Journal of Organometallic Chemistry 791 (2015) 107–118

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Ruthenium complexes containing hexamethylbenzene and butadienesulfonyl ligands: Synthesis and reactivity toward CO, nitrogen and phosphine ligands

José Ignacio de la Cruz-Cruz, M. Angeles Paz-Sandoval*

Departamento de Química, Centro de Investigación y de Estudios Avanzados del IPN, Av. IPN # 2508, Col. San Pedro Zacatenco, México D. F. 07360, Mexico

ARTICLE INFO

Article history:
Received 2 March 2015
Received in revised form
7 May 2015
Accepted 8 May 2015
Available online 23 May 2015

Keywords:
Ruthenium
Hexamethylbenzene
Butadienesulfonyl ligand
Butadienesulfinate salts
Deuterated nitrogen ligands

ABSTRACT

The heterometallic tetranuclear complexes [(HMB)Ru(Cl)$_2$(5-η-CH$_2$CHCRCHSO$_2$)(Li)(THF)]$_2$ [R = H, **3**; Me, **4**] were synthesised by reaction of [(HMB)Ru(μ-Cl)Cl]$_2$ (**1**) (HMB = η^6-C$_6$Me$_6$) and an excess of [CH$_2$CHCRCHSO$_2$Li] (R = H, Me), whereas mononuclear complexes [(HMB)Ru(Cl)(1,2,5-η-CH$_2$CHCRCHSO$_2$)] (R = H, **7**; Me, **8**) were obtained when [CH$_2$CHCRCHSO$_2$K] was used. Complex [(HMB)Ru(Cl)$_2$(5-η-CH$_2$CHCHCHSO$_2$)(K)(THF)]$_2$ (**5**) was spectroscopically detected by ^{1}H and ^{13}C NMR. Solution experiments demonstrated that the above mentioned compounds transform into new ones by simply dissolving or standing in solution. Isolation of the ion pair complex [(HMB)Ru(Cl)(5-η-CH$_2$CHCHCHSO$_2$)(5-η-CH$_2$CHCHCHSO$_2$K)] (**9**) and subsequent addition of AgBF$_4$ results in the formation of [(HMB)Ru(1,2,5-η-CH$_2$CHCHCHSO$_2$)(5-η-CH$_2$CHCHCHSO$_2$)] (**10**). Further reactivity of complexes **7** and **8** showed the addition reactions of a variety of ligands such as CO, deuterated and non-deuterated pyridine and acetonitrile, resulting in complexes of the type [(HMB)Ru(Cl)(5-η-CH$_2$CHCRCHSO$_2$)L] [R = H, L = CO, **11**; Py, **12**, Py-d$_5$, **12D**; R = Me, L = Py, **13**, Py-d$_5$, **13D**; R = H, L = CD$_3$CN, **14D**]. Treatment with phosphines afforded the addition products [(HMB)Ru(Cl)(5-η-CH$_2$CHCHCHSO$_2$)L] (L = PMe$_3$, **15**; PPh$_3$, **16**; PHPh$_2$, **17**) and the formation of the dichloride complexes [(HMB)Ru(Cl)$_2$PR$_3$] **15Cl**, **16Cl** and **17Cl**, respectively, as by-products. Compounds **8** and **15** were characterized by single crystal X-ray crystallography. Additionally, a comparative study with isoelectronic and related compounds was undertaken.

1. Introduction

In the past few years, many "half-open sandwich" and "half-sandwich" compounds have been prepared based on the well-known cyclic cyclopentadienyl (Cp) or pentamethylcyclopentadienyl (Cp*) and the acyclic heteropentadienyl ligands [1,2]. The latter type of ligands incorporate heteroatoms such as oxygen [3–5], nitrogen [6] and sulfur [7] into the pentadienyl fragment. In spite of some achievements [8,9], the development of the analogue chemistry to the above mentioned five-membered ligands, with the ancillary arene ligand HMB (HMB = η^6-C$_6$Me$_6$) remain poorly studied. The potential of this chemistry needs to be evaluated because of the advantage offered by the coordination of bioligands to the (η^6-arene)Ru fragment in comparison to Cp*Ru(II) sandwich compounds [10]. Compounds based on Cp*MCl fragment, such as (Cp*RuCl)$_4$ and [Cp*M(μ-Cl)Cl]$_2$ (M = Rh, Ir) react, in THF, with lithium butadienesulfinate salts [CH$_2$CHCRCHSO$_2$Li] (R = H, **2Li**, Me **2Li–Me**) affording tetrameric [Cp*Ru(Cl)(1,2,5-η-CH$_2$CHCRCHSO$_2$)(Li)]$_4$ (**A**, Scheme 1) [11] and heterometallic tetranuclear [Cp*M(Cl)$_2$(5-η-CH$_2$CHCHCHSO$_2$)(Li)(THF)]$_2$ (M = Rh, **3Cp*Rh** [12]; Ir, **3Cp*Ir** [13], Scheme 1) compounds. The tetrameric **A** and **3Cp*Ir** can be easily transformed into the mononuclear [Cp*Ru(1-5-η-CH$_2$CHCRCHSO$_2$)] (**B**) and [Cp*Ir(Cl)(1,2,5-η-CH$_2$CHCHCHSO$_2$)] (**7Cp*Ir**) by displacement of LiCl and THF, Scheme 1, or using directly the potassium butadienesulfinate in presence of Cp*MCl$_n$ moieties. The size of the alkali-metal is crucial in determining the nuclearity of the resulting complexes. The reactions with an excess of potassium butadienesulfinate afford labile mononuclear ion pairs, such as [Cp*Ru(1,2,5-η-CH$_2$CHCHCHSO$_2$)(5-η-CH$_2$CHCHCHSO$_2$K)] (**9Cp*Ru**) [11] and [Cp*Rh(Cl)(5-η-CH$_2$CHCHCHSO$_2$)(5-η-CH$_2$CHCHCHSO$_2$K)] (**9Cp*Rh**) [12]. The latter reacts with AgBF$_4$ to give the corresponding [Cp*Rh(1,2,5-η-

* Corresponding author.
E-mail address: mpaz@cinvestav.mx (M.A. Paz-Sandoval).

http://dx.doi.org/10.1016/j.jorganchem.2015.05.023
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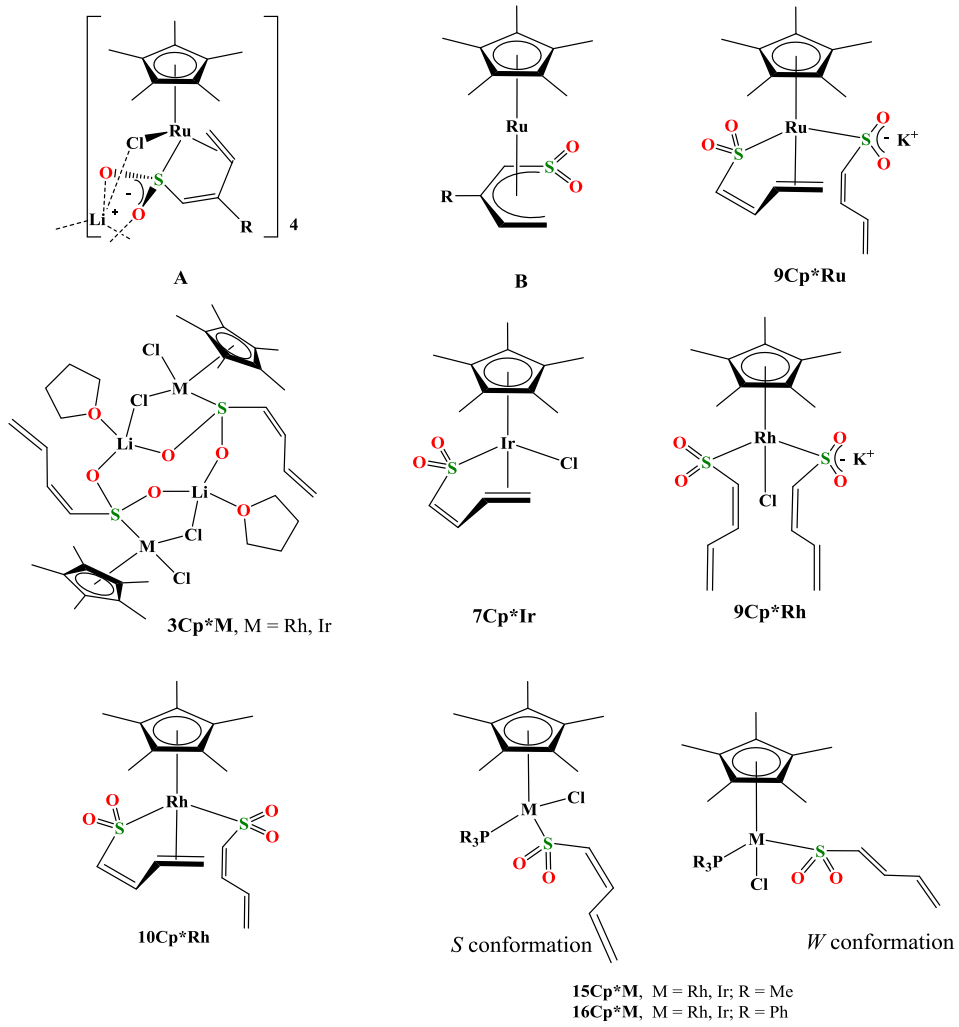


Scheme 1. Examples of half-open sandwich and half-sandwich compounds with butadienesulfonyl and butadienesulfinate ligands [11–14].

$CH_2CHCHCHSO_2$)(5-η-$CH_2CHCHCHSO_2$)] (**10Cp*Rh**) [12], Scheme 1.

The metathesis reaction with $Cp^*MCl_2PR_3$ (M = Rh, Ir, R = Me, Ph) takes place in the presence of [$CH_2CHCHCHSO_2K$] (**2K**) to afford [$Cp^*M(Cl)(5\text{-}\eta\text{-}CH_2CHCHCHSO_2)(PR_3)$] (M = Rh, Ir, R = Me, **15Cp*M**; R = Ph, **16Cp*M**, Scheme 1) [14] where the butadiensulfonyl ligand adopts both *S* (*ZE*) and *W* (*EE*) conformations, the former being the kinetic product whereas the latter the thermodynamic. Addition of PMe_3 and PPh_3 to compound **B** (Scheme 1) affords [$Cp^*Ru(1,2,5\text{-}\eta\text{-}CH_2CHCRCHSO_2)(PR'_3)$] (R = H, Me, R′ = Me, Ph) [15].

Related ruthenium sulfur chemistry of sandwich compounds containing HMB and thiophene ligands, such as [(HMB)Ru(η^5-C_4R_4S)][OTf]$_2$ and [(HMB)Ru(η^4-C_4HR_4S)][PF_6] [R = H, Me] have shown unique and varied bonding modes, as well as ready accessibility of the $Ru^{II/0}$ redox couple in (HMB)Ru(η^4-C_4R_4S) [R = H, Me] [16]. The protonated reduced thiophene complex leads to C–S cleavage, affording the ring-opened thiapentadienyl complex [(HMB)Ru(η^5-C_4H_5S)][PF_6] [17,18].

Due to the known similarity in many aspects of the [(HMB)Ru(μ-Cl)Cl]$_2$ chemistry to that of the neutral isoelectronic [Cp^*M(μ-Cl)Cl]$_2$ (M = Rh, Ir), as nicely and extensively shown by Bennett [19], Maitlis [20] and co-workers, we decided to do a comparative study between these precursors and their reactivity towards the butadienesulfonyl ligand.

Herein, we expand the chemistry of arene ruthenium compounds bearing a butadienesulfonyl or butadienesulfinate ligands, by describing a new series of compounds (HMB)Ru(Cl)L, (HMB)Ru(Cl)$_2$L′, (HMB)Ru(Cl)(L)(L′), (HMB)Ru(Cl)(L)(L″) and (HMB)Ru(L)$_2$ (L = butadiensulfonyl, L′ = butadiensulfinate; L″ = $2e^-$ donor). The study also includes some derivatives with π and σ complementary ligands, such as CO and phosphines; nitrogen ligands, such as pyridine, acetonitrile and their corresponding deuterated species; as well as ion-pair derivatives from the butadienesulfinate lithium and potassium salts. Therefore, a detailed analysis of the steric and electronic effects, as well as the influence of the substituents in different ligands is described.

2. Results and discussion

2.1. Synthesis and spectroscopic characterization of (Hexamethylbenzene)Ruthenium(butadienesulfonyl) complexes

*2.1.1. Tetranuclear ruthenium-alkali-metal compounds **3**–**5** and mononuclear ruthenium compounds **6**–**10***

The chloro arene ruthenium dimer [(HMB)Ru(μ-Cl)Cl]$_2$ (**1**) reacted with an excess of lithium butadienesulfinate

[$CH_2CHCRCHSO_2Li$] (R = H, **2Li**; Me, **2Li**–**Me**) in THF to give the heterometallic complexes [(HMB)Ru(Cl)$_2$(5-η-$CH_2CHCRCHSO_2$)(-Li)(THF)]$_2$ [R = H, **3**, 53%; Me, **4**, 40%], Scheme 2.

The K-analogue of complex **3**, namely compound **5**, was detected spectroscopically by ^{1}H and ^{13}C NMR in a tube-scale experiment. It was prepared by mixing potassium butadienesulfinate-based ligand **2K** and **1**. When **2K** and **2K**–**Me** are used in the reaction with **1**, instead of lithium salts **2Li** and **2Li**–**Me**, mononuclear yellow-orange **7** and yellow mustard **8** compounds are obtained in 54 and 46% yield, respectively, as described in Scheme 2. The formation rate of **7** and **8** depends on the dielectric constant of the solvent employed, being faster in chloroform (ε = 4.7, 1 h, **7**; 30 min, **8**) than in THF (ε = 7.4, 3 h, **7**; 2h, **8**) or acetone (ε = 20.7, 6 h, **7**), suggesting that the limiting step occurs *via* a neutral transition state. In Scheme 3 a proposed mechanism for the formation of compound **7** is described, where the addition of **2K** to **1** afforded the tetranuclear compound **5**, spectroscopically observed, followed by the elimination of THF which gave the saturated ion pair **i**. After that, due to the loss of KCl, the ion pair **i** converts into the coordinatively unsaturated intermediate **ii** with the immediate coordination of the terminal double bond to afford **7**. The same mechanism is proposed for compound **8**.

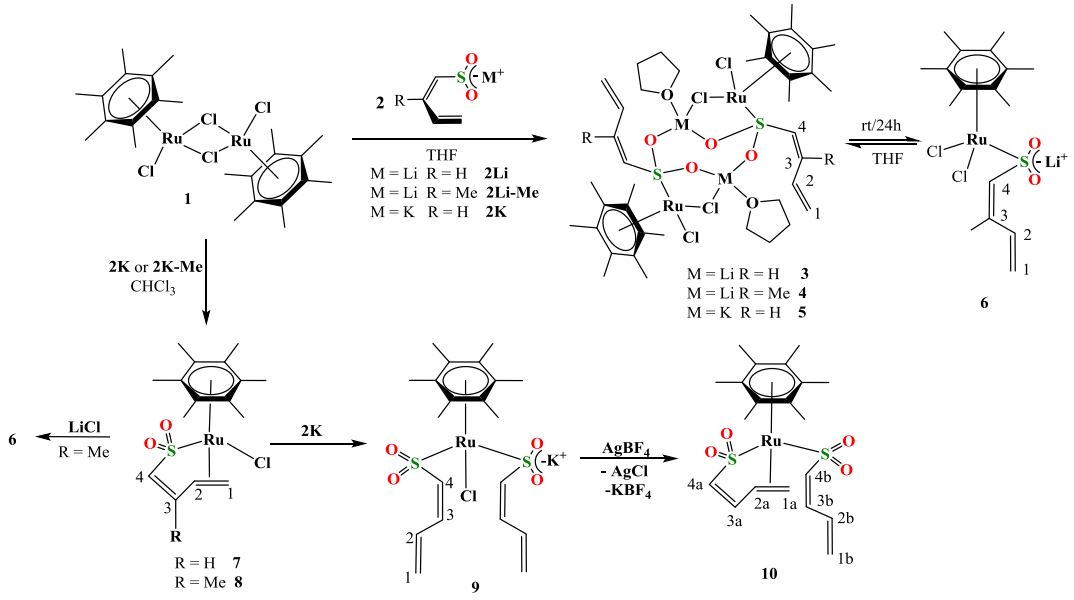
The ion-pair complexes **6** and **9** (Scheme 2) were isolated from the addition of 1.5 equiv of LiCl to **8** and the reaction of **7** with **2K** in a molar ratio 1:10 in 62.4% and 65.3%, respectively. In contrast, when complex **8** was treated with **2K**–**Me** under otherwise identical conditions as described for **9**, an intractable mixture of (HMB)Ru-containing complexes was obtained. Nonetheless, complex [(HMB)Ru(Cl)(5-η-$CH_2CHCMeCHSO_2$)(5-η-$CH_2CHCMeCHSO_2K$)] (**9Me**) was detected by NMR spectroscopy. Addition of $AgBF_4$ to **9** in acetone solution resulted in the formation of [(HMB)Ru(1,2,5-η-$CH_2CHCHCHSO_2$)(5-η-$CH_2CHCHCHSO_2$)] (**10**) in 53.4% yield, Scheme 2.

Compound **7** crystallizes from CH_2Cl_2/hexane (1:2) solution at −20 °C, in the monoclinic space group P21/a, with four crystallographically independent molecules in the asymmetric unit. The quality of the crystals was poor and, unfortunately, no detailed structural information could be obtained. Nevertheless, there was no doubt about the composition and connectivity of the atoms in this molecule, as described in the Supporting information. In contrast to the molecular structure of **7**, the methyl-substituted compound **8** gave unquestionable evidence of the molecular structure. The ruthenium atom is found in a distorted-octahedral geometry and coordinated to one HMB ligand and one $\eta^{1,2,5}$-butadienesulfonyl ligand through the terminal double bond and sulfur atom; the chloride atom completes the electronic demand for a coordinatively saturated complex **8**, (Fig. 1).

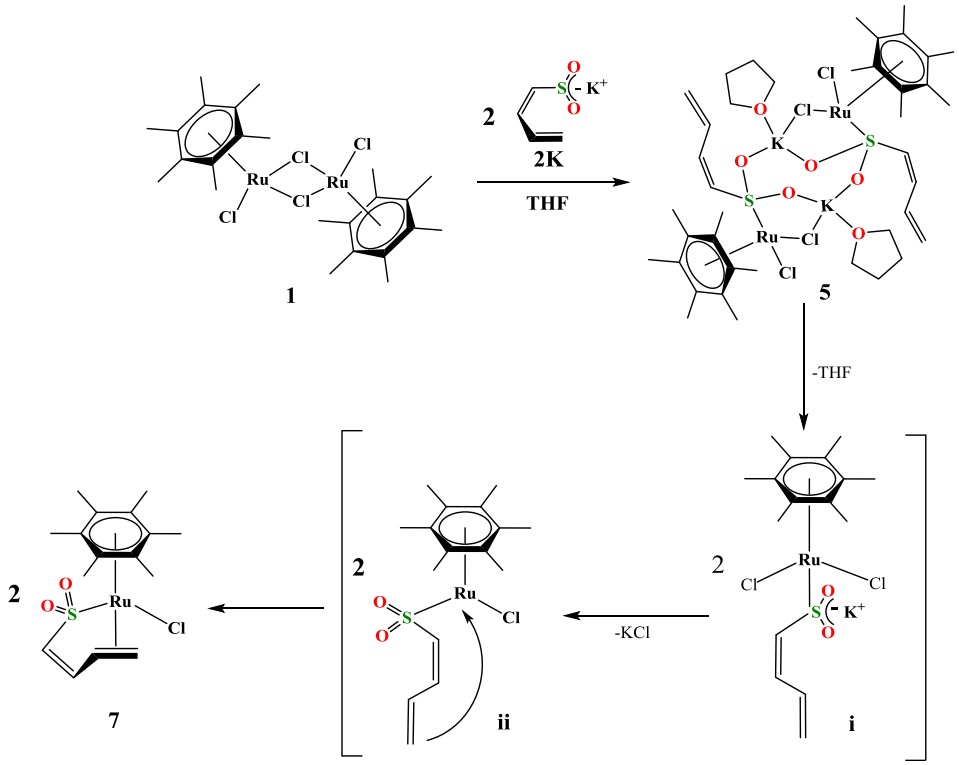
Compound **8** crystallizes in a monoclinic system with a space group C 2/c with four molecules in the asymmetric unit and THF as solvate. The bond lengths C1–C2 and C3–C4 [1.405(8), 1.303(9) Å] shown that the terminal double bond of the butadienesulfonyl ligand was coordinated to the ruthenium center, which was clearly demonstrated by the enlargement of the bond length due to the retrodonation of C1–C2; while the internal C3–C4 double bond distance is in agreement with the typical sp^2 bond length. The C4–S1, S1–O1 and S1–O2 bond lengths of 1.772(6), 1.459(5) and 1.472(4) Å reflect the typical values observed in **7Cp*Ir** [13] and tetranuclear complexes **3Cp*M** [M = Rh [12], Ir [13]] (Scheme 1).

The steric effect in the butadienesulfonyl ligand of **8** were reflected by the torsion angle [C1–C2–C3–C4 98.69(0.80)°], which is similar than those of Cp*Ru(1,2,5-η-$CH_2CHCHCHSO_2$)(PPh_3) [97.13(76)°] and wider compared with the carbonyl complex Cp*Ru(1,2,5-η-$CH_2CHCHCHSO_2$)(CO) [88.52(27)°] [15a]. The lack of planarity of the butadienesulfonyl ligand was reflected by the least-squares planes [64.689 (0.579)°].

The IR spectra of **3** and **4** for the vibration modes of the SO_2 in the region of 1154–1016 cm^{-1} showed strong and broad bands, due to the coordination of the lithium atom, those for **4** (ν_{as}1154, 1124; ν_s1021 cm^{-1}) were at higher wavenumber than those of **3** (ν_{as}1147, 1104; ν_s1016 cm^{-1}). The corresponding vibration modes of the SO_2 group in the IR of the mononuclear compounds **7** (ν_{as}1187, 1111, 1080; ν_s1047 cm^{-1}) and **8** (ν_{as}1182, 1118, 1071; ν_s1043 cm^{-1}) show narrow bands and, as expected, higher frequency values than those of **3** and **4** (see Supporting information). The ion-pair complexes **6** (ν_{as}1143, 1122, 1074; ν_s1029 cm^{-1}) and **9** (ν_{as}1156, 1110; ν_s1039 cm^{-1}) also showed broad bands, due to the alkali-metal interaction with the O=S=O fragment, as observed for compounds **3** and **4**. The IR was quite useful in order to identify indirectly the presence or absence of the alkali-metal in the butadienesulfinate and butadienesulfonyl complexes, as it has been



Scheme 2. Hexamethylbenzene ruthenium complexes with butadienesulfonyl and butadienesulfinate ligands.



Scheme 3. Proposed mechanism for the formation of compound **7**.

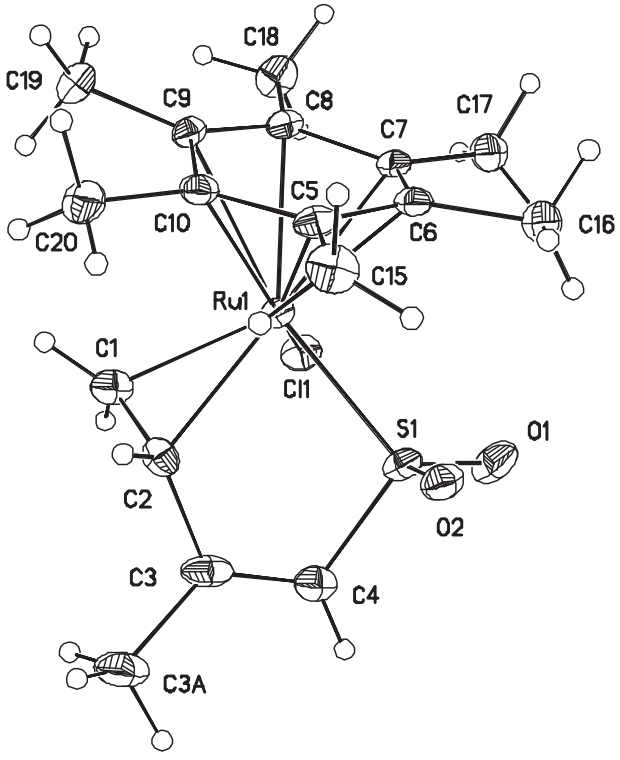
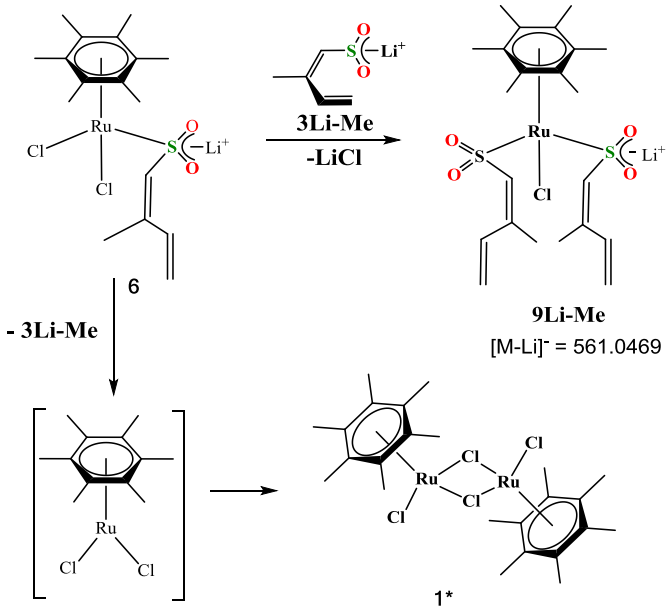


Fig. 1. Molecular structure of (HMB)Ru(Cl)(1,2,5-η-$CH_2CHCMeCHSO_2$) (**8**). Thermal ellipsoids at 45% probability level. Selected bond distances (Å): C1–C2, 1.405(8); C2–C3, 1.491(9); C3–C4, 1.303(9); C4–S1, 1.772(6); S1–O1, 1.459(5); S1–O2, 1.472(4); Ru1–S1, 2.3144(15); Ru1–Cl1, 2.4088(15). Selected bond angles (°): S1–Ru1–Cl1, 84.60(5); C1–C2–C3, 119.8(6); C2–C3–C4, 120.7(6); C3–C4–S1, 114.4(5). HMB(centroid)-Ru,1.7839 Å.

established for different sorts of derivatives, some of them described in Scheme 1. Compound **10** showed broader bands at ν_{as} 1179, 1112; ν_s1046 cm^{-1}, this was attributed to the presence of two different butadienesulfonyl ligands coordinated to the ruthenium atom.

The lability of compounds **3** and **4** hampered the detection of the molecular ion in the mass spectra. However, compound **3** showed, through the $(FAB)^+$technique, a peak detected at 989 m/z assigned to $[\mathbf{3}\text{-THF}]^+$, (see Supporting information). This data supports the presence of a higher molecular weight than those expected for discrete mononuclear entities. After several unsuccessful attempts to get the molecular ion or the crystalline structure of compound **3**, complementary qualitative electrochemical and physical Dynamic Laser-Light Scattering (DLS) techniques were carried out, in order to support the nature of **3**. The results obtained from both techniques, support the higher aggregation state of **3** compare to the mononuclear compound **7**, as described in detail in the Supporting information. Further characterization of complexes **7**–**10** was accomplished by ESI + TOF-MS. In the case of complex **6** it was possible to detect a peak at m/z = 561, in the ESI-TOF-MS mode, assigned to [(HMB)Ru(Cl)(5-η-$CH_2CHCMeCHSO_2$)(5-η-$CH_2CHCMeCHSO_2Li$)] (**9Li**–**Me**), without lithium, analogous to the potassium derivative **9** (see Supporting information). This result suggests the rearrangement of **6**, under the ionization process involved, to afford compound **1** along with **9Li**–**Me**, as described in Scheme 4.

2.1.1.1. Solution reactivity and NMR spectroscopic characterization of 3–10. ^1H and ^{13}C NMR spectra obtained from THF-d_8 solution support the proposed structure for **3** and **4** in which the butadienesulfonyl ligand shows typical chemical shifts for an non-coordinated unsaturated diene fragment (*e.g.* δ 5.18, H1; 5.15, H1'; 8.00, H2; 5.89, H3 and 6.46, H4, for compound **3**, which could be compared with the chemical shifts of the precursor salt **2Li**, 5.38,



Scheme 4. Mass spectrometry fragments observed in the rearrangement of **6**. *Observed by ^{1}H and $^{13}C\{^{1}H\}$ NMR.

H1; 5.31, H1'; 5.89, H2; 6.38, H3; 6.96, H4) [21a]. The highest frequency signal, assigned to H2, suggested an interaction between H2 and one of the oxygen atoms from the SO_2 moiety, this kind of interaction is also observed in solution and in the solid state for compound [(HMB)Ru(Cl)(5-η-$CH_2CHCHCHSO_2$)(PMe_3)] (**15**) [H2···O1, 2.3278 Å] (*vide infra*, Section 2.1.3) and in similar derivatives previously reported [12]. An *S* conformation of the butadienesulfonyl ligand in solution has been established for compound **3** by a *t*-ROESY experiment, which confirms the *trans* and *cis* coupling of the *S* conformer, showing spatial interaction between hydrogens H4 and H3, H3 and H1, and H2 and H1′, (see Supporting information). A singlet at δ 1.96 is assigned to the coordinated HMB, and two pairs of signals at δ 1.75, 3.59 as multiplets and 1.71, 3.56 as singlets are assigned to coordinated THF and the solvent residual signal, respectively. The corresponding carbon resonances of **3** for C1, C2, C3 and C4 at δ 119.8, 133.5, 128.6 and 138.2 confirm that the diene fragment is not coordinated.

According to the almost identical chemical shifts and coupling constants of compounds **3** and **4** we proposed similar molecular structures in solution. Moreover, the ^{7}Li NMR spectra of **3** and **4** showed broad singlets at 0.18 and 0.17 ppm. The analogy between the NMR spectroscopy data of **5** with **3** and **4** (except H3 and C3 in **4**) is indicative that the alkali-metal (M = Li, K) is interacting exclusively with the sulfonyl group, where a charge is delocalized along the O–S–O atoms, as it has been reported for other butadienesulfinate derivatives [21a,22].

Based on the similar chemical, spectroscopic and structural behavior of **3** and **4** with **3Cp*M** (M = Rh [12], Ir [13]) (Scheme 1), and the qualitative results obtained by electrochemical and DLS experiments, we propose analogue molecular structures for **3** and **4** to those confirmed for the Cp* derivatives, where the lithium butadienesulfinate ligand is solely added to the corresponding precursors.

Compound **3** exhibited the highest stability in THF-d_8 solution compared to **4** which showed partial transformation in THF-d_8 solution to the highly hygroscopic **6**, Scheme 2. Isolated compound **6** gave evidence of the partial transformation to compound **4** after 24 h in THF-d_8 (see Scheme 2 and Supporting information). The presence of lithium in **6** was confirmed through the ^{7}Li NMR spectrum as a sharp signal at 0.21 ppm (Δν = 18.2 Hz), which contrast to the broad signals observed in the heterometallic tetranuclear complexes **3** (Δν = 65.4 Hz) and **4** (Δν = 79.5 Hz). It should be mentioned that, in deuterated acetone, the ^{1}H and ^{13}C NMR spectra of compound **6** do not have evidence of coordinated THF, and it showed immediate transformation to produce starting material **1** after losing **2Li**–**Me**, and also the regeneration of compound **8** after losing LiCl (see Supporting information).

The ^{1}H and ^{13}C NMR spectra showed that when **5** remained in THF-d_8 for 1h, a mixture of **5** and **7** in a 1:1 ratio is observed. After 3h there was a mixture of the potassium ion-pair **9** and **5**, **7** in a 1.0:1.6:1.6 ratio, respectively; finally, a 1.0:2.7:2.0 ratio was observed after 24 h (see Supporting information). Compound **9** has only one set of signals for η^1-butadienesulfonyl and the η^1-butadienesulfinate ligands, which suggested that they were magnetically equivalent, as observed in other ion-pair complexes [11,12]. The integration of 2:1 with respect to the HMB ligand in **9** confirms the chemical similarity between both ligands (see Supporting information). Compound **9** showed similar hydrogen and carbon chemical shifts as those of **3**–**6**, which supported the same η^1 coordination of the corresponding butadienesulfinate ligands (see NMR data in the experimental section).

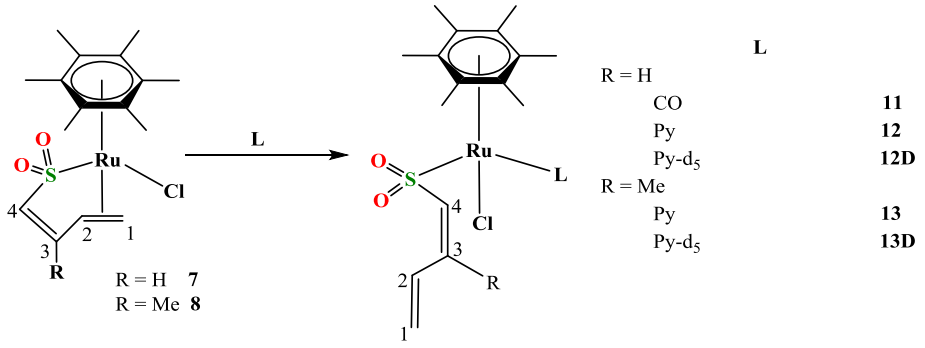
The bonding mode of the butadienesulfonyl ligand in **7** and **8** is evident from NMR spectroscopy. The ^{1}H NMR spectrum of **7** exhibit one signal of the HMB ligand at δ 2.12, and five hydrogens of the butadienesulfonyl ligand that confirms the preferred η^2 coordination mode of the terminal double bond (δ = 3.61, H1; 3.73, H1'; 5.04, H2) at lower frequencies, than those of the non-coordinated internal double bond (δ 5.86, H3; 6.40, H4), a similar spectrum was detected for **8**. This type of bonding was also confirmed in the ^{13}C NMR spectrum for both complexes, where complex **8** exhibits signals at higher frequencies corresponding to C3 and C4 non-coordinated internal carbon atoms at 141.5, 149.2 ppm, respectively, whereas the terminal-coordinated carbon atoms, C1 and C2, resonate at 65.8, 93.4 ppm, respectively. ^{1}H and ^{13}C $\{^{1}H\}$ NMR spectra of **10** were consistent with the different coordination modes of both η^1 and $\eta^{1,2,5}$ butadienesulfonyl ligands to the ruthenium atom.

2.1.2. Reactivity of compounds 7 and 8 with CO and nitrogen donor ligands

The synthesis of Ru(II) compounds of general formula [(HMB)Ru(Cl)(5-η-$CH_2CHCRCHSO_2$)L] [R = H, L = CO, **11**; Py, **12**, Py-d_5, **12D**; R = Me, L = Py, **13**, Py-d_5, **13D**] was carried out by mixing compounds **7** or **8** and the corresponding ligand L, under mild conditions, which yielded **11**–**13, 12D and 13D** ranging 51.9–81.3%, Scheme 5. All compounds are readily soluble in THF, CH_2Cl_2, acetone and chloroform. These derivatives were fairly stable in the solid state at room temperature and hygroscopic.

Further reactivity in solution was observed for complex **7**. Addition of carbon monoxide, at 1 atm, to a solution of **7** in $CHCl_3$ at ~40 °C gave, after 30 min, a deep yellow solution from which **11** was isolated in 81.3% yield. An IR spectrum in KBr revealed the presence of a carbonyl ligand in **11** showing a strong band at 1982 cm^{-1}. This result suggests a higher capability of back-bonding of the CO in comparison to [Cp*Ru(1,2,5-η-$CH_2CHCRCHSO_2$)CO] (R = H, 1991; Me, 1986 cm^{-1}) [15], and [(HMB)Ru(Cl)$_2$CO] (νCO, 1996 cm^{-1}) [23].

The reaction of **7** and **8** with pyridine and deuterated pyridine in $CHCl_3$ or CD_3CN solution at room temperature yielded yellow-orange products **12**, **12D**, **13** and **13D** which were isolated in 73.8, 65.5, 58.4 and 51.9%, respectively. The addition of MeCN or CD_3CN to **7** failed to give stable adducts, namely **14** and **14D**. It was possible to determine by ^{1}H NMR spectroscopy in CD_3CN at room temperature that the reaction between **7** and CD_3CN was not complete even after ten days, instead, an equilibrium of **7**:**14D** was observed



Scheme 5. Synthesis of compounds **11**–**13** and **12D**–**13D**.

in a 1:3 ratio (see Supporting information). The facile dissociation of CH_3CN in **14** compared to CD_3CN in **14D**, is significantly more evident. Nevertheless, attempts to isolate **14D** failed because of the lability of CD_3CN, and only compound **7** was recovered. The reaction of **8** with CD_3CN showed only traces of the corresponding deuterated adduct. The ^1H and ^{13}C NMR spectra of **11**–**13** and **12D**–**14D** displayed some general features and support the characteristic *S* conformation in the butadienesulfonyl ligand, as described in Section 2.1.1.1.

The ^1H and ^{13}C NMR chemical shifts at the highest frequencies were observed for **11**, where the proton (δ = 2.28) and the quaternary carbon (δ = 112.1) chemical shifts of the HMB ligand reflected the low contribution of π-acceptor capability of this arene ligand. In general, the quaternary carbon resonances of the HMB were diagnostic and clearly reflected the contribution of the donor ligands involved. The σ-nitrogen donor ligands in **12**–**13** and **12D**–**14D** and alkali-metal derivatives **3**–**6** showed chemical shifts for quaternary carbons in the range of δ = 94.7–98.3, whereas in complexes **7**, **8**, **10** and **11** more electron deficient quaternary carbon atoms of the HMB ligands (δ = 102.8–116.6) were found. An exception was the chemical shift of **9** (δ = 103.7), which can be explained due to a second butadienesulfonyl ligand coordinated to the ruthenium atom. According to these chemical shift values, the ^{13}C NMR spectra were quite useful, as they gave indirect information of other ligands coordinated to the ruthenium atom as well. In addition, both butadienesulfonyl and the butadienesulfinate are acting as better π-acceptor ligands than the ancillary arene ligands in **7**–**11**; while the opposite was observed for the σ-donor adducts.

The IR spectra of the neutral compounds **11**–**13** and **12D**, **13D** showed sharp bands, and significant differences in the corresponding stretching S=O frequencies: **11** (ν_{as}1201, 1055; ν_s1010 cm^{-1}); **12** (ν_{as}1162, 1071, 1109; ν_s1028 cm^{-1}); **12D** (ν_{as}1163, 1071, 1108; ν_s1030; cm^{-1}); **13** (ν_{as}1194, 1116, 1165; ν_s1037 cm^{-1}); **13D** (ν_{as}1189, 1119, 1159; ν_s1034 cm^{-1}) which was interpreted as the push–pull interplay of the different ligands, that is the π-acceptor CO and the σ-donor nitrogen ligands, according to the stretching vibrations at higher wavenumber in **11** compared to **12** and **13**.

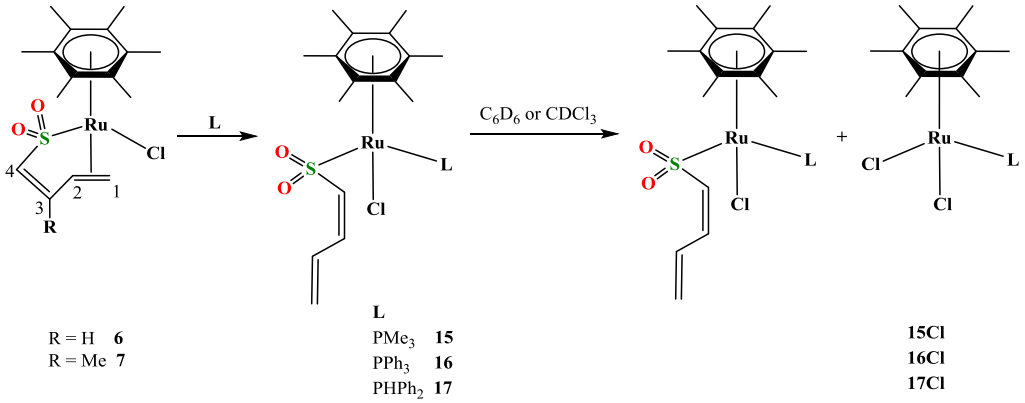
2.1.3. Reactivity of Compound 7 with phosphine ligands

The addition reaction of **7** with PMe_3 and $PHPh_2$ in THF and PPh_3 in benzene at room temperature afforded compounds [(HMB)Ru(Cl)(5-η-$CH_2CHCHCHSO_2$)L] (L = PMe_3, **15**; PPh_3, **16** and $PHPh_2$, **17**) in 65.6, 67.5 and 49.3% yield, respectively. These compounds in solution were always accompanied by the formation of the corresponding dichloride derivatives (HMB)$Ru(Cl)_2$L (L = PMe_3, **15Cl**; PPh_3, **16Cl** and $PHPh_2$, **17Cl**), Scheme 6.

The ^1H and ^{31}P NMR spectra showed each pair of compounds in a ratio **15**:**15Cl** (14.5:1.0), **16**:**16Cl** (10.5:1.0) and **17**:**17Cl** (10.2:1.0). Nonetheless the phosphine base adducts were fully characterized in solid state and in solution. The assignment of **15**–**17** through $^{31}P\{^1H\}$ NMR spectroscopy confirms the phosphorus coordination, and ^1H and ^{13}C spectroscopy gave evidence of the η^1 coordination (*e. g.* ^1H δ = 5.07, J = 17.2 Hz, H1; 5.10, J = 8.7 Hz, H1'; 8.44, J = 17.2, 10.5, 1.1, H2; 5.81, J = 11.1 Hz, H3; 7.20, J = 11.0 Hz, H4; and ^{13}C δ = 120.4, J = 156.8 Hz, C1; 134.0 J = 162.2, 10.8, 3.8 Hz, C2; 128.1 J = 158.4 Hz, C3; 140.8, J = 172.7 Hz, C4 for compound **15**) and the exclusive *S* conformation of the butadienesulfonyl ligand as described in Section 2.1.1.1 (see Supporting information). The isoelectronic compounds **15Cp*M** (M = Rh, Ir; PMe_3) and **16Cp*M** (M = Rh, Ir; PPh_3) have shown mixtures of isomers, where an *S* conformation of the butadienesulfonyl ligand can be transformed to the corresponding *W*, by heating the samples in solution [14]. In contrast, compounds **15** and **16** did not show any isomerization after two days in $CDCl_3$ solution even after heating the sample in an oil-bath at 65 °C for three days. During this treatment, a small quantity of **15Cl** was observed at early stages and reaching a 2:1 ratio of **15**:**15Cl** by the end of the reaction. This result suggested the presence of the electron deficient species (HMB)Ru(Cl)(PR_3) [24], which can easily coordinate another chloride, and gives evidence for the relatively weak ruthenium–sulfur bond. A similar trend has been observed in the reaction mixtures of **15Cp*M** and **16Cp*M** (M = Rh, Ir) and the corresponding Cp*M$(Cl)_2(PR_3)$ (M = Rh, Ir; R = Me, Ph) [14], and in a mixture of (HMB)Ru(CO)(CH_2=CH_2), (HMB)$Ru(Et)_2$ and [(HMB)$Ru(I)_2$(CO)] [25]. Unsuccessful results were obtained in the addition of phosphines to compound **8** due to the stronger coordination of the terminal double bond to the ruthenium atom. It should be mentioned that the metathesis reaction of (HMB)$Ru(Cl)_2PPh_3$ and **2K** was not useful as a synthetic alternative in the formation of **16**. In contrast to this result, the isoelectronic Cp*M$(Cl)_2PPh_3$ (M = Rh, Ir) reacts with **2K** more efficiently to give the corresponding **16Cp*M** [14].

The IR spectra of phosphine derivatives **15**–**17** showed the highest wavenumber for the S=O symmetric stretching frequencies, for **16** (ν_s 1051; ν_{as} 1091, 1192 cm^{-1}), while **15** (ν_s 1040; ν_{as} 1069, 1110, 1168 cm^{-1}) and **17** (ν_s 1041; ν_{as} 1070, 1103, 1178, cm^{-1}) were quite similar, in spite of the different σ and π-capabilities of the corresponding PMe_3 and $PHPh_2$. While electronic factors may be significant, it is worth noting that the higher cone angle [26] of the PPh_3 ligand (145°) relative to the $PHPh_2$ (126°) or PMe_3 (118°) was sufficient to rationalize the different behavior observed.

Complex **15** was isolated as an air-stable yellow solid, which was recrystallized from methylene chloride/hexane at −30 °C. Adduct **15** crystallizes in an orthorombic system with a space group Pna21 with four molecules in the asymmetric unit and water as solvate. The molecular structure of **15** is shown in Fig. 2, and full data is provided in the Supporting information.



Scheme 6. Synthesis of compounds **15**–**17** and dichloride derivatives **15Cl**–**17Cl**.

The crystal structure shows a *pseudo*-octahedral geometry about the metal center with the HMB ligand occupying three coordination sites, with the other three sites occupied by one chloride, one trimethylphosphine and one butadienesulfonyl ligands.

The same chemical structure was confirmed in solution and in solid state, which was supported by the effective intramolecular interaction observed between H(2) and O(1) [2.3278 Å] of the 5-η-$CH_2CHCHCHSO_2$ coordinated ligand (van der Waals radius of 2.95 Å). A shorter distance was also observed from the intramolecular interaction between H(4) and Cl(1), (2.7444 Å) where van der Waals radius is 3.35 Å. The bond angles of this piano stool fragment gave evidence of the similar influence of the different ligands [S(1)-Ru(1)-P(1) 87.35(4)°, P(1)-Ru(1)-Cl(1) 87.70(4)°, S(1)-Ru(1)-Cl(1) 87.49(4)°]. Comparatively, the (HMB)Ru(Cl)$_2$PMe$_3$ [27] and (HEB)Ru(Cl)$_2$PMe$_3$ (HEB = Hexaethylbenzene) [28,29] complexes showed less symmetric coordination angles: 82.04(11) and 82.11(3)°; 84.96(11) and 82.11(3)°; 90.31(10) and 90.35(5)° for the P(1)–Ru(1)–Cl(1), P(1)–Ru(1)–Cl(2), and Cl(2)–Ru(1)–Cl(1) units, respectively. The torsional angle C1–C2–C3–C4 [−177.06(1.55)°] gave evidence of the *S* conformation of the butadienesulfonyl ligand and the planarity reflected by 4.37 (1.03)°.

The Ru–P [2.3417(11) Å] and Ru–Cl [2.4151(11) Å] bond lengths were in the expected range of typical mixed half-sandwich compounds, such as (HMB)Ru(Cl)$_2$PMe$_3$ [27] and (HEB)Ru(Cl)$_2$PMe$_3$ [28,29] where the corresponding bond lengths are Ru–P [2.343(3) and 2.343(1) Å] and Ru–Cl [2.422(3), 2.424(3) and 2.4181(9) Å]. The Ru–S distance [2.2996(11) Å] in **15** can be compared with the values of **15Cp*M** [M = Rh, 2.307(3); Ir, 2.301(3) Å] [14]. According to the bond lengths of the HMB coordinated ligand to the ruthenium atom [C(5)-Ru(1) 2.291 (4), C(6)-Ru(1) 2.233(4), C(7)-Ru(1) 2.253(4), C(8)-Ru(1) 2.307(3), C(9)-Ru(1) 2.277(4), C(10)-Ru(1) 2.267(4) Å], and in comparison with those of **15Cp*Ir** [C(5)-Ru(1) 2.165 (11), C(6)-Ru(1) 2.255(10), C(7)-Ru(1) 2.236(10), C(8)-Ru(1) 2.219(10), C(9)-Ru(1) 2.265(11) Å] it is clear that the (HMB)Ru moiety has lower π-acceptor capability compared to the Cp* ancillary ligand.

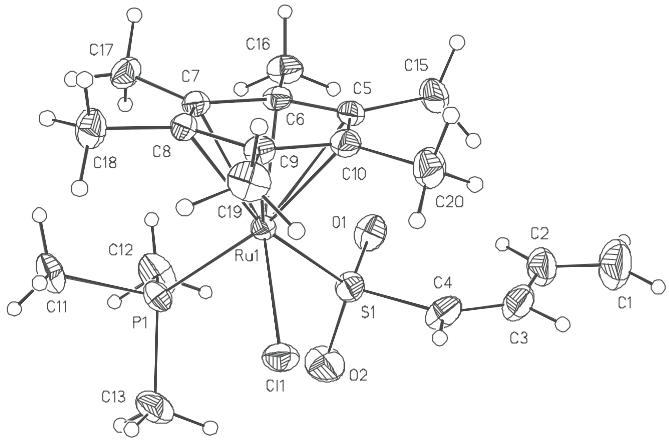


Fig. 2. Molecular structure of [(HMB)Ru(Cl)(5-η-$CH_2CHCHCHSO_2$)PMe$_3$] (**15**). Thermal ellipsoids at the 45% probability level. Selected bond distances (Å): C1–C2, 1.342(8); C2–C3, 1.435(8); C3–C4, 1.323(7); C4–S1, 1.794(5); S1–O1, 1.455(3); S1–O2, 1.462(4); Ru1–S1, 2.2996(11); Ru1–P1, 2.3417(11); Ru1–Cl1, 2.4151(11); P1–C13, 1.818(5). Selected bond angles (°): S1–Ru1–Cl1, 87.49(4); P1–Ru1–Cl1, 87.70(4); S(1)-Ru(1)-P(1) 87.35(4); C1–C2–C3, 124.7(6); C2–C3–C4, 130.4(5); C3–C4–S1, 128.4(4). HMB(centroid)-Ru, 1.7684 Å.

3. Conclusions

Representative examples of the butadienesulfonyl and butadienesulfinate ligands with the (HMB)RuCl fragment were synthesized and a comparative study was established with the analogue isoelectronic complexes **15Cp*M** and **16Cp*M** (M = Rh [12,14], Ir [14], and Cp*Ru(1,2,5-η-butadienesulfonyl)(L) [15].

The thermodynamic stability of the (HMB)Ru(Cl)(1,2,5-η-butadienesulfonyl) and (HMB)Ru(Cl)(5-η-butadienesulfonyl)(L) complexes is attributed, in part, to the steric bulk and electron-donating properties of the HMB ligand. In contrast, and as expected, the presence of the butadienesulfinate complexes in **3**–**6** and **9** induce low thermal stability, with **3** and **9** being the most stable at room temperature. Our preliminary experience with the Cp*M moieties (M = Ru [11], Rh [12,14], Ir [13,14]) and the butadienesulfinate and butadienesulfonyl ligands indicated that the latter ligand is less prone to hydrolysis compared to the (HMB)Ru derivatives, where even neutral derivatives **7**, **8**, **10**–**17** were found to be hygroscopic in the presence of traces of water. In the chemistry of the (HMB)Ru complexes it was possible to detect, at least spectroscopically, the potassium complex **5**, while no evidence of potassium derivatives was observed in the corresponding chemistry with the Cp*M (M = Ru, Rh, Ir) moiety.

The reactivity of **7** and **8** showed a strong reaction dependence on the nature of the substituent at the central carbon atom (C3) in the presence of nitrogen donor ligands and their corresponding deuterated analogues. The methyl group substituted in the butadienesulfonyl ligand of compound **8** favored equilibrium reactions.

The previous synthetic methods which have been exploited in the Cp*Ru(heteropentadienyl) [3–5,30] chemistry were not useful in the development of the analogous chemistry of the (HMB)Ru moiety [8,9].

More extensive exploration of the chemistry of these dioxo-

sulfur-based ligands with other transition metals may be of special interest because of their potential relevance in biological and synthetic processes, and current work in our laboratory is focused on the study of the cationic complexes [(HMB)Ru(1-5-η-$CH_2CHCRCHSO_2$)][X] (R = H, Me; X = BF_4, OTf).

4. Experimental section

Standard inert-atmosphere techniques were used for all synthetic procedures. The solvents were dried by standard methods (hexane and pentane with CaH_2 and THF with Na/benzophenone. CH_2Cl_2 and $CHCl_3$ with $CaCl_2$, benzene and toluene with Na, CH_3CN with P_2O_5) and distilled under argon prior to use. Compounds [(η^6-*p*-cymene)Ru(μ-Cl)Cl]$_2$ [31], [(HMB)Ru(μ-Cl)Cl]$_2$ (**1**) [31b] and the salts ($CH_2CHCRCHSO_2M$) (M = Li, R = H, **2Li**; M = Li, R = Me, **2Li**–**Me**; M = K, R = H, **2K**; M = K, R = Me, **2K**–**Me**) [21] were prepared according to literature procedures. All other chemicals were used as purchased from Pressure Chemical, Sigma–Aldrich, Strem Chemical, Merck, and J. T. Baker (industrial grade). All compressed gases were obtained from Infra. Argon (>99.9%), nitrogen (>99.5%) and carbon monoxide (>99.5%) were used as supplied without purification. IR spectra were recorded using KBr pellets (4000–400 cm^{-1}). Melting points are uncorrected. The ^1H, ^{13}C, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ and ^7Li NMR spectra are referenced internally using the residual protio and carbon solvent resonances relative to tetramethylsilane with deoxygenated deuterated solvents. External standard for ^{31}P was H_3PO_4 and LiCl/H_2O (9.7 mM) for ^7Li. Routine 2-D sequences in NMR were used for all assignments. High-resolution mass spectra were obtained by LC/MSD TOF with APCI as ionization source. LR/FAB Finnigan MAT95 $(FAB)^+$ mass spectrometer. Elemental analyses were performed in the Chemistry Department at Cinvestav.

4.1. General method for the synthesis of [(HMB)Ru(Cl)$_2$(5-η-$CH_2CHCRCHSO_2$)(Li)(THF)]$_2$ [R = H, 3; Me, 4]

Compound **1** (150 mg, 0.224 mmol) and the corresponding lithium salt **2Li** (84.0 mg, 0.677 mmol) or **2Li**–**Me** (144.0 mg, 1.043 mmol) were placed into a Schlenk flask equipped with a stir bar and the mixture was left under vacuum for 5 min. THF (50 mL) was added, and the mixture was stirred for 2h, changing from orange–brick to brown-amber. The THF solution was filtered through Celite (2.5 × 3.5 cm) before the resulting brown-amber filtrate was cannula filtered to a Schlenk flask. The THF was reduced under vacuum to ~3 mL, and pentane was added. After stirring this solution, a light-brown or dark-beige precipitate, respectively, appeared. The solid was filtered, rinsed with pentane (5 mL) and dried under vacuum affording compounds **3** (127.0 mg, 0.120 mmol, 53%) and **4** (98.0 mg, 0.090 mmol, 40%). Compounds **3** and **4** did not melt until 300 °C, and decomposed at 170 °C and 142 °C, respectively. Compound **3**: ^1H NMR (500 MHz, THF-d_8) δ = 5.18 (d, *J* = 17.0 Hz, H1), 5.15 (d, *J* = 10.2 Hz, H1′), 8.00 (dt, *J* = 10.6, 17.0 Hz, H2), 5.89 (t, *J* = 11.1 Hz, H3), 6.46 (d, *J* = 11.3 Hz, H4), 1.96 (s, C_6Me_6), 1.71, 3.56 (s, THF), 1.75, 3.59 (m, THF). ^7Li NMR (194 MHz, THF-d_8) δ = 0.18 (s, br). $^{13}C\{^1H\}$ NMR (125 MHz, THF-d_8) δ = 119.8 (C1), 133.5 (C2), 128.6 (C3), 138.2 (C4), 95.0 (C_6Me_6), 14.5 (C_6Me_6), 25.5, 67.3 (s, THF), 24.4, 67.5 (quintet, THF). IR(KBr): 3081(w), 2916(s,br), 2730(w,br), 2448(w,br), 2047(w,br), 1963(w,br), 1846(w,br), 1748(w,br), 1627(s), 1572(s), 1445(s), 1384(vs), 1293(w), 1236(w), 1147(vs), 1104(vs), 1071(vs,sh), 1016(vs,br), 918(s), 819(w), 786(m), 722(w), 672(vs), 551(s), 474(s). Anal Calcd for $C_{40}H_{62}Cl_4Li_2O_4Ru_2S_2 \cdot 4H_2O$ (1132.93): C, 42.41; H, 6.23. Found: C, 42.11; H, 6.32. Compound **4**: ^1H NMR (500 MHz, THF-d_8) δ = 5.27 (d, *J* = 17.5 Hz, H1), 5.13 (d, *J* = 11.0 Hz, H1′), 8.23 (dd, *J* = 10.8, 17.7 Hz, H2), 1.83 (s, Me3), 6.43 (s, H4), 1.95 (s, C_6Me_6), 1.70, 3.55 (s, THF), 1.75, 3.59 (m, THF). ^7Li NMR (194 MHz, THF-d_8) δ = 0.17 (s, br). $^{13}C\{^1H\}$ NMR (125 MHz, THF-d_8) δ = 115.1 (C1), 134.6 (C2), 132.8 (C3), 18.2 (Me3), 137.4 (C4), 95.0 (C_6Me_6), 14.5 (C_6Me_6), 24.4, 66.5 (quintet, THF), 25.5, 67.3 (s, THF). IR(KBr): 3023(w), 2914(s), 2863(m,sh), 2725(w,br), 2384(w,br), 2216(w,br), 1948(w,br), 1844(w,br), 1763(w,br), 1637(vs), 1575(s), 1439(vs), 1384(vs), 1251(w), 1154(vs), 1124(vs), 1021(vs,br), 922(m,sh), 835(s), 778(m,sh), 701(m,sh), 615(vs,br), 546(vs,br), 502(vs,br).

4.2. Identification of [(HMB)Ru(Cl)$_2$(5-η-$CH_2CHCHCHSO_2$)(K)(THF)]$_2$ (5)

An NMR tube containing 30.0 mg (0.045 mmol) of **1** and 14.0 mg (0.09 mmol) of **2K** in THF-d_8 was monitored by ^1H NMR for 24 h. ^1H NMR (500 MHz, THF-d_8) δ = 5.15 (d, *J* = 15.6 Hz, H1), 5.12 (d, *J* = 8.6 Hz, H1′), 8.03 (dt, *J* = 10.4, 17.2 Hz, H2), 5.84 (t, *J* = 11.2 Hz, H3), 6.37 (d, *J* = 11.3 Hz, H4), 1.94 (s, C_6Me_6), 1.70, 3.56 (s, THF). $^{13}C\{^1H\}$ NMR (125 MHz, THF-d_8) (in mixture with **7** and **9**, *vide supra*) δ = 119.3 (C1), 133.7 (C2), 127.1 (C3), 141.0 (C4), 94.7 (C_6Me_6), 14.6 (C_6Me_6), 24.2, 66.7 (quintet, THF).

4.3. Synthesis of [(HMB)Ru(Cl)$_2$(5-η-$CH_2CHCMeCHSO_2Li$)] (6)

Compound **8** (47.0 mg, 0.109 mmol) and 7.0 mg of LiCl (0.164 mmol) were placed into a Schlenk flask equipped with a stir bar and the mixture was left under vacuum for 5 min at room temperature. THF (10 mL) was added and gave a yellow-orange solution which turned amber after stirred 50 min at room temperature. After filtration, the THF was reduced under vacuum to ~2 mL, and pentane was added in order to induce precipitation of an orange solid, which was filtered, rinsed with pentane (2 × 5 mL), filtered again, and dried under vacuum. This afforded a yellow-orange compound **6** in 62.4% (31.2 mg, 0.068 mmol) which melted at 92–94 °C with decomposition. **6** was unstable at room temperature and was also quite hygroscopic. Compound **6**: ^1H NMR (500 MHz, THF-d_8) δ = 5.30 (d, *J* = 17.5 Hz, H1), 5.17 (d, *J* = 11.9 Hz, H1′), 8.26 (dd, *J* = 10.9, 17.8 Hz, H2), 1.87 (s, Me3), 6.46 (s, H4), 1.98 (s, C_6Me_6). ^7Li (194 MHz, THF-d_8) NMR δ = 0.21 (s). $^{13}C\{^1H\}$ NMR (125 MHz, THF-d_8) δ = 115.2 (C1), 134.6 (C2), 132.9 (C3), 18.2 (Me3), 137.4 (C4), 95.0 (C_6Me_6), 14.6 (C_6Me_6). ^1H NMR (500 MHz, $(CD_3)_2CO$) δ = 5.37 (dd, *J* = 0.9, 17.7 Hz, H1), 5.22 (dt, *J* = 1.6, 10.9 Hz, H1′), 8.16 (dd, *J* = 10.9, 17.7 Hz, H2), 1.88 (d, *J* = 1.2 Hz, Me3), 6.32 (s, H4), 1.98 (s, C_6Me_6). ^7Li NMR (194 MHz, $(CD_3)_2CO$) δ = 1.29 (s). $^{13}C\{^1H\}$ NMR (125 MHz, $(CD_3)_2CO$) δ = 116.5 (C1), 134.0 (C2), 134.1 (C3), 18.4 (Me3), 137.0 (C4), 95.3 (C_6Me_6), 14.8 (C_6Me_6). ESI-TOF: m/z 561.0469, error: 0.172732 ppm, DBE: 6.5, (see Scheme 4). IR(KBr): 2043(w,br), 1706(sh), 1634(vs,br), 1438(s,br), 1385(s,br), 1287 (w,br), 1253(w,br), 1152(s,br), 1124(sh), 1031(vs,br), 926(sh), 839(s,br), 724(w,br), 616(w,br), 497(w,br). Anal Calcd for $C_{17}H_{25}Cl_2LiO_2RuS \cdot 2H_2O$ (508.40): C, 40.16; H, 5.75. Found: C, 40.11; H, 5.79.

4.4. General method for the synthesis of [(HMB)Ru(Cl)(1,2,5-η-$CH_2CHCRCHSO_2$)] [R = H, 7; Me, 8]

Compound **1** (150 mg, 0.224 mmol) and the corresponding potassium salt **2K** (70.0 mg, 0.448 mmol) or **2K**–**Me** (92.0 mg, 0.540 mmol) were placed into a Schlenk flask equipped with a stir bar and the mixture was left under vacuum for 5 min $CHCl_3$ (40 mL) was added, and the mixture was stirred for 1h or 30 min, respectively, changing from orange–brick to yellow-orange or yellow-apple. The solution was filtered through Celite (2.5 × 3.5 cm) before the peach-yellow or brilliant-tangerine filtrate was cannula filtered to a Schlenk flask. The chloroform was reduced under vacuum to ~3 mL, and pentane was added; after stirring the

solution, a yellow-orange or orange precipitate appeared. The solid was filtered, rinsed with pentane (2 × 5 mL) and dried under vacuum, thus affording compounds **7** (101.0 mg, 0.243 mmol, 54%) and **8** in (88.0 mg, 0.205 mmol, 46%). Compounds **7** and **8** did not melt until 300 °C, and decomposed at 185 °C and 190 °C, respectively. Compound **7**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.61 (d, *J* = 13.3 Hz, H1), 3.73 (d, *J* = 9.7 Hz, H1′), 5.04 (dd, *J* = 10.0, 11.5 Hz, H2), 5.86 (t, *J* = 6.3 Hz, H3), 6.40 (d, *J* = 6.3 Hz, H4), 2.12 (s, C_6Me_6). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 67.2 (dd, *J* = 157.3, 166.9 Hz, C1), 91.0 (ddd, *J* = 158.8, 8.6, 4.8 Hz, C2), 129.9 (d_{ap}, *J* = 160.3 Hz, C3), 154.8 (dt, *J* = 180.4, 4.8 Hz, C4), 108.2 (s, C_6Me_6), 15.5 (q, 128.8 Hz, C_6Me_6). ESI + TOF: m/z 417.0225; error: 0.3508, DBE: 4.5. IR(KBr): 3040(w), 2927(w), 2865(w), 2612(w,br), 2180(w,br), 1743(w,br), 1662(w,br), 1625(w,br), 1452(m,br), 1386(s), 1290(m), 1264(w,sh), 1187(vs), 1111(m,sh), 1080(s,sh), 1047(vs), 966(w,sh) 808(m), 741(m), 656(m), 631(m), 538(s), 445(m). Anal Calcd for $C_{16}H_{23}ClO_2RuS$ (415.95): C, 46.20; H, 5.57. Found: C, 45.94; H, 5.20. Compound **8**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.72 (d, *J* = 13.4 Hz, H1), 3.71 (d, *J* = 9.2 Hz, H1′), 5.13 (dd, *J* = 9.9, 13.1 Hz, H2), 1.96 (s, Me3), 6.20 (s, H4), 2.11 (s, C_6Me_6). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 65.8 (C1), 93.4 (C2), 141.5 (C3), 19.6 (Me3), 149.2 (C4), 108.2 (C_6Me_6), 15.5 (C_6Me_6). ESI + TOF: m/z 431.0379; error: −0.1827, DBE: 4.5. IR(KBr): 3025(w), 2969(w), 2911(w), 2863(w), 2347(w,br), 2273(w,br), 1947(w,br), 1640(m), 1439(s), 1386(s), 1250(w), 1182(vs), 1118(s), 1071(s,sh), 1043(vs), 823(m), 775(w), 540(m), 500(m). Anal Calcd for $C_{17}H_{25}ClO_2RuS{\cdot}0.5H_2O$ (438.97): C, 46.52; H, 5.97; S, 7.30. Found: C, 46.51; H, 5.31; S, 7.40.

4.5. Synthesis of [(HMB)Ru(Cl)(5-η-$CH_2CHCHCHSO_2$)(5-η-$CH_2CHCHCHSO_2K$)] (9)

Compound **7** (117.0 mg, 0.281 mmol) and the corresponding potassium salt **2K** (470.0 mg, 3.01 mmol) were placed into a Schlenk flask equipped with a stir bar and the mixture was left under vacuum for 5 min and the temperature stabilized at 20 °C. THF (50 mL) was added, and the mixture was stirred 21 h at this temperature. The solution was filtered through Celite (2.5 × 3.5 cm) and the yellow-orange solution was filtered again with a cannula to a Schlenk flask. The THF was reduced under vacuum to ~3 mL, and pentane was added; after stirring this solution, a light-yellow precipitate appeared. The cream-yellow solid was filtered, rinsed with pentane (2 × 3 mL) and dried under vacuum to afford compound **9** in 65.3% (105.0 mg, 0.184 mmol) which decomposes at 210 °C. Compound **9**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.27 (d, *J* = 17.0 Hz, H1), 5.26 (d, *J* = 9.9 Hz, H1′), 7.74 (dt, *J* = 10.7, 16.3 Hz, H2), 5.94 (t, *J* = 11.1 Hz, H3), 6.48 (d, *J* = 11.0 Hz, H4), 1.98 (s, C_6Me_6). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 122.6 (t, *J* = 156.4 Hz, C1), 132.7 (dd, *J* = 161.7, 9.1 Hz, C2), 129.6 (d_{ap}, *J* = 154.5 Hz, C3), 139.5 (d, *J* = 172.7 Hz, C4), 103.7 (s, C_6Me_6), 15.8 (q, *J* = 128.8 Hz, C_6Me_6). ESI-TOF: m/z 533.0167, error: 0.0898 ppm, DBE: 6.5. IR(KBr): 3082(w), 3043(w), 3000(w), 2923(m), 2345(vw), 2169(w,br), 1966(w,br), 1847(w,br), 1709(w,br), 1627(m,br), 1571(m), 1440(m,br), 1385(m), 1307(m,br), 1156(vs), 1110(s,sh), 1039(vs), 918(m), 789(m), 715(w), 664(vs), 543(s), 474(m). Anal Calcd for $C_{20}H_{28}ClKO_4RuS{\cdot}H_2O$ (590.19): C, 40.70; H, 5.12. Found: C, 40.96; H, 5.26.

4.6. Synthesis of [(HMB)Ru(1,2,5-η-$CH_2CHCHCHSO_2$)(5-η-$CH_2CHCHCHSO_2$)] (10)

Compound **9** (50.0 mg, 0.087 mmol) and $AgBF_4$ (17.0 mg, 0.087 mmol) were placed into a Schlenk flask equipped with a stir bar; the solid mixture was left under vacuum for 5 min, then it was cooled at −110 °C (N_{2liq}/EtOH). Acetone (5 mL) was added, and the cooling bath was removed 5 min later, whereupon the resulting yellow solution was stirred until it reached room temperature plus an additional 1 h, in order to afford a lemon-yellow suspension. The solution was filtered and the solvent removed until dryness. The solid residue was dissolved in $CHCl_3$ (5 mL), stirred 5 min and filtered; then the solution evaporated until dryness, in order to give a yellow-beige solid in 53.4% (23.2 mg, 0.047 mmol). This solid decomposed at 173 °C, without melting below 250 °C. Compound **10**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.13 (d, *J* = 12.4 Hz, H1a), 5.33 (d, *J* = 16.3 Hz, H1b), 3.43 (d, *J* = 9.2 Hz, H1'a), 5.32 (d, *J* = 8.1 Hz, H1'b), 4.88 (t, *J* = 10.8 Hz, H2a), 7.64 (dt, *J* = 11.0, 16.3 Hz, H2b), 6.01 (d, *J* = 6.0 Hz, H3a), 5.96 (t, *J* = 11.0 Hz, H3b), 6.29 (d, *J* = 6.0 Hz, H4a), 6.47 (d, *J* = 10.6 Hz, H4b), 2.20 (s, C_6Me_6). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 62.5, (C1a), 124.1 (C1b), 87.1 (C2a), 131.4 (C2b), 130.3 (C3a), 132.2 (C3b), 152.5 (C4a), 135.7 (C4b), 116.6 (C_6Me_6), 16.4 (C_6Me_6). ESI + TOF: m/z 499.054559, error: 0.063640 ppm, DBE: 6.5. IR(KBr): 3056(w,br), 3001(w,br), 2926(m,br), 2863(w,br), 2608(w,br), 2379(w,br), 2214(w,br), 1966(w,br), 1723(m,br), 1627(s), 1571(m), 1448(m,br), 1386(s), 1293(m), 1179(vs,br), 1112(s,br), 1046(vs,br), 931(m,sh), 803(m), 744(m), 665(s), 540(s), 475(m). Anal Calcd for $C_{20}H_{28}O_4RuS_2{\cdot}0.5CHCl_3$ (557.33): C, 44.18; H, 5.15. Found: C, 44.09; H, 5.38.

4.7. Synthesis of [(HMB)Ru(Cl)(5-η-$CH_2CHCHCHSO_2$)(CO)] (11)

Compound **7** (53.0 mg, 0.127 mmol) was placed into a glass reactor equipped with a stir bar under vacuum for 5 min at room temperature. $CHCl_3$ (15 mL) was added, and then CO was introduced at 1 atm. The reaction mixture was warmed in an oil bath and stirred at 55–60 °C (~40 °C) for 30 min. The solution turned from bright-yellow to deep-yellow. After replacement of CO by an argon atmosphere, the solution was filtered and the volume of $CHCl_3$ was reduced to ~3 mL; pentane was added in order to induce the precipitation of a deep yellow solid, which was filtered, rinsed with 5 mL of pentane, filtered again, and dried under vacuum for 2 h. Compound **11** was obtained in 81.3% (46.0 mg, 0.104 mmol); it decomposed at 183 °C, without melting below 300 °C. Compound **11**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.33 (d_{ap}, *J* = 16.9 Hz, H1), 5.31 (d_{ap}, *J* = 10.1 Hz, H1′), 7.64 (m, *J* = 1.1, 10.7, 17.0 Hz, H2), 6.05 (t, *J* = 11.1 Hz, H3), 6.53 (dd, *J* = 0.8, 11.0 Hz, H4), 2.28 (s, C_6Me_6). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 123.9 (t_{ap}, *J* = 158.4, 5.8 Hz, C1), 131.7 (ddd, *J* = 162.7, 10.1, 3.8 Hz, C2), 132.1 (t_{ap}, *J* = 154.5 Hz, C3), 139.3 (d, *J* = 175.6 Hz, C4), 112.1 (s, C_6Me_6), 16.5 (Hz q, 130.0, C_6Me_6), 195.5 (s, *C*O). ESI + TOF: m/z 445.0174, error: 0.2509 ppm, DBE: 5.5. IR(KBr): 2925(m,br), 2068(m), 1982(vs), 1625(w), 1572(m), 1444(m,br), 1385(s), 1201(vs), 1055(vs), 1010(m,sh), 928(m), 780(s), 723(m), 669(vs), 636(s), 535(s), 477(m). Anal. Calcd for $C_{17}H_{23}ClO_3RuS{\cdot}H_2O$ (461.96): C, 44.20; H, 5.45; S, 6.94. Found: C, 44.21; H, 5.06; S, 6.70.

4.8. Synthesis of [(HMB)Ru(Cl)(5-η-$CH_2CHCHCHSO_2$)(C_5H_5N)] (12)

Compound **7** (50.0 mg, 0.120 mmol) was placed into a Schlenk flask equipped with a stir bar under vacuum for 5 min at room temperature. $CHCl_3$ (10 mL) was added, followed by 10.0 μL of pyridine (9.51 mg, 0.120 mmol). The mixture was stirred for 1.2 h at room temperature changing from yellow to orange. After filtration, the $CHCl_3$ was reduced under vacuum to ~2 mL; pentane was added in order to induce precipitation of a yellow-orange solid, which was filtered, rinsed with pentane (2 × 3 mL), filtered again, and dried under vacuum. This afforded compound **12** in 73.8% (43.9 mg, 0.089 mmol) which melted with decomposition at 163–164 °C. Compound **12**: ^{1}H NMR (500 MHz, CD_3CN) δ = 5.01 (m, *J* = 17.1 Hz, H1), 5.11 (m, *J* = 10.1 Hz, H1′), 7.64 (dt, *J* = 11.0, 17.3 Hz, H2), 5.48 (t, *J* = 11.1 Hz, H3), 5.65 (d, *J* = 11.4 Hz, H4), 1.89 (s, C_6Me_6), 8.85 (d, 5.0, 1.4 Hz, Hα), 7.37 (m, 7.6, 6.7 Hz, Hβ), 7.80 (tt, 7.7, 1.6 Hz, Hγ). ^{13}C{^{1}H} NMR (125 MHz, CD_3CN) δ = 120.8 (C1), 132.6 (C2), 129.3 (C3), 138.5 (C4), 97.7 (C_6Me_6), 14.6 (C_6Me_6), 155.1 (Cα), 125.3 (Cβ), 137.9 (Cγ).

ESI + TOF: m/z = 496.064604; error: 0.1030; DBE: 7.5. IR(KBr): 3065(m), 3037(m), 2985(m), 2922(m), 2454(w,br), 2044(w,br), 1850(w,br), 1627(w), 1603(w), 1568(m), 1483(m), 1449(s), 1385(s), 1289(w), 1222(w), 1162(vs), 1109(m), 1071(vs), 1028(vs), 921(m), 770(s), 704(s), 660(vs), 537(m), 469(m). Anal. Calcd for $C_{21}H_{28}ClNO_2RuS\cdot H_2O$ (513.05580): C, 49.16; H, 5.89; N, 2.73. Found: C, 49.08; H, 5.84; N, 2.34.

4.9. Synthesis of [(HMB)Ru(Cl)(5-η-$CH_2CHCHCHSO_2$)(C_5D_5N)] (12D)

The synthesis was carried out in an NMR tube, using **7** (55.0 mg, 0.13 mmol) and 11.7 μL of Py-d_5 (12.2 mg, 0.15 mmol) in deuterated acetonitrile (1.2 mL); the mixture was stirred for 1h, filtered and the CD_3CN evaporated. The solid was rinsed with pentane (2 × 5 mL), filtered and dried under vacuum. The yellow-orange solid was obtained in 65.5% yield (43.3 mg, 0.087 mmol). Compound **12D** melted with decomposition at 163–165 °C. Compound **12D**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.97 (d, *J* = 17.3 Hz, H1), 5.07 (d, *J* = 10.2 Hz, H1′), 7.66 (dt, *J* = 10.6, 17.0 Hz, H2), 5.51 (t, *J* = 11.3 Hz, H3), 5.75 (d, *J* = 11.3 Hz, H4), 1.95 (s, C_6Me_6). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 121.6 (C1), 132.4 (C2), 130.9 (C3), 137.6 (C4), 97.8 (C_6Me_6), 15.4 (C_6Me_6), 154.6 (t, *J* = 28.3, Cα), 124.7 (t, *J* = 25.4, Cβ), 137.1 (t, *J* = 25.0 Hz, Cγ). ESI + TOF: m/z = 501.096585; error: 0.1895. IR(KBr): 2921(m), 2283(d), 1626(d), 1562(m), 1443(m), 1385(mf), 1320(m), 1163(f), 1108(m), 1071(m), 1030(f), 920(m), 840(md), 780(m), 712(d), 661(f), 542(mf), 471(d). Anal. Calcd for $C_{21}H_{23}D_5ClNO_2RuS\cdot H_2O$ (518.09): C, 48.69; H, 4.86; N, 2.70; S, 6.19. Found; C, 48.79; H, 5.52; N, 2.66; S, 6.26.

4.10. Synthesis of [(HMB)Ru(Cl)(5-η-$CH_2CHCMeCHSO_2$)(C_5H_5N)] (13)

The synthesis was carried out using **8** (40.0 mg, 0.09 mmol) and 11.3 μL of Py (11.0 mg, 0.14 mmol) in CD_3CN (1.2 mL) and stirred in a Vortex for 2h in an NMR tube, followed by a new addition of 3.8 μL of Py (3.68 mg, 0.05 mmol) and stirring for 1 h. The solution was transferred into a Schlenk tube, and after filtration, evaporation of CD_3CN and washing with pentane (2 × 5 mL), a yellow-orange solid was isolated in 58.4% yield (27.7 mg, 0.054 mmol). **13** melts with decomposition at 173–174 °C. Compound **13**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.10 (d, *J* = 17.3 Hz, H1), 5.11 (d, *J* = 11.7 Hz, H1′), 7.89 (dd, *J* = 11.0, 17.1 Hz, H2), 1.40 (s, Me3), 5.71 (s, H4), 1.96 (s, C_6Me_6), 8.97 (d, 5.3 Hz, Hα), 7.72 (t, 7.6 Hz, Hβ), 7.29 (t, 6.9 Hz, Hγ). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 116.8 (dd, *J* = 156.9, 156.9 Hz, C1), 134.6 (t_{ap} *J* = 167.5 Hz, C2), 135.9 (s, C3), 19.0 (q, *J* = 127.6 Hz, Me3), 137.0 (dd, *J* = 170.8, 6.7, 4.8 Hz, C4), 97.7 (s, C_6Me_6), 15.4 (q, *J* = 129.6 Hz, C_6Me_6), 155.2 (d, *J* = 185.2 Hz, Cα), 125.0 (dt, *J* = 167.0, 6.7 Hz, Cβ), 137.4 (dt, *J* = 165.1, 6.7 Hz, Cγ). ESI + TOF: m/z = 510.079752, error: 0.7849, DBE: 7.5. IR(KBr): 3025(m), 2917(m), 1602(d), 1573(md), 1448(mf), 1384(mf), 1194(m), 1165(f), 1116(m), 1037(f), 910(m), 833(m), 768(m), 705(m), 655(d), 609(f), 544(m), 506(m). Anal. Calcd for $C_{22}H_{30}ClNO_2RuS$ (509.07): C, 51.91; H, 5.94; N, 2.75. Found; C, 51.68; H, 6.01; N, 2.63.

4.11. Synthesis of [(HMB)Ru(Cl)(5-η-$CH_2CHCMeCHSO_2$)(C_5D_5N)] (13D)

The synthesis was carried out as described for **13**, using **8** (40.0 mg, 0.09 mmol) and 11. 2 μL of Py-d_5 (11.7 mg, 0.14 mmol) in CD_3CN (1.2 mL) and stirred for 1.5 h in a Vortex. However, two extra independent additions of Py-d_5 (3.7 μL, 3.91 mg, 0.05 mmol) were required, stirring in each case for ~ 2h. The solution was transferred into a Schlenk tube, and after filtration, evaporation of CD_3CN and washing with pentane (2 × 5 mL), a yellow-orange solid was isolated in 51.9% yield (24.8 mg, 0.05 mmol). This solid melted with decomposition at 172–174 °C. Compound **13D**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.11 (d, *J* = 17.0 Hz, H1), 5.12 (d, *J* = 10.6 Hz, H1′), 7.89 (dd, *J* = 11.0, 16.6 Hz, H2), 1.41 (s, Me3), 5.72 (s, H4), 1.98 (s, C_6Me_6). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 116.8 (C1), 133.9 (C2), 135.9 (C3), 19.0 (Me3), 137.0 (C4), 97.7 (C_6Me_6), 15.4 (C_6Me_6), 154.8 (t, *J* = 27.8 Hz, Cα), 124.5 (t, *J* = 25.0 Hz, Cβ), 137.0 (t, *J* = 25.0 Hz, Cγ). ESI + TOF: m/z = 515.112011, error: −0.2504 ppm. IR(KBr): 2015(m), 225(md), 1570(m), 1441(m), 1384(mf), 1319(md), 1189(f), 1159(f), 1119(md), 1034(f), 917(m), 827(m), 729(f), 645(md), 613(mf), 543(mf), 504(m). Anal. Calcd for $C_{22}H_{25}D_5ClNO_2RuS$ (514.10): C, 51.40; H, 4.90; N, 2.72. Found; C, 50.88; H, 5.19; N, 2.62.

4.12. Identification of [(HMB)Ru(Cl)(5-η-$CH_2CHCHCHSO_2$)(CD_3CN)] (14D)

The synthesis was carried out in an NMR tube, using **7** (30.0 mg, 0.07 mmol) and excess of CD_3CN (0.6 mL). The orange solution was monitored through the ^{1}H NMR, showing that after 1h and even after 10 days a 1:3 ratio (**7**:**14D**) remained in the CD_3CN solution. Compound **14D**: ^{1}H NMR (500 MHz, CD_3CN) δ = 5.21 (m, *J* = 17.0 Hz, H1), 5.18 (m, *J* = 10.7 Hz, H1′), 7.63 (m, *J* = 17.2, 10.6, 1.2, 1.0 Hz, H2), 5.91 (t_{ap}, J = 11.2 Hz, H3), 6.11 (m, *J* = 11.2, 1.9, 1.2 Hz, H4), 2.03 (s, C_6Me_6). $^{13}C\{^1H\}$ NMR (125 MHz, CD_3CN) δ = 121.1 (C1), 132.7 (C2), 129.6 (C3), 139.4 (C4), 98.3 (C_6Me_6), 15.0 (C_6Me_6), 0.5 (CD_3CN), 117.5 (CD_3CN).

4.13. Synthesis of [(HMB)Ru(Cl)(5-η-$CH_2CHCHCHSO_2$)(PMe_3)] (15)

Compound **7** (58.0 mg, 0.140 mmol) was placed into a Schlenk flask equipped with a stir bar under vacuum for 5 min at room temperature. THF (10 mL) was added, followed by 14.4 μL of PMe_3 (10.61 mg, 0.14 mmol); the mixture was stirred 2h. After filtration, the THF was reduced under vacuum to ~1 mL, and cold pentane was added in order to induce the precipitation of a yellow-orange solid, which was filtered, rinsed with 2 mL of cold pentane, filtered again, and dried under vacuum in order to afford compound **15** in 65.6% (45.0 mg, 0.09 mmol), which melted at 90–93 °C, with decomposition. Compound **15** with traces of **15Cl** (**15**:**15Cl**, 14.5:1.0): ^{1}H NMR (500 MHz, C_6D_6) δ = 5.07 (d, *J* = 17.2 Hz, H1), 5.10 (d, *J* = 8.7 Hz, H1′), 8.44 (dt_{ap}, *J* = 17.2, 10.5, 1.1 Hz, H2), 5.81 (t, J = 11.1 Hz, H3), 7.20 (d, *J* = 11.0 Hz, H4), 1.71 (s, C_6Me_6), 1.39 (d, *J* = 10.6 Hz, PMe_3), $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6) δ = 6.8 (s). ^{13}C NMR (125 MHz, C_6D_6) δ = 120.4 (t_{ap}, *J* = 156.8, 5.4 Hz, C1), 134.0 (ddd, *J* = 162.2, 10.8, 3.8 Hz, C2), 128.1 (d, *J* = 158.4 Hz, C3), 140.8 (d, *J* = 172.7 Hz, C4), 102.8 (s, C_6Me_6), 15.9 (q, *J* = 129.1 Hz, C_6Me_6), 16.8 (q, J = 129.9 Hz, PMe_3). ESI + TOF ($C_{19}H_{32}O_2NaPSClRu^+$): m/z = 515.0487; error: 0.3862; DBE: 3.5. IR(KBr): 2041(w,br), 1628(m,br), 1571(m), 1427(m,br), 1385(s), 1283(m), 1168(vs), 1110(m), 1069(m,sh), 1040(vs), 959(vs), 857(w), 787(m), 732(m), 661(vs), 540(m), 470(m). Anal. Calcd for $C_{19}H_{32}ClO_2PRuS$ (492.02): C, 46.38; H, 6.56; S, 6.52. Found: C, 45.99; H, 6.76; S, 5.99.

4.14. Synthesis of [(HMB)Ru(Cl)(5-η-$CH_2CHCHCHSO_2$)(PPh_3)] (16) and [(HMB)Ru(Cl)$_2$(PPh_3)] (16Cl)

Compound **7** (50.0 mg, 0.120 mmol) and PPh_3 (47.0 mg, 0.18 mmol) were placed into a Schlenk flask equipped with a stir bar under vacuum 5 min at room temperature. Benzene (20 mL) was added and the mixture was stirred 1.5h. After filtration, the benzene was reduced under vacuum until ~2 mL, and pentane was added in order to induce the precipitation of an orange-yellow solid, which was filtered, rinsed with pentane (5 × 5 mL), filtered again and dried under vacuum in order to afford compound **16** in 67.5% (55.0 mg, 0.08 mmol), which melted at 242–245 °C with

decomposition. Compound **16** with **16Cl** (**16**:**16Cl**, 10.5:1.0): ^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.03 (d, *J* = 17.0 Hz, H1), 5.07 (d, *J* = 10.2 Hz, H1′), 7.51 (dt, *J* = 17.0, 10.6 Hz, H2), 5.38 (t, J = 11.1 Hz, H3), 6.17 (d, *J* = 11.3 Hz, H4), 1.79 (s, C_6Me_6), 7.15–7.75 (m, P*Ph*$_3$). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$) δ = 35.4 (s). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 120.7 (C1), 133.1 (C2), 128.6 (C3), 138.3 (C4), 105.0 (s, C_6Me_6), 15.7 (C_6Me_6), 134.0 (d, *J* = 17.3 Hz, *o*, P*Ph*$_3$), 128.9 (d, *J* = 8.6 Hz, *m*, P*Ph*$_3$), 130.0 (s, *p*, P*Ph*$_3$). ESI + TOF ($C_{34}H_{38}O_2$N-aPSClRu$^+$): m/z = 701.0963; error 1.2304; DBE 15.5. IR(KBr): 3055(m), 2897(m,br), 2616(w,br), 2346(w), 2188(w,br), 1988(w,br), 1828(w,br), 1743(w), 1711(w), 1625(w), 1572(w), 1483(m), 1435(s), 1384(m), 1317(w), 1264(w), 1192(vs), 1091(s), 1051(vs,br), 914(m), 797(m), 753(s), 700(vs), 667(vs), 527(vs), 491(vs), 468(m), 425 (vw). Anal. Calcd for $C_{34}H_{38}ClO_2PRuS$ (678.23): C, 60.21; H, 5.65. Found: C, 60.59; H, 5.28.

4.15. Synthesis of [(HMB)Ru(Cl)(5-η-$CH_2CHCHCHSO_2$)(P*H*P*h*$_2$)] (17) and [(HMB)Ru(Cl)$_2$(P*H*P*h*$_2$)] (17Cl)

Compound **7** (50.0 mg, 0.12 mmol) was placed into a Schlenk flask equipped with a stir bar under vacuum 5 min at room temperature. THF (10 mL) followed by 0.33 mL of $PHPh_2$ (223.8 mg, 1.20 mmol, 10% w in hexane) were added; then the mixture was stirred 1.5 h. After filtration of the golden solution, the THF was reduced under vacuum until ~2 mL, and pentane was added in order to induce the precipitation of an orange-yellow solid, which was filtered, rinsed twice with 5 mL of pentane, filtered again, recrystallized with $CHCl_3$/pentane, and dried under vacuum in order to afford compound **17** in 49.3% (35.5 mg, 0.06 mmol), which melts at 118–120 °C, with decomposition. Compound **17** with **17Cl** (**17**:**17Cl**, 10.2:1.0): ^{1}H NMR (500 MHz, C_6D_6) δ = 4.98 (d, *J* = 17.3 Hz, H1), 5.01 (d, *J* = 9.9 Hz, H1′), 8.21 (dt, *J* = 17.0, 11.0 Hz, H2), 5.72 (t, J = 11.0 Hz, H3), 6.92 (d, *J* = 11.3 Hz, H4), 1.61 (s, C_6Me_6), 6.96–7.20 (m, PH*Ph*$_2$), 7.70–7.79 (m, PH*Ph*$_2$), 7.09 (d, *J* = 422.8 Hz, P*H*Ph$_2$). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6) δ = 28.9 (s). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6) δ = 120.6 (C1), 133.6 (C2), 129.1 (C3), 138.9 (C4), 103.1 (s, C_6Me_6), 15.0 (C_6Me_6), 135.8 (d, *J* = 10.6 Hz, *o*, PH*Ph*$_2$), 133.0 (d, *J* = 7.7 Hz, *o*, PH*Ph*$_2$), 130.5 (br, *J* = 1.9 Hz, *m*, PH*Ph*$_2$), 129.6 (br, *J* = 1.9 Hz, *m*, PH*Ph*$_2$), 128.1 (s, *p*, PH*Ph*$_2$), 128.0 (s, *p*, PH*Ph*$_2$). ESI + TOF: m/z = 603.082177, error: -0.02575 ppm, DBE: 11.5. IR (KBr): 3052(m), 2920(m), 2347(w), 1966(w), 1821(w), 1626(m), 1571(m), 1480(m), 1437(s), 1384(m), 1312(w), 1178(vs), 1103(m), 1070(m), 1041(vs), 894(m), 859(m), 789(m), 743(s), 697(s), 663(vs), 539(m), 502(s), 477(m). Anal. Calcd for $C_{28}H_{34}ClO_2PRuS\cdot0.5CHCl_3$ (661.82): C, 51.72; H, 5.25; S, 4.84. Found: C, 51.62; H, 5.01; S, 4.62.

4.16. Crystal structure determinations

X-ray diffraction measurements were made at 293(2) K (**7**) and 173(2) K (**15**) on an Enraf Nonius-Kappa CCD diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), and at 123(2) K (**8**) in a Agilent Nova Cu Kα radiation (λ = 1.54056 Å). The structures were solved by direct methods, using SHELXS-2014 included in WinGX v.2014.1 and refined by a full-matrix least-squares method based on F^2 [32]. Absorption corrections were performed by Multi-Scan. All non-hydrogen atoms were refined with anisotropic thermal displacement coefficients unless specified otherwise. The crystallographic information file (CIF) of compounds **7**(CCDC-1036731), **8**(CCDC-1036729) and **15**(CCDC-1036730) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

This work was financially supported by the National Council of Science and Technology (Conacyt, 152280). J.I.C.C. is grateful for a scholarship from Conacyt and Cinvestav. We thank Dr. Armando Ramirez-Monroy, José Rosas from BUAP and Marco Antonio Leyva from Cinvestav for use and assistance with the crystal structure determinations, and Patricia Juarez-Saavedra and M. Teresa Cortez-Picasso for technical support in the chemical microanalysis, IR and NMR experiments, respectively. The authors would also like to thank Dr. Juan Olguín for valuable comments, Dr. Felipe Gonzalez-Bravo and Daniel Morales Martinez, and Josué Israel Alemán Vega for performing the electrochemical and DLS experiments, respectively.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2015.05.023.

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