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Introduction

During the last two decades, the synthesis of half-sandwich ruthenium(II) complexes containing functionalized η^6 -arene ligands has received increasing attention¹ due to their potential applications as metallopharmaceuticals^{2,3} as well as catalysts in synthetic organic chemistry.⁴ The introduction of a functional group on the arene not only allows the modulation of steric and electronic properties of the resulting complexes but also confers other interesting features for their use in catalysis. For example, the presence of an adequate functionality can enhance significantly their solubility in water⁵ or ionic liquids,⁶ improve their thermal stability⁷ or allow their immobilization onto a solid support.8 On the other hand, a side chain containing a coordinating group offers an easy entry to tethered arene-ruthenium(II) derivatives, a huge number being obtained through different methodologies in recent years.^{4,9} In this context, most of the synthetic endeavors have been focused on the preparation of complexes with a tethering

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Functionalized arene–ruthenium(II) complexes: dangling *vs.* tethering side chain†

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The reactivity of compounds $[RuCl_2(\eta^6-C_6H_5OCH_2CH_2OH)(L)]$ (L = phosphine or phosphite) towards the chloride abstractor AgSbF₆ has been investigated. Thus, the treatment of the triphenylphosphite complex $[RuCl_2(\eta^6-C_6H_5OCH_2CH_2OH){P(OPh)_3}]$ with one equivalent of AgSbF₆ gave rise to the formation of the dinuclear dichloro-bridged species $[{Ru(\mu-Cl)(\eta^6-C_6H_5OCH_2CH_2OH){P(OPh)_3}}_2]^{2+}$ as the hexafluoro-antimonate salt. On the other hand, the triphenylphosphine analog $[RuCl_2(\eta^6-C_6H_5OCH_2CH_2OH)(PPh_3)]$ led, under the same experimental conditions, to the di-ruthenium derivative $[{RuCl(\eta^6-C_6H_5OCH_2CH_2OH)(PPh_3)}_2(\mu-Cl)][SbF_6]$ containing only one Cl-bridge. In sharp contrast, treatment of precursors $[RuCl_2(\eta^6-C_6H_5CH_2CH_2OH)(L)]$ (L = P(OPh)_3, PPh_3, P(OEt)_3) with AgSbF_6 resulted in the clean formation of the tethered compounds $[RuCl\{\eta^6:\kappa^1(O)-C_6H_5CH_2CH_2CH_2OH\}(L)][SbF_6]$. The differences in reactivity observed have been rationalized by theoretical calculations.

chiral side chain, potentially able to promote asymmetric organic transformations.¹⁰ Much less studied is the ability of the tethered arenes to act as hemilabile ligands. Thus, only a few studies have demonstrated that when the pendant group is poorly coordinating, such as alcohol or amine functions, reversible coordination/decoordination processes can occur depending on the experimental conditions.^{9b,f,10a,11}

We recently showed that the water-soluble derivatives $[RuCl_2(\eta^6-C_6H_5OCH_2CH_2OH)(L)]$ (L = phosphite or phosphine), containing an η^6 -coordinated phenoxyethanol arene ligand, are highly efficient catalysts for the isomerization of a number of allylic substrates in aqueous media.^{5b,12} Like for other arene-ruthenium(II) species,¹³ the cleavage of at least one Ru-Cl bond is a prerequisite for achieving good catalytic performances in these C=C bond migration processes.¹⁴ Hence, in order to further improve the efficiency of catalysts [RuCl_2(η^6 -C₆H₅OCH_2CH_2OH)(L)], we considered the possibility of removing one of the chloride ligands of these precursors before use. One would anticipate that the vacant site liberated by Cl⁻ would be temporarily occupied by the hydroxyl side chain of the arene giving rise to the formation of complexes of type **A** (Fig. 1). The rupture of the Ru–O bond in such derivatives is



Fig. 1 Structure of complexes of type A

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 $[\]dagger$ Electronic supplementary information (ESI) available: Synthesis of complex 5c [SbF₆]; CIF file giving crystallographic data for compounds 2[SbF₆]₂, 3[SbF₆] and 5a[SbF₆]; details on the chemical behavior of 1b and 4b in water; Cartesian coordinates and total energies of 1M and 4M. CCDC 908513, 908514 and 908515. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt33051f

expected to be easy,^{9b,f,10a} and can readily provide unsaturated species under catalytic conditions, enabling the rapid coordination of the substrates and their further transformation onto the metal.

With this idea in mind, here we describe the reactivity of precursors $[RuCl_2(\eta^6-C_6H_5OCH_2CH_2OH)(L)]$ (L = P(OPh)₃ (1a), P(OEt)₃ (1b) or PPh₃ (1c)) towards chloride abstractors. Unexpectedly, the coordination of the arene side chain onto the metal does not occur, dinuclear Cl-bridged species, instead of complexes of type **A**, being generated. To better understand the reluctance of the C₆H₅OCH₂CH₂OH arene to coordinate through an $\eta^6:\kappa^1(O)$ -mode, the reactivity of analogous compounds $[RuCl_2(\eta^6-C_6H_5CH_2CH_2OH_2OH)(L)]$ (L = P(OPh)₃ (4a), P(OEt)₃ (4b) or PPh₃ (4c)) was also explored.

Results and discussion

Synthesis and characterization of compound [{Ru(μ -Cl)-(η^{6} -C₆H₅OCH₂CH₂OH){P(OPh)₃}₂][SbF₆]₂

The treatment of a dichloromethane solution of complex $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\{P(OPh)_3\}]$ (1a) with one equivalent of AgSbF₆ at room temperature gave rise to the di-ruthenium salt $[\{Ru(\mu\text{-}Cl)(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\{P(OPh)_3\}\}_2][SbF_6]_2$ (2[SbF₆]_2), instead of the expected tethered derivative of type A (Scheme 1). The formation of compound 2[SbF₆]_2 results from the abstraction of one chloride ligand in 1a and the further coupling of two units of the resulting $[RuCl(\eta^6\text{-}C_6H_5OCH_2\text{-}CH_2OH)\{P(OPh)_3\}]^+$ unsaturated fragments through two Cl-bridges.

The dinuclear structure of compound $2[SbF_6]_2$ has been unequivocally determined by X-ray diffraction studies. An ORTEP view is shown in Fig. 2, and selected bond distances and angles are listed in the caption. The molecule possesses a center of inversion located in the center of the Ru₂Cl₂ square. The geometry around each ruthenium atom can be described as a distorted octahedron in which the arene ligand occupies three positions of coordination. The Ru–Cl bond distances (2.429(1) and 2.436(1) Å) and the Ru(1)–Cl(1)–Ru(1a) (100.09(5)°) and Cl(1)–Ru(1)–Cl(1a) (79.91(5)°) bond angles are similar to those previously reported for other ruthenium dimers bearing two chloride bridges.¹⁵ Around each ruthenium atom, the OCH₂CH₂OH dangling arm and the triphenylphosphite ligand point toward almost opposite sides (torsion



Scheme 1 Synthesis of compound 2[SbF₆]₂.



Fig. 2 ORTEP-type view of the structure of the dication $[\{Ru(\mu-CI)(\eta^6 C_6H_5OCH_2CH_2OH\}(P(OPh)_3\}\}_2]^{2+}$ (**2**) showing the crystallographic labeling scheme. Hydrogen atoms, except the OH ones, and SbF₆⁻ anions are omitted for clarity. Atoms labeled with an "a" are generated by a crystallographic center of symmetry. Thermal ellipsoids are drawn at 20% probability level. Selected bond distances (Å) and angles (°): Ru(1)–Cl(1) = 2.429(1); Ru(1)–Cl(1a) = 2.436(1); Ru(1)–P(1) = 2.284(2); Ru(1)–C* = 1.7488(4); Cl(1)–Ru(1)–Cl(1a) = 79.91(5); Cl(1)–Ru(1)–P(1) = 88.75(5); Cl(1a)–Ru(1)–P(1) = 92.93(5); Cl(1)–Ru(1)–C* = 128.66(4); P(1)–Ru(1)–C* = 127.56(4); Cl(1a)–Ru(1)–C* = 124.93(4); Ru(1)–Cl(1)–Ru(1a) = 100.09(5). C* = centroid of the arene ring (C(1), C(2), C(3), C(4), C(5) and C(6) carbon atoms). Symmetry code related to moiety: –*x*, –*y*, –*z*.

angle P(1)-Ru(1)-C*-C(4) = 131.3°), probably to minimize the steric hindrance between both groups.

Compound 2[SbF₆]₂ has also been characterized by means of standard spectroscopic techniques (¹H and ³¹P{¹H} NMR) as well as elemental analyses, all data being consistent with the proposed formulation. In particular, in complete accord with the symmetry of the molecule, the ³¹P{¹H} NMR spectrum shows a unique singlet signal at 112.7 ppm, the chemical shift falling within the expected range for a phosphite ligand coordinated to a ruthenium center.¹⁶ The ¹H NMR spectrum also reflects the equivalency of both [Ru(η^6 -C₆H₅OCH₂CH₂OH)-{P(OPh)₃}] moieties of the molecule. However, the two *ortho* as well as the two *meta* hydrogen nuclei of the η^6 -phenoxyethanol ligand resonate at different chemical shifts (see details in the Experimental section). This inequivalency is probably due to the limited rotation of the arene as a consequence of the high steric hindrance.

Finally, note that we have observed by NMR spectroscopy the formation of a similar dinuclear derivative starting from the triethylphosphite precursor $[RuCl_2(\eta^6-C_6H_5OCH_2CH_2OH)-{P(OEt)_3}]$ (1b).¹⁷ However, all our attempts to isolate this compound in pure form have failed.

$\label{eq:synthesis} \begin{array}{l} Synthesis and characterization of compound [{RuCl- (\eta^6-C_6H_5OCH_2CH_2OH)(PPh_3)}_2(\mu\text{-}Cl)][SbF_6] \end{array}$

Surprisingly, unlike the triphenylphosphite derivative **1a**, the treatment of the triphenylphosphine analog $[RuCl_2(\eta^6-C_6H_5OCH_2CH_2OH)(PPh_3)]$ **(1c)** with one equivalent of AgSbF₆ in dichloromethane at room temperature led to the selective formation of the monocationic dinuclear compound [{RuCl(η^6 -



 $C_6H_5OCH_2CH_2OH)(PPh_3)\}_2(\mu-Cl)][SbF_6]$ (3[SbF₆]), which contains only one Cl-bridge (Scheme 2). The formation of the dicationic derivative [{Ru(μ -Cl)(η^6 - $C_6H_5OCH_2CH_2OH$)(PPh_3)}_2]-[SbF_6]_2, structurally related to 2[SbF_6]_2, was not observed even after a long reaction time. The use of more drastic conditions to force the generation of a second Cl-bridge, *i.e.* reflux temperature or large excess of AgSbF_6, only gave rise to a decomposition mixture.¹⁸

Crystals of compound 3[SbF₆] suitable for X-ray analysis were obtained from an acetone solution layered with diethyl ether. Once again, the ORTEP view shows the classical pseudooctahedral "three-legged piano-stool" geometry around each ruthenium atom (Fig. 3). However, according to the presence of only one Cl-bridge in the molecule, the Cl(1)-Ru(1)-Cl(2)and Ru(1)-Cl(1)-Ru(1a) bond angles adopt higher values when compared with those found in 2 (91.45(3)° vs. 79.91(5)° and 117.59(6)° vs. 100.09(5)°, respectively). Therefore, in this way, the two ruthenium fragments are located farther from each other (Ru-Ru distance = 4.152 Å (3) vs. 3.730 Å (2)), thus minimizing the steric congestion. Apparently, the formation of one-Cl vs. two-Cl bridged derivatives seems to be governed by the steric repulsions between the P-donor ligand and the arene. In accord with this, easy access to the two-Cl bridged compounds $[{Ru(\mu-Cl)(\eta^6-C_6Me_6)(L)}_2]$ [PF₆]₂ has been previously described with relatively small phosphines (L = PMe₃, PMePh₂), while the related derivative $[{Ru(\mu-Cl)(\eta^6-C_6Me_6)(PPh_3)}_2][PF_6]_2$, containing a bulkier P-donor ligand (i.e. PPh3), could not be obtained.¹⁹ On the other hand, dimers with highly sterically demanding phosphines, such as $[{Ru(\mu-Cl)(\eta^6-C_6H_6)(PCy_3)}_2]$ $[BF_4]_2$, are known but only with small arene ligands like benzene.²⁰ Hence, in the present case, it is not surprising that the two Cl-bridged compound [{ $Ru(\mu-Cl)(\eta^6-C_6H_5OCH_2CH_2OH)$ - ${P(OPh)_3}_2$ [SbF₆]₂ (2[SbF₆]₂), including the small triphenylphosphite, could be easily generated, but the counterpart with the larger PPh₃ ligand is not accessible (Tolman angles for P(OPh)₃ and PPh₃: 128° and 145°, respectively).

Synthesis and characterization of mononuclear compounds $[RuCl_2(\eta^6:\kappa^1(O)-C_6H_5CH_2CH_2CH_2OH)(L)][SbF_6] (L = P(OPh)_3, PPh_3, P(OEt)_3)$

The reluctance of the $-OCH_2CH_2OH$ side arm of compounds **1a-c** to coordinate the metal center was unexpected since related derivatives readily generated tethered η^6 : $\kappa^1(O)$ -arene



Fig. 3 ORTEP-type view of the structure of the cation $[\{RuCl(\eta^6-C_6H_5OCH_2-CH_2OH)(PPh_3)\}_2(\mu-CI)]^+$ (**3**). Hydrogen atoms, except the OH ones, SbF_6⁻ anion and diethyl ether molecule are omitted for clarity. Atoms labeled with an "a" are generated by a crystallographic 2-fold symmetry axis. Thermal ellipsoids are drawn at 20% probability level. Selected bond distances (Å) and angles (°): Ru(1)–Cl(2) = 2.4144(1); Ru(1)–Cl(1) = 2.4271(8); Ru(1)–P(1) = 2.341(1); Ru(1)–C* = 1.722(3); Cl(1)–Ru(1)–Cl(2) = 91.45(3); Cl(2)–Ru(1)–P(1) = 86.28(4); Cl(1)–Ru(1)–P(1) = 86.80(4); Cl(2)–Ru(1)–C* = 124.38(3); Cl(1)–Ru(1)–C* = 124.82(2); P(1)–Ru(1)–C* = 130.53(3); Ru(1)–Cl(1)–Ru(1a) = 117.59(6). C* = centroid of the arene ring (C(1), C(2), C(3), C(4), C(5) and C(6) carbon atoms). Symmetry code related to moiety: –*x*, *y*, –*z* + 3/2.



Scheme 3 Synthesis of the tethered compounds 5a-c[SbF₆].

complexes under similar reaction conditions.^{9b,10a} Thus, for comparative purposes, and to better understand the factors which govern this particular chemical behavior, the reactivity of compounds $[RuCl_2(\eta^6-C_6H_5CH_2CH_2CH_2OH)(L)]$ (L = P(OPh)₃ (4a), P(OEt)₃ (4b), PPh₃ (4c)), structurally similar to 1a-c, was also explored. In accordance with literature precedents,²¹ the treatment of these derivatives with one equivalent of AgSbF₆ resulted in the expected formation of the mononuclear tethered derivatives [RuCl(n⁶:κ¹(0)-C₆H₅CH₂CH₂CH₂OH)(L)][SbF₆] $(L = P(OPh)_3 (5a[SbF_6]), P(OEt)_3 (5b[SbF_6]), PPh_3 (5c[SbF_6])),$ which result from the elimination of one chloride ligand and the coordination of the pendant arm onto the ruthenium center (Scheme 3). Their NMR spectroscopic data are in complete agreement with the proposed structure (see details in the Experimental section and the ESI⁺). In particular, due to the generation of a stereogenic center on the ruthenium atom, the hydrogen nuclei of each methylenic group become diastereotopic.

The molecular structure of complex $[RuCl(\eta^6:\kappa^1(O)-C_6H_5CH_2CH_2CH_2OH)\{P(OPh)_3\}]^+$ (5a) was unequivocally confirmed by X-ray diffraction analysis of a single crystal of 5a [SbF₆] (Fig. 4). The Ru(1)–O(1) distance (2.145(5) Å) is



Fig. 4 ORTEP-type view of the structure of the cation $[RuCl(\eta^{6}:\kappa^{1}(O)-C_{6}H_{5}CH_{2}CH_{2}CH_{2}OH){P(OPh)_{3}}]^{+}$ **(5a)** showing the crystallographic labeling scheme. Hydrogen atoms, except the OH one, SbF₆⁻⁻ anion and acetone molecule are omitted for clarity. Thermal ellipsoids are drawn at 20% probability level. Selected bond distances (Å) and angles (°): Ru(1)–Cl(1) = 2.384(2); Ru(1)–O(1) = 2.145(5); Ru(1)–C^* = 1.7006(4); Ru(1)–P(1) = 2.297(1); Cl(1)–Ru(1)–P(1) = 84.41(5); Cl(1)–Ru(1)–O(1) = 84.0(2); P(1)–Ru(1)–O(1) = 88.3(2); C^*-Ru(1)–Cl(1) = 127.95(5); C^*-Ru(1)–P(1) = 130.45(4); C^*-Ru(1)–O(1) = 126.5(1). C^* = centroid of the arene ring (C(1), C(2), C(3), C(4), C(5) and C(6) carbon atoms).

Table 1 Formal potential of complexes 1a-c and 4a-c^a

Entry	Complex	Formal potential
1	$[\operatorname{RuCl}_2(\eta^6-C_6H_5\operatorname{OCH}_2\operatorname{CH}_2\operatorname{OH})\{\operatorname{P}(\operatorname{OPh})_3\}], \mathbf{1a}$ $[\operatorname{RuCl}_2(\eta^6-C_6H_5\operatorname{OCH}_2\operatorname{CH}_2\operatorname{OH})\{\operatorname{P}(\operatorname{OFt})_3\}], \mathbf{1b}$	$0.86 V^{b}$ $0.77 V^{b}$
3	$[\text{RuCl}_2(\eta^6\text{-}C_6\text{H}_5\text{OCH}_2\text{CH}_2\text{OH})(\text{PPh}_3)]$, 1	0.71 V^b
4 5	[RuCl ₂ (η° -C ₆ H ₅ CH ₂ CH ₂ CH ₂ CH ₂ OH){P(OPh) ₃ }], 4a [RuCl ₂ (η° -C ₆ H ₅ CH ₂ CH ₂ CH ₂ CH ₂ OH){P(OEt) ₃ }], 4b	0.84 V 0.76 V
6	$[RuCl_2(\eta^6-C_6H_5CH_2CH_2CH_2OH)(PPh_3)], 4c$	0.70 V

^{*a*} Ru(π)/Ru(π) potential values (in V) *vs.* the ferrocenium–ferrocene redox couple. ^{*b*} Values reported in ref. 5*b*.

comparable to that observed in analogous tethered η^6 : $\kappa^1(O)$ -arene-ruthenium complexes and fully consistent with the coordination of the hydroxyl group onto the metal center.^{9b,f,10a}

Rationalization of chemical behavior

The experiments described above clearly show the difference in reactivity between the precursors $[RuCl_2(\eta^6-C_6H_5OCH_2-CH_2OH)(L)]$ (1) and $[RuCl_2(\eta^6-C_6H_5CH_2CH_2CH_2OH)(L)]$ (4) despite their great structural similarity.²² This could not be ascribed to different electron-donating abilities of both arenes, since, for a given P-donor ligand, complexes 1 and 4 present almost identical redox potentials (Table 1, entries 1 vs. 4, 2 vs. 5 and 3 vs. 6), reflecting therefore similar electron densities on the metal centers.

The particular chemical behavior of derivatives **1** may be rather ascribed to the participation of the oxygen lone pairs to the delocalized π -system of the η^6 -phenoxyethanol arene ligand. In favor of this hypothesis is the fact that the oxygen atom adjacent to the arene ring adopts an sp²-hybridization, as inferred by the values of the C_{*ipso*}-O-C_(CH₂) bond angles

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Table 2 Structural data of different η^{6} -	phenoxyethanol complexes
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Complex	C-O-C ^a	θ^b
$ \begin{split} & [RuCl_2(C_6H_5OCH_2CH_2OH)\{P(OEt)_3\}], \mathbf{1b}^c \\ & [\{Ru(\mu\text{-}Cl)(C_6H_5OCH_2CH_2OH)\{P(OPh)_3\}\}_2]^{2^+}, 2 \\ & [\{RuCl(C_6H_5OCH_2CH_2OH)(PPh_3)\}_2(\mu\text{-}Cl)]^+, 3 \\ & [\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\}_2]^d \\ & [RuCl(C_6H_5OCH_2CH_2OH)\{TsNCH(Ph)CH(Ph)NH_2\}]^e \end{split} $	121.4(3)° 119.5(5)° 119.6(6)° 119(1)° 120(1)°	$2.1(5)^{\circ}$ $0.6(8)^{\circ}$ $4.6(9)^{\circ}$ $5(2)^{\circ}$ $1(2)^{\circ}$

^{*a*} Bond angle C_{ipso} -O- $C_{(CH_2)}$. ^{*b*} θ = dihedral angle C_{ortho} - C_{ipso} -O- $C_{(CH_2)}$ in the functionalized arene. ^{*c*} Values reported in ref. 5*b*. ^{*d*} Values reported in ref. 23*a*. ^{*e*} Values reported in ref. 23*b*.

about 120° (see Table 2). Moreover, the electronic delocalization forces the neighboring C_{ortho} , C_{ipso} , O and $C_{(CH_2)}$ atoms to be roughly coplanar, giving rise to a dihedral angle C_{ortho} - C_{ipso} -O- $C_{(CH_2)}$ (θ) near 0°. Such structural parameters are observed for the precursor [RuCl₂(η^6 -C₆H₅OCH₂CH₂OH)-{P(OEt)₃}]^{5b} (**1b**) as well as for dinuclear derivatives 2 and 3 (Table 2). Similar features were also found for the previously reported η^6 -phenoxyethanol ruthenium(II) complexes [{RuCl-(μ -Cl)(η^6 -C₆H₅OCH₂CH₂OH)}₂] and [RuCl(η^6 -C₆H₅OCH₂-CH₂OH){ κ^2 -(N,N)-TsNCH(Ph)CH(Ph)NH₂}] (Table 2),²³ and other organometallic derivatives with a different η^6 -PhOR ligand like [{Ru(η^6 -C₆H₅OEH)}₂(μ -Cl)₃][BPh₄].^{23a}

In contrast, in compounds containing the η^{6-} C₆H₅(CH₂)₃OH arene ligand, the related dihedral angles C_{ortho}-C_{ipso}-C_(CH₂)-C_(CH₂) adopt values ranging from 11.3° to 89.2°, ^{9b,24} indicating a higher flexibility of the side chain.

In order to rationalize the structural differences observed between the η^6 -C₆H₅OCH₂CH₂OH and η^6 -C₆H₅CH₂CH₂CH₂OH ruthenium derivatives, Density Functional Theory (DFT) calculations at the BP86/def2-SVP level on complexes [RuCl₂(η^6 -C₆H₅-X-CH₂CH₂OH){P(OMe)₃}] with X = O (1M) or X = CH₂ (4M), as models for derivatives 1 and 4, respectively, were carried out (see details in the Experimental section and in the ESI[†]).

Our calculations nicely agree with the above conclusions based on the different structural features of complexes 1 and 4. Thus, the computed hybridization of the oxygen atom in the model complex 1M is approximately sp² (computed value of sp^{1.76} for the C_{ipso} -O bond and sp^{2.48} for the O-C_(CH,) bond), therefore suggesting a significant participation of the oxygen lone pairs to the delocalized π -system of the η^6 -phenoxyethanol arene ligand. Indeed, the second order perturbation theory (SOPT) of the natural bond orbital (NBO) method indicates a quite remarkable stabilizing delocalization of the out-of-plane oxygen lone-pair to the π^* (C_{ipso}=C_{ortho}) molecular orbital (associated SOPT energy of $\Delta E^{(2)} = -32.1$ kcal mol⁻¹, Fig. 5). For complex 4M, the NBO method locates a similar delocalization from the σ (C–H) molecular orbital to the π^* system coupled to the reverse $\pi(C=C)$ to $\sigma^*(C-H)$ delocalization (see Fig. 5). However, and as expected for these hyperconjugative interactions,²⁵ their corresponding strengths are much weaker (associated SOPT energies, $\Delta E^{(2)}$, of *ca.* -3.1 kcal mol⁻¹) than the LP(O) to $\pi^*(C=C)$ conjugative delocalization present in complex 1M. Although the latter stabilizing delocalization can



Fig. 5 Two-electron stabilizing delocalizations (associated SOPT energies, $\Delta E^{(2)}$) in complexes **1M** and **4M**.



Fig. 6 Relative energies of derivatives [RuCl₂($\eta^{6-}C_{6}H_{5-}X-CH_{2}CH_{2}OH$){P(OMe)₃}] (X = O (**1M**), CH₂ (**4M**)) as a function of the dihedral angle C_{ortho}-C_{ipso}-X-C_(CH₂) (θ). All data have been computed at the BP86/def2-SVP level.

be also found in alkoxy-substituted aryl compounds like anisol, the presence of the metal moiety enhances the π -acceptor ability of the coordinated aryl fragment. For this reason, the computed $\Delta E^{(2)}$ (LP(O) $\rightarrow \pi^*(C=C)$) value in the parent anisol (C₆H₅-OMe, $\Delta E^{(2)}$) = -28.2 kcal mol⁻¹) is clearly lower than in **1M** ($\Delta E^{(2)}$ = -32.1 kcal mol⁻¹).

The occurrence of this stabilizing delocalization plays an important role in the structure and reactivity of these complexes, as described above. As a consequence of this interaction, a more restricted rotation around the Cortho-Cipso-X- $C_{(CH_2)}$ moiety for X = O compared to X = CH₂ should be expected. In fact, our calculations indicate that such rotation, which is needed to form the tethered compounds, is associated with a much higher energetic cost for 1M (being essentially free for 4M). Fig. 6 shows the relative energies determined for different conformers with a Cortho-Cipso-X- $C_{(CH_2)}$ dihedral angle (θ) ranging from 0° to 90°.²⁶ For X = O, the lowest energies correspond to small θ values (minimum for $\theta = 9.2^{\circ}$), *i.e.* for an almost coplanar disposition of the C_{ortho} , C_{ipso} , O and $C_{(CH_2)}$ atoms. An increase of θ results in remarkably higher relative energies, the conformer with θ = 90° being the less stable ($\Delta E = 4.5 \text{ kcal mol}^{-1}$). In contrast, for $X = CH_2$ the stability of the molecule does not show a marked dependence on the θ angle ($\Delta E_{\text{max}} = 1.5 \text{ kcal mol}^{-1}$). Moreover,

the orientation of the oxygen downwards to the metal center is an energy minimum.

Therefore, it becomes clear that the rotation of the arene side chain around the C_{ipso} -X axis is more favorable for η^6 -phenylpropanol complexes **4** than for η^6 -phenoxyethanol derivatives **1**, facilitating in the former the approach of the OH group to the metal and its coordination. Although the energy required to rotate the pendant -OCH₂CH₂OH group in **1** is not very high, it seems to be enough to avoid access to tethered compounds [RuCl(η^6 : $\kappa^1(O)$ -C₆H₅OCH₂CH₂OH)(PR₃)][SbF₆] (PR₃ = P(OPh)₃, P(OEt)₃, PPh₃) and favor the formation of diruthenium Cl-bridged derivatives.

Conclusions

In this work, we have demonstrated that a subtle change in the structure of η^6 -arene ligands can dramatically modify their coordination ability and induce, therefore, a difference in reactivity of the resulting complexes. Thus, C₆H₅OCH₂CH₂OH showed to be reluctant to act as an η^6 : $\kappa^1(O)$ -coordinated ligand and the treatment of its complexes $[RuCl_2(\eta^6-C_6H_5OCH_2 CH_2OH$ {P(OPh)₃}] (1a) and $[RuCl_2(\eta^6-C_6H_5OCH_2CH_2OH)-$ (PPh₃)] (1c) with a chloride abstractor exclusively led to diruthenium Cl-bridged compounds, namely [{Ru(μ -Cl)(η^6 - $C_6H_5OCH_2CH_2OH$ {P(OPh)₃}₂ [SbF₆]₂ (2[SbF₆]₂) and [{RuCl(η^6 - $C_6H_5OCH_2CH_2OH$ (PPh₃) $_2(\mu$ -Cl) [SbF₆] (3[SbF₆]), in which the arene is linked to the metal only through the aromatic ring. In contrast, the phenylpropanol complexes [RuCl₂(η^6 - $C_6H_5CH_2CH_2CH_2OH(L)$ (L = P(OPh)₃ (4a), P(OEt)₃ (4b), PPh₃ (4c)) cleanly furnished the expected mononuclear tethered derivatives $[RuCl(\eta^6:\kappa^1(O)-C_6H_5CH_2CH_2CH_2OH)(L)][SbF_6]$ (L = P(OPh)₃ (5a[SbF₆]), P(OEt)₃ (5b[SbF₆]), PPh₃ (5c[SbF₆])) under the same conditions. The particular behavior of complexes 1 seems to be a direct consequence of the participation of the oxygen lone pairs to the delocalized π -system of the η^6 -phenoxyethanol arene ligand. This fact limits the rotation of the side chain around the Cipso-O axis, avoiding the approach of the OH unit to the ruthenium center.

Experimental

The manipulations were performed under an atmosphere of dry nitrogen using a vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers with the exception of compounds $[RuCl_2(\eta^6:\kappa^1(O)-C_6H_5CH_2CH_2CH_2OH)]$,²⁷ $[RuCl_2(\eta^6-C_6H_5OCH_2-CH_2OH)(L)]$ (L = P(OPh)₃ (1a), P(OEt)₃ (1b), PPh₃ (1c))^{5b} and $[RuCl_2(\eta^6-C_6H_5CH_2CH_2OH)(PPh_3)]$ (4c),^{9b} which were prepared by following the methods reported in the literature. The C, H elemental analyses were carried out with a Perkin-Elmer 1720-XFT spectrometer, and NMR spectra with a Bruker DPX300 instrument at 300 MHz (¹H), 121.5 MHz (³¹P)

or 75.4 MHz (¹³C) using SiMe₄ or 85% H₃PO₄ as standards. Cyclovoltammetric measurements were performed at 20 °C with a "µAutolab type III" apparatus equipped with a threeelectrode system. Platinum disk electrode, spiral-shaped platinum wire and silver wire were used as working-, counter- and reference-electrodes, respectively. CV experiments were carried out with CH₂Cl₂ solutions of the appropriate complex (0.5 × 10^{-3} M) and [NⁿBu₄][PF₆] (0.1 M) as the electrolyte. Formal CV potentials (*E*°′) are referenced relative to the potential of the ferrocenium/ferrocene couple (*E*° = 0.184 V) run under identical conditions (*E*°′ = *E*°(complex⁺/complex) – *E*°([Cp₂Fe]⁺/[Cp₂Fe])). A scan rate of 0.5 V s⁻¹ has been employed.²⁸

Preparation of [{Ru(μ -Cl)(η^6 -C₆H₅OCH₂CH₂OH){P(OPh)₃}}_2]-[SbF₆]₂ (2[SbF₆]₂)

To a solution of 0.130 g (0.210 mmol) of $[RuCl_2(\eta^6-C_6H_5OCH_2 CH_2OH$ {P(OPh)₃} (1a) in dichloromethane (20 mL), a solution of AgSbF₆ (0.072 g, 0.210 mmol) in 1 mL of methanol was added and the mixture was stirred at room temperature for 2 h. Then, the suspension was filtered through Kieselguhr and the filtrate was evaporated to dryness. The residue was washed with diethyl ether and the resulting yellow brownish solid was dried in vacuum. Yield: 0.146 g (85%). Anal. calcd for C₅₂H₅₀Cl₂F₁₂O₁₀P₂Ru₂Sb₂: C, 38.05; H, 3.07. Found: C, 38.28; H, 2.99. ${}^{31}P{}^{1}H{}$ NMR, acetone-d₆, δ : 112.8 (s). ${}^{1}H{}$ NMR, acetone-d₆, δ: 7.52-7.31 (m, 30 H, OPh), 6.38 and 6.30 (both m, 2 H each, CH_{meta}), 5.47 (d, 2 H, ${}^{3}J_{HH}$ = 6.6, CH_{ortho}), 4.97 (d, 2 H, ${}^{3}J_{\rm HH}$ = 6.3, CH_{ortho}), 4.17 (apparent t, 2 H, ${}^{3}J_{\rm HH} \approx {}^{3}J_{\rm HH} \approx$ 6.4, CH_{para}), 3.94 and 3.84 (both m, 4 H each, CH₂CH₂); OH signal was not observed. ${}^{13}C_1^{1}H$ NMR spectra were not recorded due to the low solubility of this compound.

Preparation of [{RuCl(η^6 -C₆H₅OCH₂CH₂OH)(PPh₃)}₂(µ-Cl)]-[SbF₆] (3[SbF₆])

Compound **3** was prepared as a clear orange solid using a similar procedure starting from 0.100 g (0.175 mmol) of $[RuCl_2(\eta^6-C_6H_5OCH_2CH_2OH)(PPh_3)]$ (**1c**), 0.060 g (0.175 mmol) of AgSbF₆, 20 mL of dichloromethane and 1 mL of methanol. Yield: 0.101 g (86%). Anal. calcd for $C_{52}H_{50}Cl_3F_6O_4P_2Ru_2Sb$: C, 46.43; H, 3.75. Found: C, 46.25; H, 3.66. ³¹P{¹H} NMR, acetone-d₆, δ : 34.1 (s). ¹H NMR, acetone-d₆, δ : 7.79–7.45 (m, 30 H, Ph), 6.03 and 5.73 (both broad s, 4 H each, CH_{meta} and CH_{ortho}), 4.98 (broad s, 2 H, CH_{para}), 4.21 and 3.91 (both m, 4 H each, CH₂CH₂); OH signal was not observed. ¹³C{¹H} NMR spectra were not recorded due to the low solubility of this compound.

Preparation of $[RuCl_2(\eta^6-C_6H_5CH_2CH_2CH_2OH){P(OPh)_3}]$ (4a)

A suspension of $[\text{RuCl}_2(\eta^6:\kappa^1-(O)-\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})]$ (0.500 g, 1.62 mmol) and P(OPh)₃ (0.55 mL, 2.10 mmol) in 100 mL of dichloromethane was stirred at room temperature till complete dissolution (*ca.* 2 h). Then, solvent was evaporated and the solid residue was washed 3 times with 30 mL of a 1:1 mixture of diethyl ether: hexane. The resulting orange solid was dried under vacuum. Yield: 0.965 g (96%). Anal. calcd for C₂₇H₂₇Cl₂O₄PRu: C, 52.44; H, 4.40. Found: C, 52.31; H, 4.60. ³¹P{¹H} NMR, CDCl₃, δ : 110.1 (s). ¹H NMR, CDCl₃, δ: 7.46–7.20 (m, 15 H, OPh), 5.14 (m, 4 H, CH_{ortho} and CH_{meta}), 4.33 (m, 1 H, CH_{para}), 3.73 (t, 2 H, ${}^{3}J_{HH}$ = 5.8, CH₂OH), 2.58 (t, 2 H, ${}^{3}J_{HH}$ = 7.5, PhCH₂), 1.84 (tt, 2 H, ${}^{3}J_{HH}$ = 7.5, ${}^{3}J_{HH}$ = 5.8, CH₂CH₂OH); OH signal was not observed. ${}^{13}C{}^{1}H$ NMR, CDCl₃, δ: 151.2 (d, ${}^{2}J_{PC}$ = 9.1, C_{ipso} OPh), 129.7 (s, C_{meta} OPh), 125.4 (s, C_{para} OPh), 121.8 (d, ${}^{2}J_{PC}$ = 4.0, C_{ortho} OPh), 116.7 (d, ${}^{2}J_{PC}$ = 8.1, C_{ipso}), 89.6 (s, CH_{ortho} or CH_{meta}), 89.3 (d, ${}^{2}J_{PC}$ = 9.1, CH_{ortho} or CH_{meta}), 61.3 (s, CH₂OH), 31.1 and 29.1 (both s, PhCH₂CH₂). IR, ν_{OH} = 3426 cm⁻¹.

Preparation of $[RuCl_2(\eta^6-C_6H_5CH_2CH_2CH_2OH){P(OEt)_3}]$ (4b)

Complex **4b** was prepared as a red solid using a similar procedure using 0.500 g (1.62 mmol) of $[RuCl_2(\eta^6:\kappa^1(O)-C_6H_5CH_2CH_2CH_2OH)]$, 0.36 mL (2.10 mmol) of P(OEt)₃, and 100 mL of dichloromethane. Yield: 0.670 g (87%). Anal. calcd for $C_{15}H_{27}Cl_2O_4PRu$: C, 37.98; H, 5.74. Found: C, 38.11; H, 5.63. ³¹P{¹H} NMR, CDCl₃, δ : 114.0 (s). ¹H NMR, CDCl₃, δ : 5.56 (t, 2 H, ³J_{HH} = 5.1, CH_{meta}), 5.48 (d, 2 H, ³J_{HH} = 5.1, CH_{ortho}), 5.31 (t, 1 H, ³J_{HH} = 5.1, CH_{para}), 4.16 (dq, 6 H, ³J_{PH} = 7.1, ³J_{HH} = 7.1, POCH₂), 3.78 (t, 2 H, ³J_{HH} = 4.5, CH₂OH), 2.74 (t, 2 H, ³J_{HH} = 6.8, PhCH₂), 1.95 (m, 2 H, CH₂), 1.85 (broad s, 1 H, OH), 1.29 (t, 9 H, ³J_{HH} = 7.1, POCH₂Me). ¹³C{¹H} NMR, CDCl₃, δ : 114.4 (d, ²J_{PC} = 8.1, C_{ipso}), 89.9 (d, ²J_{PC} = 8.1, CH_{ortho} or CH_{meta}), 88.3 (s, CH_{ortho} or CH_{meta}), 81.1 (s, CH_{para}), 63.2 (d, ²J_{PC} = 6.0, POCH₂), 61.1 (s, CH₂OH), IR, ν_{OH} = 3434 cm⁻¹.

Preparation of [RuCl(η^6 : $\kappa^1(O)$ -C₆H₅CH₂CH₂CH₂OH){P(OPh)₃}]-[SbF₆] (5a[SbF₆])

A solution of 4a (0.100 g, 0.16 mmol) in 20 mL of dichloromethane was treated with AgSbF₆ (0.072 g, 0.21 mmol, dissolved in 1 mL of MeOH). After stirring for 0.5 h at room temperature, the suspension was filtered on Kieselguhr, and the filtrate was evaporated to dryness. The residue was washed 3 times with 10 mL of diethyl ether and the resultant yellow solid was dried in vacuum. Yield: 0.099 g (76%). Anal. calcd for C₂₇H₂₇ClF₆O₄PRuSb: C, 39.61; H, 3.32. Found: C, 39.75; H, 3.42. ${}^{31}P{}^{1}H$ NMR, acetone-d₆, δ : 110.2 (s). ${}^{1}H$ NMR, acetoned₆, δ: 7.53–7.34 (m, 15 H, OPh), 6.67 (dd, 1 H, ${}^{3}J_{HH}$ = 5.6, ${}^{3}J_{PH}$ = 4.0, CH_{ortho} arene), 6.33 (apparent t, 1 H, ${}^{3}J_{HH} = {}^{3}J_{HH} = 5.6$, CH_{meta} arene), 6.12 (t, 1 H, ${}^{3}J_{HH}$ = 2.8, OH), 5.97 (d of apparent t, 1 H, ${}^{3}J_{PH} = 5.7$, ${}^{3}J_{HH} = {}^{3}J_{HH} = 5.6$, CH_{meta} arene), 5.02 (d, 1 H, ${}^{3}J_{HH} = 5.6$, CH_{ortho} arene), 4.04 (m, 1 H, OCH₂), 3.89 (apparent t, 1 H, ${}^{3}J_{HH} = {}^{3}J_{HH} = 5.6$, CH_{para} arene), 3.61 (m, 1 H, OCH₂), 2.91 (ddd, 1 H, ${}^{2}J_{HH}$ = 10.0, ${}^{3}J_{HH}$ = 7.6, ${}^{3}J_{HH}$ = 3.6, CH₂Ph), 2.47 (m, 1 H, CH₂Ph), 2.24 (m, 1 H, CH₂CH₂O), 2.10 (m, 1 H, CH_2CH_2O , overlapped by the solvent). Attributions were confirmed by ${}^{1}H{}^{-1}H$ correlation. ${}^{13}C{}^{1}H{}$ NMR, acetone-d₆, δ : 151.1 (d, ${}^{2}J_{PC}$ = 9.6, C_{ipso} OPh), 130.6 (s, C_{meta} OPh), 126.5 (s, C_{para} OPh), 121.7 (d, ${}^{3}J_{PC}$ = 4.6, C_{ortho} OPh), 110.1 (d, ${}^{2}J_{PC}$ = 1.8, C arene), 104.4 (d, ${}^{2}J_{PC}$ = 6.3, CH arene), 94.2 (d, ${}^{2}J_{PC}$ = 19.7, CH arene), 87.1, 82.4 and 71.1 (all s, CH arene), 65.1 (s, CH₂OH), 29.3 and 27.7 (both s, CH₂). IR, ν_{OH} = 3186 cm⁻¹.

Preparation of $[RuCl(\eta^6:\kappa^1(O)-C_6H_5CH_2CH_2CH_2OH){P(OEt)_3}]-$ [SbF₆] (5b[SbF₆])

Compound $5b[SbF_6]$ was prepared as a yellow solid using a similar procedure starting from 0.100 g (0.21 mmol) of 4b and 0.076 g (0.21 mmol) of AgSbF₆. Yield: 0.111 g (78%). Anal. calcd for C15H27ClF6O4PRuSb: C, 26.71; H, 4.03. Found: C, 26.62; H, 4.25. ³¹P{¹H} NMR, acetone-d₆, δ: 116.0 (s). ¹H NMR, acetone-d₆, δ : 6.66 (broad d, 1 H, ${}^{3}J_{HH}$ = 6.6, CH_{ortho}), 6.48 (dd, 1 H, ${}^{3}J_{HH}$ = 6.6, ${}^{3}J_{HH}$ = 5.4, CH_{meta}), 6.17 (apparent t of d, 1 H, ${}^{3}J_{HH} = {}^{3}J_{HH} = 5.4$, ${}^{3}J_{PH} = 5.1$, CH_{meta}), 5.95 (dd, 1 H, J = 6.3, J = 6.33.3, OH), 5.77 (broad d, 1 H, ${}^{3}J_{HH}$ = 5.4, CH_{ortho}), 5.39 (apparent t, 1 H, ${}^{3}J_{HH} = {}^{3}J_{HH} = 5.4$, CH_{para}), 4.18 (m, 6 H, POCH₂), 4.07 and 3.34 (both m, 1 H each, CH₂O), 3.03 (ddd, 1 H, ${}^{2}J_{HH}$ = 13.8, ${}^{3}J_{HH} = 4.8$, ${}^{3}J_{HH} = 3.3$, $CH_{2}Ph$), 2.47 (ddd, 1 H, ${}^{2}J_{HH} = 13.8$, ${}^{3}J_{\rm HH}$ = 11.1, ${}^{3}J_{\rm HH}$ = 4.2, CH₂Ph), 2.30 and 2.12 (both m, 1 H each, CH_2CH_2Ph), 1.34 (t, 9 H, ${}^{3}J_{HH}$ = 7.2, OCH_2CH_3). Attributions were confirmed by $^1\text{H}\text{-}^1\text{H}$ correlation. $^{13}\text{C}\{^1\text{H}\}$ NMR, acetone-d₆, δ : 104.7 (d, ²J_{PC} = 9.8, CH arene), 101.9 (s, C arene), 96.5 (d, ${}^{2}J_{PC}$ = 17.4, CH arene), 85.8, 84.0 and 72.8 (all s, CH arene), 64.7 (s, CH₂O), 63.2 (d, ²J_{PC} = 6.0, CH₂OP), 28.8 and 27.4 (both s, CH₂), 15.4 (d, ${}^{3}J_{PC}$ = 6.8, OCH₂CH₃). IR, ν_{OH} = 3163 cm^{-1} .

X-ray crystal structure determination of complexes 2[SbF₆]₂, 3[SbF₆] and 5a[SbF₆]

Single crystals suitable for X-ray diffraction analyses were obtained by slow diffusion of diethyl ether through saturated solutions of $2[SbF_6]_2$, $3[SbF_6]$ or $5a[SbF_6]$ in acetone. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication Nos CCDC 908513 ($2[SbF_6]_2$), 908514 ($3[SbF_6]$), 908515 ($5a[SbF_6]$).

Computational details

All the calculations reported in this paper were obtained with the GAUSSIAN 09 suite of programs.²⁹ The geometry of **1M** and **4M** were optimized at the gradient-corrected DFT level of theory by using Becke's exchange functional³⁰ in conjunction with Perdew's correlation functional³¹ (BP86) using the double- ξ valence plus polarization basis set def2-SVP³² for all atoms. This protocol is denoted BP86/def2-SVP and has been successfully applied to different organic and organometallic species.³³ Zero point vibrational energy (ZPVE) corrections have been computed at the same level (BP86/def2-SVP) and have not been corrected. Complexes **1M** and **4M** were characterized by frequency calculations,³⁴ and have a positive defined Hessian matrix indicating that both complexes are minimum on the potential energy surface.

Donor–acceptor interactions have been computed using the natural bond orbital (NBO) method.³⁵ The energies associated with these two-electron interactions have been computed according to the following equation:

$$\Delta E^{(2)}_{\phi\phi^*} = n_{\phi} rac{\langle \phi^* | \hat{F} | \phi
angle^2}{arepsilon_{\phi^*} - arepsilon_{\phi}}$$

where \hat{F} is the DFT equivalent of the Fock operator and ϕ and

 ϕ^* are two filled and unfilled natural bond orbitals having ε_{ϕ} and ε_{ϕ^*} energies, respectively; n_{ϕ} stands for the occupation number of the filled orbital.

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- 16 See, for example: B. Demerseman, R. Le Lagadec,B. Guilbert, C. Renouard, P. Crochet and P. H. Dixneuf, Organometallics, 1994, 13, 2269.
- 17 The reaction of the precursor $[RuCl_2(\eta^6-C_6H_5OCH_2CH_2OH) \{P(OEt)_3\}$ (1b), under the same experimental conditions (*i.e.* r.t., CH₂Cl₂, 1 equiv. of AgSbF₆ per Ru), seems to generate predominantly the derivative [{Ru(μ -Cl)(η^6 -C₆H₅OCH₂- CH_2OH {P(OEt)₃}₂[SbF₆]₂ analogous to compound 2 $[SbF_6]_2$. However, the presence of inseparable impurities did not allow the isolation of a pure sample of this derivative. Structure assignation is based on the similarity of NMR data with those of compound 2[SbF₆]. Spectroscopic data: ${}^{31}P{}^{1}H$ NMR, acetone-d₆, δ : 116.6 (s). ${}^{1}H$ NMR, acetone-d₆, δ : 6.52 and 6.33 (both m, 2 H each, CH_{meta}), 5.60 (d, 2 H, ${}^{3}J_{HH}$ = 6.4, CH_{ortho}), 5.06 (d, 2 H, ${}^{3}J_{HH}$ = 6.6, CH_{ortho}), 4.35 (apparent t, 2 H, ${}^{3}J_{HH} \approx {}^{3}J_{HH} \approx 5.8$, CH_{para}), 4.09 (m, 12 H, POCH₂), 3.89 and 3.79 (both m, 4 H each, CH_2CH_2), 1.32 (t, 18 H, ${}^{3}J_{HH}$ = 6.9, POCH₂Me); OH signal was not observed.
- 18 On the other hand, all our attempts to generate [{RuCl-(η^6 -C₆H₅OCH₂CH₂OH){P(OPh)₃}₂(μ -Cl)][SbF₆], structurally related to 3[SbF₆], from 1a failed. The use of only half an equivalent of AgSbF₆ per Ru gave rise to a mixture of 2 [SbF₆]₂ and the starting material 1a.
- 19 A mixture of $[\{Ru(\eta^6-C_6Me_6)\}_2(\mu\text{-Cl})_3][PF_6]$ and $[Ru-(\eta^6-C_6Me_6)(\eta^6-C_6H_5PPh_2)][PF_6]$ was rather obtained. See: H. Werner, H. Kletzin and C. Burschka, J. Organomet. Chem., 1984, 276, 231.
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- 21 Complex **5c** was previously obtained as the corresponding tetrafluoroborate salt. See ref. 9*b*.
- 22 This difference in reactivity is also exemplified by their behavior in the aqueous medium. The dissolution of $[RuCl_2(\eta^6-C_6H_5OCH_2CH_2OH){P(OEt)_3}]$ (1b) in D₂O gave rise to a mixture of $[RuCl(D_2O)(\eta^6-C_6H_5OCH_2CH_2OH) {P(OEt)_3}][Cl]$ and the starting product 1b, due to partial dissociation of one chloride ligand. In contrast, aqueous solutions of the analog 4b contain three species: (*i*) the starting material 4b, (*ii*) the aquo-complex $[RuCl(D_2O)(\eta^6-C_6H_5CH_2CH_2CH_2OH){P(OEt)_3}][Cl]$, generated by displacement of a Cl ligand by a molecule of water and, (*iii*) the tethered derivative $[RuCl(\eta^6:\kappa^1(O)-C_6H_5CH_2CH_2CH_2OH) {P(OEt)_3}][Cl]$, formed through Cl⁻ release and coordination of the hydroxyl group of the arene side chain onto the metal center (see NMR data in the ESI⁺).

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- 26 Since complexes $[RuCl_2(\eta^6-C_6H_5OCH_2CH_2OH){P(OMe)_3}]$ and $[RuCl_2(\eta^6-C_6H_5CH_2CH_2CH_2OH){P(OMe)_3}]$ present a plane of symmetry, relative energies for $90^\circ \le \theta \le 180^\circ$ are identical to those calculated for a dihedral angle of $180^\circ - \theta$.
- 27 Although this compound has been initially described as the dimer [{RuCl(μ -Cl)(η^6 -C₆H₅CH₂CH₂CH₂OH)}₂], its monomeric structure, at least in solid state, has been recently evidenced. See ref. 9*b* and *f*.
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