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Ruthenium(II) Arene Complexes Bearing Tris(pyrazolyl)methanesulfonate Capping Ligands. Electrochemistry, Spectroscopic, and X-ray Structural Characterization

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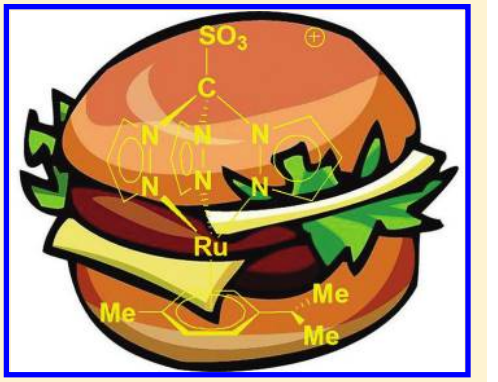
Supporting Information

ABSTRACT: Novel [Ru(L)(Tpms)]Cl and [Ru(L)(Tpms^{Ph})]Cl complexes (L = *p*-cymene, benzene, or hexamethylbenzene, Tpms = tris(pyrazolyl)-methanesulfonate, Tpms^{Ph} = tris(3-phenylpyrazolyl)methanesulfonate) have been prepared by reaction of $[Ru(L)(\mu\text{-}Cl)_2]_2$ with Li[Tpms] and Li[Tpms^{Ph}], respectively. [Ru(*p*-cymene)(Tpms)]BF_4 has been synthesized through a metathetic reaction of [Ru(*p*-cymene)(Tpms)]Cl with $AgBF_4$. [RuCl(cod)-(Tpms)] (cod = 1,5-cyclooctadiene) and [RuCl(cod)(Tpms^{Ph})] are also reported, being obtained by reaction of $[RuCl_2(cod)(MeCN)_2]$ with Li[Tpms] and Li[Tpms^{Ph}], respectively. The structures of the complexes and the coordination modes of the ligands have been established by IR, NMR, and single-crystal X-ray diffraction (for [RuL(Tpms)]X (L = *p*-cymene or HMB, X = Cl; L = *p*-cymene, X = BF_4)) studies. Electrochemical studies showed that each complex undergoes a single-electron $Ru^{II} \rightarrow Ru^{III}$ oxidation at a potential measured by cyclic voltammetry, allowing to compare the electron-donor characters of the tris(pyrazolyl)methanesulfonate and arene ligands, and to estimate, for the first time, the values of the Lever E_L ligand parameter for Tmps^{Ph}, HMB, and cod.

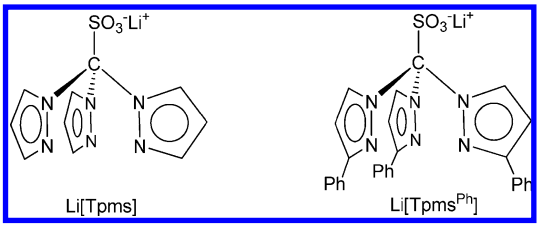


INTRODUCTION

Transition metal complexes stabilized by tripodal capping ligands, which also contain labile monodentate or bidentate ligands, are potentially useful in catalytic processes with biological or industrial significance.[1] We have been interested in the coordination chemistry of the "scorpionate" nitrogen donor ligands, and we have previously reported the synthesis and spectroscopic characterization of Ru derivatives of pyrazolylalkanes[2] and pyrazolylborates,[3] showing that this family could find application in hydrogen transfer[2] and in the catalytic Henry reaction.[3a] Recently we have devoted our attention to the coordination chemistry of tris(pyrazolyl)-methane $HC(pz)_3$[4] and its C-substituted sulfonate derivative tris(pyrazolyl)methanesulfonate, $SO_3C(pz)_3^-$,[4a−e,5] (or Tpms, Chart 1).

The hydrophilic Tpms and its derivatives[5] have been indicated as the analogous counterpart of tris(pyrazolyl)borate (Tp), bearing the C−SO_3 group instead of the B−H moiety,

Chart 1



both being able to act as monoanionic C_{3v}-symmetrical nitrogen-donor ligands.[6] However, unlike the Tp derivatives, insoluble in water and unstable toward hydrolysis, Tpms has a methanesulfonate unit, which imparts an increased solubility in polar solvents and a very good stability in aqueous media over a

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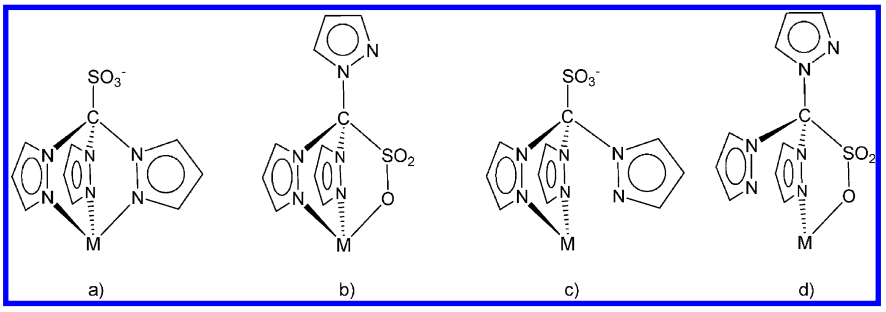
Chart 2. Possible Coordination Modes for the Tpms Ligand: (a) Tripodal N,N,N (κ^3-*N,N,N*); (b) Tripodal N,N,O (κ^3-*N,N,O*); (c) Bipodal N,N (κ^2-*N,N*); (d) Bipodal N,O (κ^2-*N,O*)



wide range of pH.[5] The κ^3-Tpms and κ^3-Tp can often be compared with the isoelectronic pentahapto cyclopentadienyl (Cp) ligand.[7] However, as shown recently,[7] Tpms can act not only as a tripodal ligand but also as a bipodal one. In the former case, it can exhibit either a N,N,N or a N,N,O coordination, whereas Tpms can coordinate in the bidentate fashion through either N,N or N,O[5] (Chart 2).

A "second generation" of tris(pyrazolyl)methanesulfonate ligands,[7,8] in which the pyrazolyl rings contain bulky substituents, especially at the 3-position, offers the opportunity to tune the coordination behavior toward different metal centers. Tpms derivatives bearing a phenyl ring at the 3-position of pyrazolyl rings (Tpms^{Ph}, Chart 1) are not largely explored. When bonded to a metal center, such bulky species would be expected to provide a "sterical control" on the other coordination position(s) of the complex, selecting the suitable ligands on the opposite side, namely, preventing the formation of "sandwich" complexes (with two of such scorpionate ligands).[9] The lack or rarity of half-sandwich Tpms and Tpms^{Ph} complexes with arene ruthenium(II), as well as the knowledge of the important role played by this metal in catalytic organic chemistry[10] and in biology,[11] encouraged us to attempt the preparation of complexes with such a metal and ligands. We report here the result of these studies, leading, to our knowledge, to the preparation of the first examples of half-sandwich Tpms and Tpms^{Ph} complexes of ruthenium.

EXPERIMENTAL SECTION

Materials and Methods. The synthetic work was carried out under an oxygen-free dinitrogen atmosphere, using standard Schlenk techniques. All solvents were degassed and distilled prior to use. $[RuCl(p\text{-cymene})(\mu\text{-Cl})]_2$ was purchased from Aldrich (Milwaukee) and used as received.

Hydrotris(1-pyrazolyl)methane (Tpm),[12a] hydrotris(3-phenylpyrazolyl)methane (Tpm^{Ph}),[5e] lithium tris(1-pyrazolyl)-methanesulfonate (Li[Tpms]),[5a] and lithium (3-phenylpyrazolyl)-methanesulfonate (Li[Tpms^{Ph}])[5e] were prepared by published procedures. $[RuCl(benzene)(\mu\text{-Cl})]_2$ and $[RuCl(HMB)(\mu\text{-Cl})]_2$ were synthesized as previously reported.[13] $[RuCl_2(cod)(MeCN)_2]$ was synthesized by following a procedure reported in the literature.[14] C, H, N, and S analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Infrared spectra (4000−400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets. Reflectance IR spectra were recorded from 4000 to 400 cm^{-1} using a Perkin-Elmer system Spectrum One 100 FT-IR spectrometer. ^1H and ^{31}P NMR spectra were recorded at UNICAM on a 400 Mercury Plus Varian spectrometer operating at room temperature (400 MHz for ^1H and 162.1 MHz for ^{31}P). ^1H and ^{13}C NMR spectra were measured at IST on Bruker 300 and 400 UltraShield spectrometers. ^1H and ^{13}C chemical shifts δ are expressed in ppm relative to $Si(Me)_4$. ^{31}P chemical shifts are reported in ppm versus 85% H_3PO_4. Coupling constants are in Hz; abbreviations: s, singlet; d, doublet; m, complex multiplet; vt, virtual triplet; br, broad. ESI^+/ESI^- mass spectra were obtained on a Varian 500-MS LC ion trap mass spectrometer (solvent: water; flow: 20 μL/min; needle spray voltage: ±5 kV, capillarity voltage: ±100 V; nebulizer gas (N_2): 35 psi; drying gas (N_2): 10 psi; drying gas temperature: 350 °C). The electrochemical experiments were performed on an EG&G PAR 273A potentiostat/galvanostat connected to a personal computer through a GPIB interface. Cyclic voltammetry (CV) studies were undertaken in 0.2 M $[^nBu_4N][BF_4]/CH_3CN$, at a platinum disk working electrode (d = 0.5 mm) and at room temperature. Controlled-potential electrolyses (CPE) were carried out in electrolyte solutions with the above-mentioned composition, in a three-electrode H-type cell. The compartments were separated by a sintered glass frit and equipped with platinum gauze working and counter electrodes. For both CV and CPE experiments, a Luggin capillary connected to a silver wire pseudoreference electrode was used to control the working electrode potential. A Pt wire was employed as the counter-electrode for the CV cell. The CPE experiments were monitored regularly by cyclic voltammetry, thus assuring no significant potential drift occurred along the electrolyses. The solutions were saturated with N_2 by bubbling this gas before each run, and the redox potentials of the complexes were measured by CV in the presence of ferrocene as the internal standard. Their values are quoted relative to the SCE by using the $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$ redox couple ($E^{ox}_{1/2}$ = 0.420 V vs SCE).[15]

*Synthesis of [Ru(p-cymene)(Tpms)]Cl (**1**).* $[Ru(Cl)(p\text{-cymene})(\mu\text{-}Cl)]_2$ (0.306 g, 0.5 mmol) was dissolved in methanol (20 mL), and the solution stirred 30 min. Then Li[Tpms] (0.300 g, 1.0 mmol) was added to the red solution, which immediately changed to orange. After 24 h stirring at room temperature the solvent was removed *in vacuo*, the residue dissolved in dichloromethane (10 mL), and the solution filtered to remove lithium chloride. The solution was then evaporated to dryness and redissolved in diethyl ether (5 mL). Slow evaporation afforded a brown powder, which was dried under reduced pressure and identified as compound **1**. It is very soluble in water and alcohols and slightly soluble in chlorinated solvents, acetone, and acetonitrile. Yield: 0.38 g, 65%. Mp: 300 °C dec. Anal. Calcd for $C_{20}H_{23}ClN_6O_3SRu\cdot H_2O$ (M_w 582.04 g mol^{-1}): C, 41.27; H, 4.33; N, 14.44; S, 5.5. Found: C, 40.78; H, 4.55; N, 14.20; S, 5.43. IR (KBr, cm^{-1}): 3172w $\nu(C_{arom}-H)$, 1518s $\nu(C{=}N)$, 1286vs br, 1113s, 1071s $\nu(SO_3)$. ^1H NMR (CD_3OD, 298 K): δ 1.22d, 1.25d (6H, $CH_3-C_6H_4-CH(CH_3)_2$), 2.49s (3H, $CH_3-C_6H_4-CH(CH_3)_2$), 3.12 m (1H, $CH_3-C_6H_4-CH(CH_3)_2$), 6.30dt 6.50 (4H, AA'BB' system, $CH_3-C_6H_4-CH(CH_3)_2$), 6.72dd (3H, 4-H (pz)), 8.82d (3H, 3-H (pz)), 8.91d (3H, 5-H (pz)). $^{13}C\{^1H\}$ NMR (CD_3OD): δ 16.3s ($CH_3-C_6H_4-CH(CH_3)_2$), 19.7s ($CH_3-C_6H_4-CH(CH_3)_2$), 28.8s ($CH_3-C_6H_4-CH(CH_3)_2$), 84.9s, 85.5s, ($CH_3-C_6H_4-CH(CH_3)_2$), 106.6 (s, 4-C (pz)), 108.1 (s, O_3SC), 134.9 (s, 5-C (pz)), 146.3 (s, 3-C (pz)).

*Synthesis of [Ru(benzene)(Tpms)]Cl (**2**).* Compound **2** was prepared following a procedure similar to that reported for **1** by using $[RuCl(benzene)(\mu\text{-Cl})]_2$ (0.250 g, 1.0 mmol) and Li[Tpms] (0.300 g, 1.0 mmol). It is very soluble in water and alcohols but practically insoluble in chlorinated solvents or acetone. Yield: 0.25 g, 50%. Mp: 194 °C dec, color changed from greenish to brown. Anal. Calcd for $C_{16}H_{15}ClN_6O_3SRu$ (M_w 507.92 g mol^{-1}): C, 37.84; H, 2.98;

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N, 16.55; S, 6.31. Found: C, 37.15; H, 2.99; N, 15.99; S, 6.11. IR (KBr, cm^{-1}): 3148w $\nu(C_{arom}-H)$, 1518s $\nu(C{=}N)$, 1286vs, 1114s, 1073s $\nu(SO_3)$. ^1H NMR (CD_3OD, 298 K): δ 4.99s (6H, C_6H_6), 5.13dd (3H, 4-H (pz)), 7.31d (3H, 3-H (pz)), 7.36d (3H, 5-H (pz)). ^1H NMR (CD_3OD, 273 K): δ 4.99s (6H, C_6H_6), 5.13dd (3H, 4-H (pz)), 7.31d (3H, 3-H (pz)), 7.36d (3H, 5-H (pz)). ^1H NMR (CD_3OD, 253 K): δ 4.99s (6H, C_6H_6), 5.13dd (3H, 4-H (pz)), 7.31d (3H, 3-H (pz)), 7.36d (3H, 5-H (pz)). ^1H NMR (CD_3OD, 233 K): δ 4.99s (6H, C_6H_6), 5.13dd (3H, 4-H (pz)), 7.31d (3H, 3-H (pz)), 7.36d (3H, 5-H (pz)). ^1H NMR (CD_3OD, 213 K): δ 4.99s (6H, C_6H_6), 5.13dd (3H, 4-H (pz)), 7.31d (3H, 3-H (pz)), 7.36d (3H, 5-H (pz)). $^{13}C\{^1H\}$ NMR (CD_3OD, 298 K): δ 90.2 (s, C_6H_6), 109.3 (s, 4-C (pz)), 137.4 (s, 5-C (pz)), 149.8 (s, 3-C (pz)). ESI^+-MS (CH_3CN): m/z 472 $[Ru(benzene)(Tpms)]^+$.

*Synthesis of [Ru(HMB)(Tpms)]Cl (**3**).* $[RuCl(HMB)(\mu\text{-}Cl)]_2$ (0.334 g, 0.5 mmol) was dissolved in methanol (20 mL), the solution stirred for 30 min, and then Li[Tpms] (0.300 g, 1.0 mmol) was added to the red solution, which immediately changed to orange. After 24 h stirring at room temperature the solvent was removed *in vacuo*, the residue redissolved in dichloromethane (10 mL), and the solution filtered to remove lithium chloride. The solution was then evaporated to dryness and redissolved in diethyl ether (5 mL). Slow evaporation afforded a brown powder, which was dried under reduced pressure and identified as **3**. It is very soluble in alcohols, chlorinated solvents, acetone, and acetonitrile and only slightly soluble in water. Yield: 0.39 g, 62%. Mp: 250 °C dec, color changed from yellow to gray. Anal. Calcd for $C_{22}H_{27}ClN_6O_3SRu{\cdot}1/2CH_2Cl_2$ (M_w 634.54 g mol^{-1}): C, 42,59; H, 4.45; N, 13.24; S, 5.05. Found: C, 42.91; H, 4.82; N, 13.54; S, 4.99. IR (KBr, cm^{-1}): 3185w, 3132w, $\nu(C_{arom}-H)$, 1520s $\nu(C{=}N)$, 1291vs br, 1114s, 1057s $\nu(SO_3)$. ^1H NMR (CD_3OD, 298 K): δ, 2.40s (18H, C_6-$(CH_3)_6$), 6.74dd (3H, 4-H (pz)), 8.52d (3H, 3-H (pz)), 8.94d (3H, 5-H (pz)). $^{13}C\{^1H\}$ NMR (CD_3OD, 298 K): δ 16.93 (s, C_6-$(CH_3)_6$), 98.71 (s, C_6-$(CH_3)_6$), 109.6 (s, 4-C (pz)), 138.0 (s, 5-C (pz)), 147.6 (s, 3-C (pz)).

*Synthesis of [Ru(p-cymene)(Tpms)]BF_4 (**4**).* A mixture of compound **1** (0.580 g, 1 mmol) and silver tetrafluoroborate, $AgBF_4$ (0.194 g, 1 mmol), was stirred in chloroform (10 mL) for 24 h at room temperature. The silver chloride precipitate was separated by filtration. Then the solvent was removed *in vacuo*, and the residue redissolved in dichloromethane (10 mL) and hexane. Slow evaporation yielded a yellow crystalline powder, identified as **4**. It is very soluble in water, alcohols, chlorinated solvents, acetone, and acetonitrile. Yield: 0.30 g, 48%. Mp: 300 °C dec. Anal. Calcd for $C_{20}H_{23}N_6O_3SRuBF_4$ (M_w 615.37 g mol^{-1}): C, 39.04; H, 3.77; N, 13.66; S, 5.21. Found: C, 38.65; H, 3.50; N, 13.22; S, 5.31. IR (KBr, cm^{-1}): 3161w, 3123w $\nu(C_{arom}-H)$, 1521s $\nu(C{=}N)$, 1278vs, 1098s $\nu(SO_3)$, 1028vs br $\nu(BF_4)$. ^1H NMR (CD_3OD, 298 K): δ, 1.22d, 1.24d (6H, $CH_3-C_6H_4-CH(CH_3)_2$), 2.49s (3H, $CH_3-C_6H_4-CH(CH_3)_2$), 3.12 m (1H, $CH_3-C_6H_4-CH(CH_3)_2$), 6.30dt 6.50 (4H, AA′BB′ system, $CH_3-C_6H_4-CH(CH_3)_2$), 6.71dd (3H, 4-H (pz)), 8.82d (3H, 3-H (pz)), 8.91d (3H, 5-H (pz)).

*Synthesis of [Ru(p-cymene)(Tpms^{Ph})]Cl (**5**).* $[RuCl(cymene)(\mu\text{-}Cl)]_2$ (0.306 g, 0.5 mmol) was dissolved in methanol (20 mL), the solution was stirred for 30 min, and then Li[Tpms^{Ph}] (0.528 g, 1.0 mmol) was added. After 24 h stirring at room temperature and 24 h stirring at reflux, a red-brown precipitate formed, which was removed by filtration, dried under vacuum, and identified as the derivative **5**. It is soluble in chlorinated solvents. Yield: 0.59 g, 74%. Mp: 320 °C dec. Anal. Calcd for $C_{38}H_{35}ClN_6O_3SRu$ (M_w 792.32 g mol^{-1}): C, 57.61; H, 4.45; N, 10.61; S, 4.05. Found: C, 57.18; H, 4.32; N, 10.34; S, 3.81. IR (KBr, cm^{-1}): 3124w, 3058w $\nu(C_{arom}-H)$, 1533s $\nu(C{=}N)$, 1232vs, 1042s $\nu(SO_3)$. ^1H NMR ($CDCl_3$, 298 K): δ 1.28d, 1.35d (6H, $CH_3-C_6H_4-CH(CH_3)_2$), 2.15s, 2.28s (3H, $CH_3-C_6H_4-CH(CH_3)_2$), 2.95 m, 3.08 m (1H, $CH_3-C_6H_4-CH(CH_3)_2$), 5.29dd, 5.38d, 5.56dd, 5.62d (4H, AA′BB′ system, $CH_3-C_6H_4-CH(CH_3)_2$), 6.55d, 6.63d (3H, 4-*H* (pz)), 7.55 m (9H, *m*-*H* and *p*-*H* (Ph)), 7.88 m (6H, *o*-*H* (Ph)), 7.96d, 8.11d (3H, 5-*H* (pz)). ESI^+-MS (CH_3CN): m/z 757 $[Ru(cymene)(Tpms^{Ph})]^+$.

*Synthesis of [Ru(benzene)(Tpms^{Ph})]Cl (**6**).* $[RuCl(benzene)(\mu\text{-}Cl)]_2$ (0.250 g, 0.5 mmol) was dissolved in methanol (20 mL) and stirred 30 min. Then Li[Tpms^{Ph}] (0.528 g, 1.0 mmol) was added to the solution. After 24 h stirring at room temperature and 24 h stirring at reflux, a red-brown precipitate formed, which was removed by filtration, dried under vacuum, and identified as the derivative **6**. It is soluble in acetone and acetonitrile. Yield: 0.44 g, 58%. Mp: 320 °C dec. Anal. Calcd for $C_{34}H_{27}ClN_6O_3SRu$ (M_w 736.21 g mol^{-1}): C, 55.47; H, 3.70; N, 11.42; S, 4.36. Found: C, 55.21; H, 3.77; N, 11.13; S, 4.35. IR (KBr, cm^{-1}): 3186w $\nu(C_{arom}-H)$, 1533s $\nu(C{=}N)$, 1291vs, 1245vs, 1193vs, 1051vs $\nu(SO_3)$. ^1H NMR (acetone-d_6, 298 K): δ 5.25s (6H, C_6H_6), 6.49d (3H, 4-*H* (pz)), 7.34–7.30 m (9H, *m*-*H* and *p*-*H* (Ph)), 7.53d (6H, *o*-*H* (Ph)), 9.21d (3H, 5-*H* (pz)). ^1H NMR (acetone-*d*, 273 K): δ 5.25s (6H, C_6H_6), 6.49d (3H, 4-*H* (pz)), 7.34–7.30 m (9H, *m*-*H* and *p*-*H* (Ph)), 7.53d (6H, *o*-*H* (Ph)), 9.21d (3H, 5-*H* (pz)). ^1H NMR (acetone-d_6, 253 K): δ 5.25s (6H, C_6H_6), 6.49d (3H, 4-*H* (pz)), 7.34–7.30 m (9H, *m*-*H* and *p*-*H* (Ph)), 7.53d (6H, *o*-*H* (Ph)), 9.21d (3H, 5-*H* (pz)). ^1H NMR (acetone-d_6, 233 K): δ 5.25s (6H, C_6H_6), 6.49d (3H, 4-*H* (pz)), 7.34–7.30 m (9H, *m*-*H* and *p*-*H* (Ph)), 7.53d (6H, *o*-*H* (Ph)), 9.21d (3H, 5-*H* (pz)). $^{13}C\{^1H\}$ (acetone-d_6, 298 K): δ 79.3s (C_6H_6), 127.2 (s, *m*-C (Ph)), 131.7s (*o*-C (Ph)), 137s (5-C (pz)). ESI^+-MS (CH_3CN): m/z 701 [Ru(benzene)-(Tpms^{Ph})]$^+$.

*Synthesis of [Ru(cod)Cl(Tpms)] (**7**).* $[RuCl_2(cod)(MeCN)_2]$ (0.362 g, 1.0 mmol) was dissolved in acetonitrile (20 mL), and the solution was stirred for 30 min. Then a methanol solution (30 mL) of Li[Tpms] (0.528 g, 1.0 mmol) was added, and the reaction mixture was stirred at reflux for 24 h, whereafter the solvents were removed *in vacuo* and the residue was redissolved in chloroform (10 mL). After filtration to remove lithium chloride, slow evaporation yielded a yellow crystalline powder, which was dried under vacuum and identified as the derivative **7**. It is soluble in water, alcohols, acetone, acetonitrile, and chlorinated solvents. Yield: 0.33 g, 68%. Mp: 60 °C dec. Anal. Calcd for $C_{18}H_{21}ClN_6O_3SRu{\cdot}H_2O$ (M_w 556.00 g mol^{-1}): C, 38.88; H, 4.17; N, 15.12; S, 5.77. Found: C, 39.36; H, 4.18; N, 15.26; S, 5.32. IR (KBr, cm^{-1}): 3464br $\nu(H_2O)$, 3131w $\nu(C_{arom}-H)$, 1663br $\delta(H_2O)$, 1520s $\nu(C{=}N)$, 1239vs br, 1041s $\nu(SO_3)$. ^1H NMR (CD_3OD, 298 K): δ 2.54 m, 2.69d (8H, CH_2-cod), 2.85br (H_2O), 4.20dbr, 4.55dbr (4H, *CH*-cod), 6.42t (3H, 4-*H* (pz)), 7.59d (3H, 5-*H* (pz)), 7.92d (3H, 3-*H* (pz)).

*Synthesis of [Ru(cod)Cl(Tpms^{Ph})] (**8**).* $[RuCl_2(cod)(MeCN)_2]$ (0.362 g, 1.0 mmol) was dissolved in acetonitrile (20 mL), and the solution was stirred for 30 min. Then a methanol solution (30 mL) of Li[Tpms^{Ph}] (0.528 g, 1.0 mmol) was added, and the reaction mixture stirred at reflux for 24 h, whereafter the solvents were removed *in vacuo* and the residue was redissolved in chloroform (10 mL). After filtration to remove lithium chloride, slow evaporation yielded a yellow crystalline powder, which was dried under vacuum and identified as the derivative **8**. It is soluble in alcohols, acetone, acetonitrile, and chlorinated solvents. Yield: 0.45 g, 59%. Mp: 134–137 °C. Anal. Calcd for $C_{36}H_{33}ClN_6O_3SRu$ (M_w 766.28 g mol^{-1}): C, 56.43; H, 4.34; N, 10.97; S, 4.18. Found: C, 56.15; H, 4.26; N, 11.10; S, 4.42. IR (KBr, cm^{-1}): 3150w $\nu(C_{arom}-H)$, 1532s $\nu(C{=}N)$, 1223vs br, 1041s $\nu(SO_3)$. ^1H NMR (CD_3OD, 298 K): δ 2.41 m, 2.49d (8H, CH_2-cod), 3.35dbr, 3.70dbr (4H, *CH*-cod), 6.82d (3H, 4-*H* (pz)), 7.32 m (9H, *m*-*H* and *p*-*H* (Ph)), 7.88 m (6H, *o*-*H* (Ph)), 8.13d (3H, 5-*H* (pz)).

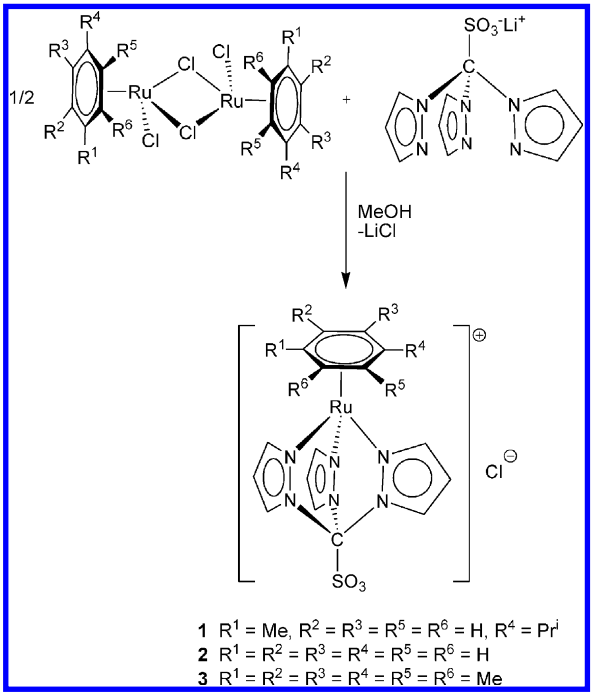
Crystals of **1**, **3**, and **4** suitable for X-ray diffraction were obtained from 1/1 methanol/diethyl ether mixtures. Crystallographic data have been deposited at the CCDC and allocated the deposition numbers CCDC 837586–837588.

General Procedure for Catalytic Oxidation of Styrene by H_2O_2. Styrene (0.25 mmol, 0.026 g) and **1** (0.0025 mmol, 0.0014 g) were dissolved in acetone (1.5 mL). Aqueous hydrogen peroxide [0.1214 g, 35% (w/w), 1.25 mmol] was then added in one portion, and the reaction mixture was stirred under dinitrogen at ambient temperature for 12 h. Then a sample (20 μL) of the resultant solution was diluted to 1 mL and analyzed by GC-MS. Control experiments without either the catalyst or H_2O_2 were performed under identical conditions. An identical reaction procedure was performed using **5** as catalyst.

RESULTS AND DISCUSSION

Synthesis and Spectroscopic Characterization of Compounds 1−8. Complexes [Ru(*p*-cymene)(Tpms)]Cl (**1**), [Ru(benzene)(Tpms)]Cl (**2**), and [Ru(HMB)(Tpms)]Cl (**3**) were synthesized by reactions of the lithium salt Li[Tpms] with the appropriate [RuCl(arene)(μ-Cl)]$_2$ dimers (arene = *p*-cymene, benzene, or hexamethylbenzene = HMB) in methanol, at room temperature (Scheme 1).

Scheme 1



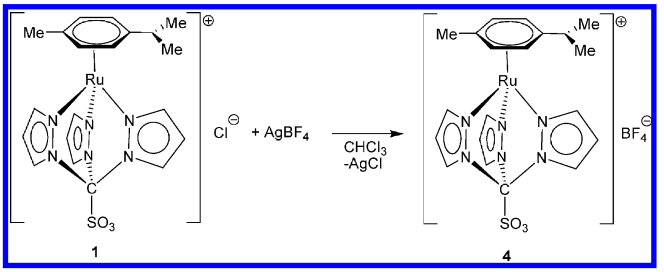
These complexes, as well as the other new ones discussed below, appear to provide, to our knowledge, the first examples of half-sandwich tris(1-pyrazolyl)methanesulfonate complexes of Ru. Moreover, they display a high solubility in water, an important feature toward their application as catalysts or catalyst precursors in aqueous media and which may also be of particular significance for further biological activity tests. They have been isolated as orange, air-stable solids, well soluble in water and MeOH, and have been characterized by elemental analysis, IR, NMR, and ESI-MS spectroscopies, and X-ray diffraction.

Their ^{1}H and ^{13}C{^{1}H} NMR and IR spectra confirm the presence of the Tpms ligand and the organometallic fragment. The NMR resonances of the Tpms hydrogen atoms are weakly shifted relative to the Li[Tpms]. The detection of only one set of signals for each equivalent group of protons, also at low temperature, suggests the absence of fluxionality and that coordination of Tpms in the N$_2$O-donor fashion is unlikely also in solution. For complexes **1**, **2**, and **3** the ν(S═O) and ν(S−C) bands of the methanesulfonate group, as well as ν(C═C) and ν(C═N) bands of the pyrazolyl rings, are observed at the usual ranges 1113−1071, 636−620, and 1636−1518 cm^{-1}, while in the far-IR region the disappearance of the ν(Ru−Cl) band at 280 cm^{-1} confirms the substitution of the chloride ligand for one pyrazolyl group.

^{1}H and ^{13}C{^{1}H} NMR spectra show the typical set of resonances of the arene fragment and the equivalence of the pyrazolyl groups, deshielded with respect to those of the reagents. This pattern for the complex [Ru(benzene)(Tpms)]Cl (**2**) essentially remains unchanged upon cooling until 200 K, thus indicating the preservation of the N$_3$-coordination also at low temperature.

Compound **1** has been converted to [Ru(*p*-cymene)(Tpms)]BF$_4$ (**4**) through a metathesis reaction with AgBF$_4$ (Scheme 2). It has been isolated as an orange, air-stable solid,

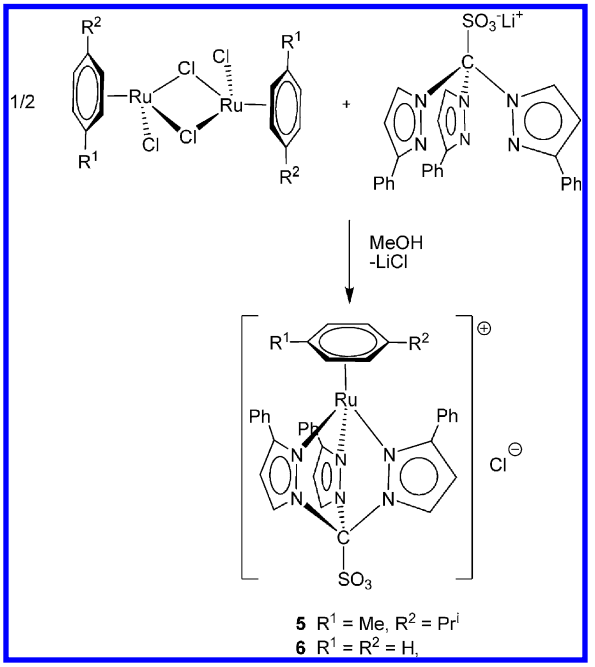
Scheme 2



which is well soluble in water (which may be of particular significance for further biological activity tests), MeOH, CH_3CN, acetone, and $CHCl_3$. Complex **4** has been characterized by elemental analysis, IR, NMR spectroscopies, and X-ray diffraction.

When the phenyl-substituted Li[Tpms^{Ph}] compound was used instead of the unsubstituted one, Li[Tpms], the reactions with [RuCl(*p*-cymene)(μ-Cl)]$_2$ and [RuCl(benzene)(μ-Cl)]$_2$ proceeded similarly in methanol, to yield, although upon solvent refluxing, the corresponding products bearing the anionic Tpms^{Ph} ligand, i.e., [Ru(*p*-cymene)(Tpms^{Ph})]Cl (**5**) and [Ru(benzene) (Tpms^{Ph}) Cl] (**6**) (Scheme 3). These

Scheme 3



complexes have also been characterized by NMR and IR spectroscopies and elemental analysis. The ^{1}H and ^{13}C{^{1}H} NMR spectra confirm the presence of the ligands, the NMR resonances of Tpms^{Ph} being shifted with respect to those of the starting Li[Tpms^{Ph}]. The IR spectra also show the presence of

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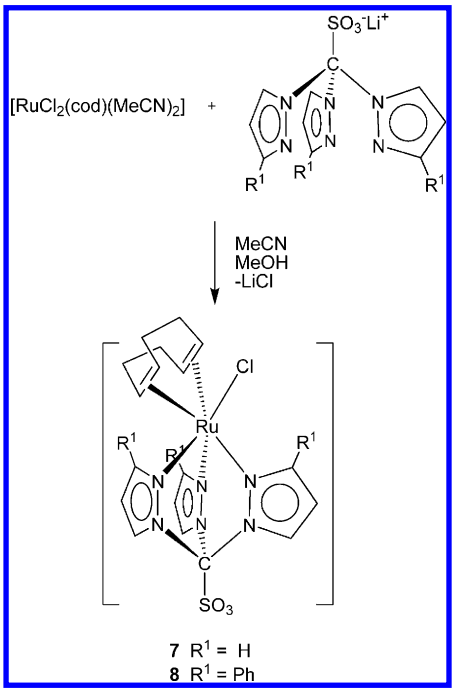
Tpms^{Ph} (e.g., stretching bands at 1533 (C═N) and 1042 or 1051 (SO) cm^{-1}).

By using the 1,5-cyclooctadiene (cod) complex [$RuCl_2$(cod)-$(MeCN)_2$] as the starting reagent in the reactions with Li[Tpms] or Li[Tpms^{Ph}], the corresponding [Ru(cod)Cl-(Tpms)] (**7**) and [Ru(cod)Cl(Tpms^{Ph})] (**8**) complexes are obtained from refluxing MeCN/MeOH solutions (Scheme 4).

Scheme 4



They have been characterized by elemental analysis and IR and NMR spectroscopies, which confirm the presence of the organic ligands. These species are fluxional in solution, where conversion between coordinated and uncoordinated pyrazolyl rings is fast on the ^{1}HNMR time scale, resulting in averaging of all pyrazolyl resonances, in accordance with previous observations for similar Rh(cod)Tp species.[3b]

We have also attempted the reactions of **1** and **2** with phosphorus monodentate donors such as PPh_3 and PCy_3, but in all the cases the starting reagents were fully recovered unreacted. Aiming to synthesize mixed phosphino arene Tpms complexes, we have also tried the reactions between [Ru(*p*-cymene)(PR_3)Cl_2] and Li[Tpms] or Li[Tpms^{Ph}], in various solvents (acetone, methanol, and dichloromethane), but again the starting reagents were always identified unreacted.

Compounds **1** and **5** were preliminarily investigated as catalysts toward the homogeneous styrene oxidation, in acetone, with H_2O_2 (see Experimental Section for details). All reactions were run with a 1.0 mol % of Ru catalyst/substrate ratio. The preliminary tests show that they are poorly active, benzaldehyde (isolated in 20% yield) being the only observed product. In that solvent, the use of higher amounts of the Ru catalyst improves the styrene conversion only slightly.

X-ray Diffraction Studies of Compounds 1, 3, and 4. The X-ray molecular structures of the compounds are shown in Figures 1−3, and relevant bond lengths and angles are reported in the corresponding legends. The Ru−N bond distances adopt values of 2.088(2)−2.098(2) Å (**1**·H_2O), 2.082(2)−2.101(2) (**4**), and 2.111(5) Å (**3**); they are in the range of values found

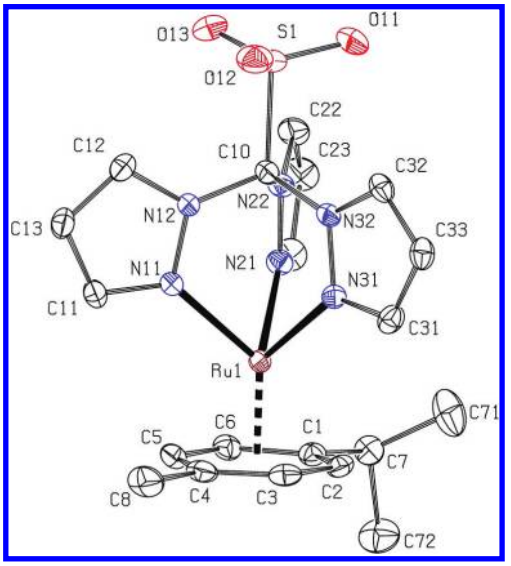


Figure 1. ORTEP diagram of the [Ru(*p*-cymene)(Tpms)]$^+$ cation in **1**·H_2O, with atomic numbering scheme. Ellipsoids are drawn at 50% probability. Hydrogen atoms, chloride counterion, and water molecule are omitted for clarity. Selected bond distances (Å) and angles (deg): N11−Ru1 2.089(2), N21−Ru1 2.098(2), N31−Ru1 2.088(2), N11−N12 1.372(3), N21−N22 1.375(3), N31−N32 1.366(3), C10−S1 1.898(3); N31−Ru1−N11 83.10(8), N31−Ru1−N21 82.82(8), N11−Ru1−N21 80.72(8).

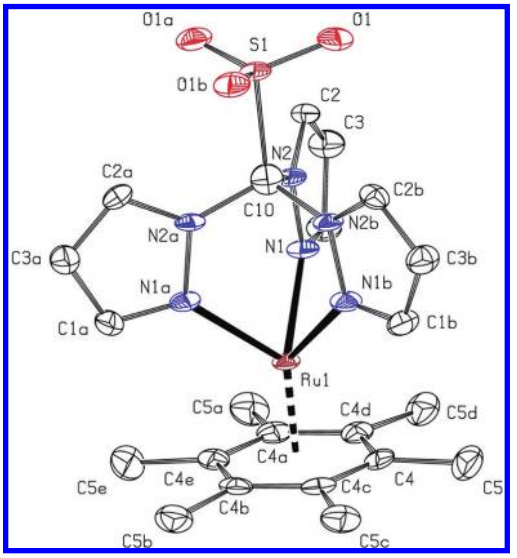


Figure 2. ORTEP diagram of the [Ru(HMB)(Tpms)]$^+$ cation in **3**, with atomic numbering scheme. Ellipsoids are drawn at 50% probability. Hydrogen atoms and chloride counterion are omitted for clarity. Selected bond distances (Å) and angles (deg): Ru1−N1 2.111(5), N1−N2 1.375(6), C10−S1 1.910(11); N1−Ru1−N1*a* 82.2(2). Symmetry operations to generate equivalent atoms: (a) 1−*y*, *x*−*y*, *z*; (b) 1−*x*+*y*, 1−*x*, *z*; (c) 1−*y*, 1−*x*, *z*; (d) *x*, *x*−*y*, *z*; (e) 1−*x* +*y*, *y*, *z*.

for Ru(II) complexes with the related Tpm ligand.[16,17] The ruthenium centers adopt highly distorted tetrahedral geometries, with the scorpionate ligands occupying three of the coordination positions and binding in the N_3-mode. The fourth position can be envisaged as being occupied by the *centroid* of the aromatic ring of the arene ligand. Such distortions result from the chelation of the Tpms ligand, which shows bite angles in the 79.34(9)−84.44(9)° range; consequently, the *centroid*−

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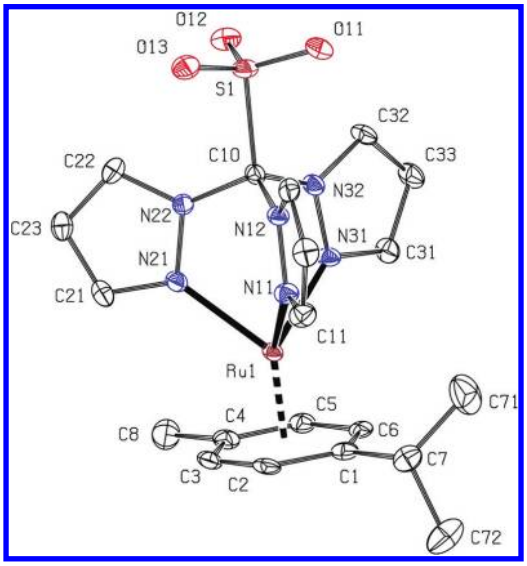

Figure 3. ORTEP diagram of the $[Ru(p\text{-cymene})(Tpms)]^+$ cation in **4**, with atomic numbering scheme. Ellipsoids are drawn at 50% probability. Hydrogen atoms and BF_4^- counterion are omitted for clarity. Selected bond distances (Å) and angles (deg): N11–Ru1 2.101(2), N21–Ru1 2.092(2), N31–Ru1 2.082(2), N11–N12 1.372(3), N21–N22 1.374(3), N31–N32 1.362(3), C10–S1 1.894(3); N21–Ru1–N11 79.34(9), N31–Ru1–N11 83.03(8), N31–Ru1–N21 84.44(9).

Ru–N angles widen to 129.01–132.64° (**1**·H_2O), 130.62–130.67° (**3**), and 128.07–131.92° (**4**).

In every complex cation of this study, the pyrazole rings are entirely planar; however, only in **3**, and as a result of symmetry imposition, does the Ru atom to which they are bound lie in the planes of all rings, which, unavoidably, are mutually inclined at 60°. In the structures of **1** and **4** it is interesting to notice that the counterion has an effect on those parameters; indeed, while in **1** the metal atom deviates 0.007, 0.058, and 0.073 Å from the planes of the pyrazole rings, in **4** those deviations are of 0.007, 0.037, and 0.223 Å. Besides, the pyrazole rings are mutually inclined at 55.06°, 60.59°, and 64.43° (in **1**) or 46.58°, 63.83°, and 69.92° (in **4**). Templeton et al.[18] proposed the M–{N–N}–$C_{methine}$ dihedral angles as a method for measuring such distortions of the pyrazole rings, which would equal 0° for an undistorted geometry. As expected on the basis of the above discussion, this is the situation for **3**, but for **1** such angles are −1.0°, 2.0°, and 6.4°, and for **4** they assume values of −1.6°, 3.5°, and −10.3°, therefore reinforcing the fact that the metal atom is shifted away from the planes of the pyrazole rings in the latter cases.

Electrochemical Studies. The redox properties of compounds **1**–**8** were investigated by cyclic voltammetry, at a Pt disk electrode, in a 0.2 M $[^nBu_4N][BF_4]/CH_3CN$ solution, at 25 °C. They exhibit a single-electron oxidation wave assigned[19−31] to the $Ru^{II} \rightarrow Ru^{III}$ oxidation. The wave meets the reversibility criteria[32] except for compounds **3** and **5**, where it is irreversible due to a chemical reaction that follows the electron transfer. The oxidation potential values ($E^{ox}_{1/2}$ or $E^{ox}_{p/2}$, for the reversible or irreversible waves, respectively, in the range 0.95–1.37 V vs SCE) are given in Table 2 (Figure 4 for compound **4** as a typical case). For the compounds with Cl^- as the counterion an irreversible oxidation wave is observed at $E^{ox}_p \approx 1.25$ V vs SCE, being assigned to the oxidation of Cl^-. Compounds **1**–**8** also show a single-electron irreversible reduction wave in the −0.87 to −1.27 V vs SCE range assigned[33] to the $Ru^{II} \rightarrow Ru^{I}$ reduction, which was not investigated further. The occurrence of a single-electron oxidation (or reduction) has been confirmed by exhaustive controlled potential electrolysis at a potential slightly anodic (or cathodic) to that of the corresponding peak potential. No redox process for free Tpms and $Tpms^{Ph}$ could be detected under the experimental conditions of this study.

Compounds **1** and **4** display redox waves at identical potentials, as expected, since they differ only in their counterions.

The values of the $Ru^{II/III}$ oxidation potential of the complexes are expected[19−31] to reflect the electron-donor characters of their ligands. In fact, for the cationic complexes **1** (or **4**) and **2**, with the common $\{Ru(Tpms)\}^+$ center, the order of the oxidation potentials follows that (in the opposite direction) of

Table 1. Crystallographic Data for Compounds $[Ru(p\text{-cymene})(Tpms)]Cl\cdot H_2O$ (1·H_2O), $[Ru(HMB)(Tpms)]Cl$ (3), and $[Ru(p\text{-cymene})(Tpms)]BF_4$ (4)

	1·H_2O	3	4
empirical formula	$C_{20}H_{23}N_6O_3RuS,H_2O$, Cl	$C_{22}H_{27}N_6O_3RuS,Cl$	$C_{20}H_{23}N_6O_3RuS,BF_4$
fw	582.04	592.08	615.38
cryst syst	monoclinic	trigonal	triclinic
space group	$P2_1/c$	$P\bar{3}m1$	$P\bar{1}$
a (Å)	9.222(4)	12.115	8.8436(10)
b (Å)	16.392(7)	12.115	10.5078(10)
c (Å)	15.534(6)	10.3377(9)	12.6238(14)
α (deg)	90	90	89.147(6)
β (deg)	104.201(2)	90	74.966(7)
γ (deg)	90	120	86.404(6)
V (Å^3)	2276.5(16)	1314.02(11)	1130.7(2)
Z	4	2	2
density(calcd) (Mg/m^3)	1.698	1.497	1.807
absorp coeff (mm^{-1})	0.939	0.812	0.857
F(000)	1184	604	620
reflns collected/unique	19970/4071 [R(int) = 0.0360]	4445/799 [R(int) = 0.0399]	8840/3578 [R(int) = 0.0222]
goodness-of-fit on F^2	1.042	1.115	1.084
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0278, wR_2 = 0.0592	R_1 = 0.0509, wR_2 = 0.1278	R_1 = 0.0276, wR_2 = 0.0638

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Table 2. Cyclic Voltammetric Data[a] for Complexes [RuL(Tpms^R)]$^+$ and [Ru(cod)Cl(Tpms^R)] (R = H or Ph; L = *p*-cymene, benzene, or HMB)

	anodic wave[b] $E^{ox}_{1/2}$ ($E^{ox}_{p/2}$)		cathodic wave E^{red}_p
complex	V vs SCE	V vs NHE	V vs SCE
1, [Ru(*p*-cymene)(Tpms)]Cl	0.95	1.20	−0.97
2, [Ru(benzene)(Tpms)]Cl	1.07	1.32	−0.87
3, [Ru(HMB)(Tpms)]Cl	(0.95)	(1.20)	−1.11
4, [Ru(*p*-cymene)(Tpms)]BF_4	0.96	1.21	−0.97
5, [Ru(*p*-cymene)(Tpms^{Ph})]Cl	(1.02)	(1.27)	−1.00
6, [Ru(benzene)(Tpms^{Ph})]Cl[c]	1.37	1.62	−0.92
7, [RuCl(cod)(Tpms)]	0.96	1.21	−1.10
8, [RuCl(cod)(Tpms^{Ph})]	0.99	1.24	− 1.27

[a]Potential values in volts ± 0.02, in a 0.2 M [^{n}Bu$_4$N][BF_4]/CH_3CN solution, at a Pt disk working electrode determined by using the [Fe(η^5-C_5H_5)$_2$]$^{0/+}$ redox couple ($E^{ox}_{1/2}$ = 0.420 V vs SCE)[15] as internal standard at a scan rate of 200 mVs^{-1}; for irreversible oxidation waves, the values of $E^{ox}_{p/2}$ (half-peak oxidation potential) are given in parentheses; the values can be converted to the NHE reference by adding +0.245 V. [b]E^{ox}_p (Cl$^-$): 1.25 (**1**), 1.27 (**2** and **3**), and 1.24 V (**5**). [c]A reversible single-electron oxidation wave at 0.81 V vs SCE is also observed (see text).

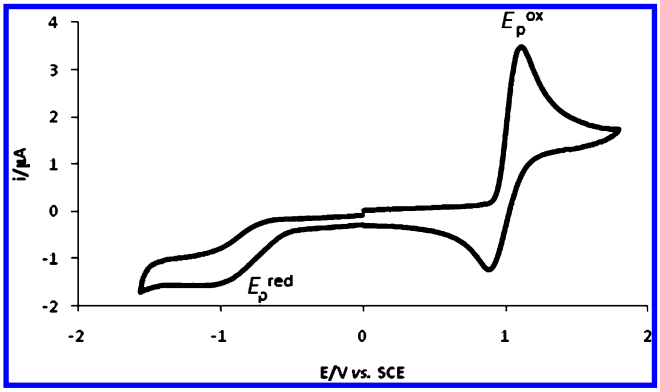

Figure 4. Cyclic voltammogram of [Ru(*p*-cymene)(Tpms)]BF_4 (**4**), in a 0.2 M [^{n}Bu$_4$N][BF_4]/ NCMe solution, at a Pt disk working electrode (d = 0.5 mm), run at a scan rate of 200 mV s^{-1}, starting with the anodic sweep (potential in V vs SCE).

the electron-releasing character of the corresponding variable ligand (cymene > benzene) as measured by the electrochemical Lever E_L ligand parameter (see below) (+1.48 and +1.59 V vs NHE for cymene and benzene, respectively[27]). One should note that E_L is a measure of the electron-donor character of the ligand; the stronger this character, the lower the E_L. Moreover, the above experimental oxidation potentials are in accordance with those predicted from the knowledge of E_L values for cymene,[27] benzene,[27] and Tpms[4e] by applying the Lever method (see below).

Accordingly, the higher oxidation potentials of [Ru(benzene)(Tpms^{Ph})]Cl (**5**) or [RuCl(cod)(Tpms^{Ph})] (**8**), bearing the 3-phenyl-substituted tris(pyrazolyl)methane ligand, than those of the analogous [Ru(benzene)(Tpms)]Cl (**2**) or [RuCl(cod)(Tpms)] (**7**) reflect the expected weaker electron-donor character of the Tpms^{Ph} ligand in comparison with that of Tpms. Hence, the former ligand should present (see also below) a higher E_L value than the latter (−0.09 V vs NHE, per each 2e-donor arm).[4e]

For [Ru(benzene)(Tpms^{Ph})]Cl (**6**) ($E^{ox}_{1/2}$ = 1.37 V vs SCE), another reversible oxidation wave is observed at a lower oxidation potential ($E^{ox}_{1/2}$ = 0.81 V vs SCE), being assigned to the oxidation of the proposed neutral chloro complex [RuCl(benzene)(Tpms^{Ph})] conceivably formed in the electrolyte solution, upon coordination, to some extent, of the Cl$^-$ counterion. The solution would contain a mixture of both complexes, the postulated chloro species having a lower oxidation potential on account of the strong electron-donor character[19] of the chloro ligand.

On the basis of the Lever linear relationship (eq 1), valid for octahedral-type complexes, which relates the redox potential (V vs NHE) with the sum of the E_L values for all of the ligands ($\sum E_L$, two-electron donors, with additive contributions), we propose the estimate of E_L for the tris(3-phenylpyrazolyl)-methanesulfonate (Tpms^{Ph}), hexamethylbenzene (HMB), and 1,5-cyclooctadiene (cod) ligands, by assuming that expression 1 is also valid for half-sandwich arene-type complexes, as we have previously proposed.[3,27] The slope (S_M) and intercept (I_M) are dependent upon the metal, redox couple, spin state, and stereochemistry, being 0.97 and 0.04 V vs NHE, respectively, for the standard octahedral Ru$^{II/III}$ couple.[19] The already known E_L values are as follows: −0.24 (Cl$^-$),[19] −0.09 (Tmps, per each 2e-donor arm),[4e] +1.48 (cymene, overall),[27] and +1.59 (benzene, overall)[27] V vs NHE. The estimated E_L values are collected in Table 3 and have been obtained as indicated below.

Table 3. E_L Ligand Parameter Values Estimated for Tpms^{Ph}, HMB, and cod[a]

	E_L/V vs NHE	
ligand	overall	per each 2e-donor arm
Tpms^{Ph}	−0.15	−0.05
HMB	1.54	0.51[b]
cod	1.71	0.86

[a]From Lever's eq 1. [b]Should be taken cautiously in view of the irreversible character of the oxidation wave of **3**.

$$E = S_M(\sum E_L) + I_M \quad (1)$$

First, we checked the validity of eq 1 for the type of our complexes by estimating the oxidation potential for compounds [Ru(*p*-cymene)(Tpms)]$^+$ (**1** or **4**) and [Ru(benzene)-(Tmps)]$^+$ (**2**) from the knowledge of the E_L values of all their ligands. The estimated values (1.21 and 1.32 V vs NHE, respectively) are in perfect accord with the measured ones (1.20 and 1.32 V vs NHE, correspondingly). In view of this agreement, we then proceeded toward the estimate of the unknown E_L values for the other ligands.

Application of eq 1 to [RuCl(cod)(Tpms)] (**7**) ($E^{ox}_{1/2}$ = 0.96 V vs SCE = 1.21 V vs NHE) with the known values of S_M and I_M and of E_L for Tpms and Cl$^-$ (see above) allows us to estimate the following overall E_L parameter for 1,5-cyclo-octadiene (cod): 1.71 V vs NHE (Table 3). This corresponds to E_L = 0.86 V vs NHE per each 2e-donor olefinic bond, which is comparable to the known value (0.76 V vs NHE)[19] for ethylene, the latter acting as a slightly stronger electron donor.

At this stage, the E_L parameter for the Tpms^{Ph} ligand can be estimated from the oxidation of [RuCl(cod)(Tpms^{Ph})] (**8**), [Ru(benzene)(Tpms^{Ph})]Cl (**6**), and [Ru(*p*-cymene)(Tpms^{Ph})]Cl (**5**) (although cautiously in view of its irreversibility). The obtained average value of −0.05 V vs NHE (for each

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coordinating pyrazolyl arm assuming additive contributions) is in agreement with the expected slightly weaker electron-donor character of $Tpms^{Ph}$ relative to Tpms (E_L = −0.09 V vs NHE),[4e] due to the phenyl substituent at the pyrazolyl rings in the former ligand.

Moreover, application of eq 1 to [Ru(HMB)(Tpms)]Cl (**3**) leads to the estimate of 1.54 V vs NHE for the overall E_L parameter of HMB. This value is slightly lower than that of benzene (1.59 V vs NHE),[27] in accordance with the stronger electron-donor character of HMB imparted by the methyl substituents. However, E_L(HMB) is slightly higher than that of cymene (1.48 V vs NHE).[27] Nevertheless, the estimated E_L value for HMB should be taken cautiously since it is based on the oxidation potential of an irreversible wave.

CONCLUSIONS

Novel [Ru(L)(L′)]X complexes (L = *p*-cymene, benzene or hexamethylbenzene, cyclooctadiene, L′ = tris(pyrazolyl)-methanesulfonate or the 3-phenylpyrazolyl-substituted derivative, X = Cl or BF_4) have been synthesized, and NMR spectroscopy has been employed to investigate the complexes' stability in solution and reactivity. These compounds, very soluble in water and in most organic solvents, are very stable and unreactive, for example, toward PR_3 and S-donor species, in accordance with the lack of catalytic activity for styrene oxidation. The external chloride in [Ru(arene)(Tpms)]Cl can be easily replaced by other counterions such as BF_4^-, through metathetic reaction, but no displacement of arene and Tpms from the Ru coordination center is possible under the conditions we have employed. The Tpms and $Tpms^{Ph}$ ligands' coordination mode has been established by IR and single-crystal X-ray studies: in all cases the N_3 coordination has been found, with no evidence for N_2O and N_2 coordination being detected.

The electrochemical study has allowed comparing the electron-donor characters of C-scorpionate and arene ligands and estimating, for the first time, the E_L values for $Tpms^{Ph}$, HMB, and cod. However, one should be cautious with the obtained values since, with the exception of $Tpms^{Ph}$, each of them is based on a single complex and, moreover, in the case of HMB, the oxidation potential is not the thermodynamic one in view of the irreversibility of the oxidation wave.

It was also assumed that the S_M and I_M values for the octahedral $Ru^{II/III}$ redox couple (used in eq 1) are also valid for the half-sandwich complexes of the present study, what is in agreement with our previous proposal[3,27] and with the checked validity of that expression for the complexes of the current work bearing ligands with already known E_L values. Nevertheless, this hypothesis has still to be checked for a broader variety of arene-type complexes.

ASSOCIATED CONTENT

Supporting Information

This material is available free of charge via the Internet at http://pubs.acs.org.

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