NEt_3 (50 μL) was added to a solution of dimer **2a** (42 mg) in 10 mL acetone. The reaction mixture was stirred for 4 h then the solution was concentrated under vacuum. Addition of diethyl ether gave a yellow microcrystalline solid. The product was separated washed with diethylether then dried under vacuum (yield 40 mg, 87%).

^{1}H NMR (250 MHz, $(CD_3)_2CO$) δ, 6.70 (dd, 2H, H_{meta}), 6.55 (t, 1H, H_{para}), 5.66 (d, 2H, H_{ortho}, J_{H-H} = 7.5 Hz, J_{H-H} = 8.5 Hz), 2.22 (s, 15H, Me-Cp).

^{13}C NMR (62.86 MHz, $(CD_3)_2CO$) δ, 161.95 (s, phenyl -C=O), 106.72 (d, -C=C-, -Cp*, J_{Rh-C} = 7.8 Hz), 105.12, 93.39, 89.76 (phenyl C_{meta}, C_{ortho}, C_{para}, each d, J_{Rh-C} = 5.6 Hz), 9.94 (s, Cp-Me).

IR (CH_2Cl_2) ν(C=O) 1 637, ν(C=C) 1 625, ν(B-F) 1 010.

Anal calc for $C_{16}H_{22}O_2BF_4Rh$: C, 44.03; H, 5.04. Found: C, 43.87; H, 5.00.

*Synthesis of [Cp*Ir(η^5-PhO · H_2O)][BF_4]* **4b**

This compound was prepared in a similar fashion to that of **4a**. Complex **4b** was obtained quantitatively as an off-white precipitate (yield 80%).

^{1}H NMR (250 MHz), $(CD_3)_2CO$) δ, 6.75 (t, 1H, H_{para}), 6.60 (t, 2H, H_{meta}), 5.70 (d, 2H, H_{ortho}, J_{H-H} = 7.5 Hz, J_{H-H} = 8.5 Hz), 2.35 (s, 15H, Me-Cp).

^{13}C NMR (62.86 MHz, $(CD_3)_2CO$) δ, not observed (phenyl -C=O), 100.35 (s, -C=C-, -Cp*), 95.97, 81.30, 84.68 (phenyl C_{meta}, C_{ortho}, C_{para}, each s), 9.76 (s, Cp-Me).

IR (CH_2Cl_2) ν(C=O) 1 652, ν(C=C) 1 630, ν(B-F) 1 046.

Anal calc for $C_{16}H_{22}O_2BF_4Ir$: C, 36.50; H, 4.18. Found: C, 37.40; H, 4.20.

*Synthesis of [Cp*Rh(η^6-PhOH)][BF_4][CF_3SO_3]* **8a**

This compound was prepared by adding 30 μL of $MeCF_3SO_3$ to a solution of [Cp*Rh(η^5-PhO) · H_2O][BF_4] **4a** (30 mg, 0.07 mmol) in 10 mL acetone and the mixture was stirred for only 10 min. The solvent was concentrated under vacuum. Addition of 20 mL of diethyl ether afforded a white precipitate. This unstable compound was separated then washed with diethyl ether and dried under vacuum.

^{1}H NMR (250 MHz), $(CD_3)_2CO$) δ, 7.50 (t, 2H, H_{meta}) 7.27 (t, 1H, H_{para}) 7.13 (d, 2H, H_{ortho}, J_{H-H} = 7.5 Hz, J_{H-H} = 8.5 Hz), 2,35 (s, 15H, Me-Cp), presence of free phenol.

IR(KBr disc) 1 250cm^{-1}, 1 224cm^{-1}, free CF_3SO_{3-}. This compound was unstable, and analyses were not obtained.

*Synthesis of [Cp*Ir(η^6-PhOH)][BF_4][CF_3SO_3]* **8b**

This compound was prepared in a similar way to that of **8a** and isolated as a white microcrystalline solid (yield 80%).

^{1}H-NMR (250 MHz), $(CD_3)_2CO$) δ, 7.25 (m, 3H, H_{meta} and H_{para}), 6.92 (d, 1H, H_{ortho}), 2,45 (s, 15H, Me-Cp).

^{13}C NMR (62.86 MHz, $(CD_3)_2CO$) δ 149.80 (s, phenol -C-OH), 104 (s, -C=C-, -Cp*), 97.10, 92.40, 85.30 (phenol C_{meta}, C_{para}, C_{ortho}, each s), 10.10 (s, Cp-Me).

IR (KBr disc) 1 256 cm^{-1}, 1 222 cm^{-1} free CF_3SO_{3-}.

Anal calc for $C_{17}H_{21}O_4BF_7SIr$: C, 31.00; H, 3.19. Found: C, 30.10; H, 3.10.

*Synthesis of (α,β)-[Cp*Rh(η^6-estradiol)][BF_4]$_2$* **12ab** *and (α,β)-[Cp*Rh(η^5-estradienonyl)][BF_4]* **13ab**

A solution of $AgBF_4$ (195 mg, 1 mmol) in 5 mL THF was added to a red solution of [Cp*$RhCl_2$]$_2$ (155 mg, 0.25 mmol) in 10 mL acetone, to give rapidly a white precipitate (AgCl); the mixture was stirred for 15 min. The orange-yellow solution ([Cp*Rh(S)$_3$][BF_4]$_2$) was then filtered into a dry Schlenk tube. To the latter was added a solution of estradiol (136 mg, 0.5 mmol) in 10 mL THF and the mixture was stirred at room temperature for 2 h. The initial yellow-orange solution decolorized and a white precipitate was formed identified as α-[Cp*Rh(η^6-estradiol)][BF_4]$_2$ **12a** and α-[Cp*Rh(η^5-estradienonyl)][BF_4] **13a**, while the supernatant phase gave the β-isomers **12b** and **13b**. Separation of the α- and β-isomers of the different forms was achieved by fractional crystallization using an acetone/THF/ether mixture; due to solubility and stability factors the dienonylic forms were much easier to obtain.

• *Spectroscopic data for* **12a**

^{1}H NMR (250 MHz, (CD_3CN)) δ, 6.90 (d, 1H, H-1, J_{H1-H2} = 7.5 Hz), 6.57 (dd, 1H, H-2, J_{H1-H2} = 7.5 Hz, J_{H2-H4} = 2.5 Hz), 6.47 (d, 1H, H-4, J_{H2-H4} = 2.5 Hz), 2.03 (s, 15H, -Cp*), 0.72 (s, 3H, -$C_{18}H_3$).

Anal calc for $C_{28}H_{39}O_2B_2F_8Rh$: C, 49.12; H, 5.70. Found: C, 49.70; H, 5.69.

• *Spectroscopic data for* **12b**

^{1}H NMR (250 MHz, (CD_3CN)) δ, 6.86 (d, 1H, H-1, J_{H1-H2} = 7.5 Hz), 6.45 (dd, 1H, H-2, J_{H1-H2} = 7.5 Hz, J_{H2-H4} = 2.5 Hz), 6.53 (d, 1H, H-4, J_{H2-H4} = 2.5 Hz), 2.08 (s, 15H, -Cp*), 0.73 (s, 3H, -$C_{18}H_3$).

• *Spectroscopic data for* **13a**

^{1}H NMR (250 MHz, (CD_3CN)) δ, 6.42 (d, 1H, H-1, J_{H1-H2} = 7.5 Hz), 5.47 (dd, 1H, H-2, J_{H1-H2} = 7.5 Hz, J_{H2-H4} = 2.5 Hz), 5.35 (d, 1H, H-4, J_{H2-H4} = 2.5 Hz), 2.09 (s, 15H, -Cp*), 0.75 (s, 3H, -$C_{18}H_3$).

IR (KBr disc) ν(C=O) 1 596 cm^{-1}, ν(B-F) 1 010 cm^{-1}.

Anal calc for $C_{28}H_{38}O_2BF_4Rh$: C, 56.37; H, 6.37; B, 1.8; F, 12.75. Found: C, 56.62; H, 6.35; B, 1.78; F, 12.46.

• *Spectroscopic data for* **13b**

^{1}H NMR (250 MHz, (CD_3CN)) δ, 6.35 (d, 1H, H-1, J_{H1-H2} = 7.5 Hz), 5.10 (dd, 1H, H2, J_{H1-H2} = 7.5 Hz, J_{H2-H4} = 2.5 Hz), 5.26 (d, 1H, H4, J_{H2-H4} = 2.5 Hz), 1.97 (s, 15H, -Cp*), 0.71 (s, 3H, -$C_{18}H_3$).

*Synthesis of (α,β)-[Cp*Rh(η^6-estradiol)][CF_3SO_3]$_2$* **14ab**

The preparation of the triflate salt [Cp*Rh(S)$_3$][CF_3SO_3]$_2$ is similar to that described for [Cp*Rh(S)$_3$][BF_4]$_2$ in the previous section. A solution of 17β-estradiol (137 mg, 0.5 mmol) in 10 mL THF was added to a yellow solution of [Cp*Rh(S)$_3$][CF_3SO_3]$_2$ (0.5 mmol) in 10 mL acetone. The reaction mixture was stirred for 3 h and then the pale yellow solution was concentrated under vacuum followed by addition of diethyl ether to give an oil-like product. This compound was separated and washed several times with ether and dried under vacuum to give a pale yellow powder identified as **14a**. The mother liquor was collected and solvent was removed under vacuum to afford the β-isomer **14b**. Overall yield (320 mg, 79%) (α/β ratio 87:13).

• *Spectroscopic data for* **14a**

^{1}H NMR (250 MHz, (CD_3OD)) δ, 7.03 (d, 1H, H-1, J_{H1-H2} = 7.5 Hz), 6.32 (dd, 1H, H-2, J_{H1-H2} = 7.5 Hz,

J_{H2-H4} = 2.5 Hz), 6.27 (d, 1H, H-4, J_{H2-H4} = 2.5 Hz), 2.09 (s, 15H, -Cp*), 0.80 (s, 3H, $-C_{18}H_3$).

IR (KBr disc) 1 254 cm^{-1}, 1 222 cm^{-1} free $CF_3SO_3^-$.

Anal calc for $C_{30}H_{39}O_8F_6S_2Rh$: C, 44.55; H, 4.82. Found: C, 43.83; H, 5.24.

- *Spectroscopic data for* **14b**

^1H NMR (250 MHz, (CD_3OD)) δ, 6.92 (d, 1H, H-1, J_{H1-H2} = 7.5 Hz), 6.00 (dd, 1H, H-2, J_{H1-H2} = 7.5 Hz, J_{H2-H4} = 2.5 Hz), 6.13 (d, 1H, H-4, J_{H2-H4} = 2.5 Hz), 2.12 (s, 15H, -Cp*), 0.89 (s, 3H, $-C_{18}H_3$).

IR (KBr disc) 1 254 cm^{-1}, 1 222 cm^{-1} free $CF_3SO_3^-$.

Synthesis of
*(α,β)-[Cp*Rh(η^6-estradiol)][CF_3SO_3][BF_4]* **15ab**

$MeCF_3SO_3$ (60 μL) was added to a suspension of (α,β)-[Cp*Rh(η^5-estradienonyl)][BF_4] **13ab** (50 mg, 0.084 mmol) in 10 mL of acetone and the reaction mixture was stirred for 15 min. During this time the precipitate dissolved completely to give a yellow-orange solution. The solvent was concentrated under vacuum then diethylether was added to afford an orange precipitate. The compound was separated then washed with diethyl ether and dried under vacuum.

- *Spectroscopic data for* **15a**

^1H NMR (250 MHz, $(CD_3)_2CO$) δ, 7.40 (d, 1H, H-1, J_{H1-H2} = 7.5 Hz), 6.85 (dd, 1H, H-2, J_{H1-H2} = 7.5 Hz, J_{H2-H4} = 2.5 Hz), 6.80 (d, 1H, H-4, J_{H2-H4} = 2.5 Hz), 2.25 (s, 15H, -Cp*), 0.80 (s, 3H, $-C_{18}H_3$).

IR (KBr disc) 1 250 cm^{-1}, 1 220 cm^{-1} free $CF_3SO_3^-$.

- *Spectroscopic data for* **15b**

^1H NMR (250 MHz, $(CD_3)_2CO$) δ, 7.25 (d, 1H, H-1, J_{H1-H2} = 7.5 Hz), 6.65 (d, 1H, H-4, J_{H2-H4} = 2.5 Hz), 6.55 (dd, 1H, H-2, J_{H1-H2} = 7.5 Hz, J_{H2-H4} = 2.5 Hz), 2.30 (s, 15H, -Cp*), 0.90 (s, 3H, $-C_{18}H_3$).

X-ray crystallography

Suitable crystals of [Cp*Rh(η^5-PhO · H_2O)][BF_4] **4a**, were obtained by recrystallization from acetone/hexane solution. Crystallographic data are collected in table III. Accurate cell dimensions and orientation matrices were obtained by least-squares refinement of 25 accurately centered reflections on a Nonius CAD4 diffractometer equipped with graphite-monochromated Mo$K\alpha$ radiation. No significant variations were observed in the two check reflections during data collection. The data were corrected for Lorentz and polarization effects; an empirical absorption correction (DIFABS) [12] was applied. Computations were performed by using CRYSTALS [13] modified locally for a Microvax II computer. Scattering factors and corrections for anomalous absorption were taken from reference [14]. The structure was solved by direct methods (SHELXS) [15] and refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were then located on a difference Fourier map and their coordinates refined with an isotropic thermal parameter. The structure was refined to $R = 0.0358$ and $R_w = 0.0385$ with use of 2 642 reflections for 470 least-squares parameters. Final atomic coordinates and selected bond distances and angles are listed in tables IV, V and VI.

Acknowledgments

We thank CNRS for supporting this work and the reviewers for their perceptive comments.

Supplementary material available

Anisotropic displacement parameters (table S1), table of bond distances and angles (table S2); table S3, observed and calculated structure factors (17 pages). Supplementary material data have been deposited with the British Library, Document Supply Center at Boston Spa, Wetherby, West Yorkshire, UK as supplementary publication N° SUP 90395 and is available on request from the Document Supply Center.

References

1 Collman JP, Hegedus LS, Norton JR, Finke RG, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987, pp 921-940

2 a) Semmelhack MF, *Pure Appl Chem* (1981) 53, 2379
b) Pike RD, Ryan WJ, Carpenter GB, Sweigart DA, *J Am Chem Soc* (1989) 111, 8535
c) Krow GR, Miles WH, Smiley PM, Lester WS, Kim YG, *J Org Chem* (1992) 57, 4040

3 a) Chaudret B, He X, Huang Y, *J Chem Soc, Chem Commun* (1989) 1844
b) Koelle U, Wang MJ, Raabe G, *Organometallics* (1991) 10, 2573

4 a) Jaouen G, Vessieres A, Top S, Ismail AA, Butler IS, *J Am Chem Soc* (1985) 107, 4778
b) Vichard D, Gruselle M, El Amouri H, Jaouen G, Vaisserman J, *Organometallics* (1992) 11, 976
c) Vichard D, Gruselle M, El Amouri H, Jaouen G, *J Chem Soc, Chem Commun* (1991) 46
d) Urbanos F, Halcrow MA, Fernandez-Baeza J, Dahan F, Labroue D, Chaudret B, *J Am Chem Soc* (1993) 115, 3484
e) Moriarty RM, Ku Yi Yin, Gill US, Giraldi R, Perrier RE, McGlinchey MJ, *Organometallics* (1989) 8, 960

5 El Amouri H, Gruselle M, Jackson PA, Jaouen G, Vaissermann J, *Organometallics* (1990) 9, 2871

6 White C, Thompson SJ, Maitlis PM, *J Chem Soc, Dalton Trans* (1977) 1654

7 White C, Thompson SJ, Maitlis PM, *J Organomet Chem* (1977) 127, 415

8 Cole-Hamilton DJ, Young RG, Wilkinson G, *J Chem Soc, Dalton Trans* (1976) 1995

9 We appreciate the insight of a reviewer who pointed this out

10 He XD, Chaudret B, Dahan F, Huang YS, *Organometallics* (1991) 10, 970

11 Kopach ME, Kelsh LP, Stork KC, Harman WD, *J Am Chem Soc* (1993) 115, 5322

12 Walker N, Stuart D, *Acta Crystallogr* (1983) A39, 159

13 Watkin DJ, Carruthers JR, Betteridge PW, *Crystals User Guide*; Chemical Crystallography Laboratory: University of Oxford, Oxford, England, 1986

14 *International Tables for X-ray Crystallography*, Kynoch, Birmingham, England, 1974, Vol IV

15 Sheldrick GM, SHELXS86, *Program for Crystal Structure Solution*, University of Göttingen, 1986