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New Ruthenium(II) Complexes with Enantiomerically Pure Bis- and Tris(pinene)-Fused Tridentate Ligands. Synthesis, Characterization and Stereoisomeric Analysis

Xavier Sala,[†] Albert Poater,[‡] Alexander von Zelewsky,[§] Teodor Parella,[||] Xavier Fontrodona,[†] Isabel Romero,[†] Miquel Solà,*[,†] Montserrat Rodríguez,*[,†] and Antoni Llobet*[,||,⊥]

Departament de Química, Institut de Química Computacional, and Serveis Tecnics de Recerca, Universitat de Girona, Campus de Montilivi, E-17071 Girona, Spain, Modeling Laboratory for Nanostructures and Catalysis (MoLNaC), Dipartimento di Chimica, Università di Salerno, Via Ponte Don Melillo, E-84084 Fisciano (Salerno), Italy, Department of Chemistry, University of Fribourg, Pérolles, 1700 Fribourg, Switzerland, Departament de Química and Servei de RMN, Universitat Autònoma de Barcelona, Cerdanyola del Vallès, E-08193 Barcelona, Spain, and Institut Català d'Investigació Química (ICIQ), Av. Països Catalans 16, E-43007 Tarragona, Spain

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A new set of Ru−Cl complexes containing either the pinene[5,6]bpea ligand (**L1**) or the C_3 symmetric pinene[4,5]tpmOMe (**L2**) tridentate ligand in combination with the bidentate (B) 2,2′-bipyridine (bpy) or 1,2-diphenylphosphinoethane (dppe) with general formula $[RuCl(L1 \text{ or } L2)(B)]^+$ have been prepared and thoroughly characterized. In the solid state, X-ray diffraction analysis techniques have been used. In solution, cyclic voltammetry (CV) and 1D and 2D NMR spectroscopy have been employed. DFT calculations have been also performed on these complexes and their achiral analogues previously reported in our group, to interpret and complement experimental results. Whereas isomerically pure complexes ($[Ru^{II}Cl(L2)(bpy)](BF_4)$, **5** and $[Ru^{II}Cl(L2)(dppe)](BF_4)$, **6**) are obtained when starting from the highly symmetric $[Ru^{III}Cl_3(L2)]$, **2**, isomeric mixtures of *cis,fac*-$[Ru^{II}Cl(L1)(bpy)](BF_4)$ (**3b**/**3b′**), *trans,fac*- (**3a**) and *up/down,mer*- (**3c**, **3d**) isomers are formed when bpy is added to the less symmetric $[Ru^{III}Cl_3(L1)]$, **1**, in contrast to the case of the bulky dppe ligand that, upon coordination to **1**, leads to the *trans,fac*-$[Ru^{II}Cl(L1)(dppe)](BF_4)$ (**4a**) complex as a sole isomer due to steric factors.

Introduction

Ruthenium complexes are gathering a great deal of attention because of their multiple applications in many fields of science.[1] In particular, they are being used extensively as catalysts for a myriad of different processes including oxidative and reductive reactions.[2] In the field of asymmetric catalysis mediated by chiral transition-metal complexes, the ligands attached to the metal center play a key role, governing the catalyst performance (selectivity and efficiency) and its ability to produce enantioenriched compounds. Despite the huge number of enantiopure ligands reported, only some privileged ones have shown a wide range of applicability.[3] Therefore, the design of new chiral ligands to adequately influence reactivity is one of the most important challenges

* To whom correspondence should be addressed. E-mail: montse.rodriguez@udg.edu (M.R.), allobet@iciq.es (A.L.), miquel.sola@udg.edu (M.S.).
† Universitat de Girona.
‡ Università di Salerno.
§ University of Fribourg.
|| Universitat Autònoma de Barcelona.
⊥ Institut Català d'Investigació Químca (ICIQ).

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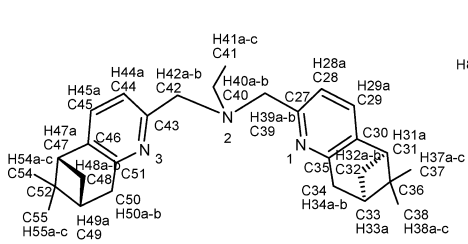
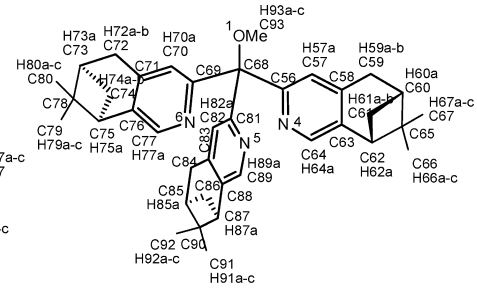
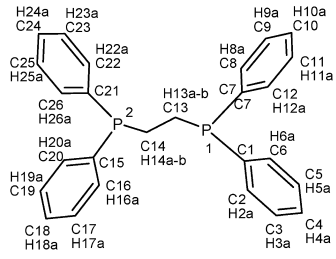
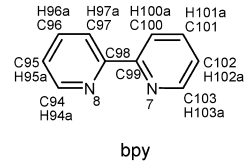
Chart 1. Drawing of the Ligands Used in This Work









nowadays in this field.[4] Working in this direction, we have recently reported the synthesis of a new family of polypyridylic chiral ligands where the chirality emerges from the monoterpene chiral pool.[5]

Rational design of effective catalysts for asymmetric transformations is then a pivotal issue nowadays. When a given enantiopure ligand coordinates octahedral transition-metal precursors (e.g., ruthenium(II) compounds), a set of isomeric complexes may be formed.[6] The understanding of both steric and electronic interactions around the metal ion can allow us to design synthesis where a major isomer is favored or even to generate only one isomer.[7] The latter would be extremely useful because it would allow us to prepare the catalyst in situ by just mixing the metal precursor and the chiral ligand.

Pinene[5,6]bpea (Chart 1) in combination with N- and P-donor bidentate ligands provides an excellent scenario to evaluate and understand how steric and electronic factors govern the final isomer outcome of these catalyst preparations.

Here on, we present the ruthenium coordination chemistry of the above-mentioned set of chiral tridentate ligands together with N- and P-donor bidentate ones (bpy and dppe). Ru−Cl complexes with the general formula [RuCl(L1 or L2)(B)]$^+$ (L1 is the pinene[5,6]bpea ligand; L2 is the C_3 symmetric pinene[4,5]tpmOMe ligand; B is bpy or dppe; Chart 1) have been prepared, thoroughly characterized, and stereoisomerically analyzed by comparison with their achiral analogues previously reported by our group.[8]

Experimental Section

Materials. All reagents used in the present work were obtained from Aldrich Chemical Co. and were used without further purification. Reagent grade organic solvents were obtained from SDS, and high-purity deionized water was obtained by passing distilled water through a nanopure Mili-Q water purification system. $RuCl_3 \cdot 2H_2O$, was supplied by Johnson and Matthey Ltd. and was used as received.

Preparations. The synthesis of the pinene[5,6]bpea (**L1**) and pinene[4,5]tpmOMe (**L2**) ligands (Chart 1) has been carried out as recently reported by our group.[5] All synthetic manipulations were routinely performed under a nitrogen atmosphere using Schlenck tubes and vacuum-line techniques. Electrochemical experiments were performed under either N_2 or argon atmosphere with degassed solvents.

[$Ru^{III}Cl_3$(L1)], 1. A sample of **L1** (100 mg, 0.241 mmol) was added to a 10 mL round-bottomed flask containing a solution of $RuCl_3 \cdot 2H_2O$ (59 mg, 0.241 mmol) in dry EtOH (3 mL) under magnetic stirring, and the mixture was heated at reflux for 3.5 h. The hot solution was filtered off in a frit, and the volume reduced to 1 mL in a rotary evaporator under reduced pressure. Then, water (2 mL) was added, and a green precipitate appeared. The solid obtained in this manner was filtered in a frit, washed with cold water and Et_2O, and dried under vacuum. Yield: 65% (98 mg, 0.157 mmol). ESI-MS (*m*/*z*) 587.6 [M-Cl]$^+$. $E_{1/2}$ (III/II)/(IV/III): (CH_2Cl_2) 0.113 V/1.36 V vs SSCE; elemental Anal. Calcd (%) for $C_{28}H_{37}N_3Cl_3Ru \cdot 2H_2O$: C 51.03, H 6.27, N 6.38; found: C 51.15, H 6.38, N 6.22.

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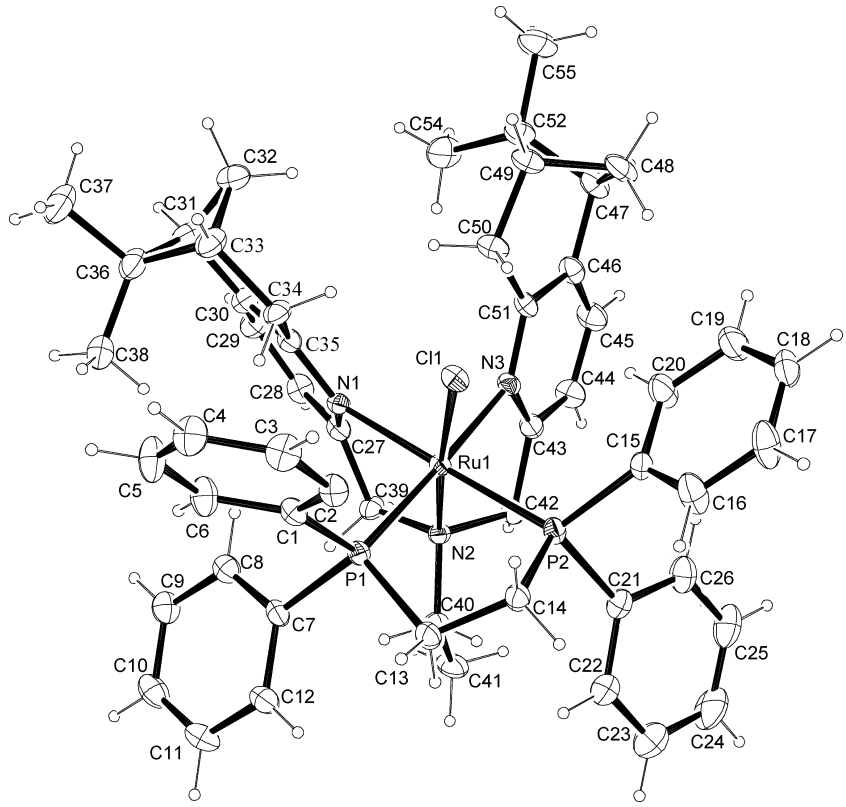


Figure 1. *ORTEP* view (ellipsoids are drawn at 50% probability level) of the molecular structure of cation **4a** including the atom numbering scheme.

[$Ru^{III}Cl_3$(L2)], 2. A sample of **L2** (55 mg, 0.099 mmol) was added to a 50 mL round-bottomed flask containing a solution of $RuCl_3 \cdot 2H_2O$ (24.2 mg, 0.099 mmol) in dry EtOH (19.3 mL) under magnetic stirring, and the mixture was heated at reflux for 2.5 h. The hot solution was filtered off in a frit and the volume reduced to 1 mL in a rotary evaporator under reduced pressure. Then, water (2 mL) was added and a green precipitate appeared. The solid obtained in this manner was filtered in a frit, washed with cold water and Et_2O, and dried under vacuum. Yield: 77.5% (62 mg, 0.076 mmol). ESI-MS (*m*/*z*) 731.4 $[M\text{-}Cl]^+$. $E_{1/2}$ (III/II)/(IV/III)(CH_2Cl_2): −0.224 V/ 1.34 V vs SSCE; elemental Anal. Calcd (%) for $C_{38}H_{45}Cl_3N_3Ru \cdot 2.5H_2O$: C 56.19, H 6.20, N 5.17; found: C 56.18, H 6.52, N 5.11.

***trans*,*fac*-[Ru^{II}Cl(L1)(bpy)](BF_4), 3a.** A sample of **1**·$2H_2O$ (55 mg, 0.084 mmol) was added to a 50 mL round bottomed flask containing a solution of LiCl (11 mg, 0.263 mmol) in EtOH/H_2O (3:1) (22 mL), under N_2 atmosphere. Then, NEt_3 (0.013 mL) was added and the reaction mixture stirred at room temperature for 30 min at which point bpy (13.5 mg, 0.086 mmol) was added and then heated at reflux for 1 h. The hot solution was filtered off in a frit and the volume reduced in a rotary evaporator under reduced pressure to remove the ethanol after the addition of an aqueous saturated solution of $NaBF_4$ (1.5 mL). A brown-red dust is obtained, which is filtered in a frit, washed with Et_2O, and dried under vacuum. The solid obtained in this manner was a mixture of isomeric complexes *trans*,*fac*-[Ru^{II}Cl(L1)(bpy)](BF_4), **3a**, and *cis*,*fac*-[Ru^{II}Cl(L1)(bpy)](BF_4), **3b/3b′** (in a molar ratio of 72:28, respectively), together with traces of the *up*,*mer*-[Ru^{II}Cl(L1)-(bpy)](BF_4), **3c** isomer, with an overall yield of 86.3%. Subsequently, recrystallization from a $CHCl_3/Et_2O$ mixture allows one to obtain the *trans*,*fac*- **3a** complex, in solution, as a sole isomer. Yield: 22% (15 mg, 0.019 mmol). ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C) δ = 0.48 (s, 3H, $H_{Me\text{-}pinene}$), 0.87 (s, 3H, $H_{Me\text{-}pinene}$), 0.94 (t, $^3J_{41ac\text{-}40a} = {}^3J_{41ac\text{-}40b}$ = 5.5 Hz, 3H, $H41_{a\text{-}c}$), 1.42 (s, 3H, $H_{Me\text{-}pinene}$), 1.45 (s, 3H, $H_{Me\text{-}pinene}$), 2.01 (q, $^3J_{40a\text{-}41ac}$ = 4.5 Hz, 1H, H40a), 2.12 (q, $^3J_{40b\text{-}41ac}$ = 4.5 Hz, 1H, H40b), 2.42 (m, 2H, H50a, H34a) 2.67 (m, 2H, H48a, H32a), 2.76 (m, 2H, H48b, H32b), 2.92 (t, 2H, H47a, H31a), 3.48 (d,$^3J_{34a\text{-}33a}$ = 8.2 Hz, 1H, H34b), 3.52 (d, $^3J_{50a\text{-}49a}$ = 7.3 Hz, 1H, H50b), 3.86 (d, $^3J_{42a\text{-}42b}$ = 9.3, 1H, H42a), 3.94 (d, $^3J_{39a\text{-}39b}$ = 9.6, 1H, H39a), 3.97 (d, $^3J_{42b\text{-}42a}$ = 9.3 Hz, 1H, H42b), 4.06 (d, $^3J_{39b\text{-}39a}$ = 9.6 Hz, 1H, H39b), 7.22 (d, $^3J_{44a\text{-}45a}$ = 7.2 Hz, 1H, H44a), 7.24 (d, $^3J_{28a\text{-}29a}$ = 7.1 Hz, 1H, H28a), 7,37 (m, 1H, H102a), 7.39 (m, 1H, H95a), 7.42 (d, $^3J_{29a\text{-}28a} = {}^3J_{45a\text{-}44a}$ = 7.2 Hz, 2H, H29a, H45a), 7.89 (m, 1H, H96a), 7.92 (m, 1H, H101a), 8.02 (dd, $^3J_{103a\text{-}102a}$ = 8.2 /$^4J_{103a\text{-}101a}$ = 3.5 Hz, 1H, H103a), 8.03 (dd, $^3J_{94a\text{-}95a}$ = 8.1 /$^4J_{94a\text{-}96a}$ = 3.1 Hz, 1H, H94a), 8.30 (dd, $^3J_{100a\text{-}101a}$ = 7.5 /$^4J_{100a\text{-}102a}$ = 2.9 Hz, 1H, H100a), 8.34 (dd, $^3J_{97a\text{-}96a}$ = 8.6,$^4J_{97a\text{-}95a}$ = 3.7 Hz, 1H, H97a). ^{13}C NMR (CD_2Cl_2): δ = 7.9 (C41), 20.7 (C38), 21.5 (C55), 25.1 (C37), 25.3 (C54), 31.2 (C32), 31.6 (C48), 38.8 (C50), 40.6 (C49, C33, C34), 47.3 (C31, C47), 56.2 (C40), 63.5 (C42), 64.6 (C39), 119.2 (C44), 119.5 (C28), 123.4 (C100), 123.6 (C97), 126.3 (C102), 126.4 (C95), 134.7 (C29, C45), 135.3 (C101), 135.4 (C96), 152 (C103), 152.1 (C94), 160.2 (C98), 160.4 (C99). ESI-MS (*m*/*z*) 708.3 $[M\text{-}BF_4]^+$; $E_{1/2}$ (III/II) (CH_2Cl_2) = 0.807 V vs SSCE; elemental Anal. Calcd (%) for $C_{38}H_{45}N_5RuClBF_4$: C 57.4; N 8.81; H 5.70; found: C 57,1; N 8.45; H 6.06.

For the NMR assignments of the complexes, we use the same labeling scheme used in Chart 1 and in the crystal structure shown in Figure 1.

***trans*,*fac*-[Ru^{II}Cl(L1)(dppe)](BF_4), 4a.** A sample of **1**·$2H_2O$ (75 mg, 0.114 mmol) was added to a 100 mL round-bottomed flask containing a solution of LiCl (11 mg, 0.526 mmol) in EtOH/H_2O (3:1) (35 mL), under N_2 atmosphere. Then, NEt_3 (0.036 mL) was added and the reaction mixture stirred at room temperature for 30 min, at which point dppe (49.2 mg, 0.123 mmol) was added and then heated at reflux for 2 h. The hot solution was filtered off in a frit, and the ethanol was completely removed in a rotary evaporator

under reduced pressure after the addition of an aqueous saturated solution of $NaBF_4$ (1.5 mL). A yellowish dust was then obtained, which was filtered in a frit washed with Et_2O and dried under vacuum. Yield: 85% (100 mg, 0.096 mmol). ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C) δ = 0.0 (s, 3H, H55a-c), 0.43 (t, $^3J_{41ac\text{-}40a}$ = $^3J_{41ac\text{-}40b}$ = 7.5 Hz, 3H, H41a-c), 0.64 (s, 3H, H38a-c), 1.09 (m, 1H, H32a), 1.28 (s, 3H, H54a-c), 1.32 (s, 3H, H37a-c), 1.36 (m, 1H, H48a) 1.93 (m, 1H, H33a), 2.17 (m, 1H, H49a), 2.24−2.27 (m, 2H, H40a, H40b), 2.50 (m, 1H, H32b), 2.65−2.67 (m, 2H, H34a, H48b), 2.71−2.76 (m, 3H, H50a, H31a, H47a), 2.85−3.41 (m, 4H, H14a, H14b, H13a, H13b), 3.55 (d, $^2J_{42a\text{-}42b}$ = 10.5 Hz, 1H, H42a), 3.83 (d, $^2J_{39a\text{-}39b}$ = 9.7 Hz, 1H, H39a), 4.05 (d, $^2J_{42b\text{-}42a}$ = 9.8 Hz, 1H, H42b), 4.16 (d, $^2J_{39b\text{-}39a}$ = 9.7 Hz, 1H, H39b), 7.06 (d, $^3J_{28a\text{-}29a}$ = 7.3 Hz, 1H, H28a), 7.14 (d, $^3J_{29a\text{-}28a}$ = 7.3 Hz, 1H, H29a), 7.17 (d, $^3J_{45a\text{-}44a}$ = 6.9 Hz, 1H, H45a), 7.30 (d, $^3J_{44a\text{-}45a}$ = 6.9 Hz, 1H, H44a), 7.44−7.75 (m, 20H, H2−H25). ^{13}C NMR (CD_2Cl_2): δ = 8.49 (C41), 21.4 (C38), 21.5 (C55), 25.2 (C54), 25.5 (C37), 28.1 (C14), 28.3 (C13), 30.0 (C32), 31.6 (C48), 37.7 (C34), 37.8 (C50), 39.9 (C49), 40.2 (C33), 46.3 (C31), 46.6 (C47), 61.6 (C40), 68.4 (C39), 68.9 (C42), 118.1 (C28), 120.0 (C44), 126.9 (C29), 127.5 (C45), 127.8 (C17, C19), 128.1 (C11, C9), 128.7 (C24), 129.0 (C5, C3), 129.6 (C18), 129.9 (C10), 130.7 (C22, C26), 131.0 (C4), 131.1 (C23, C25), 132.1 (C8, C12), 133.5 (C16, C20), 134.2 (C2, C6). ^{31}P NMR (CD_2Cl_2, 202 MHz, 25 °C): δ, 60.7 (s, P1, P2). ESI-MS (*m*/*z*) 950.2 $[M\text{-}BF_4]^+$; $E_{1/2}$ (III/II) (CH_2Cl_2) = 1.06 V vs SSCE. Elemental Anal. Calcd (%) for $C_{54}H_{61}N_3RuClBF_4$: C 62.53; N 4.05; H 5.93; found: C 62.25; N 3.84; H 6.17.

[Ru^{II}Cl(L2)(bpy)](BF$_4$), 5. A sample of **2** (60 mg, 0.074 mmol) was added to a 25 mL round-bottomed flask containing a solution of LiCl (8 mg, 0.263 mmol) in EtOH/H_2O (3:1) (12 mL), under N_2 atmosphere. Then, NEt_3 (0.023 mL) was added and the reaction mixture stirred at room temperature for 30 min, at which point bpy (12 mg, 0.077 mmol) was added and then heated at reflux for 1 h. The hot solution was filtered off in a frit and the volume reduced in a rotary evaporator under reduced pressure to remove the ethanol after the addition of an aqueous saturated solution of $NaBF_4$ (1.5 mL). A brown-red dust is obtained, which is filtered in a frit washed with Et_2O and dried under vacuum. Yield: 58% (40 mg, 0.043 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ = 0.37 ppm (s, 3H, H91a-c), 0.61 (s, 3H, H80a-c), 0.77 (s, 3H, H66a-c), 0.95 (m, 1H, H86a), 1.21 (s, 3H, H92a-c), 1.24 (m, 1H, H61a), 1.38 (m, 1H, H47a), 1.39 (s, 3H, H79a-c), 1.46 (s, 3H, H67a-c), 2.20 (m, 1H, H85a), 2.25 (t, $^3J_{87a\text{-}86a}$ = $^3J_{87a\text{-}86b}$ = 9.6 Hz, 1H, H87a), 2.39 (m, 2H, H60a, H73a), 2.69 (m, 1H, H61b), 2.82 (m, 1H, H74b), 2.90 (t,$^3J_{62a\text{-}61a}$ = $^3J_{62a\text{-}61b}$ = 7.5 Hz, 1H, H62a), 2.97−2.99 (m, 2H, H75a, H84), 3.17 (d, $^3J_{59ab\text{-}60a}$ = $^3J_{72ab\text{-}73a}$ = 7.8 Hz, 2H, H59a-b, H72a-b), 4.11 (s, 3H, H93a-c), 6.20 (s, 1H, H89a), 7.36−7.40 (m, 2H, H95a, H102a), 7.79 (s, 1H, H82a), 7.80 (s, 1H, H57a), 8.04−8.15 (m, 4H, H103a, H96a, H101a, H94a), 8.60 (dd, $^3J_{97a\text{-}96a}$ = $^3J_{100a\text{-}101a}$ = 7.6 Hz / $^4J_{97a\text{-}95a}$ = $^4J_{100a\text{-}102a}$ = 3.7 Hz, 2H, H97a, H100a), 8.81 (s, 1H, H77a), 8.83 (s, 1H, H64a). ^{13}C NMR ($CDCl_3$): δ = 21.1 (C91), 21.8 (C80, C66), 25.3 (C91), 25.8 (C79, C67), 31.1 (C86), 31.2 (C61), 31.6 (C74), 32.8 (C84), 33.2 (C59, C72), 38.0 (C78), 38.4 (C90), 39.0 (C65), 39.4 (C85), 39.7 (C60, C73), 43.5 (C87), 44.2 (C62, C75), 57.9 (C93), 88.9 (C88), 121.2 (C82), 121.4 (C57), 121.5 (C70), 124.1 (C100, C97), 125.3 (C95, C102), 136.5 (C96), 136.7 (C101), 148.0 (C89), 151.2 (C94, C103), 152.0 (C64), 152.2 (C77). ESI-MS (*m*/*z*) 852.1 $[M\text{-}BF_4]^+$;$E_{1/2}$ (III/II) (CH_2Cl_2) = 0.741 V vs SSCE; elemental Anal. Calcd (%) for $C_{48}H_{53}N_5O_1RuClBF_4$: C 58.57; N 7.11; H 5.94; found: C 58.25; N 6.97; H 6.33.

[Ru^{II}Cl(L2)(dppe)](BF$_4$)·7H$_2$O, 6. A sample of **2** (55 mg, 0.068 mmol) was added to a 25 mL round-bottomed flask containing a solution of LiCl (7.3 mg, 0.349 mmol) in EtOH/H_2O (3:1) (12 mL), under N_2 atmosphere. Then, NEt_3 (0.022 mL) was added and the reaction mixture stirred at room temperature for 30 min, at which point dppe (29 mg, 0.073 mmol) was added. The reaction mixture was then heated at reflux for 1.5 h. The hot solution was filtered off in a frit and the ethanol completely removed in a rotary evaporator under reduced pressure after the addition of an aqueous saturated solution of NH_4PF_6 (1.0 mL). A yellowish dust is then obtained, which is filtered in a frit, washed with Et_2O, and dried under vacuum. Yield: 54% (50 mg, 0.040 mmol). ^{1}H NMR (500 MHz, acetone-d_6, 25 °C) δ = −0.19 (s, 3H, H92a-c), 0.20 (m, 1H, H86a), 0.48 (s, 6H, H66a-c, H80a-c), 0.88 (s, 3H, H91a-c), 0.96 (m, 1H, H74a), 1.01 (m, 1H, H61a), 1.24 (s, 3H, H79a-c), 1.25 (t, $^3J_{87a\text{-}86a}$ = $^3J_{87a\text{-}86b}$ = 8.2 Hz, 1H, H87a), 1.27 (s, 3H, H67a-c), 1.86 (m, 1H, H85a), 1.93 (t, $^3J_{62a\text{-}61a}$ = $^3J_{62a\text{-}61b}$ = 7.7 Hz, 1H, H62a), 2.04 (m, 1H, H86b), 2.23 (m, 2H, H60a, H73a), 2.25 (t, $^3J_{75a\text{-}74a}$ = $^3J_{75a\text{-}74b}$ = 7.9 Hz, 1H, H75a), 2.50 (m, 1H, H61b), 2.64 (m, 1H, H74b), 2.70 (d, $^3J_{84a\text{-}85a}$ = 8.2 Hz, 1H, H84a), 2.85 (m, 1H, H14a), 3.06−3.08 (m, 3H, H59a, H72a, H13a), 3.15 (d, $^3J_{59b\text{-}60a}$ = $^3J_{72b\text{-}73a}$ = 9.0 Hz, 2H, H59b, H72b), 3.26 (m, 1H, H14b), 3.31 (m, 1H, H13b), 3.39 (s, 3H, H93a-c), 6.12 (s, 1H, H89a), 6.92 (m, 1H, H18a), 7.13−7.14 (m, 4H, H22a, H23a, H26a, H25a), 7.21 (m, 2H, H20a, H16a), 7.33−7.48 (m, 12H, H19a, H18a, H17a, H8a, H9a, H10a, H11a, H12a, H6a, H5a, H3a, H2a), 7.71 (m, 1H, H4a), 7.80 (S, 1H, H82a), 7.98 (s, 1H, H57a), 8.00 (s, 1H, H70a), 8.07 (s, 1H, H64a), 8.15 (s, 1H, H77a). ^{13}C NMR (CD_2Cl_2): δ = 21.0 (C66. C80), 21.7 (C92), 25.0 (C67, C79, C91), 28.1 (C14), 28.3 (C13), 30.3 (C61), 31.3 (C74), 31.8 (C86), 32.2 (C84), 32.7 (C59, C72), 38.0 (C65, C78, C90), 39.0 (C85), 39.7 (C60), 39.8 (C73), 43.2 (C87), 43.7 (C62), 43.9 (C75), 57.1 (C93), 88.5 (C68), 119.9 (C82), 123.1 (C57), 123.8 (C70), 127.8 (C17, C19), 128.1 (C9, C11), 129.0 (C3, C5), 129.6 (C18), 129.9 (C10), 131.0 (C4), 132.1 (C8, C12), 133.5 (C16, C20), 134.2 (C6, C2), 151.6 (C64, C77), 156.6 (C89). ^{31}P NMR (Acetone-d_6, 202 MHz, 25 °C): δ, 70.0 (d, J_{P1-P2}= 7.45 Hz, P1), 71.1 (d, P2). ESI-MS (*m*/*z*) 1094 $[M\text{-}PF_6]^+$; $E_{1/2}$ (III/II)(CH_2Cl_2)= 1.02 V vs SSCE. Elemental Anal. Calcd (%) for $C_{64}H_{69}N_3O_1RuClPF_6 \cdot 7H_2O$: C 56.28; N 3.07; H 6.13; found: C 56.55; N 2.69; H 6.17.

Instrumentation and Measurements. Cyclic voltammetric (CV) experiments were performed in a IJ-Cambria IH-660 potentiostat, using a three-electrode cell. Glassy carbon disk electrodes (3 mm diameter) from BAS were used as a working electrode, platinum wire as auxiliary, and SSCE as the reference electrode. Cyclic voltammograms were recorded at 100 mV/s scan rate under nitrogen atmosphere. The complexes were dissolved in previously degassed dichloromethane containing the necessary amount of (n-Bu_4N)(PF_6), used as supporting electrolyte, to yield a 0.1 M ionic strength solution. All $E_{1/2}$ values reported in this work were estimated from cyclic voltammetry as the average of the oxidative and reductive peak potentials ($E_{p,a}$ + $E_{p,c}$)/2. Unless explicitly mentioned, the concentration of the complexes were approximately 1 mM.

The ^{1}H NMR spectroscopy was performed on a Bruker DPX 200 MHz, a Bruker DPX 250 MHz, or a Varian VRX 500 MHz. Samples were run in $CDCl_3$, CD_2Cl_2 or acetone-d_6 with internal references (residual protons and/or tetramethylsilane or DSS respectively). Elemental analyses were performed using a CHNS-O Elemental Analyzer EA-1108 from Fisons. The ESI mass spectroscopy experiments were performed on a VG-QUATTRO from Fisons Instruments.

X-ray Structure Determination. Suitable crystals of **4a** were grown from slow diffusion of ethyl ether into a solution of the compound in CH_2Cl_2. *Data Collection:* A crystal of **4a** was mounted on a nylon loop and used for low-temperature (100(2) K) X-ray

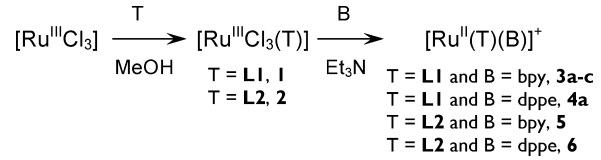
structure determination. The measurement was carried out on a Bruker *SMART* APEX CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) from an X-ray tube. The measurements were made in the range 2.02 to 28.28° for θ. Full-sphere data collection was carried out with ω and φ scans. A total of 20 557 reflections were collected, of which 12 340 [R(int) = 0.0143] were unique. Programs used: data collection, *Smart* version 5.631 (Bruker AXS 1997−02); data reduction, *SAINT+* version 6.36A (Bruker AXS 2001); absorption correction, *SADABS* version 2.10 (Bruker AXS 2001). *Structure Solution and Refinement*. Program *SHELXTL* Version 6.14 (Bruker AXS 2000−2003) was used. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in geometrically optimized positions and forced to ride to the atom to which they are attached.

Computational Details. The density functional theory (DFT) calculations have been carried out with the hybrid B3PW91 density functional,[9,10] as implemented in the *Gaussian 03* package.[11] The ruthenium atoms have been represented with the quasi relativistic effective core pseudopotentials (RECP) of the Stuttgart group and the associated basis sets augmented with a *f* polarization function ($\alpha = 1.235$).[12,13] The remaining atoms (carbon, nitrogen, phosphorus, chlorine, and hydrogen) have been represented with 6−31G(d,p) basis sets.[14] The B3PW91 geometry optimizations were performed without any symmetry constraints, and the nature of minima was checked by analytical frequency calculations. The energies given throughout the paper are electronic energies without ZPE corrections (inclusion of the ZPE corrections does not significantly modify the results) or Gibbs free energy values computed at 298 K and 1 atm.

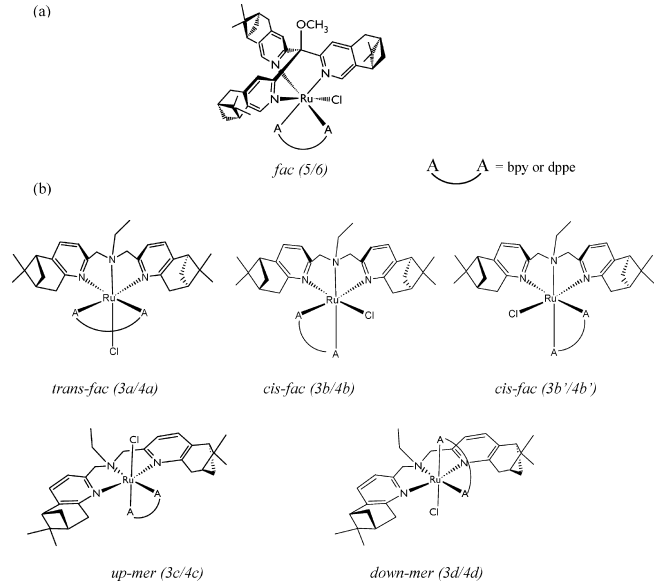
Results and Discussion

The synthetic strategy followed for the preparation of the complexes described in the present article is outlined in Scheme 1. The chiral tripodal ligands **L1** and **L2** (Chart 1) have been prepared following the synthesis recently reported by us.[5] $RuCl_3 \cdot 2H_2O$ is used as starting material for the complexation of **L1** and **L2**, leading to the trichloro ruthenium complexes [$RuCl_3$(pinene[5,6]bpea)], **1**, and [$RuCl_3$(pinene[4,5]tpmOMe)], **2**, in good yields. Dramatic solubility differences can be observed by comparing **1** and **2** with their counterparts bearing nonchiral ligands.[15] The highly organic content of the pineno-fused ligands originates an enhanced solubility in a wide range of solvents, facilitating the use of **1** and **2** as starting materials for the coordination of further ligands. Therefore, through reduction with NEt_3 in presence of a bidentate ligand B, a collection of [RuCl(L1 or L2)(B)]$^+$ chiral complexes can be generated. 2,2′-bipyridine (bpy) and 1,2-bis(diphenylphosphino)ethane (dppe) have been our choice for the present work, and a set of chloro complexes have been synthesized: **3a**−**c** and **4a** containing **L1**, and **5** and **6** containing **L2** (Scheme 1).

Scheme 1. Synthetic Strategy for the Preparation of **1**−**6**



Scheme 2. Possible Stereoisomers for [RuCl(L2)(A−A)]$^+$ (a) and [RuCl(L1)(A−A)]$^+$ (b)



The substitution of two chlorine ligands in **1** and **2** by a symmetrical bidentate *N*,*N*- or *P*,*P*-donor ligand such as bpy or dppe can potentially lead to multiple stereoisomers that are shown in Scheme 2. First of all, pinene[5,6]bpea, **L1**, is a sufficiently flexible tridentate ligand that can potentially coordinate in a meridional or in facial fashion,[16] whereas the more rigid pinene[4,5]tpmOMe, **L2**, acts only in the latter mode. Second, whereas the C_3 symmetric **2** can only lead to a single stereoisomer upon coordination of a bidentate ligand

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(16) See for instance Romero, I.; Rodríguez, M.; Llobet, A.; Collomb-Dunand-Sauthier, M. N.; Deronzier, A.; Parella, T.; Stoeckli-Evans, H. *J. Chem. Soc., Dalton Trans.* **2000**, *168*, 9–1694, or ref 8a for some examples of facial coordination of the analogous achiral bpea ligand, and ref 8b for the same ligand coordinated in a meridional fashion.

Table 1. Crystal Data for Complex *trans,fac*-[Ru^{II}Cl(L1)(dppe)](BF_4), **4a**

empirical formula	$C_{58}H_{71}BClF_4N_3OP_2Ru$
fw	1111.45
cryst syst, space group	triclinic, *P*1
a, Å	10.695(2)
b, Å	11.316(2)
c, Å	12.455(3)
α,°	63.165(3)°
β,°	87.923(3)°
γ,°	87.683(3)°
V, Å^3	1343.6(5)
formula Units/Cell	1
temperature, K	100(2)
λ Mo Kα, Å	0.71073
ρ_{calcd}, g cm^{-3}	1.374
μ, mm^{-1}	1.104
R1[a]	0.0309
wR2[b]	0.0896

[a] $R_1 = \Sigma|||F_o| - ||F_c|||/\Sigma|F_o|$. [b] $wR2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0042P)^2]$ and $P = (F_o^2 + 2F_c^2)/3$.

(part a of Scheme 2), **1**, with lower symmetry, can potentially lead to four more stereoisomers, as depicted in part b of Scheme 2.

From now on, the nomenclature used to name isomers where the bpea or the pinene[5,6]bpea ligand acts in a facial fashion will consider the relative position of the Ru−Cl bond with regard to the Ru−$N_{aliphatic}$ bond of the tridentate ligand. Therefore, isomer **3a** will be named *trans,fac*-, **3b/3b′** will be the *cis,fac*-, and the two meridional isomers will be named *up,mer*- (**3c**) and *down,mer*- (**3d**), where the notation up and down refers to the orientation of the chlorine ligand with respect to the ethyl group of the bpea ligand (Scheme 2).

The reaction of equimolar amounts of **1** and the neutral bpy ligand in EtOH/H_2O at reflux for 1 h under nitrogen atmosphere produces isomeric **3a** and **3b/3b′** in a molar ratio of 72:28, respectively. Traces of the mer **3c** are also observed by NMR, being 86.3% the overall isolated yield. Subsequent recrystallization from $CHCl_3$/Et_2O allows the isolation of **3a** in 22% yield. It is worth mentioning here that the synthesis of the analogous complex containing the nonchiral bpea ligand, [RuCl(bpea)(bpy)]$^+$, **7**, recently reported by us,[8a] leads to the *trans,fac*- **7a** as single isomer. On the other hand, reaction of equimolar amounts of **1** and the P-bidentate dppe ligand under similar conditions leads to the exclusive formation of the *trans,fac*-[RuCl(L1)(dppe)](BF_4) isomer **4a**, in a 85% yield. The remaining dppe ligand produces the neutral [$RuCl_2$(dppe)$_2$] complex as a side product. However, in this case, the synthesis of analogous complexes containing the achiral bpea ligand affords quite more complex mixtures containing the *trans,fac*-, *cis,fac*- and *mer*-isomers.[8b,17] To deepen in these significant product differences, theoretical calculations for the whole set of compounds synthesized from **1** as well as for the potential isomers of complexes [RuX(bpea)(bpy)]$^{n+}$ (X = Cl, **7a**−**d**; X = H_2O, **8a**−**d**) have been performed and will be discussed later on.

The crystal structure of **4a** has been solved by X-ray diffraction analysis. Main crystallographic data are reported in Table 1 together with selected bond distances and angles that can be found in Table 3. An *ORTEP* plot for the molecular structure of **4a** is depicted in Figure 1.

The redox properties of **1**−**6** were investigated by means of cyclic voltammetry (Figures S7−S9 in the Supporting Information). Trichloro **1** and **2** show a double wave pattern, which corresponds to the $Ru^{III/II}$ and $Ru^{IV/III}$ couples, at $E_{1/2}$ values of 0.113/1.36 and −0.224/1.34 V, respectively. The stronger *σ*-donating and lower *π*-accepting capability of **L2** with regard to **L1** is clearly manifested by a shift of 0.337 V to lower potentials on the (III/II) wave in complex **2**. However, this electronic effect is clearly reduced upon coordination of a bidentate ligand. Thus, chlorido **3a** and **5** show a simple chemically and electrochemically reversible wave in dichloromethane, corresponding to the Ru^{III}/Ru^{II} couple, at $E_{1/2}$ values of 0.802 and 0.741 V, respectively. Analogous **4a** and **6**, containing the more *π*-acceptor phosphine ligand dppe instead of bpy, undergo an equivalent redox process at higher, but still closer, potential values ($E_{1/2}$ = 1.06 and 1.02 V, respectively). A plausible reason for the observed decrease on the electronic donation of **L2** to the metal center (**5** and **6**) can be found in the steric encumbrance between the bidentate ligands and the three pyridyl-pinene moieties of the tridentate itself. These interactions can produce important structural distortions, affecting the orientation of the orbitals involved in the Ru−**L2** bonding.

DFT calculations were performed for the five potential isomers of **3** (containing bpy as bidentate ligand) and for the four isomers of the analogous, previously reported compounds of general formula [Ru(X)(bpea)(bpy)]$^{n+}$ (X = Cl, **7a**−**7d**; X = H_2O, **8a**−**8d**),[8a] for purposes of comparison. The structural optimization of **8a** in the gas phase is in good agreement with the experimental X-ray data. The standard deviation for the bond distances and angles are 0.017 Å and 0.8°, respectively,[18] thus providing confidence on the reliability of the chosen method to reproduce the geometries of the studied complexes. Furthermore, DFT calculations for the five potential isomers of **4** containing dppe as bidentate ligand have been also performed. Figure 2 displays the relative energy diagram for the optimized structures of the different isomers of **3**, **4**, and **7**, whereas **8a**−**d** are gathered in the Supporting Information. Selected bond distances and angles are collected in Tables 2 and 3 together with the available experimental counterparts. To simplify the structural discussion for these sets of complexes, the plane nearly perpendicular to the Ru−X bond (X = monodentate ligand), which contains four cis coordinating atoms with regard to the mentioned Ru−X bond, will be considered as the equatorial plane of these molecules. As inferred from the calculated structures, relatively strong steric repulsions are found in the *cis,fac*- complexes **3b** and **3b′** between the bpy ligand and one of the bulky pinene groups of the pinene[5,6]bpea (**L1**) ligand (part a of Figure 2) situated, as bpy, in the mentioned equatorial plane. Consequently, a significant

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(18) Standard deviations for distances and angles: $s_{n-1} = [\sum_{i=1}^{N}(CV - EV)^2/(N-1)]^{1/2}$, where CV means calculated value, EV experimental value (X-ray data), and *N* is the number of distances or angles taken into account (distances and angles used are given in Table S1 of the Supporting Information).

Table 2. Selected Bond Distances (Angstroms) and Angles (Degrees) for X-ray Structure of **8a** and for B3PW91-Optimized Geometries of **8a**−**8d**, **7a**−**7d**, and **3a**−**3d** Isomers

	8a (X-ray)	**8a**	**8b**	**8c**	**8d**	**7a**	**7b**	**7c**	**7d**	**3a**	**3b**	**3b′**	**3c**	**3d**
Ru−N1	2.068	2.074	2.018	2.075	2.076	2.078	2.047	2.063	2.064	2.167	2.117	2.164	2.179	2.138
Ru−N2	2.110	2.120	2.177	2.192	2.166	2.173	2.188	2.189	2.172	2.160	2.179	2.177	2.195	2.170
Ru−N3	2.068	2.074	2.101	2.074	2.079	2.078	2.087	2.063	2.064	2.185	2.143	2.124	2.164	2.175
Ru−N7	2.058	2.072	2.107	2.059	2.058	2.046	2.086	2.053	2.061	2.023	2.070	2.071	2.054	2.063
Ru−N8	2.058	2.072	2.087	2.060	2.075	2.046	2.058	2.096	2.128	2.040	2.071	2.069	2.101	2.110
Ru−Z[a]	2.178	2.206	2.209	2.243	2.217	2.395	2.400	2.443	2.407	2.433	2.415	2.414	2.442	2.418
N3−Ru−N2	82.26	82.0	79.1	81.5	81.0	81.1	78.8	81.5	81.0	79.5	75.7	81.7	80.5	78.6
N3−Ru−N1	156.27	82.6	82.9	162.8	162.4	83.1	83.0	163.0	161.9	85.0	91.5	91.8	160.0	159.1
N2−Ru−N1	82.26	82.0	83.2	81.5	81.3	81.2	82.4	81.5	81.1	81.9	81.7	76.0	79.7	80.6
N2−Ru−N7	96.33	97.3	104.2	174.8	178.1	98.7	104.7	175.7	179.9	95.7	106.5	166.3	175.9	175.5
N7−Ru−N8	82.37	78.5	77.5	78.6	78.6	98.7	77.8	78.1	77.9	79.5	77.7	77.6	78.0	77.7
N7−Ru−N1	98.53	99.4	87.4	98.4	99.5	98.9	88.2	98.3	99.0	98.7	88.0	101.4	99.3	103.7
N7−Ru−N3	176.89	177.7	169.3	98.4	98.1	177.9	170.0	98.4	98.9	173.5	177.7	111.9	100.4	97.1
N8−Ru−N1	176.89	177.7	103.7	93.3	92.5	177.9	105.3	93.2	93.1	176.4	111.2	176.9	94.7	92.6
N8−Ru−N2	96.33	97.2	173.0	106.6	103.1	98.7	172.0	106.2	102.1	95.1	166.8	105.7	106.1	101.1
N8−Ru−N3	98.53	99.5	100.5	93.3	91.5	98.9	100.0	93.2	93.1	96.5	100.5	85.9	92.7	93.4
N3−Ru−Z[a]	87.22	94.0	94.2	88.0	89.6	93.9	93.2	88.5	88.8	100.6	92.2	167.2	88.0	90.2
N2−Ru−Z[a]	94.82	174.5	88.9	82.5	90.9	173.3	89.3	85.6	90.1	174.9	88.5	88.0	86.0	90.9
N1−Ru−Z[a]	86.95	93.8	172.0	88.0	90.7	81.1	171.4	88.5	88.7	103.6	168.3	93.0	88.6	88.0
N7−Ru−Z[a]	96.01	87.0	96.0	92.3	87.4	86.5	96.2	90.1	89.9	83.8	88.7	78.7	90.0	90.4
N8−Ru−Z[a]	177.89	87.1	84.2	170.9	166.0	86.5	82.8	168.2	167.8	79.9	78.9	89.7	167.9	167.9

[a] For **8a**−**8** isomers Z is oxygen; for the other complexes, Z is chlorine.

Table 3. Selected Bond Distances (Angstroms) and Angles (Deg) for X-ray Structure of **4a** and for B3PW91-Optimized Geometries of **4a**−**4d** Isomers

	4a (X-ray)	**4a**	**4b**	**4b′**	**4c**	**4d**
Ru−N1	2.222(3)	2.227	2.161	2.262	2.321	2.408
Ru−N2	2.1729(2)	2.187	2.210	2.216	2.213	2.211
Ru−N3	2.246(3)	2.283	2.298	2.227	2.256	2.199
Ru−Cl1	2.453(8)	2.448	2.430	2.425	2.469	2.433
Ru−P1	2.3072(8)	2.331	2.339	2.482	2.364	2.491
Ru−P2	2.3201(9)	2.351	2.435	2.368	2.367	2.367
N3−Ru−N2	78.36(9)	77.6	75.7	78.2	78.9	75.2
N3−Ru−N1	79.73(9)	81.0	82.2	80.9	154.1	148.8
N2−Ru−N1	80.80(9)	81.2	81.7	80.1	75.4	75.0
N3−Ru−P1	176.47(7)	176.3	101.2	105.1	107.4	104.8
N2−Ru−P1	99.46(7)	100.1	165.2	170.0	167.1	180.0
N1−Ru−P1	97.23(7)	95.8	96.4	109.6	97.1	105.0
N1−Ru−P2	177.38(7)	178.4	112.5	172.1	99.5	97.6
N3−Ru−P2	93.97(7)	97.4	101.2	96.0	90.8	94.9
N2−Ru−P2	97.62(7)	98.8	165.2	92.2	105.8	96.7
P1−Ru−P2	85.07(3)	85.8	84.1	78.1	85.6	83.3
N3−Ru−Cl1	97.93(7)	97.1	92.2	156.3	83.1	88.5
N1−Ru−Cl1	102.23(6)	100.8	167.0	78.9	91.2	82.3
N2−Ru−Cl1	174.81(7)	174.1	85.6	86.2	85.1	89.9
P1−Ru−Cl1	84.42(3)	85.3	88.1	93.3	84.6	90.1
P2−Ru−Cl1	79.19(3)	79.1	80.0	102.4	166.3	173.2

distortion from the regular octahedral geometry is found in these isomers producing a large dihedral angle between the two pyridyl rings involved, which would be almost coplanar in an ideal geometry. This effect is also observed, though in a lesser extent, even when the ligand involved is the less voluminous bpea (**7b**, part c of Figure 2). For the case of the *trans,fac*- (**3a**, **7a/8a**) and *mer*- (**3c**, **7c/8c**) complexes, the pyridyl groups of the bpea or the pinene[5,6]bpea ligands are perpendicular to the plane defined by the bpy ligand, thus reducing the degree of these steric interactions.

The relative energies of the different isomers of **7** and **8** as compared to the corresponding *trans,fac*- isomers **7a/8a** are 10.8/8.6 (**7b/8b**), 8.6/11.5 (**7c/8c**), and 12.5/12.2 (**7d/8d**) kcal·mol^{-1}, whereas for **3**, the values above the energy of isomer **3a** are 4.2/5.3 (**3b/3b′**), 3.4 (**3c**), and 4.0 (**3d**) kcal·mol^{-1} (Figure 2). These results are consistent with the experimental findings, indicating that **7a** and **8a** are the only isomers obtained, whereas for **3** the reaction yields a mixture of **3a**, **3b/3b′**, and traces of **3c**. According to experimental results, **3c** and **3d** should be the less stable isomers. It is likely that the stability of isomers **3b/3b′**, having pyridyl groups of the pinene[5,6]bpea and bpy ligands in closer contact, is underestimated by our calculations because common DFT methods do not describe correctly dispersive interactions more present in **3a/3b′** than in **3c** or **3d**.[19]

A thorough study of the solid-state and calculated gas-phase structures shows that electronic factors should be considered here, jointly with the steric ones mentioned up until now, to rationalize the results obtained. The existence of two strong hydrogen bonding interactions found in *trans,fac*-**7a** and **8a** complexes between the X atom (X = Cl, **7a**; X = O, **8a**) and the alpha atoms H51/H35 from both bpea-pyridylic rings (see **8a** X-ray structure and labeling in the Supporting Information) strongly stabilize this *trans,fac*-isomer, being the only one experimentally obtained.[8a] However, when replacing the bpea ligand by its chiral pineno-fused analogue **L1**, the electronic intramolecular stabilization disappears as H51/H35 do in the annulation process (Chart 1). Thus, the degree of steric repulsions in these isomers (**3a**−**3d**) is in this case the main factor responsible for the occurrence of **3a** as the major isomer obtained in the synthesis, which is also consistent with its lower energy, found from theoretical calculations (see values given above and Figure 2 for a qualitative diagram).

Finally, if the bulky dppe ligand is used instead of bpy in combination with **L1**, increased steric effects are found from calculations performed for the five potential isomers. Also in this case, the *trans,fac*- isomer **4a** is the most favored one both from DFT calculations and from intuitive steric arguments because this conformation keeps the pinene groups far away from the four dppe phenyl rings. The relative

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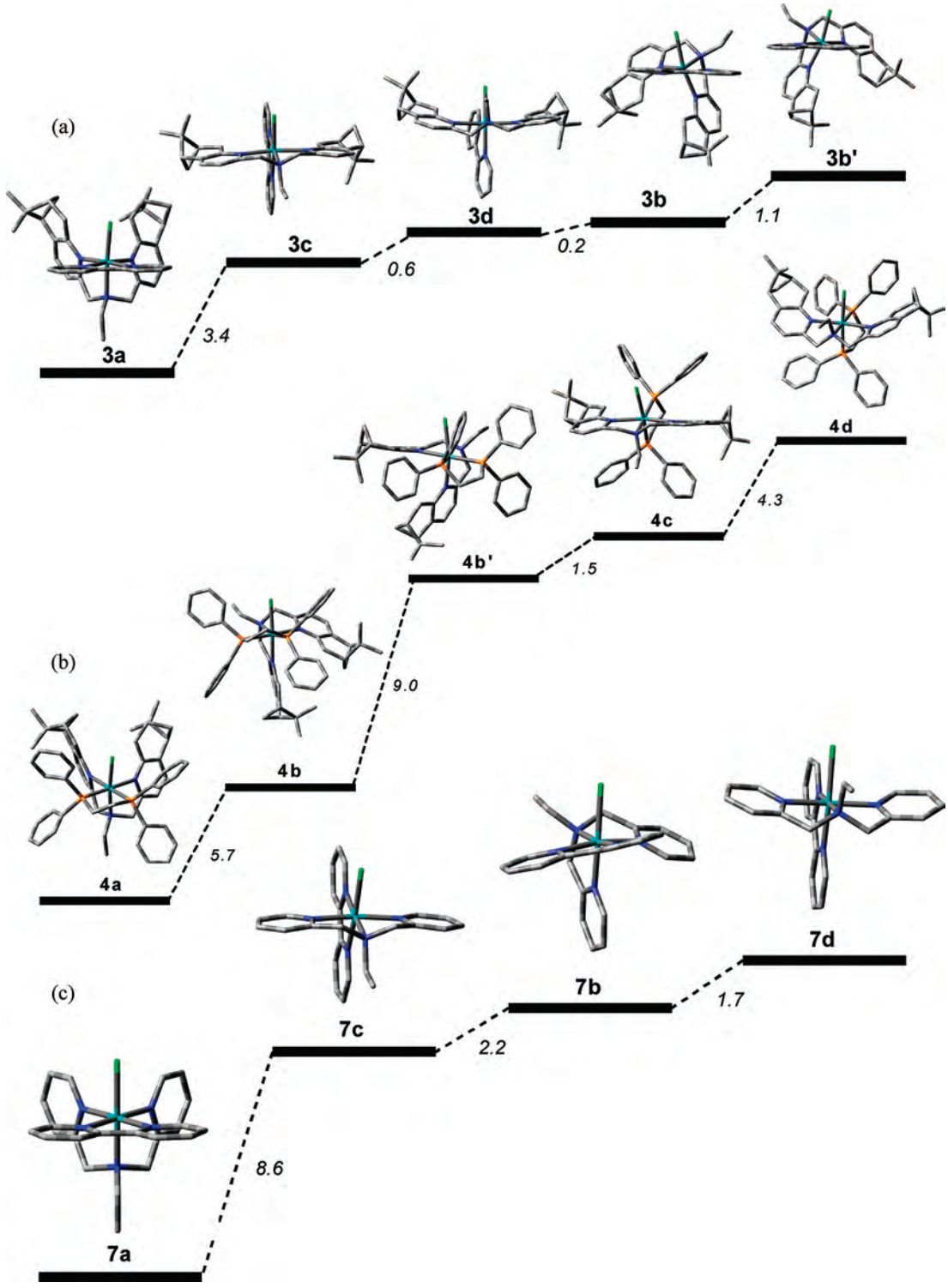

Figure 2. Relative energy diagram for the B3PW91-optimized geometries of the cationic moieties of **3a**−**3d** (a), **4a**−**4d** (b), and **7a**−**7d** (c). Energies are given in kcal mol^{-1}. Color codes: ruthenium, light blue; chlorine, green; nitrogen, blue; phosphorus, orange; carbon, gray; hydrogen, white.

energies found for the different isomers with respect to **4a** are 5.7 (**4b**), 14.7 (**4b′**), 16.2 (**4c**), and 20.5 (**4d**). The main reason for the larger stability of **4b** with regard to **4b′** is mainly due to steric hindrance. For **4b′**, the phenyl rings of the dppe and the two pinene methyl groups, situated in the upper left corner of the **4b′** drawing (part b of Figure 2), are in close proximity, whereas for **4b** the pinene group is accommodated between two phenyl rings of the dppe, leading to lower repulsion. All this is also consistent with the experimental results obtained, being only **4a** the isomer formed. It is worth mentioning here that the analogous synthetic process employing the achiral bpea ligand instead of **L1** leads to isomeric mixtures of *trans,fac*-, *cis,fac*-, and *mer*- compounds in decreasing respective molar ratio, as also deduced from DFT calculations.[8b] Thus, it can be established that the bulky pinene group introduced is responsible for the destabilization of the

cis,fac- (**4b/4b′**) and *mer* (**4c**, **4d**) isomers, allowing the synthesis of the pure *trans,fac*- (**4a**) complex.

As a conclusion, we have found that the isomeric ratio obtained in the syntheses of the complexes of general formula $[RuCl(L1 \text{ or bpea})(B)]^+$ is in all cases governed by steric factors, leading to a major occurrence of the corresponding *trans,fac*-isomer with regard to *cis,fac*- and *mer*, as stated from both experimental results and DFT calculations. However, for complexes containing the bpea ligand electronic factors also play a key role, especially favoring the formation of *trans,fac*-**7a** and **8a** complexes thanks to hydrogen-bonding interactions involving the alpha hydrogens of the bpea pyridyl rings.

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Supporting Information Available: CIF file of **4a,** together with spectroscopic (1D and 2D NMR) and electrochemical characterization for the reported complexes. This material is available free of charge via the Internet at http://pubs.acs.org. The supplementary crystallographic data can also be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax +44 1223 336033 or E-mail: deposit@ccdc.cam.ac.uk).

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