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Synthesis of New Chiral (η^6-Arene)(η^4-diene)ruthenium(0) Complexes

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Abstract

New Ru(η^6-arene)(η^4-diene) complexes, containing chiral substituents on the aromatic ring, have been prepared and characterized. The ^{1}H NMR inequivalence of the *ortho* and *meta* protons of the phenyl ring is discussed.

Introduction

(η^6-Arene)ruthenium(0) complexes are of great interest in preparative chemistry and catalysis. New simple synthetic ways have been recently reported improving studies on their chemistry and structure [1]. (η^6-Arene)(η^4-diene)ruthenium(0) complexes, containing chiral substituents on the arene ring, appeared of particular interest for their potential use in the catalytic synthesis of chiral compounds. The complexes Ru(η^6-arene)(η^4-COD) (arene = $C_6H_5CH(Et)CH_3$, $C_6H_5CH(NH_2)CH_3$ and COD = cycloocta-1,5-diene), previously prepared, pointed out an unusually high ^{1}H NMR anisochronicity of the *ortho* and *meta* protons of the phenyl ring [2].

In order to obtain a deeper insight into this phenomenon, the availability of Ru(η^6-arene)(η^4-diene) complexes having suitable chiral groups on the arene and different η^4-dienes was necessary. We report here the synthesis of new ruthenium(0) complexes of this type and some important features of their ^{1}H NMR spectra.

Experimental

All the reactions were carried out under a dry oxygen-free nitrogen atmosphere, using conventional Schlenk-tube techniques. Solvents were purified by conventional methods, distilled and stored under nitrogen.

The racemic arene ligands were prepared according to the literature methods: 2,2-dimethyl-3-phenylbutane, starting from acetophenone and t-butyl magnesium chloride [3]; 2-(4-methyl-phenyl)-butane by reaction of 4′-méthyl-propiofenone and methylene–diiodide in the presence of magnesium amalgam and subsequent hydrogenation of the resulting olefin [4]; (1-phenylethyl)ethylether, starting from 1-phenylethanol and acetylene and hydrogenation of the resulting olefin [5]; 2-phenoxybutane, by reaction of sodium phenoxide and sec-butyl bromide [6].

The complexes Ru(η^6-COT)(η^4-COD) [7] and $[RuCl_2\{\eta^6\text{-}C_6H_5CH(Et)CH_3\}]_2$ [2] were prepared according to the literature reports.

^{1}H NMR spectra were recorded on Varian T-60 and Bruker 270 MHz spectrometers, using $(CH_3)_4Si$ as internal standard (δ values). Microanalyses were performed by the Laboratorio di Microanalisi, Istituto di Chimica Organica, Facoltà di Farmacia, Università di Pisa.

Preparation of Complexes Ru(η^6-arene)(η^4-COD) (1a–d)

The Ru(η^6-arene)(η^4-COD) complexes were prepared as previously reported [2]. Only the preparation of complex **1a** will be described in detail, the experimental procedure being substantially the same for all the other compounds of the same type.

(η^6-2,2-Dimethyl-3-phenylbutane)(η^4-cycloocta-1,5-diene)ruthenium(0) (1a)

2,2-Dimethyl-3-phenylbutane (0.31 g, 1.92 mmol) was added to a solution of Ru(η^6-COT)(η^4-COD) (0.31 g, 0.99 mmol) in 5 ml of pentane. The reaction mixture was stirred at room temperature for 8 h under hydrogen (1 atm). The solvent and the excess of ligand were removed under reduced pressure and pentane (3 × 50 ml) was added to the solid residue. The yellow solution so obtained was concentrated to 10 ml and chromatographed on alumina (20 cm) using pentane as eluent. From the solution, at -78 °C, 0.28 g (0.75 mmol) of **1a** were recovered as a yellow crystalline solid ($M = 372$).

Preparation of (η^6-2-Phenylbutane)(η^4-bicyclo-2,2,1-hepta-2,5-diene)ruthenium(0), Ru$\{\eta^6\text{-}C_6H_5\text{-}CH(Et)CH_3\}(\eta^4\text{-NBD})$ (2)

To a suspension of $[RuCl_2\{\eta^6\text{-}C_6H_5CH(Et)CH_3\}]_2$ (0.12 g, 0.2 mmol) and anhydrous Na_2CO_3 (0.135 g,

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1.3 mmol) in 20 ml of isopropyl alcohol, NBD (1 ml, 9.3 mmol) was added. The mixture was refluxed for 5 h and then filtered. The pale yellow solution was evaporated to dryness under vacuum, extracted with pentane (3 X 50 ml) and chromatographed on alumina (30 cm), using pentane as

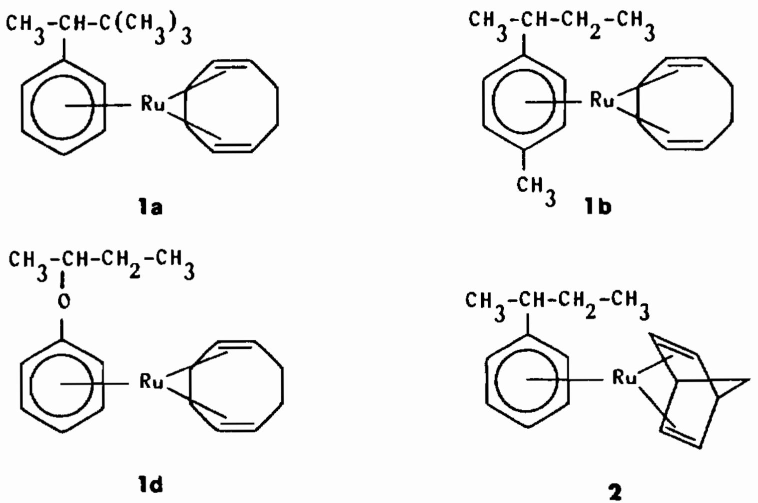
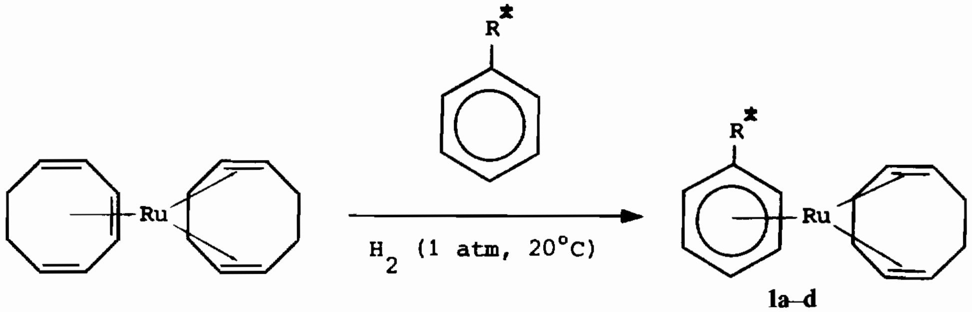
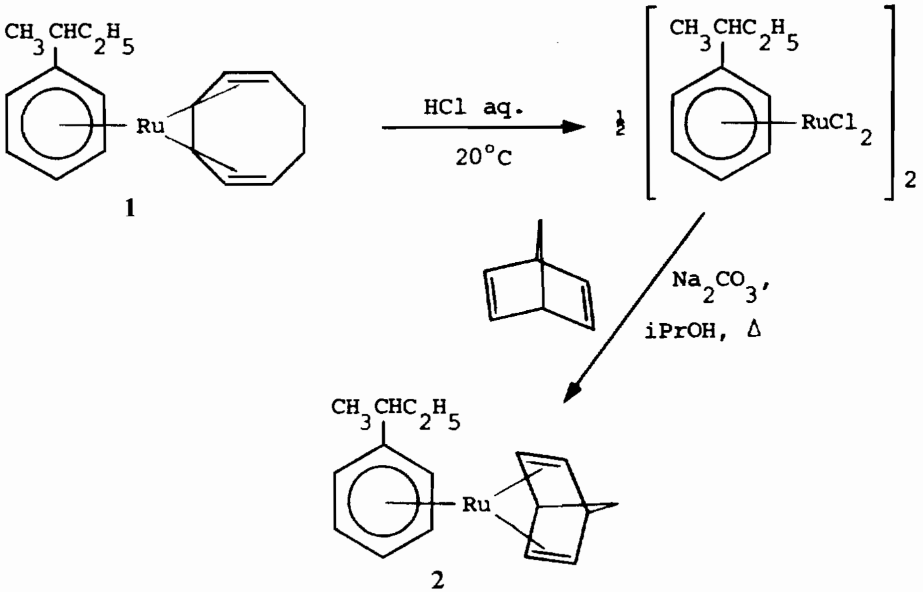


Fig. 1. Chiral (η^6-arene)(η^4-diene)ruthenium(0) complexes.



Scheme 1. Arene = a, $C_6H_5CH(^tBu)CH_3$; b, $pCH_3C_6H_4CH(Et)CH_3$; c, $C_6H_5CH(OEt)CH_3$; d, $C_6H_5OCH(Et)CH_3$.



Scheme 2.

eluent. From the solution, concentrated to 3 ml, at −78 °C, 0.055 g (0.17 mmol) of **2** were obtained as a yellow oily compound ($M = 328$).

Results and Discussion

The chiral (η^6-arene)(η^4-diene)ruthenium(0) complexes which have been prepared in the course of this study are shown in Fig. 1. They were of particular interest for structural investigations because they provide different environments around the ruthenium atom. Thus, **1a** has an asymmetric alkyl group characterized by high conformational homogeneity, **1b** contains a *para*-alkyl substituent in the phenyl ring, in **1c** there is a strong screening group in the lateral chain and in **1d** the chiral carbon atom is bonded with a spacing group to the phenyl ring. Complex **2** contains η^4-bicyclo-2,2,1-hepta-2,5-diene (NBD), which is a less flexible diene than cycloocta-1,5-diene.

Complexes **1a–d** were prepared by the reaction of Ru(η^6-COT)(η^4-COD) (COT = cycloocta-1,3,5-triene) and the corresponding arene under an atmosphere of hydrogen, as reported in Scheme 1. Complex **2** was obtained by reduction of the corresponding $[RuCl_2(\eta^6\text{-arene})]_2$ compound in the presence of NBD, according to Scheme 2.

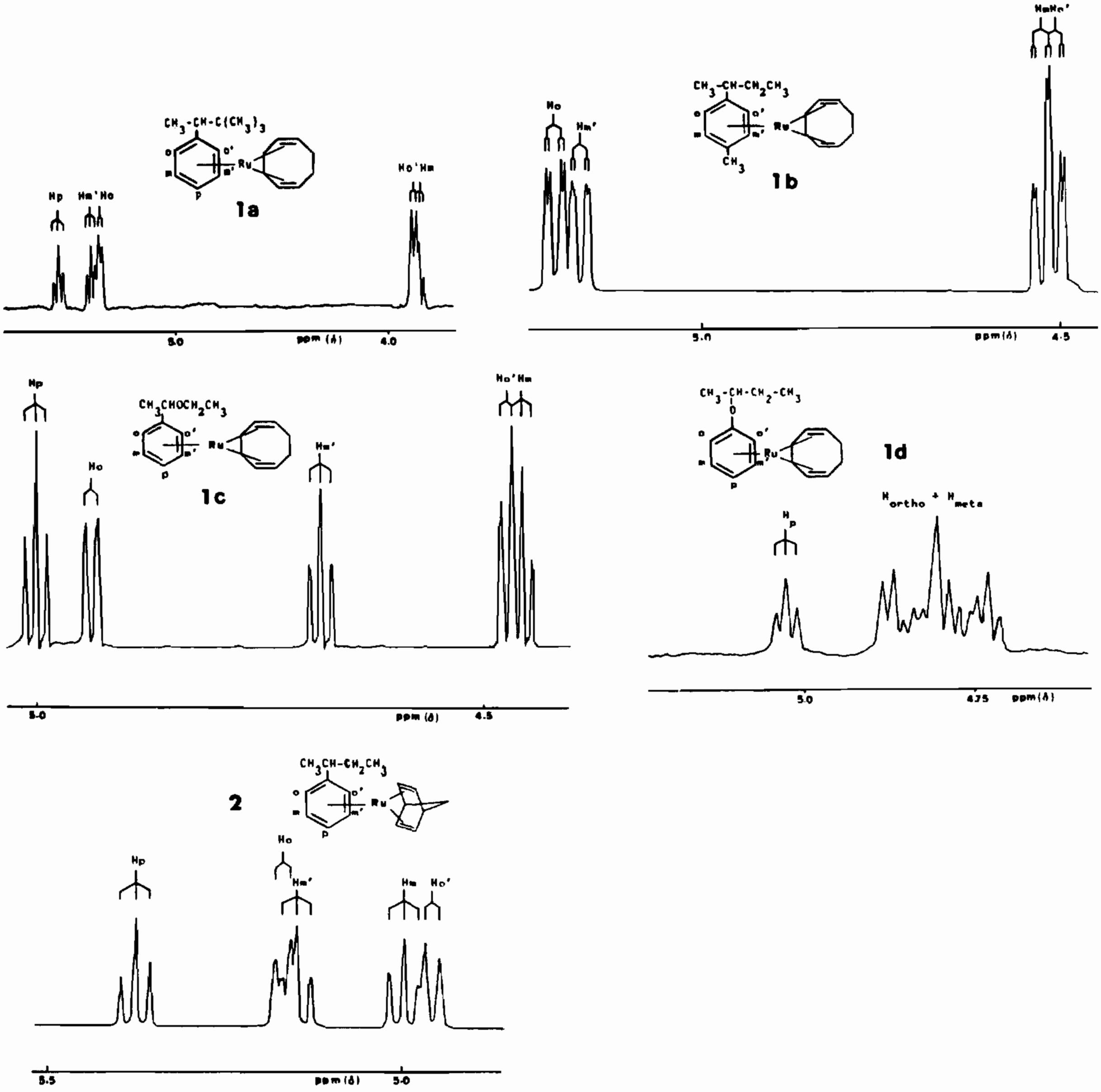
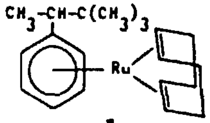
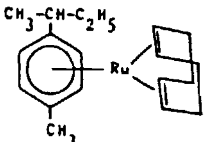
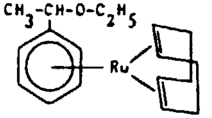
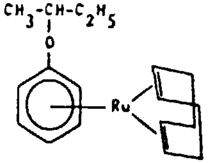
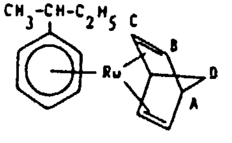


Fig. 2. ^1H NMR spectra (aromatic protons) of complexes **1a–d** and **2** at 270 MHz in C_6D_6.

TABLE I. Analytical and Spectroscopic Data of Ru(η^6-arene)(η^4-diene) Complexes

Compound	Yield (%)	Analysis[a] (%)		^{1}H NMR data[b]		
		C	H	Aromatic ligand		
				Arene protons[c]	Others	Diene
 **1a**	80	64.01 (64.69)	7.85 (8.09)	5.55 (t, 1H, Hp, $J_{pm} = J_{pm'} = 5.4$) 5.40 (t, 1H, Hm', $J_{m'p} = J_{m'o} = 6.4$) 5.35 (d, 1H, Ho, $J_{om} = 5.2$) 3.88 (d, 1H, Ho') 3.85 (t, 1H, Hm)	1.98 (q, 1H, $\mathrm{C}H$) 1.52 (d, 3H, $\mathrm{C}H_3$–CH, $J = 7.0$) 0.90 (s, 9H, $(\mathrm{C}H_3)_3\mathrm{C}$)	3.65 (m, 2H, $\mathrm{C}H$) 3.45 (m, 2H, $\mathrm{C}H$) 2.45 (m, 4H, $\mathrm{C}H_2$) 2.30 (m, 4H, $\mathrm{C}H_2$)
 **1b**	80	63.54 (63.87)	7.61 (7.84)	5.21 (dd, 1H, Ho, $J_{om} = 5.5; J_{oo'} = 1.3$) 5.17 (dd, 1H, Hm', $J_{m'o'} = 5.5; J_{mm'} = 1.2$) 4.53 (dd, 1H, Hm) 4.51 (dd, 1H, Ho')	2.18 (s, 3H, $\mathrm{C_6H_4}$–$\mathrm{C}H_3$) 2.04 (m, 1H, $\mathrm{C}H$) 1.84 (m, 1H, $\mathrm{C}H\mathrm{H}$) 1.65 (m, 1H, $\mathrm{CH}H$) 1.51 (d, 3H, CH–$\mathrm{C}H_3$, $J = 7.0$) 1.11 (t, 3H, $\mathrm{CH_2}$–$\mathrm{C}H_3$, $J = 7.4$)	3.68 (m, 2H, $\mathrm{C}H$) 3.45 (m, 2H, $\mathrm{C}H$) 2.58 (m, 8H, $\mathrm{C}H_2$)
 **1c**	50	59.92 (60.18)	7.33 (7.24)	5.00 (t, 1H, Hp, $J_{pm} = J_{pm'} = 5.5$) 4.90 (d, 1H, Ho, $J_{om} = 5.2$) 4.47 (t, 1H, Hm', $J_{m'p} = J_{m'o'} = 5.5$) 4.12 (d, 1H, Ho') 4.10 (t, 1H, Hm)	3.57 (m, 1H, $\mathrm{C}H$) 3.51 (m, 1H, $\mathrm{C}H\mathrm{H}$) 3.49 (m, 1H, $\mathrm{CH}H$) 1.12 (d, 3H, CH–$\mathrm{C}H_3$, $J = 6.5$) 0.89 (t, 3H, $\mathrm{CH_2}$–$\mathrm{C}H_3$, $J = 7.0$)	3.17 (m, 4H, $\mathrm{C}H$) 2.06 (m, 8H, $\mathrm{C}H_3$)
 **1d**	70	60.01 (60.18)	7.42 (7.24)	5.30 (t, 1H, Hp, $J_{mp} = J_{m'p} = 5.5$) 4.9–4.7 (m, 4H, Hoo'mm')	3.82 (m, 1H, $\mathrm{C}H$) 1.40 (m, 2H, $\mathrm{C}H_2$) 1.05 (d, 3H, CH–$\mathrm{C}H_3$, $J = 6.2$) 0.73 (t, 3H, $\mathrm{CH_2}$–$\mathrm{C}H_3$, $J = 7.3$)	3.36 (m, 4H, $\mathrm{C}H$) 2.26 (m, 8H, $\mathrm{C}H_2$)
 **2**	43	62.54 (62.39)	6.61 (6.72)	5.38 (t, 1H, Hp, $J_{pm} = J_{pm'} = 5.5$) 5.17 (d, 1H, Ho, $J_{om} = 5.5$) 5.16 (t, 1H, Hm', $J_{o'm'} = 5.5$) 5.01 (t, 1H, Hm) 4.96 (d, 1H, Ho')	2.25 (m, 1H, $\mathrm{C}H$) 1.78 (m, 1H, $\mathrm{C}H\mathrm{H}$) 1.62 (m, 1H, $\mathrm{CH}H$) 1.44 (d, 3H, CH–$\mathrm{C}H_3$, $J = 6.9$) 1.10 (t, 3H, $\mathrm{CH_2}$–$\mathrm{C}H_3$, $J = 7.4$)	3.67 (m, 2H, H_A, $J_{AB} = J_{AD} = 3.2; J_{AC} = 1.6$) 3.16 (m, 4H, $H_B + H_C$) 1.47 (m, 2H, H_D)

[a] Calculated values are given in parentheses. [b] Spectra were measured at 270 MHz in [^{2}H$_6$] benzene solution; δ scale; coupling constants, J, are in Hz; s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet. [c] o = *ortho*, m = *meta*, p = *para*.

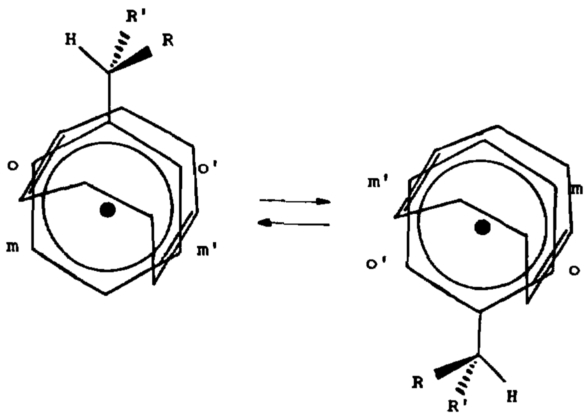


Fig. 3. Possible rotamers of the chiral complexes Ru(η^6-arene)(η^4-diene) present in solution.

These preparative routes provide access to a wide range of Ru(η^6-arene)(η^4-diene) complexes containing different arenes and/or dienes which are in most cases not easily obtained by other methods.

Complexes **1a–d** and **2** are yellow low-melting crystalline compounds, soluble in common organic solvents. They have been identified by elemental analysis and spectroscopic measurements (Table I). The aromatic region of the ^{1}H NMR spectra of these complexes, recorded at room temperature, is shown in Fig. 2; no important difference has been observed in a temperature range of +60 to −100 °C. One outstanding feature of these spectra is the large upfield shift of the ring hydrogen atoms [8] and the significant anisochronicity of both the *ortho* and *meta* protons of the arene ring. In complex **1a** the upfield coordination shifts $\Delta\delta$ ($\Delta\delta = \delta$ (free ligand) $- \delta$ (complex)) are 1.89 and 2.59 δ for the *ortho* and *ortho'* protons Ho and Ho', and 2.57 and 1.93 δ for the *meta* protons Hm and Hm'. The presence of a methyl group in the *para* position of the substituted phenyl ring (complex **1b**) does not appreciably affect such an anisochronicity, the $\Delta\delta$ values being quite similar to those found for the corresponding complex Ru{η^6-$C_6H_5CH(Et)CH_3$}(η^4-COD) [2]. When the chiral carbon atom is not directly bonded to the phenyl ring (complex **1d**) such chemical shift differences are very small, thus preventing assignment of the signals. In complex **1c**, containing an oxygen atom in the chiral group, $\Delta\delta$(Ho) is significantly less than $\Delta\delta$(Ho'), $\Delta\delta$(Hm) and $\Delta\delta$(Hm'), which suggests that Ho is close to the heteroatom of the chiral group. Inequivalence of the *ortho* and *meta* protons has been observed also in complex **2**, containing NBD as η^4-diene. This diene, in contrast to COD, cannot assume a flexible conformation, indicating that the conformation of the η^4-diene does not affect the phenomenon.

It can be seen that the inequivalence of the *ortho* and *meta* protons is present in all the reported examples and it is less evident when the chiral carbon atom is not directly bonded to the phenyl ring (**1d**). A surprising feature which appears from the ^{1}H NMR spectra is the particular value of the chemical shifts of the *ortho–meta'* and *ortho'–meta* protons, resulting in the following relationships: $\Delta\delta(\text{Ho}) \cong \Delta\delta(\text{Hm}')$ and $\Delta\delta(\text{Ho}') \cong \Delta\delta(\text{Hm})$. $\Delta\delta$(Ho) is different from $\Delta\delta$(Hm') only for complex **1c** (Fig. 2), probably because of the proximity of Ho to the heteroatom, as mentioned above. It seems reasonable to assume that the observed $\Delta\delta$ values can be related to the presence of rotamers arising from different orientations of the arene with respect to the coordinated diene. The X-ray structure of Ru(η^6-C_6H_6)(η^4-COD) shows that the planes of the η^6-arene and the coordinated double bonds of the diene are almost parallel [9]. Therefore, taking into account the similarity of the ^{1}H NMR spectra of complexes with flexible and rigid diene (**1a–d**, **2**), the presence of rotameric conformations which generate similar environments for the protons Ho, Hm' and, separately, Ho', Hm can be accounted, as pictured in Fig. 3.

^{1}H NMR studies on the corresponding isoelectronic complexes [Rh(η^6-arene)(η^4-diene)]PF_6 are in progress. Preliminary results show that the general features of the spectra are quite similar to those observed for the ruthenium complexes, indicating that the phenomenon is independent of the nature of the metal.

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