ORGANOMETALLICS

ARTICLE

pubs.acs.org/Organometallics

Coordination Chemistry of the (η^6-*p*-Cymene)ruthenium(II) Fragment with Bis-, Tris-, and Tetrakis(pyrazol-1-yl)borate Ligands: Synthesis, Structural, Electrochemical, and Catalytic Diastereoselective Nitroaldol Reaction Studies

Claudio Pettinari,*[,†] Fabio Marchetti,[‡] Adele Cerquetella,[‡] Riccardo Pettinari,[†] Magda Monari,[§] Tatiana C. O. Mac Leod,[⊥] Luísa M. D. R. S. Martins,[⊥,∥] and Armando J. L. Pombeiro*[,⊥]

[†]School of Pharmacy, University of Camerino, Via S. Agostino 1, 62032 Camerino, Italy

[‡]School of Science & Technology, University of Camerino, Via S. Agostino 1, 62032 Camerino, Italy

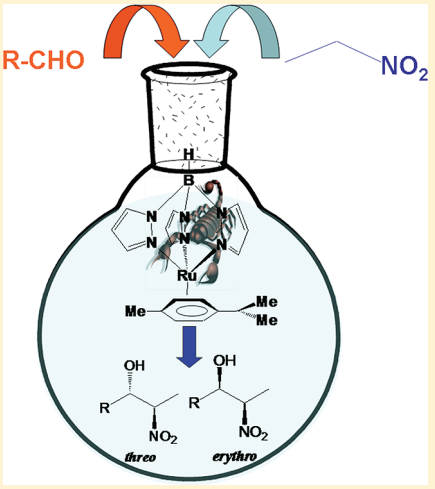
[§]Dipartimento di Chimica "G. Ciamician", Università di Bologna, Via Selmi 2, I-40126 Bologna, Italy

[⊥]Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, TU-Lisbon, Avenida Rovisco Pais, 1049-001 Lisbon, Portugal

[∥]Área Departamental de Engenharia Química, Instituto Superior de Engenharia de Lisboa, Rua Conselheiro Emídio Navarro, 1059-007, Lisboa, Portugal

Supporting Information

ABSTRACT: Novel [Ru(η^6-*p*-cymene)(κ^2-L)X] and [Ru(η^6-*p*-cymene)(κ^3-L)]X·nH$_2$O complexes (L = bis-, tris-, or tetrakis-pyrazolylborate; X = Cl, N_3, PF_6, or CF_3SO_3) are prepared by treatment of [Ru(η^6-*p*-cymene)Cl_2]$_2$ with poly(pyrazolyl)borate derivatives [M(L)] (L in general; in detail L = Ph_2Bp = diphenylbis(pyrazol-1-yl)borate; L = Tp = hydrotris(pyrazol-1-yl)borate; L = pzTp = tetrakis(pyrazol-1-yl)borate; L = Tp^{4Bo} = hydrotris(indazol-1-yl)borate, L = $Tp^{4Bo,5Me}$ = hydrotris(5-methylindazol-1-yl)borate; L = $Tp^{Bn,4Ph}$ = hydrotris(3-benzyl-4-phenylpyrazol-1-yl)borate; M = Na, K, or Tl) and characterized by analytical and spectral data (IR, ESIMS, ^{1}H and ^{13}C NMR). The structures of [Ru(η^6-*p*-cymene)(Ph_2Bp)Cl] (**1**) and [Ru(η^6-*p*-cymene)(Tp)Cl] (**3**) have been established by single-crystal X-ray diffraction analysis. Electrochemical studies allowed comparing the electron-donor characters of Tp and related ligands and estimating the corresponding values of the Lever E_L ligand parameter. The complexes [Ru(η^6-*p*-cymene)(κ^2-L)X] and [Ru(η^6-*p*-cymene)(κ^3-L)]X·nH$_2$O act as catalyst precursors for the diastereoselective nitroaldol reaction of benzaldehyde and nitroethane to the corresponding β-nitroalkanol (up to 82% yield, at room temperature) with diastereoselectivity toward the formation of the *threo* isomer.



INTRODUCTION

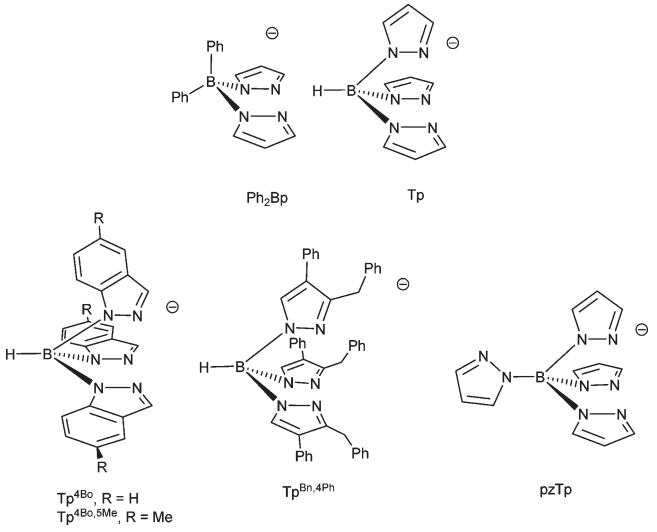
(η^6-Arene)ruthenium(II) derivatives have recently received increased attention on account of their potential as catalysts for a number of organic reactions, ranging from hydrogen transfer[1] to ring-closing metathesis,[2] from simple stoichiometric C−C couplings[3] to catalytic oxidative Heck reactions,[4] and from allyl alcohol isomerization to alkyne hydration.[5] The [Ru(η^6-arene)(chelating-ligand)Cl]-type complexes exhibit the characteristic "piano stool" structure, with the unreactive arene as a "spectator ligand" in the metal coordination sphere and the chloride as a suitable "leaving group".[6] These structural features seem favorable to afford sequential reactions involved in catalysis.

The antibacterial[7] and antitumor activity[8] presented by some water-soluble (η^6-arene) ruthenium(II) has also evoked interest in recent years. The complex [(η^6-biphenyl)Ru(en)Cl][PF_6] (en = ethylenediamine) is active in the A2780 human ovarian cancer xenograft and non-cross-resistant in the A2780cis xenograft,[9] appearing to strongly and specifically bind to guanine bases on DNA.[10]

Attempts to isolate poly(pyrazolyl)borate and poly(pyrazolyl)methane derivatives of (η^6-arene) ruthenium(II) are mainly limited to mixed-sandwich complexes incorporating the tridentate N-donor ligand acting in a κ^3 coordination mode.[11] Some half-sandwich Ru(η^6-arene) complexes containing κ^2-tris(pyrazolyl)borate and -tris(pyrazolyl)methane ligands have been isolated, where the hapticity of the potentially tridentate ligands has been modified by controlling the temperature and reaction times in acetonitrile.[12] It has been reported that the extent of dissolution of the precursor dimer [Ru(η^6-arene)Cl_2]$_2$

Received: December 6, 2010
Published: March 03, 2011

Chart 1



in a polar solvent such as MeCN has been recognized to play an important role in directing the formation of mixed-sandwich or half-sandwich Ru(II) complexes.[12] However several steps were required to isolate $[Ru(\eta^6\text{-arene})(\kappa^2\text{-Tp})Cl]$ or $[Ru(\eta^6\text{-arene})(\kappa^2\text{-HC(pz)}_3)Cl][PF_6]$ and yields were generally low, ranging from 30% to 60%, depending on the steric hindrance of the arene group.

Herein, we report a systematic investigation of the interaction between (*p*-cymene)ruthenium(II) species and the bis-, tris-, and tetrakis(pyrazolyl)borates Ph_2Bp, Tp, Tp^{4Bo}, $Tp^{4Bo,5Me}$, $Tp^{Bn,4Ph}$, and pzTp, shown in Chart 1, together with spectroscopic and structural characterization of some derivatives and electrochemical studies.

Moreover, in view of the expected coordination versatility of such ligands at the robust arene-Ru(II) center, with potential significance in catalysis, we have tested successfully those complexes as catalysts or catalyst precursors for the diastereoselective nitroaldol (Henry) reaction of a nitroalkane with an aldehyde to form the corresponding β-nitroalkanol. This reaction was selected on account of its relevance toward carbon−carbon bond formation to generate β-nitroalkanols, which are common building blocks present in biologically active natural products and pharmaceuticals.[13−15] Due to the practical importance of this reaction, much attention has been paid to its diastereoselectivity, but the stereochemical control of the two newly generated carbon centers remains a difficult task to achieve. A stereoselective synthesis of either the *threo* or *erythro* isomer would be desirable.

Various complexes of Zn(II),[16−18] Cr(III),[19] La(III),[20] Co(II),[21] and Cu(II)[22] have been shown to catalyze the nitroaldol reaction, but the diastereoselectivity has been less studied. Moreover, the use of ruthenium catalysts for this process remained unexplored before the current study, which has allowed the development of a catalytic diastereoselective nitroaldol reaction of nitroethane with benzaldedyde in the presence of the above arene ruthenium(II) complexes.

EXPERIMENTAL SECTION

Materials and Methods. The reagent $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ was purchased from Alfa (Karlsruhe) and Aldrich (Milwaukee) and used as received. Salts of the scorpionate ligands Tp^{4Bo},[23,24] $Tp^{4Bo,5Me}$,[23] pzTp,[25,26a] Ph_2Bp,[27] Tp,[25,26a] and $Tp^{Bn,4Ph}$ [26b] were synthesized as previously reported. The samples for microanalyses were dried *in vacuo* to constant weight (20 °C, ca. 0.1 Torr). Elemental analyses (C, H, N, S) were performed in-house with a Fisons Instruments 1108 CHNS-O elemental analyzer. IR spectra were recorded from 4000 to 200 cm^{-1} with a Perkin-Elmer Spectrum 100 FT-IR instrument and a Perkin-Elmer System 2000 FT-IR instrument. ^1H and ^{13}C NMR spectra were recorded on a 400 Mercury Plus Varian instrument operating at room temperature (400 MHz for ^1H and 100 MHz for ^{13}C). H and C chemical shifts (δ) are reported in parts per million (ppm) from $SiMe_4$ (^1H and ^{13}C calibration by internal deuterium solvent lock). Melting points are uncorrected and were taken on an STMP3 Stuart scientific instrument and on a capillary apparatus. The electrical conductivity measurements (Λ_M, reported as S cm^2 mol^{-1}) of acetonitrile and dichloromethane solutions of the complexes were taken with a Crison CDTM 522 conductimeter at room temperature. The positive and negative electrospray mass spectra were obtained with a Series 1100 MSI detector HP spectrometer, using an acetonitrile mobile phase. Solutions (3 mg/mL) for electrospray ionization mass spectrometry (ESI-MS) were prepared using reagent-grade acetonitrile. For the ESI-MS data, mass and intensities were compared to those calculated using IsoPro Isotopic Abundance Simulator, version 2.1.[28] Peaks containing ruthenium(II) ions are identified as the center of an isotopic cluster.

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 $[nBu_4N][BF_4]-CH_2Cl_2$, 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 ($E^{ox}_{1/2}$ = 0.525 V vs SCE).[29]

Characterization of the Salt [K(Ph_2Bp)]. $[K(Ph_2Bp)]$ was prepared by using a published procedure.[27] The compound is soluble in alcohols, acetone, and acetonitrile. Yield: 81%. Mp: 250 °C, 286−288 °C dec. Anal. Calcd for $C_{18}H_{16}BN_4K$: C, 63.91; H, 4.77; N, 16.56. Found: C, 63.61; H, 4.95; N, 16.42. IR (Nujol, cm^{-1}): 1459s, 1373m ν(C═C, C═N), 1303w, 1287m, 1272m, 1166m, 1074m, 1043m, 962m, 872w, 830w, 724m, 643w, 626w, 641m, 316m, 300m, 255w. ^1H NMR (acetone-d_6, 298 K): δ 6.00t (2H, H_{4Bp}), 7.0−7.2m br (15H, $(C_6H_5)_2Bp$), 7.30d (2H, H_{5Bp}), 7.42d (2H, H_{3Bp}). $^{13}C\{^1H\}$ (acetone-d_6): δ, 102.4s (C_{4Bp}), 124.8, 126.7, 133.7 (C_{arom}), 135.2s (C_{5Bp}), 139.0s (C_{3Bp}).

Synthesis of [Ru(η^6-*p*-cymene)(κ^2-Ph_2Bp)Cl] (1). An acetonitrile solution (30 mL) containing $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ (0.316 g, 0.5 mmol) and $[K(Ph_2Bp)]$ (0.349 g, 1.0 mmol) was stirred for 2−3 h at room temperature to yield a colorless precipitate, which was filtered off and shown to be KCl. The clear solution obtained was evaporated under vacuum. Recrystallization in methanol at 4 °C slowly yielded orange-red crystals, which were identified as **1**, soluble in alcohols, acetone, acetonitrile, DMSO, and chlorinated solvents. Yield: 86%. Mp: 265−267 °C dec. Anal. Calcd for $C_{28}H_{30}BClN_4Ru$: C, 59.01; H, 5.31; N, 9.83. Found: C, 58.96; H, 5.48, N, 9.45. Λ_M (acetonitrile, 298 K, 10^{-3} mol/L): 10.4 S cm^2 mol^{-1}. Λ_M (CH_2Cl_2, 298 K, 10^{-3} mol/L): 2.2 S cm^2 mol^{-1}.

IR (Nujol, cm^{-1}): 3064w, 3048w $\nu(C_{arom}-H)$, 1429s, 1405s, 1376m $\nu(C{=}C, C{=}N)$, 279s ν(Ru-Cl). ^1H NMR ($CDCl_3$, 298 K): δ 1.30d (6H, CH_3-C_6H_4-CH(CH_3)$_2$), 1.67s (3H, CH_3-C_6H_4-CH(CH_3)$_2$), 2.78m (1H, CH_3-C_6H_4-CH(CH_3)$_2$), 4.72dd, (4H, AA′BB′ system, CH_3-C_6H_4-CH(CH_3)$_2$), 6.30t (2H, H_{4Bp}), 6.80m (2H, (C_6H_5)$_2$Bp), 7.06d (2H, (C_6H_5)$_2$Bp), 7.2−7.3m (8H, (C_6H_5)$_2$Bp + H_{5Bp}), 7.88d (2H, H_{3Bp}). $^{13}C\{^1H\}$ ($CDCl_3$): δ 18.6s (CH_3-C_6H_4-CH(CH_3)$_2$), 22.9s, (CH_3-C_6H_4-CH(CH_3)$_2$), 30.2s (CH_3-C_6H_4-CH(CH_3)$_2$), 80.2s, 88.3s, 101.9s, 104.0s (CH_3-C_6H_4-CH(CH_3)$_2$), 105.8s (C_{4Bp}), 127.1s, 127.6s, 132.1s, 135.9s (C_{arom}), 139.1s (C_{5pz}), 145.1s (C_{3Bp}).

Synthesis of [Ru(η^6-*p*-cymene)(κ^2-Ph_2Bp)(N_3)] (2). A solution/suspension of **1** (0.090 g, 1 mmol) and NaN_3 (0.020 g, 2 mmol) was stirred in dry acetone for 3 h at room temperature to give a colorless precipitate, which was filtered off and shown to be NaCl. The clear solution obtained was evaporated under vacuum, and the residue washed with diethyl ether and identified as **2**. Yield: 95%. Mp: 100−105 °C dec. Anal. Calcd for $C_{28}H_{30}BN_7Ru$: C, 58.34; H, 5.25; N, 17.01. Found: C, 58.63; H, 5.30, N, 17.18. Λ_M (acetonitrile, 298 K, 10^{-3} mol/L): 11.4 S cm^2 mol^{-1}. Λ_M (CH_2Cl_2, 298 K, 10^{-3} mol/L): 2.8 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 2028m $\nu(N_3)$, 1460s, 1373m $\nu(C{=}C, C{=}N)$. ^1H NMR ($CDCl_3$, 298 K): δ 1.30d (6H, CH_3-C_6H_4-CH(CH_3)$_2$), 1.62s (3H, CH_3-C_6H_4-CH(CH_3)$_2$), 2.78−2.85m (1H, CH_3-C_6H_4-CH(CH_3)$_2$), 4.5dd (4H, AA′BB′ system, CH_3-C_6H_4-CH(CH_3)$_2$), 6.31t (2H, H_{4Bp}), 6.80m (2H, (C_6H_5)$_2$Bp), 7.06d (2H, (C_6H_5)$_2$Bp), 7.2−7.3m (8H, (C_6H_5)$_2$Bp + H_{5Bp}), 7.83d (2H, H_{3Bp}).

Synthesis of [Ru(η^6-*p*-cymene)(κ^2-Tp)Cl] (3). [{Ru(η^6-*p*-cymene)Cl_2}$_2$] (0.306 g, 0.5 mmol) was dissolved in dichloromethane (20 mL) and stirred for 30 min; then [Na(Tp)] (0.236 g, 1.0 mmol) was added to the red solution, which immediately turned orange. After 1 h stirring at room temperature a colorless precipitate (NaCl) slowly formed, which was removed by filtration. The filtrate was then evaporated under vacuum, and the crude residue, obtained in 78% yield, containing both [Ru(η^6-*p*-cymene)(κ^2-Tp)Cl] (**3**) and [Ru(η^6-*p*-cymene)(κ^3-Tp)]Cl (**3′**) in 2:1 ratio, was treated with *n*-hexane (10 mL). An insoluble precipitate was separated, which upon recrystallization from MeCN has been identified as **3**. Anal. Calcd for $C_{19}H_{24}BClN_6Ru$: C. 47.17; H, 5.00; N, 17.37. Found: C. 47.52; H, 5.30; N, 17.45. IR (Nujol, cm^{-1}): 3098w, 3052w $\nu(C-H_{pz})$, 2434m br ν(B−H), 1505m $\nu(C{=}C{+}C{=}N)$, 1413s, 1394m ν(B−N), 456m, 404m, 366s ν(Ru−C), 279 m ν(Ru−Cl), 247s ν (Ru−N). Λ_M (acetonitrile, 298 K, 10^{-3} mol/L): 5.9 S cm^2 mol^{-1}. Λ_M (CH_2Cl_2, 298 K, 10^{-3} mol/L): 1.3 S cm^2 mol^{-1}. ^1H NMR ($CDCl_3$): δ 1.23d (6H, CH_3-C_6H_4-CH(CH_3)$_2$), 2.3s (3H, CH_3-C_6H_4-CH(CH_3)$_2$), 2.92m (1H, CH_3-C_6H_4-CH(CH_3)$_2$), 3.50br (1H, BH_{Tp}), 5.42dd (4H, ^3J(H−H): 6.4 and 6.0 Hz, AA′BB′, CH_3-C_6H_4-CH(CH_3)$_2$), 5.99pt (2H, H_{4Tp}), 6.37pt (1H, H_{4Tp}), 6.95d, (2H, H_{5Tp}), 7.47d (2H, H_{3Tp}), 7.78d (2H, H_{5Tp} + H_{3Tp}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 19.2s (CH_3-C_6H_4-CH(CH_3)$_2$), 22.8s (CH_3-C_6H_4-CH(CH_3)$_2$), 31.2s (CH_3-C_6H_4-CH(CH_3)$_2$), 86.4s, 86.8s, 106.6s, 108.1s (CH_3-C_6H_4-CH(CH_3)$_2$), 101.7s, 107.4s (C_{4Tp}), 133.1s, 135.6s (C_{5Tp}), 142.1s, 145.4s (s, C_{3Tp}). ESI-MS (MeCN) (+): *m*/*z* (%) 448 (100) [Ru(η^6-*p*-cymene)(Tp)]$^+$, 932 (8) [{Ru(η^6-*p*-cymene)(Tp)}$_2$Cl]$^+$.

Synthesis of [Ru(η^6-*p*-cymene)(κ^3-Tp)][PF_6] (4). Derivative **3** (0.484 g, 1 mmol) was dissolved in methanol (30 mL), and $AgPF_6$ (0.253 g, 1 mmol) was added. A colorless precipitate immediately formed, which was filtered off (AgCl). From the filtered solution a residue was recovered, which was identified by analytical and spectroscopic methods (IR and ^1H NMR) as **4**, previously reported.[12]

Synthesis of [Ru(η^6-*p*-cymene)(κ^3-Tp)]$O_3SCF_3 \cdot H_2O$ (5). A mixture of **3** (0.030 g, 1 mmol) and AgO_3SCF_3 (0.016 g, 1 mmol) was stirred in dry CH_2Cl_2 for 3 h at room temperature. AgCl was immediately formed. The filtered solution was then evaporated, and the residues were washed with a mixture of dichloromethane−diethyl ether to give a colorless precipitate identified as **5**. Yield: 91%. Mp: 70 °C dec. Anal. Calcd for $C_{19}H_{26}BN_6RuO_4F_3S$: C, 37.99; H, 4.45; N, 13.99; S, 5.40. Found: C, 37.82; H, 4.34; N, 13.93; S, 5.31. IR (Nujol, cm^{-1}): 3490br ν(O−H), 3133w, 3074w, $\nu(C_{arom}-H)$, 2500m ν(B−H), 1629m δ(O−H), 1504m, 1470m, 1411s $\nu(C{=}C, C{=}N)$, 1155s, 759s $\nu(O_3SCF_3)$. Λ_M (acetonitrile, 298 K, 10^{-3} mol/L): 128.5 S cm^2 mol^{-1}. Λ_M (CH_2Cl_2, 298 K, 10^{-3} mol/L): 26.6 S cm^2 mol^{-1}. ^1H NMR ($CDCl_3$, 298 K): δ 1.18−1.21d (6H, CH_3-C_6H_4-CH(CH_3)$_2$), 2.34s (3H, CH_3-C_6H_4-CH(CH_3)$_2$), 2.98 m (1H, CH_3-C_6H_4-CH(CH_3)$_2$), 6.0dd (4H, ^3J(H−H): 6.3 and 6.0 Hz,4H, AA′BB′ system, CH_3-C_6H_4-CH(CH_3)$_2$), 6.31t (3H, H_{4Tp}), 7.56d (3H, H_{5Tp}), 8.31d (3H, H_{3Tp}). ESI-MS (MeCN) (+): *m*/*z* (%) 448 (100) [Ru(η^6-*p*-cymene)(Tp)]$^+$, 466 (50) [Ru(η^6-*p*-cymene)(Tp)(H_2O)]$^+$, 489 (70) [Ru(η^6-*p*-cymene)-(Tp)(MeCN)]$^+$.

Synthesis of [Ru(η^6-*p*-cymene)(κ^2-Tp)(N_3)] (6). A mixture of **3** (0.472 g, 1 mmol) and NaN_3 (0.020 g, 2 mmol) was stirred in dry acetone for 3 h at room temperature to give a colorless precipitate, which was filtered off and shown to be NaCl. The clear solution obtained was evaporated under vacuum, and the residue identified as **6**. Yield: 71%. Mp: 100 °C dec. Λ_M (acetonitrile, 0.24 × 10^{-3} M): 3.4 S cm^2 mol^{-1}. Anal. Calcd for $C_{19}H_{24}BN_9Ru$: C, 46.54; H, 4.93; N, 25.71. Found: C. 46.13; H, 4.75; N, 25.76. IR (Nujol, cm^{-1}): 3114w ν(C−H), 2483m br ν(B−H), 2025vs $\nu(N_3)$, 1499m $\nu(C{=}C + C{=}N)$, 1401s ν(B−N). Λ_M (acetonitrile, 298 K, 10^{-3} mol/L): 12.6 S cm^2 mol^{-1}. Λ_M (CH_2Cl_2, 298 K, 10^{-3} mol/L): 3.3 S cm^2 mol^{-1}. ^1H NMR ($CDCl_3$): δ 1.52d (6H, CH_3-C_6H_4-CH(CH_3)$_2$), 1.98s (3H, CH_3-C_6H_4-CH(CH_3)$_2$), 2.95 m (1H, CH_3-C_6H_4-CH(CH_3)$_2$), 3.20br (1H, BH_{Tp}), 6.10 m (4H, AA′BB′, CH_3-C_6H_4-CH(CH_3)$_2$), 6.37dd (2H, ^2J(H−H): 1.6 Hz), 6.44dd (1H, ^2J(H−H): 1.6 Hz) (H_{4Tp}), 7.18d (2H, ^2J(H−H): 2.5 Hz), 7.40d (1H, ^2J(H−H): 2.4 Hz) (H_{5Tp}), 7.69d (2H, ^2J(H−H): 1.7 Hz), 7.82d (1H, ^2J(H−H): 1.6 Hz) (H_{3Tp}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 20.1 (s, CH_3-C_6H_4-CH(CH_3)$_2$), 22.6 (s, CH_3-C_6H_4-CH(CH_3)$_2$), 32.3 (s, CH_3-C_6H_4-CH(CH_3)$_2$), 85.2s, 86.5s, 107.7s, 108.0s (CH_3-C_6H_4-CH-(CH_3)$_2$), 106.9s 107.4s (C_{4Tp}), 135.6s, 137.6s (C_{5Tp}), 144.1s, 145.8s (C_{3Tp}). ESI-MS (MeCN) (+): *m*/*z* (%) 448 (100) [Ru(η^6-*p*-cymene)-(Tp)]$^+$, 466 (60) [Ru(η^6-*p*-cymene)(Tp)(H_2O)]$^+$.

Synthesis of [Ru(η^6-*p*-cymene)(κ^2-Tp^{4Bo})Cl] (7). To a CH_2Cl_2 solution (15 mL) containing [Ru(η^6-*p*-cymene)Cl_2]$_2$ (0.053 g, 0.5 mmol) was added [Tl(Tp^{4Bo})] (0.100 g, 1.0 mmol), and the suspension was stirred for 3 h at room temperature. A colorless precipitate was formed, which was filtered off and shown to be TlCl. The clear solution obtained was evaporated under vacuum, and the crude residue recrystallized from methanol at 4 °C slowly to yield an orange-red microcrystalline compound, which was identified as **7**. The compound is soluble in alcohols, acetone, acetonitrile, DMSO, and chlorinated solvents. Yield: 91%. Mp: 140−142 °C dec. Anal. Calcd for $C_{31}H_{30}BClN_6Ru$: C, 58.73; H, 4.77; N, 13.26. Found: C, 58.40; H, 4.88, N, 12.96. Λ_M (acetonitrile, 298 K, 10^{-3} mol/L): 10.0 S cm^2 mol^{-1}. Λ_M (CH_2Cl_2, 298 K, 10^{-3} mol/L): 2.8 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 2403w ν(B−H), 1614m, 1493m $\nu(C{=}C, C{=}N)$, 279s ν(Ru−Cl). ^1H NMR ($CDCl_3$, 298 K): δ 1.25d (6H, CH_3-C_6H_4-CH(CH_3)$_2$), 1.79s (3H, CH_3-C_6H_4-CH(CH_3)$_2$), 2.95m (1H, CH_3-C_6H_4-CH(CH_3)$_2$), 5.20d (2H, H_{Tp4Bo}), 5.54dd (4H, AA′BB′ system, CH_3-C_6H_4-CH-(CH_3)$_2$), 6.69m, 6.85m, (4H, H_{Tp}), 7.0br (2H, H_{Tp4Bo}), 7.51d (2H, H_{Tp}), 7.6−7.8m (2H, H_{Tp}), 8.35s (1H, H_{Tp}), 8.48s (2H, H_{Tp}). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 18.4s (CH_3-C_6H_4-CH(CH_3)$_2$), 22.6s, (CH_3-C_6H_4-CH(CH_3)$_2$), 30.7s (CH_3-C_6H_4-CH(CH_3)$_2$), 84.3s, 86.8s (CH_3-C_6H_4-CH(CH_3)$_2$), 101.1, 106.5 (C_{Tp4Bo}) 112.3s, 113.1s, 119.2s, 120.6s, 124.3s, 125.6s, 125.8s, 126.3s (C_{arom} + C_{Tp}), 135.9s, 140.8d, 145.5s (C_{Tp}). ESI-MS (MeCN) (+): *m*/*z* (%) 598 (100) [Ru(η^6-*p*-cymene)(Tp^{4Bo})$_3$]$^+$.

Synthesis of [Ru(η^6-*p*-cymene)(κ^2-$Tp^{4Bo,5Me}$)Cl] (8). Compound **8** was prepared following a procedure similar to that reported for **7** by using [Ru(η^6-*p*-cymene)Cl_2]$_2$ and [Tl($Tp^{4Bo,5Me}$)]. **8** is soluble in alcohols, acetone, acetonitrile, DMSO, and chlorinated solvents. Yield:

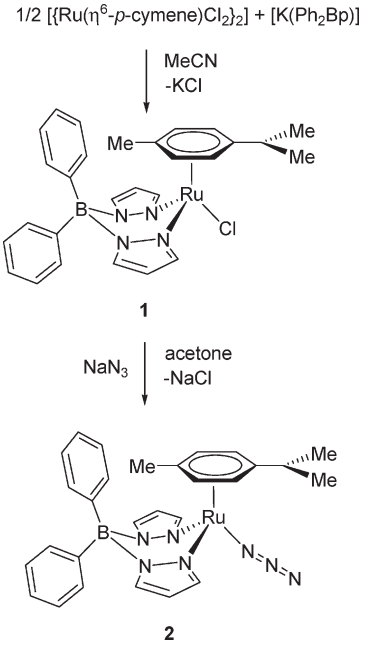
72%. Mp: 128−130 °C dec. Anal. Calcd for $C_{34}H_{36}BClN_6Ru$: C, 60.41; H, 5.37; N, 12.43. Found: C, 60.23; H, 5.25, N, 12.17. Λ_M (acetonitrile, 298 K, 10^{-3} mol/L): 8.3 S cm^2 mol^{-1}. Λ_M (CH_2Cl_2, 298 K, 10^{-3} mol/L): 3.0 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 2403w ν(B−H), 1627m, 1506m ν(C═C, C═N), 271s ν(Ru−Cl). ^{1}H NMR ($CDCl_3$, 298 K): δ 1.28d (6H, CH_3-C_6H_4-CH(CH_3)$_2$), 1.83s (3H, CH_3-C_6H_4-CH(CH_3)$_2$), 2.25s (6H, CH_{3Tp}), 2.35s (3H, CH_{3Tp}), 2.95 m (1H, CH_3-C_6H_4-CH(CH_3)$_2$), 5.17d, (3H, H_{Tp}), 5.55dd (4H, AA′BB′ system, CH_3-C_6H_4-CH(CH_3)$_2$), 6.54s (1H, H_{Tp}), 6.58s (1H, H_{Tp}), 6.72br (2H, H_{Tp}), 7.30s (2H, H_{Tp}), 7.51s (1H, H_{Tp}), 8.25s (1H, H_{Tp}), 8.39s (2H, H_{Tp}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ, 18.4s (CH_3-C_6H_4-CH(CH_3)$_2$), 21.2s, 21.5s (CH_3-C_6H_4-CH(CH_3)$_2$), 22.6s (CH_{3Tp}), 30.7s (CH_3-C_6H_4-CH(CH_3)$_2$), 84.1s, 86.8s, (CH_3-C_6H_4-CH(CH_3)$_2$), 101.0s (C_{Tp}), 112.0s, 112.7s, 117.9s, 119.4s, 124.7s, 127.8s, 128.7s, 129.9s (C_{arom} + C_{Tp}), 135.1s 140.0s, 144.3s (C_{Tp}). ESI-MS (MeCN) (+): m/z (%) 640 (100) [Ru(η^6-p-cymene)($Tp^{4Bo,5Me}$)]$^+$.

Synthesis of [Ru(η^6-*p*-cymene)(κ^3-$Tp^{Bn,4Ph}$)Cl] (9). Compound **9** has been prepared following a procedure similar to that reported for **7** by using [Ru(η^6-p-cymene)Cl_2]$_2$, [Tl($Tp^{Bn,4Ph}$)], and acetonitrile. The compound is soluble in alcohols, acetone, acetonitrile, DMSO, and chlorinated solvents. Yield: 90%. Mp: 131−134 °C dec. Anal. Calcd for $C_{58}H_{54}BClN_6Ru$: C, 70.71; H, 5.54; N, 8.55. Found: C, 70.45; H, 5.65, N, 8.24. Λ_M (acetonitrile, 298 K, 10^{-3} mol/L): 118.7 S cm^2 mol^{-1}. Λ_M (CH_2Cl_2, 298 K, 10^{-3} mol/L): 21.5 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 2431w ν(B−H), 1603m, 1533m, 1493m ν(C═C, C═N), 280s ν(Ru−Cl). ^{1}H NMR ($CDCl_3$, 298 K): δ 0.99d (6H, CH_3-C_6H_4-CH(CH_3)$_2$), 2.17s (3H, CH_3-C_6H_4-CH(CH_3)$_2$), 2.99m (1H, CH_3-C_6H_4-CH(CH_3)$_2$), 4.3m, 4.5m (4H, CH_{2Tp}), 4.95m (4H, AA′BB′ system, CH_3-C_6H_4-CH(CH_3)$_2$), 5.05m (2H, CH_{2Tp}), 7.12−7.34m br (30H, Ph_{Tp}), 7.55s (2H, H_{5Tp}), 8.01s, (1H, H_{5Tp}). ESI-MS (MeCN) (+): m/z (%) 947 (100) [Ru(η^6-p-cymene)($Tp^{Ph,Bn}$)$_3$)]$^+$.

Synthesis of [Ru(η^6-*p*-cymene)(κ^2-pzTp)Cl] (10). Compound **10** has been prepared following a procedure similar to that reported for **7** by using [Ru(η^6-p-cymene)Cl_2]$_2$, [K(pzTp)], and acetonitrile. **10** is soluble in alcohols, acetone, acetonitrile, DMSO, and chlorinated solvents. Yield: 61%. Mp: 192−194 °C. Anal. Calcd for $C_{22}H_{26}BClN_8Ru$: C, 48.06; H, 4.77; N, 20.38. Found: C, 47.83; H, 4.85, N, 19.96. Λ_M (acetonitrile, 298 K, 10^{-3} mol/L): 12.9 S cm^2 mol^{-1}. Λ_M (CH_2Cl_2, 298 K, 10^{-3} mol/L): 2.4 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 3146w, 3108w, 3061m ν(C_{arom}−H), 1502w, 1498s ν(C═C, C═N), 293s ν(Ru−Cl). ^{1}H NMR ($CDCl_3$, 298 K): δ 1.23d (6H, CH_3-C_6H_4-CH(CH_3)$_2$), 1.74s (3H, CH_3-C_6H_4-CH(CH_3)$_2$), 2.78 m (1H, CH_3-C_6H_4-CH(CH_3)$_2$), 4.90dd (4H, AA′BB′ system, CH_3-C_6H_4-CH(CH_3)$_2$), 6.21t (1H, H_{4pzTp}), 6.39 (2H, H_{4pzTp}), 6.44t (1H, H_{4pzTp}), 6.57d (1H, H_{5pzTp}), 7.1br (2H, H_{5pzTp}), 7.2br (1H, H_{5pzTp}), 7.70 (1H, H_{3pzTp}), 7.82 (1H, H_{3pzTp}), 7.86 (2H, H_{3pzTp}). ESI-MS (MeCN) (+): m/z (%) 514 (100) [Ru(η^6-p-cymene)(pzTp))]$^+$.

X-ray Crystallography. The X-ray intensity data for **1** and **3** were measured on a Bruker SMART Apex II diffractometer equipped with a CCD area detector using a graphite-monochromated Mo Kα radiation source (λ = 0.71073 Å). Cell dimensions and the orientation matrix were initially determined from a least-squares refinement on reflections measured in three sets of 20 exposures, collected in three different ω regions, and eventually refined against all data. For all crystals, a full sphere of reciprocal space was scanned by 0.3° ω steps. The software SMART[30a] was used for collecting frames of data, indexing reflections, and determination of lattice parameters. The collected frames were then processed for integration by SAINT[30a] software, and an empirical absorption correction was applied with SADABS.[30b] The structures were solved by direct methods (SIR 97)[30] and subsequent Fourier syntheses and refined by full-matrix least-squares calculations on F^2 (SHELXTL),[31] attributing anisotropic thermal parameters to the non-hydrogen atoms. All hydrogen atoms were located in the Fourier map.

Scheme 1



The hydrogens bound to C atoms were placed in calculated positions and refined with isotropic thermal parameters $U(H)$ = 1.2U_{eq}(C) and allowed to ride on their carrier carbons, whereas the H atom bound to boron was located in the Fourier map and refined isotropically [U(H) = 1.2U_{eq}(C)]. Crystal data and details of the data collection for **1** and **3** are reported in Table S1 (Supporting Information).

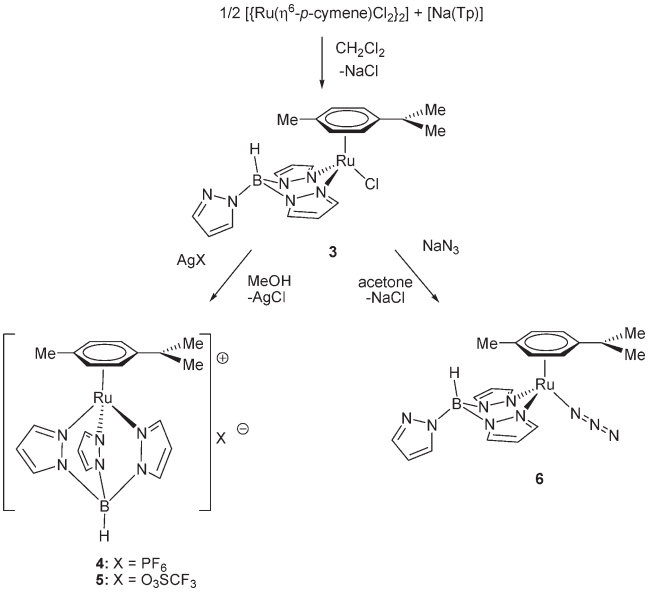
Catalytic Activity of Ruthenium Complexes 3−8 and 10. A typical nitroaldol reaction was carried out under air as follows: to 5.0 μmol of catalyst precursor contained in the reaction flask were added methanol (2.0 mL), nitroethane (4.0 mmol), and aldehyde (1.0 mmol), in that order. The reaction mixture was stirred for 24 h at 25 °C and air atmospheric pressure. After evaporation of the solvent, the residue was dissolved in DMSO and analyzed by ^{1}H NMR. The performed blank experiments confirmed that no products of nitroaldol reaction were obtained unless the catalyst was added.

RESULTS AND DISCUSSION

Synthesis and Spectroscopic Characterization of Complexes 1−10. The derivative [Ru(η^6-p-cymene)(κ^2-Ph_2Bp)Cl] (**1**) has been obtained by interaction of 1 equiv of the dinuclear [Ru(η^6-p-cymene)Cl_2]$_2$ with 2 equiv of [K(Ph_2Bp)] in acetonitrile at room temperature (Scheme 1). **1** is a high melting point solid, very soluble in most organic solvents, with the exception of aliphatic hydrocarbons. The far-IR spectrum of **1** exhibits strong and sharp absorptions due to Ru−C, Ru−Cl, and Ru−N modes in the range between 500 and 200 cm^{-1}.

The chloride in **1** can be easily replaced by the azide N_3^- group upon reaction with excess NaN_3 in acetone to afford derivative **2** (Scheme 1). In the IR of **2**, the strong absorption at 2019 cm^{-1} due to the ν(N_3)[32] and the disappearance of the band at 280 cm^{-1} due to Ru−Cl confirm the substitution of the chloride with azide. In the ^{1}H NMR spectra of **1** and **2**, all the expected resonances due to the Ph_2Bp protons occur downfield with respect to the analogous signals in the potassium salt K[Ph_2Bp]. The largest shift is found for the H_3, a proton *endo* to the ruthenium/arene fragment.

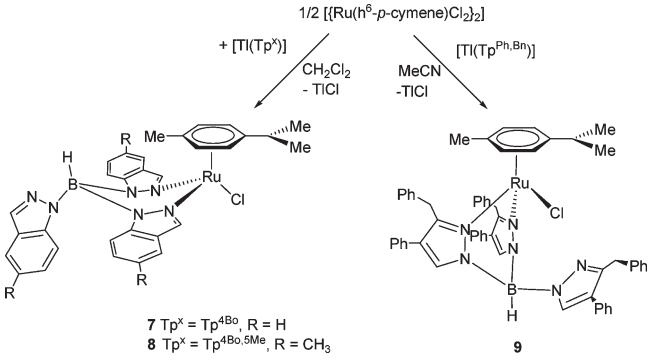
Scheme 2



By the reaction of 1 equiv of $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ with 2 equiv of [Na(Tp)] in dichloromethane at room temperature, upon recrystallization with CH_2Cl_2 and Et_2O, the derivative $[Ru(\eta^6\text{-}p\text{-cymene})(Tp)Cl]$, **3**, very soluble in most organic solvents, apart from aliphatic hydrocarbons, was obtained (Scheme 2). It is interesting to note that the not-recrystallized crude product contains both $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2\text{-Tp})Cl]$ (**3**) and $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^3\text{-Tp})]Cl$ (**3′**) species in 2:1 ratio, as evidenced by the ^1H NMR spectrum of the first precipitate afforded.[12] Conductance measurements of an acetonitrile solution of **3** indicate its nonelectrolytic nature.[33] The IR spectrum of **3** shows a medium absorption at 2434 cm^{-1} due to ν(B−H), which is at lower frequencies with respect to that of $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^3\text{-Tp})][PF_6]$, reported at 2523 cm^{-1}.[12] This is in accordance with observation that κ^3 coordination of tris(pyrazolyl)borate ligands generally leads to an increase in the frequency of B−H stretching, with respect to κ^2 coordination.[34] By careful comparison of the far-infrared region of **3** with that of the starting $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ and [Na(Tp)], we have assigned some absorptions in the 500−200 cm^{-1} range to Ru−C, Ru−Cl, and Ru−N modes.[35]

In the ^1H NMR spectrum of **3**, the *p*-cymene shows the expected resonances of the Me and *i*Pr groups, whereas the aromatic hydrogen atoms display the typical AA′BB′ system as a pair of doublets at 5.44 and 5.62 ppm, slightly deshielded with respect to the starting $[(Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$. Moreover, the spectrum shows two sets of inequivalent pyrazolyl resonances for the scorpionate ligand, with 1:2 relative intensities, as expected for a coordinated κ^2-Tp. These resonances are sharp at room temperature and remain unchanged also at low temperature (218 K), in accordance with a stereochemically rigid ligand and with absence of fluxionality around the Ru−B axis, as previously observed in related derivatives.[36] The singly degenerate signals appear at lower fields (δ, 6.45, 7.71, and 7.85) with respect to those of coordinated pyrazolyl groups (δ, 6.25, 7.03, and 7.79), whereas in the ^{13}C NMR spectrum the resonances of the unbound pyrazolyl group (δ, 101.7, 133.1, and 142.1) fall at relatively higher fields than those of the coordinated pyrazolyls

Scheme 3



(δ 107.4, 135.6, and 145.4). The most abundant signals found in the ESI-MS positive spectrum of **3**, in acetonitrile, are due to the $\{Ru(\eta^6\text{-}p\text{-cymene})(Tp)\}^+$ fragment, whereas a second minor peak arises from association of two mononuclear fragments through a bridging Cl.

From the reaction of **3** with $AgPF_6$ in methanol the compound $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^3\text{-Tp})][PF_6]$ (**4**) is obtained, showing a mixed-sandwich nature with a tricoordinated κ^3-Tp (Scheme 2).[12] Also the reaction of compound **3** with AgO_3SCF_3 in methanol leads to $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^3\text{-Tp})][O_3SCF_3]\cdot H_2O$ (**5**). Further support of our structural hypothesis for **5** comes from the observation of the characteristic absorption in the 1000−1200 cm^{-1} region, typical of a noncoordinated $[O_3SCF_3]^-$,[37] in accordance with the ionic formulation of **5** (Scheme 2). Moreover, **3** reacts with NaN_3 in acetone, affording the compound $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2\text{-Tp})(N_3)]$ (**6**) (Scheme 2). In the IR of **6**, as for **2**, a new, strong band at 2025 cm^{-1} due to the stretching mode of azide[32] is observed, together with the disappearance of the Ru−Cl mode.

In order to explore the coordination chemistry of the Ru(II)-arene fragment toward scorpionate ligands with diverse steric hindrance on pyrazole rings, we have also decided to carry out the reaction of 1 equiv of $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ with 2 equiv of differently substituted Tp^x ($Tp^x = Tp^{4Bo}$, $Tp^{4Bo,5Me}$, $Tp^{Bn,4Ph}$) in dichloromethane at room temperature, the derivatives $[Ru(\eta^6\text{-}p\text{-cymene})(Tp^x)Cl]$ **7**−**9** (**7**: Tp^{4Bo}, **8**: $Tp^{4Bo,5Me}$, **9**: $Tp^{Bn,4Ph}$) being respectively obtained (Scheme 3). The IR spectra of **7**, **8**, and **9** show at 2397, 2403, and 2431 cm^{-1}, respectively, a medium absorption due to ν(B−H), in accordance with a κ^2 coordination mode of tris(pyrazolyl)borate ligands.[29] The conductivity measurements in acetonitrile solutions suggest a nonionic nature for **7** and **8**.[33] In their proton NMR spectra one set of resonances for *p*-cymene protons and two sets of nonequivalent pyrazolyl resonances for Tp^x ligands have been found, as expected for a κ^2-coordinated Tp^x.

Conductance measurements of acetonitrile and dichloromethane solutions of **9** indicate the 1:1 electrolytic nature likely due to chloride dissociation in these solvents.[33] Additionally the ^1H NMR spectrum of **9** shows three sets of resonances for each pyrazolyl hydrogen atom, with 1:1:1 relative intensity, which could be due to the restricted rotation of the benzyl substituent due to the steric hindrance exerted by the 4-phenyl substituent.[26b]

Finally, the reaction between $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ and the tetrakis-scorpionate pzTp yields derivative **10** (Scheme 4). Conductance measurement of an acetonitrile solution of **10** indicates

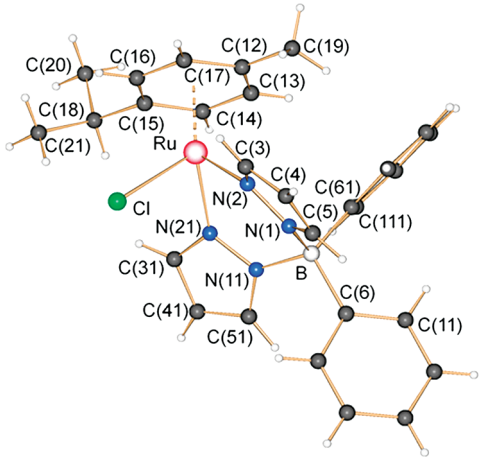
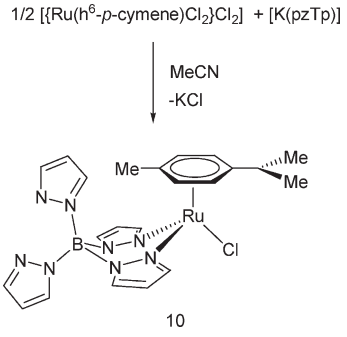


Figure 1. Molecular structure of **1** with the atom-numbering scheme. Selected bond lengths (Å) and angles (deg) for **1**: Ru−N(2), 2.086(2); Ru−N(21), 2.095(2); Ru−Cl, 2.3993(7); Ru−C(12), 2.229(2); Ru−C(13), 2.203(2); Ru−C(14), 2.190(2); Ru−C(15), 2.221(2); Ru−C(16), 2.161(2); Ru−C(17), 2.196(2); N(2)−Ru−N(21), 85.65(7); N(2)−Ru−Cl, 84.36(6); N(21−Ru−Cl, 85.19(5); N(1)−B−N(11), 107.1(2).

Scheme 4



its nonelectrolytic nature.[33] The ^{1}H NMR spectrum of this very soluble species exhibits three sets of resonances for each pyrazolyl hydrogen atom, with relative intensity of 2:1:1, supporting a nonfluxional κ^2-bonded pzTp ligand containing two unequivalent unbound pz rings. ESI-MS positive spectra of **7**−**10** always show a main peak due to the $[Ru(\eta^6\text{-}p\text{-cymene})(Tp^x)]^+$ species.

X-ray Diffraction Studies of Compounds 1 and 3. The X-ray molecular structure of **1** is shown in Figure 1, and relevant bond lengths and angles are reported in the caption of Figure 1. The ruthenium complex has a pseudo-octahedral "piano stool" geometry, with the seat being the η^6-bound arene ring of the *p*-cymene ligand, and the chloride and chelating pyrazoles of the diphenylbis(pyrazol-1-yl)borate ligands the legs. The Ru−N bond lengths are similar [Ru−N(1) 2.086 and Ru−N(3) 2.095(2) Å] and slightly longer than those found in complex **3** (*vide infra*). The Ru−C(*p*-cymene) average bond length is 2.200 Å (Ru−centroid distance 1.69 Å), whereas the Ru−Cl distance [2.3993(7) Å] is similar to those reported for analogous Ru(II) complexes. In complex **1** the chelating pyrazoles of the κ^2-coordinated Ph_2Bp ligand give rise to a six-membered metallacycle comprising Ru, N(1), N(2), B, N(4), and N(3) and adopting the boat conformation (Figure 1) with a N(2)−Ru−N(4) bite angle of 85.64(7)°. In order to alleviate the steric congestion, the two phenyl rings of the Ph_2Bp ligand are bent outward from the ruthenium and lie almost perpendicular to each other. In addition one of them lies parallel to the vector joining the "prow" and "stern" of the boat, while the one in the flagpole position is orthogonal to the chelate ring.

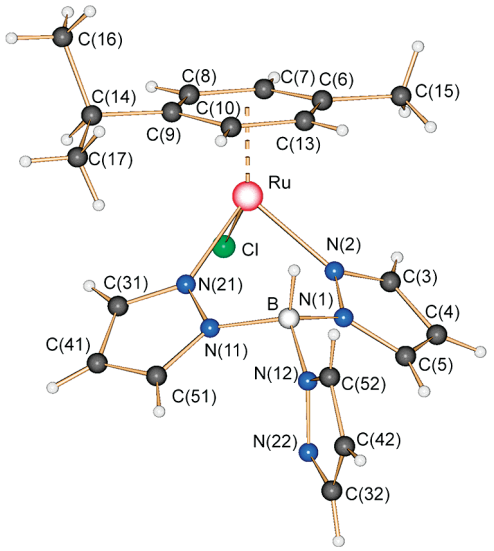


Figure 2. Molecular structure of **3** with the atom-numbering scheme. Selected bond lengths (Å) and angles (deg) for **3**: Ru−N(2), 2.092(2); Ru−N(21), 2.102(2); Ru−C(7), 2.175(2); Ru−C(8), 2.190(2); Ru−C(9), 2.235(2); Ru−Cl, 2.3976(6); N(2)−Ru−N(21), 83.35(7); N(2)−Ru−Cl, 85.92(5); N(21)−Ru−Cl, 86.21(5); N(1)−B−N(11), 107.4(2).

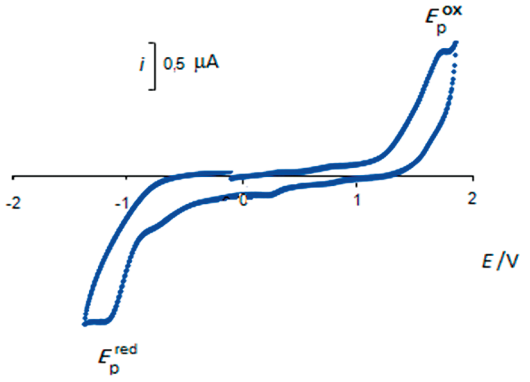
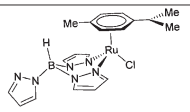
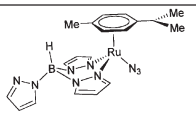
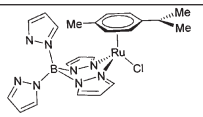
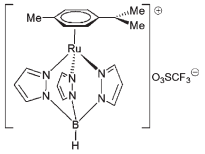
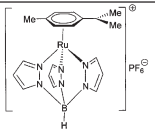
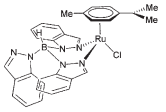
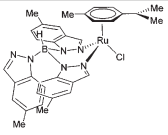
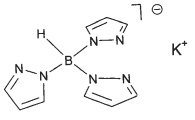
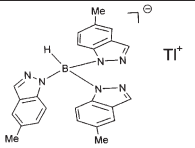


Figure 3. Cyclic voltammogram of $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2\text{-}Tp^{4Bo})Cl]$, **7**, in a 0.2 M $[nBu_4N][BF_4]-CH_2Cl_2$ solution, at a Pt disk working electrode (d = 0.5 mm), run at a scan rate of 200 mV s^{-1}.

The X-ray molecular structure of **3** is shown in Figure 2, and relevant bond lengths and angles are reported in the caption of Figure 2. Complex **3** also exhibits the pseudo-octahedral "piano stool" geometry rather common in this family of Ru(II) complexes. The Ru−C(*p*-cymene) average distance is 2.195 Å (Ru−centroid distance 1.68 Å), and the Ru−N distances [Ru−N(1) 2.092 and Ru−N(3) 2.101(2) Å] are similar and very close to those observed in complex **1** and in $[Ru(\eta^6\text{-}C_6Me_6)\{\kappa^2\text{-}HB(pz)_3\}Cl]$.[22] Also the Ru−Cl bond length [2.3981(3) Å] is almost identical to that found in **1** and in analogous Ru(II) complexes. A main difference between complexes **1** and **3** resides in the presence, in the latter, of the less bulky Tp ligand, which however is also κ^2-coordinated to the Ru atom, leaving an uncoordinated pyrazolyl ring. The κ^2-coordinated

dx.doi.org/10.1021/om101146q |*Organometallics* 2011, 30, 1616–1626

Table 1. Cyclic Voltammetric Data[a] for (η^6-*p*-Cymene)Ru^{II} Complexes with Pyrazolylborate-Type Ligands

	Complex	Anodic Wave $E^{ox}_{p/2}$ ($E^{ox}_{1/2}$)	Cathodic Waves $^{I}E^{red}_{p}$, $^{II}E^{red}_{p}$
3	 [Ru(η^6-*p*-cymene)(κ^2-Tp)Cl]	1.05	-1.45
6	 [Ru(η^6-*p*-cymene)(κ^2-Tp)(N$_3$)]	(0.93)	-1.20
10	 [Ru(η^6-*p*-cymene)(κ^2-pzTp)Cl]	1.10	-1.26
5[b]	 [Ru(η^6-*p*-cymene)(κ^3-Tp)]O$_3$SCF$_3$	1.79	-1.35
4	 [Ru(η^6-*p*-cymene)(κ^3-Tp)][PF$_6$]	1.83	-1.32
7[c]	 [Ru(η^6-*p*-cymene)(κ^2-Tp^{4Bo})Cl]	1.36	-1.23
8[c]	 [Ru(η^6-*p*-cymene)(κ^2-Tp^{4Bo,5Me})Cl]	1.24	-1.38
KTp[d]		—	-1.05
TlTp^{4Bo,5Me}[d]		—	-1.06, -1.32

[a] Potential values in volts ± 0.02 vs SCE, in a 0.2 M *n*Bu$_4$N][BF$_4$]−CH$_2$Cl$_2$ solution, at a Pt disk working electrode determined by using the [Fe(η^5-C$_5$H$_5$)$_2$]$^{0/+}$ redox couple ($E^{ox}_{1/2}$ = 0.525 V vs SCE)[29] as internal standard at a scan rate of 200 mV s^{-1}; the values can be converted to the NHE reference by adding +0.245 V.[29,37a] [b] With water of crystallization. [c] An anodic adsorption wave at E^{ox}_{p} ca. 0.45 V is generated upon addition of ferrocene. [d] Included for comparative purposes.

dx.doi.org/10.1021/om101146q |*Organometallics* 2011, 30, 1616–1626

Table 2. E_L Ligand Parameter Values Estimated for the Tp Ligands[a]

ligand	E_L/V vs NHE
$pzTp^-$	0.05
Tp^-	0.11[b]
$(Tp^{4Bo,5Me})^-$	0.12
$(Tp^{4Bo})^-$	0.19

[a] From Lever's eq 1, per ligating pyrazolyl or indazolyl arm. [b] Average value (see text).

Tp ligand generates a six-membered metallacycle in a boat conformation with a N(2)−Ru−N(4) bite angle of 83.26(8)°. The small hydrogen atom bound to the tetrahedral boron occupies the flagpole position, whereas the pyrazolyl ring is placed far from the cymene−metal unit, as it has been found in the related $[Ru(\eta^6\text{-}C_6Me_6)(\kappa^2\text{-Tp})]Cl$.[12]

Electrochemical Studies. The redox properties of our compounds have been investigated by cyclic voltammetry at a Pt electrode, in a 0.2 M $[nBu_4N][BF_4]-CH_2Cl_2$ solution, at 25 °C. They exhibit (Figure 3 for complex **7**) a single-electron irreversible oxidation (reversible only for the azide compound **6**), assigned[38] to the $Ru^{II} \rightarrow Ru^{III}$ oxidation, at the oxidation potential values ($E^{ox}_{p/2}$ or $E^{ox}_{1/2}$ in V vs SCE) given in Table 1 (in the range 0.93−1.36 and at ca. 1.8 V vs SCE for the neutral and cationic ones, respectively). The occurrence of a single-electron oxidation has been confirmed by exhaustive controlled potential electrolysis at a potential slightly anodic to that of the peak potential.

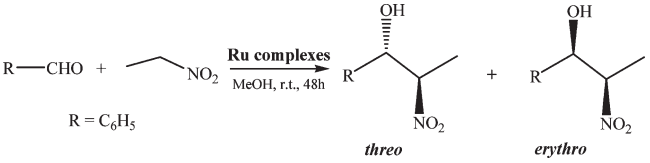
The compounds also show irreversible reduction waves in the −1.2 to −1.5 V range (Figure 3 for complex **7**), which can involve the poly(pyrazolyl)borate ligands [when uncoordinated, they undergo irreversible reductions in that range of potentials, e.g., at −1.05 V vs SCE for Tp^- and at −1.06 and −1.32 V vs SCE for $(Tp^{4Bo,5Me})^-$; see Table 1] and were not investigated further. In contrast to the reduction, no oxidation of the free ligands could be detected under the experimental conditions of this study.

The values of the $Ru^{II/III}$ oxidation potential of our complexes are expected[38,39] to reflect the electron-donor characters of their ligands, but any analysis has to be taken rather cautiously in view of the usual irreversible character of the oxidation wave. Nevertheless, for complexes **3** and **6**, with the common $\{Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2\text{-Tp})\}$ metal center, the order of the oxidation potentials (**3** > **6**) follows, as expected, that (in the opposite direction) of the electron-releasing character of the corresponding variable ligand ($Cl^- < N_3^-$) as measured by the electrochemical Lever E_L ligand parameter (−0.24 and −0.30 V vs NHE for Cl^- and N_3^-, respectively).[38a] One should note that E_L is a measure of the electron-donor character of a ligand (the stronger this character, the lower the E_L).[38a,b]

We may even try to estimate the E_L values for the Tp and related ligands of these complexes (although with the above limitation) by applying the Lever eq 1, which relates linearly the redox potential (E in V vs NHE) of an octahedral complex with the sum (ΣE_L) of the E_L ligand parameters for all the ligands (two-electron donors, assuming additive contributions), the slope S_M and the intercept I_M being dependent upon the metal, redox couple, spin state, and stereochemistry.[38a,b]

$$E = S_M(\Sigma E_L) + I_M/\text{V vs NHE} \quad (1)$$

Scheme 5. β-Nitroaldols change to β-nitroalkanol



Application of this equation to $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2\text{-Tp})(N_3)]$ (**6**) with the most reliable oxidation potential ($E^{ox}_{1/2}$ = 0.93 V vs SCE = 1.18 V vs NHE), since its oxidation wave is reversible, with the known values of S_M (0.97) and I_M (0.04 V vs NHE) for the $Ru^{II/III}$ redox center[38a] and of E_L for N_3^- (−0.30 V vs NHE)[38a] and *p*-cymene (+1.48 V vs NHE),[38j] allows us to estimate the E_L parameter for Tp as 0.00 V vs NHE (for each coordinating pyrazolyl arm assuming additive contributions; also 0.00 V for the overall ligand).

An E_L value of 0.20 V vs NHE (per each Tp arm) is obtained by applying eq 1 to complexes **4** and **5**, with an average $E^{ox}_{p/2}$ of 1.81 + 0.25 = 2.06 V vs NHE. However, the application of eq 1 to **3** leads to an E_L of 0.03 V vs NHE (per each Tp arm).

The value of 0.14 vs NHE was estimated before[37] for Tp at the phosphine complex $[Ru(Tp)Cl(PPh_3)_2]$. The variation of the estimated E_L parameter of Tp can possibly account for (i) a (slight) failure of the additive model of eq 1, (ii) the need to adjust the S_M and I_M values (proposed for the octahedral coordination)[38a] to the pseudo-octahedral half-sandwich π-arene-type coordination of the Tp complexes, (iii) the eventual dependence of the E_L value (for Tp) on the coordination metal center, and/or (iv) the irreversibility of the oxidation (in the cases of **3**, **4**, and **5**). The variation of the electron-donor properties of Tp with the metal center composition has in fact been recognized for a variety of complexes, mainly on the basis of IR and NMR spectroscopic data.[39c]

In order to get a more reliable E_L value of Tp, one should estimate (and average) it for an extended number of cases. At this stage, we propose the value of 0.11 V vs NHE as the average of the available ones mentioned above.

Further application of eq 1 to complexes $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2\text{-pzTp})Cl]$ (**10**), $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2\text{-}Tp^{4Bo,5Me})Cl]$ (**8**), and $[Ru(\eta^6\text{-}p\text{-cymene})(\kappa^2\text{-}Tp^{4Bo})Cl]$ (**7**), which bear co-ligands with known E_L values (−0.24[38a] and +1.48[38j] V vs NHE for Cl^- and *p*-cymene, respectively), allows us to roughly estimate the E_L value for each arm of the other bi- or tridentate ligands: 0.05 ($pzTp^-$), 0.12 $(Tp^{4Bo,5Me})^-$, and 0.19 $(Tp^{4Bo})^-$ V vs NHE, respectively (Table 2).

Hence, $pzTp^-$ is a slightly stronger electron donor than Tp^- (E_L of 0.05 and 0.11 V vs NHE, respectively); that is, replacement of the hydride (in the latter) by a pyrazolyl group (in the former) appears to lead to a slight increase of the electron-donor ability of the metal-ligated pyrazolyl groups.

The tetra(indazolyl)borate ligand, $(Tp^{4Bo})^-$, acts as weaker electron donor than tris(pyrazolyl)borate, i.e., each indazolyl arm (E_L = 0.19 V vs NHE) being a weaker electron releaser than each pyrazolyl arm in Tp^- (E_L = 0.11 vs NHE), in accord with the extended aromatic π-conjugation of the former. In view of the known electron-donor character of the methyl substituent, the methyl-indazolyl arm is a stronger electron donor than the unsubstituted indazolyl group (E_L = 0.12 and 0.19 V vs NHE, respectively).

dx.doi.org/10.1021/om101146q |*Organometallics* 2011, 30, 1616–1626

Table 3. Catalytic Activity of [Ru(η^6-*p*-cymene)(κ^2-Tp)(N_3)] (6) for the Nitroaldol Reaction of Benzaldehyde with Nitroethane (Henry reaction)[a]

entry	catalyst	time (h)	temp (°C)	solvent	conversion (%)[b]	selectivity *threo*/*erythro*[c]
1	blank	24	25	MeOH	–	–
Effect of solvent						
2	**6**	24	25	MeOH	82.2	62:38
3	**6**	24	25	THF	75.3	60:40
4	**6**	24	25	toluene	69.5	58:42
5	**6**	24	25	CH_3CN	80.6	61:39
Effect of reaction time						
6	**6**	1	25	MeOH	14.9	65:35
7	**6**	3	25	MeOH	29.3	64:36
8	**6**	5	25	MeOH	43.7	62:38
9	**6**	10	25	MeOH	55.4	64:36
10	**6**	24	25	MeOH	82.2	62:38
11	**6**	48	25	MeOH	83.5	62:38
Effect of temperature						
12	**6**	5	25	MeOH	43.7	62:38
13	**6**	5	50	MeOH	66.2	56:44
14	**6**	5	80	MeOH	85.8	54:46

[a] Reaction conditions: 5 μmol of catalyst precursor, methanol (2 mL), nitroethane (4 mmol), and aldehyde (1 mmol). [b] Determined by ^{1}H NMR, based on the starting aldehyde. [c] Calculated by ^{1}H NMR.

Table 4. Catalytic Activities of (η^6-Cymene)Ru^{II} Complexes with Pyrazolylborate-Type Ligands for the Nitroaldol (Henry) Reaction of Benzaldehyde with Nitroethane[a]

entry	catalyst	solvent	conversion (%)[b]	selectivity *threo*/*erythro*[c]
1	[Ru(η^6-*p*-cymene)(κ^2-Tp)Cl], **3**	MeOH	69.3	58:42
2	[Ru(η^6-*p*-cymene)(κ^2-Tp)(N_3)], **6**	MeOH	82.2	62:38
3	[Ru(η^6-*p*-cymene)(κ^2-pzTp)Cl], **10**	MeOH	31.4	53:47
4	[Ru(η^6-*p*-cymene)(κ^3-Tp)]$CF_3SO_3\cdot H_2O$, **5**	MeOH	62.7	57:43
5	[Ru(η^6-*p*-cymene)(κ^3-Tp)][PF_6], **4**	MeOH	67.4	60:40
6	[Ru(η^6-*p*-cymene)(κ^2-Tp^{4Bo})Cl], **7**	MeOH	77.0	51:49
7	[Ru(η^6-*p*-cymene)(κ^2-Tp^{4Bo,5Me})Cl], **8**	MeOH	80.5	53:47

[a] Reaction conditions: catalyst (5.0 μmol), benzaldehyde (1.0 mmol), nitroethane (4.0 mmol) in methanol (2.0 mL), 20 °C, 24 h. [b] Determined by ^{1}H NMR, based on the starting aldehyde. [c] Calculated by ^{1}H NMR.

Each pyrazolyl or indazolyl arm in these borate ligands (Tp^- and $pzTp^-$, or $(Tp^{4Bo})^-$, respectively) acts as a stronger electron donor than pyrazole (E_L = 0.20 V vs NHE)[38a] or indazole (E_L = 0.26 V vs NHE)[38h] themselves. On the basis of their E_L values, our ligands and other related ones can be ordered as follows according to their electron-donor character: tris(pyrazolyl)methanesulfonate, $SO_3Cpz_3^-$ (E_L = −0.09 V vs NHE)[40] > $pzTp^-$ (this study) > Tp^- (this study) ≈ $(Tp^{4Bo,5Me})^-$ (this study) ≈ benzoyldiazenide, $NNCOPh^-$ (E_L = 0.11 V vs NHE)[41] ≈ benzimidazole (E_L = 0.10 V vs NHE)[38g] > hydrotris(pyrazolyl)methane, $HCpz_3$ (E_L = 0.14 V vs NHE)[26] > $(Tp^{4Bo})^-$ (this study) ≈ 1-methyltriazole (E_L = 0.17 V vs NHE)[38g] ≈ 4-methylpyrazole (E_L = 0.18 V vs NHE)[38g] > NCMe (E_L = 0.34 V vs NHE).[37a]

Catalytic Studies. We have tested the catalytic activity of type [Ru(η^6-*p*-cymene)(κ^2-Tp^x)L]$^{n+}$ (L = Cl, N_3, or H_2O; *x* = H, 4Bo or 4Bo,5Me; *n* = 0 or 1) or [Ru(η^6-*p*-cymene)(κ^3-Tp)]$^+$ complexes for the Henry (nitroaldol) reaction between an aldehyde and a nitroalkane to yield the corresponding β-nitroalkanol.[16−22] Benzaldehyde and nitroethane were taken as model substrates (Scheme 5), and the various complexes are shown to exhibit good catalytic activity, even at room temperature, with an appreciable diastereoselectivity that is unusual for this type of reaction. The products are mixtures of the β-nitroalkanol diastereoisomers (*threo* and *erythro* forms), with overall conversions up to 82% (at room temperature) and predominance of the former isomer (*threo*/*erythro* molar ratios up to ca. 2:1) (Tables 3 and 4).

The effects of various factors (solvent, reaction time, and temperature) on the catalytic activity and diastereoselectivity were studied for complex [Ru(η^6-*p*-cymene)(κ^2-Tp)N_3] (**6**) as the catalyst (Table 3). Among the studied solvents (methanol, THF, toluene, and acetonitrile), methanol was found to be the best choice for this reaction (Table 3, entries 2−5). The conversion increases with the reaction time (Table 3, entries 6−11), e.g., from 15 to 84%, after 1 or 48 h, respectively, for catalyst **6**, without a considerable decrease of the diastereoselectivity. In addition, the catalytic activity is promoted by heating, and, for example, at 50 and 80 °C (5 h reaction time) the obtained conversions are 1.5 and 2 times that at 25 °C (Table 3, entries 12−14). However, a decrease of the diastereoselectivity results upon increasing the temperature.

The complexes with the hydroborate scorpionate ligand (Tp, Tp^{4Bo}, or $Tp^{4Bo,5Me}$) are markedly more active and selective than that with the tetrakis(pyrazolyl)borate (**10**), but no clear stereochemical effect of the pyrazolyl (or indazolyl) group substituent was detected.

In comparison with other reported metal catalysts[16,42−50] for the Henry reaction, those of the present study are among the best ones in terms of exhibiting a combined high activity with a relatively pronounced diastereoselectivity. Moreover, they are easier to prepare and/or cheaper than other systems, e.g., based on metals such as Rh,[43] La,[42] or Nd[42] or using an ionic liquid.[45] Nevertheless, higher selectivities have been reported[18,22,42] for some less accessible and more complex (also more expensive) catalytic systems, e.g., heterobimetallic Nd(O*i*Pr)$_3$/sodium/amide[43a] and Pd/La/Schiff base,[42e] as well as for a few others based on a bis(oxazoline)copper[22a] and some dinuclear zinc[18] catalysts.

The mechanism of the reaction is expected[51−54] to involve metal-assisted (upon coordination) (i) deprotonation of the methylene group of nitroethane (to give a nitronate species) and (ii) activation of benzaldehyde toward its electrophilic attack (with C−C coupling) to the nitronate. The cymene-Ru(II) complexes with the scorpionate ligands of the current study appear to be able to act as suitable Lewis acids for the above activations, and, in addition, the ligated (multipyrazolyl)borates can possibly behave as bases, assisting the above nitroethane deprotonation.

In an attempt to detect any possible intermediate Ru species, we have monitored by ESI-MS(+) the reaction of **7** with aldehyde and nitroalkane and observed the gradual replacement of the main peak associated with **7**, i.e., $m/z = 598$ due to $[Ru(\eta^6\text{-}p\text{-cymene})(Tp^{4Bo})]^+$, by new peaks assigned to $[Ru(Tp^{4Bo})(nitroethane)]^+$ (m/z = 539), $[Ru(Tp^{4Bo})(benzaldehyde)]^+$ (m/z = 571), and $[Ru(Tp^{4Bo})(nitroethane)(benzaldehyde)]^+$ ($m/z = 644$). These observations support the coordination of the substrates to the metal with loss of the *p*-cymene ligand.

CONCLUSIONS

Our work was aimed at the preparation of novel Ru(II) cymene pyrazolylborate derivatives, neutral and ionic ones, by using one-step procedures allowing high-yields and unique products.

NMR and IR spectroscopies, conductivity, ESI-MS, and also X-ray studies confirmed the stoichiometries and the κ^2 or κ^3 coordination modes of pyrazolylborate ligands in their metal complexes. We have demonstrated that the use of sterically hindered ligands pushes toward the synthesis of complexes containing a κ^2-Tp^x donor. The electrochemical study has allowed the comparison of the electron-donor characters of the Tp and related ligands, but although their proposed ordering is expected to be usually reliable, one should be rather cautious with the estimated E_L values. In fact, some of the E_L values were estimated from irreversible oxidation potentials rather than from the thermodynamic ones, and it was 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 this study (this has to be checked for a wider variety of π-cymene-type complexes).

Our results also show that *p*-cymene ruthenium(II) complexes with pyrazolylborates are effective catalysts for the diastereoselective nitroaldol reaction, leading to β-nitroalkanols in high yield, with predominance of the *threo* diastereoisomer. The combination of cymene-Ru(II) with a (multipyrazolyl)borate ligand, involving a Lewis acid metal center (to promote the nitroethane deprotonation and the electrophilicity of benzaldehyde) and a Brönsted base (to assist the proton loss from nitroethane), seems to be particularly favorable for that reaction. The extension of catalytic applications to other *p*-cymene (and other half-sandwich) ruthenium(II) complexes is currently underway in our laboratories.

ASSOCIATED CONTENT

Supporting Information. Detailed determination of the EL ligand parameter for Tp (each coordinating arm), crystal data and structure refinement for **1** and **3**, cif files for **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail. claudio.pettinari@unicam.it; pombeiro@ist.utl.pt

ACKNOWLEDGMENT

This work has been partially supported by the Foundation for Science and Technology (FCT) (grant BPD/46812/2008) and its PPCT program (FEDER funded) and by University of Camerino.

REFERENCES

(1) (a) Hauser, C. S.; Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K.; Xiao, L.; Weissenteiner, W. *J. Chem. Soc., Dalton Trans.* **2001**, 2989. (b) Rhyoo, H. Y.; Park, H.-J-; Chung, Y. K. *J. Chem. Soc., Chem. Commun.* **2001**, 2064.

(2) Fürstner, A.; Picquet, M.; Bruneau, C.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1998**, 1315.

(3) Faller, J. W.; Chase, K. J. *Organometallics* **1995**, *14*, 1592. Ritleng, V.; Sutter, J. P.; Pfeffer, M.; Sirlin, C *J. Chem. Soc., Chem. Commun.* **2000**, 129.

(4) Farrington, E. J.; Brown, J. M.; Barnard, C. F. J.; Rowsell, E. *Angew. Chem., Int. Ed.* **2002**, *41*, 169.

(5) Cadierno, V.; Crochet, P.; Garcia-Garrido, S. E.; Gimeno, J. *J. Chem. Soc., Dalton Trans.* **2004**, 3635.

(6) See for example: Pettinari, C.; Marchetti, F.; Martini, D. Metal Complexes as Hydrogenation Catalysts. In *Comprehensive Coordination Chemistry II*; Elsevier, 2003; Vol. 9, Chapter 9.2, pp 75−139 , and references therein.

(7) Cetinkaya, B.; Özdemir, I.; Binbasioglu, B.; Durmaz, R.; Günal, S. *Arzneim.-Forsch.* **1999**, *49*, 538.

(8) Allardyce, C. S.; Dyson, P. J.; Ellis, D. J.; Heath, S. L. *J. Chem. Soc., Chem. Commun.* **2001**, 1396. Morris, R. E.; Aird, R. E.; Murdoch, P. D. S.; Chen, H.; Cummings, J.; Hughes, N. D.; Parson, S.; Parkin, A.; Boyd, G.; Jodrell, D. I.; Sadler, P. J. *J. Med. Chem.* **2001**, *44*, 3616. Cummings, J.; Aird, R. E.; Morris, R. E.; Chen, H.; Murdoch, P. S.; Sadler, P. J.; Smith, J. F; Jodrell, D. I. *Clin. Cancer Res.* **2000**, *6*, 142. Renfrew, A. K.; Egger, A. E.; Scopelliti, R.; Hartinger, C. G.; Dyson, P. J. *C. R. Chim.* **2010**, *13*, 1144. Süss-Fink, G.; Khan, F. A.; Juillerat-Jeanneret, L.; Dyson, P. J.; Renfrew, A. K. *J. Cluster Sci.* **2010**, *21*, 313.

(9) Aird, R. E.; Cummings, J.; Ritchie, A. A.; Muir, M.; Morris, R. E.; Chen, H.; Sadler, P. J.; Jodrell, D. I. *Br. J. Cancer* **2002**, *86*, 1652.

(10) Chen, H.; Parkinson, J. A.; Parson, S.; Coxall, R. A.; Gould, R. O.; Sadler, P. J. *J. Am. Chem. Soc.* **2002**, *124*, 3064.

(11) (a) Restivo, R. J.; Ferguson, G. *J. Chem. Soc., Chem. Commun.* **1973**, 847. (b) Restivo, R. J.; Ferguson, G.; O'Sullivan, D. J.; Lalor, F. J. *Inorg. Chem.* **1975**, *14*, 3046. (c) Jones, C. J.; McCleverty, J. A.; Rothin,

A. S. *J. Chem. Soc., Dalton Trans.* **1986**, 109. (d) Bhambri, S.; Tocher, D. A. *Polyhedron* **1996**, *15*, 2763. (e) Bhambri, S.; Bishop, A.; Kaltsoyannis, N.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1998**, 3379.

(12) Bhambri, S.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1997**, 3367.

(13) Suami, T.; Tadono, K. I.; Suga, A.; Ueno, Y. *J. Carbohydr. Chem.* **1984**, *3*, 429.

(14) Williams, T. M.; Mosher, H. S. *Tetrahedron Lett.* **1985**, *26*, 6269.

(15) Bulbule, V. J.; Deshpande, V. H.; Velu, S.; Sudalai, A.; Sivasankar, Sathe, S. V. T. *Tetrahedron* **1999**, *55*, 9325.

(16) Bulut, A.; Aslan, A.; Dogan, O. *J. Org. Chem.* **2008**, *73*, 7373–7375.

(17) Lu, S. F.; Du, D. M.; Xu, J. X.; Zhang, S. W. *J. Am. Chem. Soc.* **2006**, *128*, 7418–7419.

(18) (a) Trost, B. M.; Yeh, V. S. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 861. (b) Trost, B. M.; Yeh, V. S. C.; Ito, H.; Bremeyer, N. *Org. Lett.* **2002**, *4*, 2621–2623.

(19) (a) Kowalczyk, R.; Sidorowicz, L.; Skarzewski, J. *Tetrahedron: Asymmetry* **2007**, *18*, 2581–2586. (b) Zulauf, A.; Mellah, M.; Schulz, E. *J. Org. Chem.* **2009**, *74*, 2242–2245.

(20) Sasai, H.; Suzuki, T.; Arai, S.; Arai, T.; Shibasaki, M. *J. Am. Chem. Soc.* **1992**, *114*, 4418–4420.

(21) Kogami, Y.; Nakajima, T.; Ikeno, T.; Yamada, T. *Synthesis* **2004**, 1947–1950.

(22) (a) Evans, D. A.; Seidel, D.; Rueping, M.; Lam, H. W.; Shaw, J. T.; Downey, C. W. *J. Am. Chem. Soc.* **2003**, *125*, 12692–12693. (b) Jones, M. D.; Cooper, C. J.; Mahon, M. F.; Raithbya, P. R.; Apperley, D.; Wolowska, J.; Collison, D. *J. Mol. Catal. A: Chem.* **2010**, *325*, 8–14.

(23) Rheingold, A. L.; Haggerty, B. S.; Yap, G. P. A.; Trofimenko, S. *Inorg. Chem.* **1997**, *36*, 5097–5103.

(24) Rheingold, A. L.; Yap, G.; Trofimenko, S. *Inorg. Chem.* **1995**, *34*, 759–760.

(25) Trofimenko, S. *Inorg. Synth.* **1970**, *12*, 99–205.

(26) (a) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170. (b) Rheingold, A. L.; Zakharov, L. N.; Trofimenko, S. *Inorg. Chem.* **2003**, *42*, 827–833.

(27) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 6288–6294.

(28) Senko, M. W. *IsoPro Isotopic Abundance Simulator*, Vol. *2.1*; National High Field Laboratory, Los Alamos National Laboratory: Los Alamos, NM.

(29) Pombeiro, A. J. L.; Guedes da Silva, M. F. C.; Lemos, M. A. N. D. A. *Coord. Chem. Rev.* **2001**, *80*, 219.

(30) (a) *SMART* and *SAINT* Software Reference Manuals, Version 5.051 (Windows NT Version); Bruker Analytical X-ray Instruments Inc.: Madison, WI, 1998. (b) Sheldrick, G. M. *SADABS, program for empirical absorption correction*; University of Göttingen: Germany, 1996. (c) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115–119.

(31) Sheldrick, G. M. *SHELXTLplus* Version 5.1 (Windows NT version) Structure Determination Package; Bruker Analytical X-ray Instruments Inc.: Madison, WI, 1998.

(32) (a) Neya, S.; Chang, C. K.; Okuno, D.; Hoshino, T.; Hata, M.; Funasaki, N. *Inorg. Chem.* **2005**, *44*, 1193–1195. (b) Neya, S.; Morishima, I. *J. Am. Chem. Soc.* **1982**, *104*, 5068–5661.

(33) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

(34) (a) Akita, M.; Ohta, K.; Takahashi, Y.; Hikichi, S.; Moro-oka, Y. *Organometallics* **1997**, *16*, 4121. (b) Northcutt, T. O.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1998**, *17*, 5148.

(35) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed.; Wiley & Sons: New York, 1997.

(36) (a) Bucher, U. E.; Currao, A.; Nesper, R.; Ruegger, H.; Venanzi, L. M.; Younger, E. *Inorg. Chem.* **1996**, *35*, 66. (b) de V. Steyn, M. M.; Syngleton, E.; Hietkamp, S.; Liles, D. C. *J. Chem. Soc., Dalton Trans.* **1990**, 2991. (c) Shiu, K. B.; Guo, W. N.; Peng, S. M.; Cheng, M. C. *Inorg. Chem.* **1994**, *33*, 3010. (d) Meakin, P.; Trofimenko, S.; Jesson, J. P. *J. Am. Chem. Soc.* **1972**, *94*, 5677.

(37) (a) Vitzthum, G.; Lindner, E. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 315. (b) Lindner, E.; Vitzthum, G. *Chem. Ber.* **1969**, *102*, 4062.

(38) (a) Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271.(b) Lever, A. B. P. In *Comprehensive Coordination Chemistry II*, Vol. 2; Lever, A. B. P., Ed.; Elsevier: Oxford, 2004; Chapter 2.19, pp 251−268, and references therein. (c) Pombeiro, A. J. L. In *Encyclopaedia of Electrochemistry*; Scholz, F.; Pickett, C. J., Eds.; Wiley-VCH: New York, 2006; Vol. 7A, Chapter 6, pp 77−108, and references therein. (d) Pombeiro, A. J. L. *Eur. J. Inorg. Chem.* **2007**, *11*, 1473. (e) Pombeiro, A. J. L. *J. Organomet. Chem.* **2005**, *690*, 6021. (f) Pombeiro, A. J. L. *New J. Chem.* **1997**, *21*, 649. (g) Reisner, E.; Arion, V. B.; Eichinger, A.; Kandler, N.; Geister, G.; Pombeiro, A. J. L.; Keppler, B. K. *Inorg. Chem.* **2005**, *44*, 6704, and references therein. (h) Reisner, E.; Arion, V. B.; Guedes da Silva, M. F. C.; Lichteneker, R.; Eichinger, A.; Keppler, B. K.; Kukushkin, V. Y.; Pombeiro, A. J. L. *Inorg. Chem.* **2004**, *43*, 7083. (i) Marchetti, F.; Pettinari, C.; Pettinari, R.; Cerquetella, A.; Cingolani, A.; Chan, E. J.; Kozawa, K.; Skelton, B. W.; White, A. H.; Wanke, R.; Kuznetsov, M. L.; Martins, L. M. D. R. S.; Pombeiro, A. J. L. *Inorg. Chem.* **2007**, *46*, 8245. (j) Marchetti, F.; Pettinari, C.; Cerquetella, A.; Cingolani, A.; Pettinari, R.; Monari, M.; Wanke, R.; Kuznetsov, M. L.; Pombeiro, A. J. L. *Inorg. Chem.* **2009**, *48*, 6096. (k) Bolaño, S.; Bravo, J.; Castro-Fojo, J. A.; Rodríguez-Rocha, M. M.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L.; Gonsalvi, L.; Peruzzini, M. *Eur. J. Inorg. Chem.* **2007**, *35*, 5523.

(39) (a) Silva, M. E. N. P. R. A.; Pombeiro, A. J. L.; Fraústo da Silva, J. J. R.; Herrmann, R.; Deus, M.; Bozak, R. E. *J. Organomet. Chem.* **1994**, *480*, 81. (b) Silva, M. E. N. P. R. A.; Pombeiro, A. J. L.; Fraústo da Silva, J. J. R.; Herrmann, R.; Deus, N.; Castilho, T. J.; Guedes da Silva, M. F. C. *J. Organomet. Chem.* **1991**, *421*, 75. (c) Tellers, D. M.; Skoog, S. J.; Bergman, R. G.; Gunnoe, T. B.; Harman, W. D. *Organometallics* **2000**, *19*, 2428.

(40) Alegria, E. C. B.; Martins, L. M. D. R. S.; Haukka, M.; Pombeiro, A. J. L. *Dalton Trans.* **2006**, 4954.

(41) Alegria, E. C. B.; Martins, L. M. D. R. S.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L. *J. Organomet. Chem.* **2005**, *690*, 1947.

(42) (a) Nitabaru, T.; Kumagai, N.; Shibasaki, M. *Tetrahedron Lett.* **2008**, *49*, 272. (b) Nitabaru, T.; Nojiri, A.; Kobayashi, M.; Kumagai, N.; Shibasaki, M. *J. Am. Chem. Soc.* **2009**, *131*, 13860–13869. (c) Iseki, K.; Oishi, S.; Sasai, H.; Shibasaki, M. *Tetrahedron Lett.* **1996**, *37*, 9081–9084. (d) Tosaki, S. Y.; Hara, K.; Gnanadesikan, V.; Morimoto, H.; Harada, S.; Sugita, M.; Yamagiwa, N.; Matsunaga, S.; Shibasaki, M. *J. Am. Chem. Soc.* **2006**, *128*, 11776–11777. (e) Handa, S.; Nagawa, K.; Sohtome, Y.; Matsunaga, S.; Shibasak, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 3230–3233.

(43) Kiyooka, S.; Tsutsui, T.; Maeda, H.; Kanelo, Y.; lsobe, K. *Tetrahedron Lett.* **1995**, *36*, 6531.

(44) Jammi, S.; Saha, P.; Sanyashi, S.; Sakthivel, S.; Punniyamurthy, T. *Tetrahedron* **2008**, *64*, 11724.

(45) Jiang, T.; Gao, H.; Han, B.; Zhao, G.; Chang, Y.; Wu, W.; Gao, L.; Yan, G. *Tetrahedron Lett.* **2004**, *45*, 2699.

(46) Park, J.; Lang, K.; Abboud, K. A.; Hong, S. *J. Am. Chem. Soc.* **2008**, *130*, 16484.

(47) Kim, H. Y.; Oh, K. *Org. Lett.* **2009**, *11*, 5682.

(48) Mei, L.; Ming, T. H.; Rong, L. Q.; Jie, S.; Zhong, Y. S.; Liang, L. X. *J. Chem. Sci.* **2009**, *121*, 435.

(49) Zulauf, A.; Mellah, M.; Schulz, E. *J. Org. Chem.* **2009**, *74*, 2242.

(50) Davis, A. V.; Driffield, M.; Smith, D. K. *Org. Lett.* **2001**, *3*, 3075.

(51) Boruwa, J.; Gogoi, N.; Saikia, P. P.; Barua, N. C. *Tetrahedron: Asymmetry* **2006**, *17*, 3315.

(52) Qi, N.; Liao, R.-Z.; Yu, J.-G.; Liu, R.-Z. *J. Comput. Chem.* **2009**, *31*, 1376.

(53) Liu, S.; Wolf, C. *Org. Lett.* **2008**, *10*, 1831.

(54) Qin, B.; Xiao, X.; Liu, X.; Huang, J.; Wen, Y.; Feng, X. *J. Org. Chem.* **2007**, *72*, 9323.