Ru Complexes with Chiral bis-Pinene Ligands: an Array of Subtle Structural Diversity

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ABSTRACT: A new chiral derivative of the N,N-bis(2-pyridylmethyl)ethylamine (bpea) ligand, Me-pinene[5,6]bpea (-)-**L1,** has been prepared from a new aldehyde building block (Me-pinene-aldehyde (-)-**4**) arising from the monoterpene chiral pool. The tridentate (-)-**L1** ligand has been employed to prepare a new set of Ru-Cl complexes in combination with the didentate 2,2'-bipyridine (bpy) with general formula $[RuCl((-)\text{-}\mathbf{L1})(bpy)]^{+}$. These complexes have been characterized in solution by cyclic voltammetry (CV), UV-vis and 1D and 2D NMR spectroscopy. Isomeric mixtures of *trans,fac*-**C1a** and *anti,mer*-**C1c** compounds are formed when (-)-**L1** is reacted with a $[Ru(bpy)(MeOH)Cl_3]$ precursor. DFT calculations of all the potential isomers of this reaction have been performed in order to interpret the experimental results in terms of electronic and steric effects and also to unravel the observed isomerization pathway between *anti,mer*-**C1c** and *trans,fac*-**C1a**.

Introduction

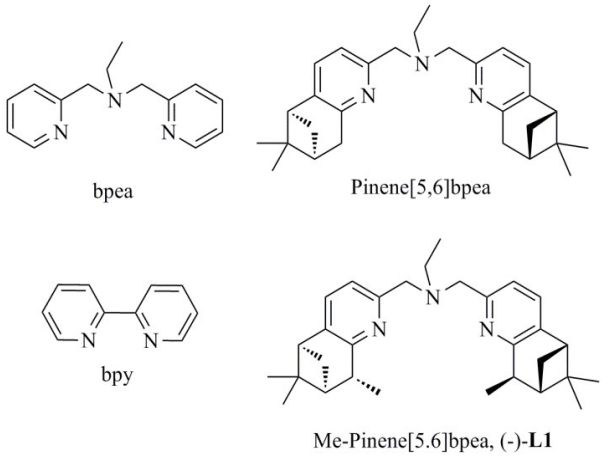
Today Ruthenium complexes have a variety of applications in many fields of science.[1] From a redox catalysis viewpoint they are excellent because they enjoy a wide range of accessible oxidation states, ranging from -2 to +8. Thus, they can be applied for both oxidative[2] and reductive[3] transformations. Furthermore, Ru complexes bearing enantiopure ligands have already been used as asymmetric catalysts giving spectacular enantiomeric excess.[4]

Within the asymmetric catalysis field, the nature of the chiral ligand plays a crucial role on the performance of the catalyst in terms of efficiency and especially in stereospecificity. However, despite the wide variety of enantiopure ligands reported so far, just a few of them have been shown to create effective asymmetric environments to a broad range of reactions and substrates.[5] Therefore, the development of new chiral ligands that could generate "*privileged*" scaffolds is one of the most important issues in enantioselective catalysis by transition metal complexes. In addition, the unraveling of the basic principles that make them "*privileged*" is also of paramount importance. With all this in mind, we have undertaken a project aiming at developing new chiral polypyridylic ligands with different geometries and denticities based on the monoterpene chiral pool.[6] Their combination with metals such as Mn, Fe and Ru has already led to interesting catalysts for diverse asymmetric oxidative transformations.[7]

Together with the nature of the ligands, their coordination arrangement around a given metal ion is also crucial for the final outcome of a catalytic reaction.[8] For chiral ligands in an octahedral environment, the formation of metal complexes can lead to a large variety of isomers, especially for second row transition metals such as Ru. This generates an additional challenge from a synthetic perspective in order to be able to separate and isolate individual pure isomers. Therefore, the rational ligand and complex design should be combined with appropriate synthetic methodologies in order to be successful in this type of endeavor.[9]

In 2008, we showed how both steric and electronic factors are key to explain the isomeric ratios obtained when combining the bpea ligand and its chiral derivative pinene[5,6]bpea (Chart 1) with N- and P-donor didentate ligands in an octahedral Ru(II) environment.[10]

Chart 1. Drawing of the Ligands Used in This Work.



Here on, we further analyze this excellent platform by preparing a new diastereoselectively alkylated Me-pinene[5,6]bpea ligand ((-)-**L1**, Chart 1) with increased bulkiness and two new stereogenic centres. Ru-Cl complexes containing this ligand combined with 2,2'-bipyridine (bpy) have been prepared, thoroughly characterized and stereoisomerically analyzed in comparison with their achiral and chiral analogues previously reported by our group.[10,11]

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. $RuCl_3 \cdot 3H_2O$ was supplied by Alfa Aesar and was used as received.

Preparations. Pinene-furan (-)-**1**,[12] and $[Ru(bpy)(MeOH)Cl_3]$[13] were prepared following the procedures described in the literature.

Me-pinene-furan (-)-**2.** A solution of n-BuLi (26 mL, 1.6 M in hexane, 41.6 mmol) was added dropwise over a solution of diisopropylamine (6.5 mL, 46.4 mmol) in dry THF (120 mL) at -40 ºC. The solution of the formed LDA was brought to 0 °C in an ice bath, stirred for 30 min and cooled again to -40 °C. A solution of the pyridine-pinene derivative (-)-**1** (4.5 g, 18.8 mmol) in THF (120 mL) was added slowly during 1 h. The resulting red solution was stirred at -40 ºC during 2 h. Then, methyl iodide (2.6 mL, 42.21 mmol) was added dropwise during 1h and the mixture was stirred overnight at room temperature. Water (310 mL) was added and the product was extracted with dichloromethane, washed with brine and dried with magnesium sulfate. The product was purified by column chromatography on silica gel using a mixture of hexane/ethyl acetate (95:5) as eluent. Compound (-)-**2** was obtained as a mixture 10:3 of Me-pinene-furan and Me-pinene-Me-furan (methylation on both the pinene and the furan moieties). This product was used without further purification in the next step. Yield: 74 % (3.5 g, 13.8 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.49 (d, *J* = 1.5 Hz, 1H, H9), 7.37 (d, *J* = 7.8 Hz, 1H, H3), 7.20 (d, *J* = 8.0 Hz, 1H, H4), 6.87 (dR, *J* = 3.4 Hz, 1H, H7), 6.5 (dd, *J* = 3.2, 1.6 Hz, 1H, H8), 3.23 (m, 1H, H13), 2.75 (t, *J* = 4.8 Hz, 1H, H10), 2.56 (m, 1H, H14), 2.16 (m, 1H, H12), 1.42 (m, 6H, H15, H16), 1.29 (d, *J* = 9.4, 1H, H14'), 0.67 (s, 3H, H17). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.8 (C, C2), 160.6 (C, C1), 154.4 (C, C6), 142.5 (CH, C9), 140.3 (C, C5), 133.1 (CH, C3), 115.4 (CH, C4), 111.8 (CH, C8), 107.2 (CH, C7), 47.1 (CH, C10), 46.8 (CH, C12), 41.4 (C, C11), 38.8 (CH, C13), 28.6 (CH2, C14), 26.3 (CH3, C16), 20.9 (CH3, C17), 18.3 (CH3, C15)); $[\alpha]_D$ -7.2 (*c* 1.5 CH_2Cl_2); ESI-MS (*m/z*) 254.1 $[M+H]^+$, 276.1 $[M+Na]^+$.

Me-pinene-COOEt (-)-**3**. (-)-**2** (23 g, 90.0 mmol) and ammonium metavanadate (1.5 g, 13.0 mmol) were mixed in water (400 mL). The mixture was heated to 65 °C and fuming nitric acid (190 mL) was added slowly. The evolved gases were trapped by connecting the reflux condenser to a solution of water and a mixture of NaOH 5 M (aq.) and H_2O_2 2-3 %. The solution was heated to reflux for 5 h. After distilling the solvent under vacuum, ethanol (175 mL) and sulfuric acid 96% (64 mL) were added. The resulting solution was heated to reflux overnight. Water (800 mL) was added and the solution was neutralized with a saturated aqueous solution of sodium carbonate. The black solid was filtered and extracted through a Soxhlet with hexane. The solvent was evaporated to obtain 14 g of (-)-**3** as a yellow oil. Yield: 60 % (14 g, 54 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.82 (d, *J* = 7.9 Hz, 1H, H4), 7.29 (d, *J* = 7.9 Hz, 1H, H3), 4.46 (m, 2H, H15), 3.32 (m, 1H, H6), 2.83 (t, *J* = 5.6 Hz, 1H, H9), 2.58 (m, 1H, H10), 2.18 (m, 1H, H7), 1.44 (m, 9H, H12, H11, H16), 1.30 (d, *J* = 9.1 Hz, 1H, H10'), 0.63 (s, 3H, H13). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.7 (C, C4), 157.6 (C, C1), 146.2 (C, C5), 145.5 (C, C2), 133.4 (CH, C3), 122.5 (CH, C4), 61.6 (CH2, C15), 46.8 (CH, C9), 40.0 (CH, C7), 39.4 (C, C8), 36.7 (CH, C6), 31.5 (CH2, C10), 25.9 (CH3, C12), 21.3 (CH3, C13), 18.1 (CH3, C11), 14.4 (CH, C16); $[\alpha]_D$ -25.4 (*c* 0.94, CH_2Cl_2); ESI-MS (*m/z*) 260.1 $[M+H]^+$.

Me-pinene-aldehyde (-)-**4**. (-)-**3** (13.7 g, 52.8 mmol) was dissolved in anhydrous THF (200 mL) and the solution was cooled to -78 °C. $LiAlH_4$ (63.4 mL, 1M in hexane, 63.4 mmol) was added during a period of 20 min with a syringe pump. The resulting solution was stirred for 1 h at the same temperature. Glacial acetic acid (27 mL) was added and the solution was left at room temperature. Hexane (400 mL) was added and the solution was poured over water (400 mL). The solution was neutralized with a saturated solution of sodium bicarbonate, extracted with hexane, washed with water and dried with magnesium sulfate. After collection and evaporation of the organic phases, a mixture of aldehyde (-)-**4** and alcohol (-)-**5** was obtained. This mixture was purified by column chromatography on silica gel. Using dichloromethane as mobile phase, 6.8 g of (-)-**4** were eluted. Yield: 60 % (6.8 g; 31.6 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.04 (s, 1H, H14), 7.68 (d, *J* = 7.5 Hz, 1H, H4), 7.34 (d, *J* = 7.5 Hz, 1H, H3), 3.27 (m, 1H, H6), 2.86 (t, *J* = 5.3 Hz, 1H, H9), 2.60 (m, 1H, H10), 2.20 (m, 1H, H7), 1.44 (m, 6H, H11, H12), 1.31 (d, 10.0 Hz, 1H, H10'), 0.64 (s, 3H, H13). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 193.6 (COH, H14), 161.8 (C, C1), 150.8 (C, C2), 147.4 (C, C5), 133.3 (CH, C3), 119.5 (CH, C4), 47.6 (CH, C9), 46.5 (CH, C7), 41.4 (C, C8), 38.7 (CH, C6), 28.2 (CH2, C10), 26.2 (CH3, C12), 20.8 (CH3, C13), 18.1 (CH3, C11); $[\alpha]_D$ -19.4 (*c* 0.98 CH_2Cl_2); ESI-MS (*m/z*) 216.1 $[M+H]^+$, 238.1 $[M+Na]^+$.

Me-pinene-OH (-)-**5**. (-)-**4** (3 g, 13.9 mmol) was dissolved in dry methanol (34 mL) and then sodium borohydride (1 g, 26.5 mmol) was added slowly. The solution was left at room temperature and the stirring was continued for 4 h. After evaporation of the solvent, dichloromethane (34 mL) and water (26 mL) were added. The product was extracted to the dichloromethane layer, washed with water and dried with magnesium sulfate. After evaporation, 2.8 g of pure (-)-**5** as a yellow solid were obtained. Yield: 92 % (2.8 g, 12.9 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.17 (d, *J* = 7.5 Hz, 1H, H3), 6.87 (d, *J* = 7.5 Hz, 1H, H4), 4.70 (b s, 2H, H14), 4.00 (b s, 1H, OH), 3.17 (m, 1H, H6), 2.75 (t, *J* = 5.4 Hz, 1H, H9), 2.55 (m, 1H, H10), 2.15 (m, 1H, H7), 1.43 (s, 3H, H12), 1.38 (d, *J* = 7.2 Hz, 3H, H11), 1.30 (d, *J* = 9.8 Hz, 1H, H10'), 0.63 (s, 3H, H13). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.6 (C, C1), 155.3 (C, C2), 140.4 (C, C5), 133.4 (CH,C3), 117.0 (CH, C4), 63.8 (CH2, C14), 46.9 (CH, C9), 46.8 (CH, C7), 41.3 (C, C8), 38.6 (CH, C6), 28.7 (CH2, C10), 26.3 (CH3, C12), 20.8 (CH3, C13), 18.1 (CH3, C11) ; $[\alpha]_D$ -22.9 (*c* 1.2 CH_2Cl_2); ESI-MS (*m/z*) 218.1 $[M+H]^+$, 240.1 $[M+Na]^+$.

Me-pinene-Cl (-)-6. (-)-**5** (5.15 g, 23.7 mmol) was dissolved in dry dichloromethane (55 mL). A solution of $SOCl_2$ (5 mL, 71 mmol) in dry dichloromethane (44 mL) was added dropwise. The solution was kept stirring overnight. The solvent was carefully evaporated. Dichloromethane (350 mL) and an aqueous solution of sodium hydroxide (0.4 M, 666 mL) were added. The product was extracted to the dichloromethane layer, washed with water and dried with magnesium sulfate. After evaporation Me-pinene-Cl (-)-**6** was obtained as yellow oil. Yield: 88 % (4.9 g, 21 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.23 (d, *J* = 7.5 Hz, 1H, H3), 7.16 (d, *J* = 7.4 Hz, 1H, H4), 4.68 (s, 2H, H14), 3.20 (m, 1H, H6), 3.78 (t, *J* = 5.7

Hz, 1H, H9), 2.57 (m, 1H, H10), 2.17 (m, 1H, H7), 1.44 (s, 3H, H12), 1.40 (d, *J* = 7.1 Hz, 3H, H11), 1.32 (d, *J* = 9.7 Hz, 1H, H10'), 0.65 (s, 3H, H13). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.4 (C, C1), 153.1 (C, C2), 141.6 (C, C5), 134.1 (CH, C3), 119.9 (CH, C4), 47.0 (CH, C9), 46.7 (CH, C7), 46.6 (CH2, C14), 41.3 (C, C8), 38.5 (CH, C6), 28.5 (CH2, C10), 26.2 (CH3, C12), 20.8 (CH3, C13), 18.3 (CH3, C11) ; $[\alpha]_D$ -16.4 (*c* 1.3 CH_2Cl_2); ESI-MS (*m/z*) 236.1 $[M+H]^+$.

Me-pinene[5,6]bpea (-)-L1. (-)-**6** (2.29 mg, 9.7 mmol) was dissolved in a mixture of acetonitrile/water 1:1 (10 mL) and ethylamine 70 % aq. (172 µl, 4.8 mmol) was added. The solution was heated to 60 °C for 5 min. Then, an aqueous solution of sodium hydroxide (10 M, 850 µl, 10.7 mmol) was added slowly. The solution was heated at 60 °C for 1 h. The product was extracted with chloroform and dried with anhydrous magnesium sulfate. The crude was purified by column chromatography of neutral alumina. Using a mixture of dichloromethane/acetone 9:1, Me-pinene[5,6]bpea was eluted. Yield: 54 % (1.17 g, 2.6 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.23 (d, *J* = 7.7 Hz, 2H, H2), 7.12 (d, *J* = 7.7 Hz, 2H, H3), 3.80 (s, 4H, H14), 3.15 (m, 2H, H12), 2.70 (t, *J* = 5.6 Hz, 2H, H6), 2.65 (q, *J* = 7.1 Hz, 2H, H15), 2.51 (m, 2H, H7), 2.12 (m, 2H, H8), 1.39 (s, 6H, H10), 1.35 (d, *J* = 7.1 Hz, 6H, H13), 1.28 (d, *J* = 9.6 Hz, 2H, H7'), 1.11 (t, *J* = 7.1 Hz, 3H, H16), 0.61 (s, 6H, H11). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ = 159.8 (C, C5), 157.1 (C, C1), 139.4 (C, C4), 133.1 (CH, C3), 119.3 (CH, C2), 59.9 (CH2, C14), 48.2 (CH2, C15), 47.0 (2CH, C6, C8), 41.3 (C, C9), 38.7 (CH, C12), 28.7 (CH2, C7), 26.3 (CH3, C10), 20.9 (CH3, C11), 18.5 (CH3, C13), 12.3 (CH3, C16); $[\alpha]_D$ -18.2 (*c* 1.4 CH_2Cl_2); ESI^+ HRMS: $[M+H]^+$ (*m/z*), Anal. Calc. for $C_{30}H_{43}N_2$: 444.3373; Found: 444.3398.

trans,*fac*-[Ru((-)-L1)(bpy)Cl]Cl (**C1a**) and **anti,*mer*-[Ru((-)-L1)(bpy)Cl]Cl** (**C1c**). To a solution of $[Ru(bpy)(MeOH)Cl_3]$ (53 mg, 0.134 mmol) and triethylamine (28 µl, 0.20 mmol) in dry ethanol (20 mL), (-)-**L1 (**56 mg, 0.134 mmol) was added. The mixture was heated to reflux during 24 h in the dark. To the resulting red solution, dry diethyl ether (50 mL) was added. The red solution was filtered and separated from a green solid. The solution was evaporated and the obtained solid was purified by column chromatography of alumina. Starting with dichloromethane, the polarity of the mobile phase was increased with methanol. With a mixture of dichloromethane/methanol 100:2 a red band was eluted. The first fractions of this band, which had a darker color and contained a mixture of **C1a** and **C1c** (11 mg), were separated. The next fractions contained pure **C1a** (37 mg; yield 36 %). Anal. Calc. for $C_{40}H_{49}ClF_6N_5PRu$: C, 54.51; H, 5.60; N, 7.95. Found; C, 54.31; H, 5.82; N, 7.68. **C1c** was isolated by purification of the mixture of **C1a** and **C1c** with an alumina semi-preparative TLC using a mixture of dichloromethane/methanol 100:2 as mobile phase, obtaining 5 mg of pure **C1c** (yield 5%). Anal. Calcd for $C_{40}H_{49}ClF_6N_5PRu$: C, 54.51; H, 5.60; N, 7.95. Found; C, 54.42; H, 5.75; N, 7.73. **C1a**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.28 (d, *J* = 8.0 Hz, 1H, H4), 8.25 (d, *J* = 7.8 Hz, 1H, H5), 7.98 (d, *J* = 5.5 Hz, 1H, H1), 7.87 (t, *J* = 7.3 Hz, 1H, H3), 7.80 (t, *J* = 7.3 Hz, 1H, H6), 7.50-7.40 (4H, H9, H10, H18, H19), 7.30 (t, *J* = 6.4 Hz, 1H, H2), 7.18 (t, *J* = 6.2 Hz, 1H, H7), 6.68 (d, *J* = 5.2 Hz, 1H, H8), 5.34 (m, 1H, H21), 4.59 (d, *J* = 15.6 Hz, 1H, 28a), 4.26 (2H, H27a, H12), 4.14 (d, *J* = 15.7 Hz, 1H, H27b), 3.78 (d, *J* = 15.7 Hz, 1H, H28b), 2.95 (dt, *J* = 10.3, 5.4 Hz, 2H, H15, H24), 2.67 – 2.58 (m, 1H, 29a), 2.58 – 2.51 (m, 2H, H14a, H23a), 2.48 (dd, *J* = 13.7, 7.0 Hz, 1H, H29b), 2.23-2.15 (m, 4H, H13, H22, H14b, H23b), 1.76 – 1.68 (m, 3H, H30), 1.47 (s, 3H, H26), 1.44 (s, 3H, H16), 1.37 – 1.26 (m, 6H, H11, H20), 0.87 (s, 3H, H25), 0.59 (s, 3H, H17). CV (CH_2Cl_2 vs. SSCE) 0.79 V. ESI^+ HRMS: $[M-2Cl]^{2+}$ (*m/z*; *z* = 2), Calc. for $C_{40}H_{49}N_5Ru$: 347.6532 found: 347.6518. CD (CH_2Cl_2) $\lambda_{min/max}$ (Δε) = 266.5 (-66.0), 280.5 (196.1), 305.0 (-96.3), 367.5 (-38.0), 418.0 (26.3), 526.5 nm (10.3 mdeg). **C1c:** ^{1}H NMR (500 MHz, CD_2Cl_2) δ 10.63 (d, *J* = 5.0 Hz, 1H, H1), 8.65 (d, *J* = 7.9 Hz, 1H, H4), 8.61 (d, *J* = 6.9 Hz, 1H, H5), 8.50 (d, *J* = 5.7 Hz, 1H, H8), 8.02 – 7.95 (m, 1H, H3), 7.80 (dd, *J* = 11.3, 4.3 Hz, 1H, H6), 7.51 (ddd, *J* = 7.4, 6.0, 1.4 Hz, 1H, H2), 7.38 – 7.32 (m, 1H, H7), 7.08 – 6.87 (m, 4H, H9 H10, H18, H19), 6.31 (d, *J* = 16.6 Hz, 1H, H28a), 5.63 (d, *J* = 13.3 Hz, 1H, H27a), 4.60 (d, *J* = 16.7 Hz, 1H, H28b), 4.52 (d, *J* = 13.4 Hz, 1H, H27b), 3.89 (dq, *J* = 13.3, 6.6 Hz, 1H, H29a), 3.24 (dq, *J* = 14.5, 7.3 Hz, 1H, H29b), 2.61 – 2.54 (m, 2H, H14a, H23a), 2.53 (dd, *J* = 6.4, 5.5 Hz, 1H, H15), 2.49 (dd, *J* = 6.4, 5.5 Hz 1H, H24), 2.27-2.19 (m, 4H, H13, H22, H14b, H23b), 1.46 (s, 3H, H16), 1.42 (s, 3H, H25), 1.24 (m, 1H, H21), 1.15 – 1.05 (m, 3H, H30), 0.75 (d, *J* = 6.9 Hz, 3H, H20), 0.65 – 0.58 (m, 1H, H12), 0.59 (s, 3H, H26), 0.55 (s, 3H, H17), -0.17 (d, *J* = 7.0 Hz, 3H, H11). $E_{1/2}$ (CH_2Cl_2, V vs. SSCE): 0.83 V. The NMR assignment for **C1a** and **C1c** has been carried out in accordance with the labeling shown in Figure S15 in the Supporting Information.

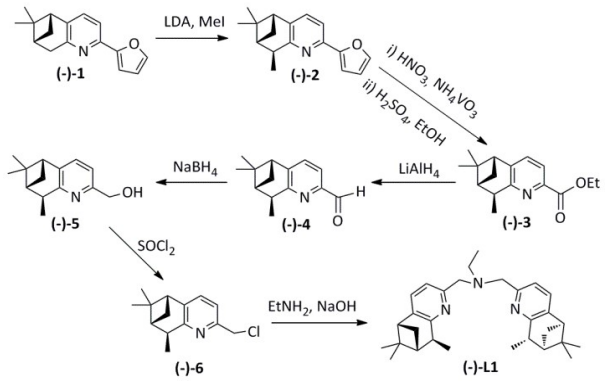
Instrumentation and Measurements. The NMR spectroscopy experiments were performed on Bruker Avance 400 and 500 Ultrashield NMR spectrometers. Samples were run in CD_2Cl_2 and CDCl3. Cyclic Voltammetry (CV) experiments were performed on an IJ-Cambria HI-660 potentiostat using a three-electrode cell. Typical CV experiments were carried out at a scan rate of 100 mV/s. A glassy carbon electrode (2 mm diameter) was used as working electrode, platinum wire as auxiliary electrode, and a SSCE as a reference electrode. Working electrodes were polished with 0.05 micron Alumina paste and washed with distilled water and acetone before each measurement. The complexes were dissolved in CH_2Cl_2 containing the necessary amount of n-Bu_4NPF_6 (TBAPF6) as supporting electrolyte to yield a 0.1 M ionic strength solution. $E_{1/2}$ values reported in this work were estimated from CV experiments as the average of the oxidative and reductive peak potentials ($E_{p,a}$ + $E_{p,c}$)/2. UV-Vis spectroscopy was performed on a Cary 50 (Varian) UV-Vis spectrophotometer in 1 cm quartz cuvettes. Mass spectrometry analysis were performed in a mass spectrometer with matrix assisted laser desorption ionization (MALDI-TOF, Bruker Autoflex). Elemental analyses were performed in EA-1108, CHNS-O elemental analyzer from Fisons Instruments (Universidad de Santiago). $[\alpha]_D$ was measured in a Jasco P-1030 polarimeter with symmetric angular oscillation for the sodium D line and photomultiplier tube detector. Angular range: ± 90ºC. A Jasco spectropolarimeter (Model J-715; Jasco Inc., Easton, MD, USA) interfaced to a computer (J700 software) was used for circular dichroism (CD) measurements at a constant temperature of 25 ºC, maintained by a Peltier PTC-351S apparatus (TE Technology Inc., Traverse City, MI, USA), in CH_2Cl_2. All spectra were recorded with 0.2 cm capped quartz cuvettes.

Computational Details. The density functional theory (DFT) calculations have been carried out with the hybrid B3PW91 density functional,[14] as implemented in the Gaussian 03 package.[15] The Ru atoms have been represented with the quasi-relativistic effective core pseudo-potentials (RECP) of the Stuttgart group and the associated basis sets augmented with an f polarization function (α = 1.235).[16] The remaining atoms (C, N, P, Cl, and H) have been represented with 6-31G(d,p) basis sets.[17] 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). These energies contain also solvent effects calculated with the polarizable continuous solvation model (PCM) using ethanol as a solvent.[18] These solvent effects include contributions of non-electrostatic terms and have been estimated in single point energy calculations on the gas phase optimized structures.

Results and Discussion

Synthesis and Characterization. The synthetic strategy that we have followed for the preparation of the Me-pinene[5,6]bpea (-)-**L1** ligand is outlined in scheme 1. This strategy is based on the diastereoselective alkylation of the pyridyl-pinene aldehyde ((-)-**4**, Scheme 1). The latter is a very convenient chiral building block intermediate for the synthesis of a wide variety of polypyridylic ligands via simple Schiff-base chemistry, as we have previously shown with related (non-alkylated) aldehyde scaffolds.[7b-d] The synthetic pathway followed started with furan-derivative (-)-**1** developed by Bernhard and co-workers[12] (Scheme 1). Methylation of (-)-**1** at the methylene group adjacent to the pyridine ring employing LDA and methyl iodide took place in a diastereoselective manner to form (-)-**2** in good yields (74 %).[19]

Scheme 1. Synthetic pathway for the **Me-pinene[5,6]bpea**, (-)-**L1** ligand.



Next step consisted on the oxidative degradation of the furan substituent employing a mixture of nitric acid and ammonium metavanadate. The carboxylic acid formed is esterified *in-situ* with sulfuric acid in methanol and compound (-)-**3** is obtained in 60% yield. Reduction of the obtained ester (-)-**3** with $LiAlH_4$ resulted in the formation of the desired Me-pinene-aldehyde (-)-**4** and Me-pinene-alcohol (-)-**5** as minor byproduct. The two products were separated by column chromatography on silica gel (see the experimental section for further details), obtaining (-)-**4** in a 60% yield. Slow and careful addition of $NaBH_4$ was then employed for the almost quantitative reduction of (-)-**4** to alcohol (-)-**5** (92% yield). Subsequent formation of (-)-**6** in quantitative yield was obtained by the slow addition of $SOCl_2$ to (-)-**5**. Finally, a double nucleophilic attack of ethylamine over (-)-**6** led to the formation of the desired Me-pinene[5,6]bpea (-)-**L1** ligand (54% yield).

(-)-**L1** was characterized by NMR (1D and 2D), ESI-MS, and optical polarimetry (see the Experimental Section and Figures S16-S21 in the Supporting Information). The ^{1}H NMR spectrum of (-)-**L1** is presented in Figure 1 together with its corresponding labeling scheme. C_2 symmetry is observed in solution and thus the two pyridine-pinene moieties are equivalent. This leads to 16 resonances that were unequivocally assigned to the corresponding protons after analysis of the homo- and hetero-nuclei bidimensional spectra.

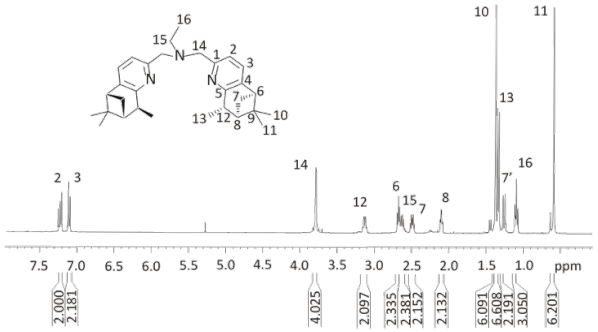
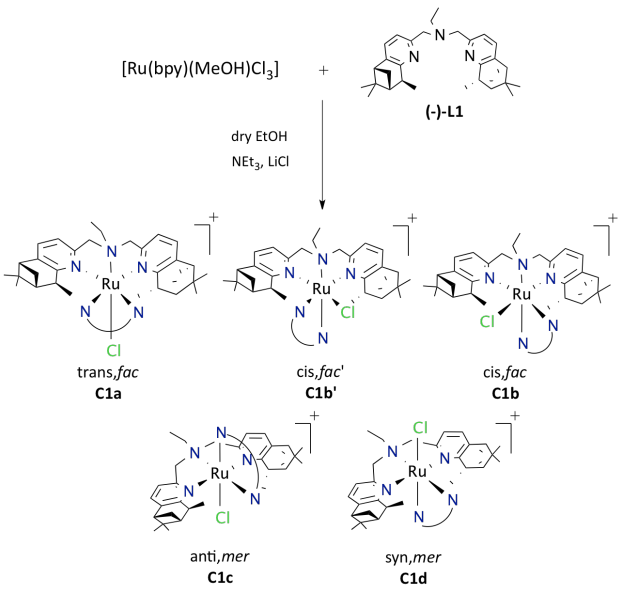


Figure 1. ^{1}H NMR spectrum of (-)-**L1** and its corresponding labeling scheme.

Scheme 2. Synthetic procedure and potential isomers of **C1.**



Ru-Cl complexes were then prepared employing $[Ru(bpy)(MeOH)Cl_3]$ as metal precursor. The sequence of ligand addition to the Ru metal center is reversed here with regard to the previously related complexes containing the pinene[5,6]bpea and bpea ligands reported earlier,[10,11] and

actually this turns out to be essential in this particular case for the preparation of the desired compounds. Attempts to coordinate the bpy ligand to a typical [Ru((-)-**L1**)Cl_3] intermediate were always unfruitful due to the increased bulkiness of the Me-pinene[5,6]bpea (-)-**L1** ligand. Therefore we used a solution of [Ru(bpy)(MeOH)Cl_3] in dry ethanol and added (-)-**L1** and triethylamine to generate the corresponding complexes (Scheme 2). The substitution of one MeOH and two chlorido ligands by a flexible[10,20] C_2-symmetric tridentate N-donor ligand such as (-)-**L1** can potentially lead to the wide range of stereoisomers as shown in Scheme 2. The flexibility of the mentioned ligands will allow them to coordinate in a facial or in a meridional manner around the octahedral d^6 Ru(II) metal center.

When the tridentate ligands act in a facial manner then *cis* and *trans* isomers can be obtained depending on whether the Ru-Cl bond is *cis* or *trans* to the Ru-$N_{aliphatic}$ bond respectively. In the particular case of *cis,fac* configuration, two possible isomers can be obtained that are depicted in Scheme 2, as **C1b** and **C1b'**. When the tridentate ligands act in a meridional fashion, two possibly isomers can be obtained depending on the relative orientation of the Ru-Cl bond with regard to the ethyl group of the aliphatic amine. These isomers are thus named *anti,mer*-**C1c** and *syn,mer*-**C1d** (Scheme 2).

Reaction of the [Ru(bpy)(MeOH)Cl_3] complex with (-)-**L1** in dry MeOH at reflux for 24h generates a mixture of complexes. A careful ^{1}H NMR analysis of the crude revealed the presence of two major complexes: *trans,fac*-**C1a** and *anti,mer*-**C1c** in a 84:16 ratio. Additionally the NMR also showed the presence of small amounts of a third complex that could not be identified, but that based on DFT could be potentially assigned to **C1d** (*vide infra*). Overall we managed to account for a 78% yield.

It is worth mentioning here that the introduction of two extra Me groups to the pinene[5,6]bpea ligand (Chart 1, (-)-**L1**), produces an enhancement of the steric effects close to the metal center in such a way that the number of isomers obtained is now substantially lower.[10] For this reason in the present case we manage to obtain the *trans,fac*-**C1a** as the major product. This was also the case for the achiral bpea ligand (Chart 1), where the main isomer obtained was *trans,fac*-[Ru(bpea)(bpy)Cl]$^+$ (**C3a)**.[11] Isolation of both **C1a** and **C1c** (Scheme 2) as pure isomers was accomplished by combining column chromatography and semi-preparative TLC, both having alumina as solid phase. Elution of the former with dichloromethane/methanol 50:1 allowed us to obtain pure **C1a** (36% yield) and a mixture of **C1a** and **C1c**. Semi-preparative TLC using the same elution conditions finally allowed us to isolate pure **C1c** (5% yield). In Figure S15 the ^{1}H NMR of the reaction crude is plotted together with the ^{1}H NMR of the isolated isomers **C1a** and **C1c**. For this type of complexes 1D and 2D NMR has been shown to be an extremely powerful tool to unambiguously identify and characterize the isolated isomers (Scheme 2). In particular, the chemical shift of the CH_2-N moieties is indicative of the presence of a facial or a meridional disposition of (-)-**L1**. A chemical shift for the CH2-N unit around 6 ppm is indicative of meridional geometry whereas a shift of more than one ppm to higher fields indicates facial coordination.[20] For **C1a** this chemical shift is 4 ppm and thus is a clear indication of facial geometry of (-)-**L1** in this compound. This is further corroborated by the absence of shifted bpy protons due to the fact that the bpy ligand is situated perpendicular to the Ru-Cl bond (See Figures S15, S22). 2D NOESY experiments allowed us to distinguish between the three potential facial isomers (**C1a**, **C1b** and **C1b'**, Scheme 2). Two interactions between bpy and (-)-**L1** protons, H8 with H15 and H1 with H20 allow to identify the *trans,fac*-**C1a** isomer (Figure S22). The assignment of the *anti,mer*-**C1c** isomer is based on three key observations. First, the chemical shift of CH_2-N at around 6 ppm suggests a meridional conformation.[20] Secondly, a deshielded doublet shifted to low fields (H1 of the bpy ligand on Figure S27) reveals the presence of the Ru-Cl bond parallel to the bpy plane. Finally, a NOE interaction between H26a of (-)-**L1** and H8 of the bpy ligand (Figure S27) clearly supports the presence of the *anti,mer*-**C1c** isomer.

The electrochemical properties of **C1a** and **C1c** were investigated by means of cyclic voltammetry in dichloromethane (Figure S32 in the Supporting Information). *Trans,fac*-**C1a** and *anti,mer*-**C1c** isomers exhibit chemically reversible and electrochemically quasi-reversible waves centered at $E_{1/2}$ = 0.79 V (ΔE_p = 90 mV) and 0.83 V (ΔE_p = 110 mV), respectively. Therefore, the sigma-donation of the tertiary amine of the Me-pinene[5,6]bpea ligand, seems to be more effective when the $N_{aliphatic}$-Ru bond is trans to the Ru-Cl bond, decreasing the Ru(III/II) redox potential by roughly 40 mV. A similar cathodic shift in the redox potentials is observed when comparing related meridional vs. facial isomers of achiral bpea complexes as has been previously reported.[20a]

In the presence of light and in a CH_2Cl_2 solution, **C1c** is not stable and isomerizes towards the *trans,fac* isomer **C1a**. This transformation has been followed by ^{1}H NMR and is shown in Figure 2. After 24 h irradiation, the *anti,mer* isomer **C1c** is no longer present in solution. The isomerization kinetics has also been followed by UV-vis spectroscopy (Figure S33). A decrease in absorbance at 395, 480 and 500 nm and the appearance of a new band at 530 nm are observed together with clean isosbestic points indicating the neat interconversion between the two species. Under the same conditions, but in the absence of light there is no transformation at all as indicated by UV-vis and ^{1}H NMR spectroscopy.

The isomerization of **C1c** to **C1a** can also be thermally promoted in the dark, by refluxing a solution of the former complex in 1,2-dichloroethane. In this case the reaction is much slower, taking 168 h to proceed (Figure S35 in the Supporting Information).

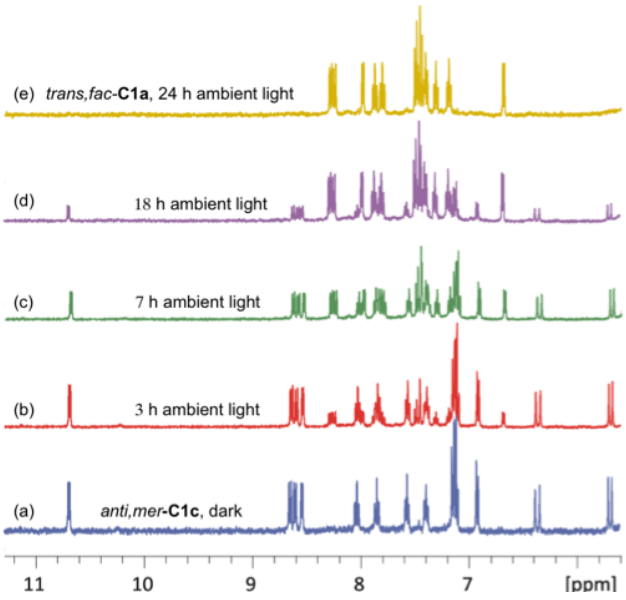


Figure 2. ^{1}H NMR monitoring (aromatic region, CD_2Cl_2) of the isomerization process of *anti,mer*-**C1c** to *trans,fac*-**C1a** triggered by ambient light irradiation.

The thermal *mer*/*fac* isomerization of a bpea ligand bound to a Ru(II) metal ion was already described by us for the [Ru(Cl)$_2$(bpea)(DMSO)] complex.[20b] In this case, a dissociative mechanism was proposed, in which one of the chlorido ligands was removed as initial step. In order to get a deeper understanding of this kind of process and assess the influence of the steric and electronic effects imposed by the ligands over the isomerization mechanism, DFT calculations were carried out for the **C1c→C1a** thermal process, where the facial isomer **C1a** is slightly more stable (1.3 kcal/mol) than the meridional **C1c**. Two possible dissociative mechanisms were proposed as initial hypothesis; a first one based on the dissociation of a pyridylic arm of the (-)-**L1** ligand (pathway (a), Figure 3) and a second one based on the removal of the chlorido ligand (pathway (b), Figure 3). The energies of the different calculated species involved in both mechanisms are represented in Figure 3. Following pathway (a), one pyridyl ring of (-)-**L1** is firstly decoordinated to reach the transition state **TSI** by means of 34.4 kcal/mol. On the other hand, release a chlorido ligand from **C1c** (pathway (b)) leads first to the formation of intermediate **II** and subsequently to a pentacoordinated transition state **TSIII** through a highly energetically demanding reorganization process (44.1 kcal/mol). Further ligand reorganization allows gathering species **III** with already facial coordination of (-)-**L1**. In general, the decoordination of an "arm" of a quelating ligand is disfavored with regard to the decoordination of a monodentate ligand.[20b] In this case, the steric hindrance exerted by the pinene moieties precludes the reorganization of the pentacoordinated species up to 44.1 kcal/mol, hampering the viability of this mechanism. However, the decoordination of one pyridyl ring gives rise to a much more flexible intermediate, less sterically hindered and easier to reorganize to its facial form. These steric arguments would also explain why in the case of the previously reported [Ru(Cl)$_2$(bpea)(DMSO)] complex, in which no bulky ligands are used, the proposed *mer* to *fac* isomerization mechanism was based on the initial removal of a chlorido ligand.[20b]

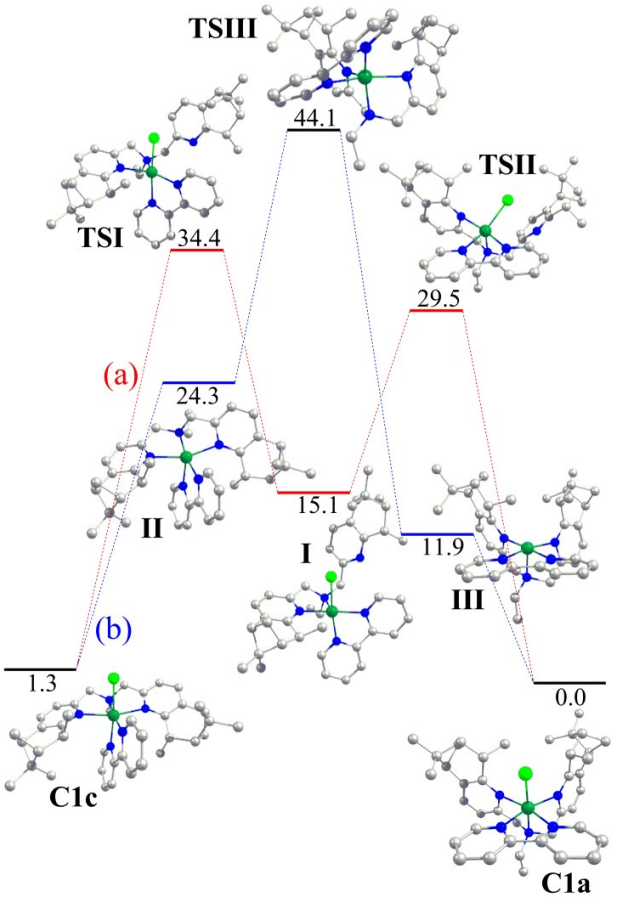


Figure 3. Relative energy diagram for the BPW91 **C1c→C1a** isomerization.

Stereoisomeric Analysis. DFT calculations were performed for the five potential isomers of **C1** and their relative energy diagram is shown in Figure 4(a). In the same figure the relative energy diagram is compared with the ones reported recently for the two analogous complexes [Ru(pinene[5,6]bpea)(bpy)Cl]$^+$, **C2**, Figure 4(b)) and ([Ru(bpea)(bpy)Cl]$^+$, **C3**, Figure 4(c), containing, respectively, non-alkylated and achiral bpea scaffolds.[10] Selected bond distances and angles are collected in Table S1 for all the optimized structures of **C1** together with reported data for **C2** and **C3**, for purposes of comparison. To simplify the structural discussion for these complexes, the plane nearly perpendicular to the Ru-X bond (X = monodentate ligand), will be considered as the equatorial plane.

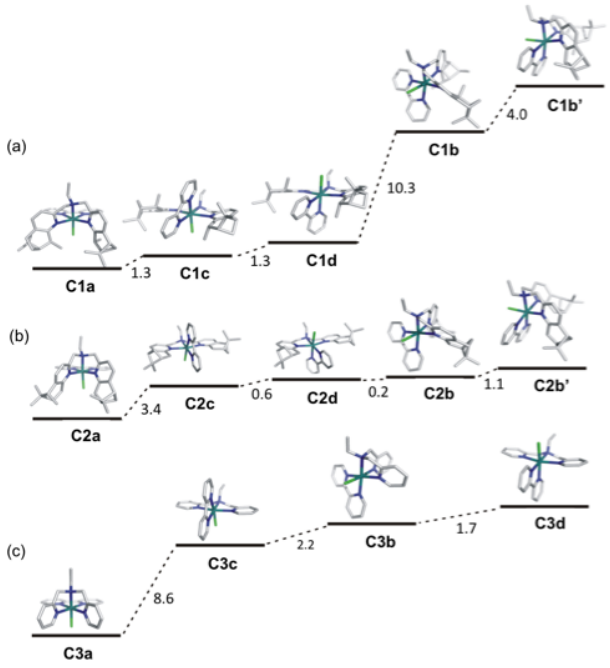


Figure 4. Relative energy diagram for the B3PW91-optimized geometries of the cationic moieties of (a) **C1a**-**C1d**, (b) **C2a**-**C2d** and (c) **C3a**-**C3d**. Energies are given in kcal/mol. Color codes: ruthenium, light blue; chlorine, green; nitrogen, blue; carbon, gray.

For the **C3** complexes containing the achiral bpea ligand, only the **C3a** isomer is obtained experimentally. This is due to the absence of strong steric interaction and the presence of hydrogen bonding between the chlorido ligand and the CH groups situated in the alpha position with regard to the N atoms of the bpea pyridyl rings (See Figure 4c).[10] Introduction of a pinene moiety in the 5,6 positions of the pyridylic bpea rings (pinene[5,6]bpea, Chart 1) produces large steric interactions and removes the potential hydrogen bonding mentioned above. As a consequence of this the relative energies of the potentials isomers are relatively similar and thus synthetically we obtain a mixture of isomers: *trans,fac*-**C2a**, *cis,fac*-**C2b**/**C2b'** and *up,mer*-**C2d** (Figure 4b).[10] Finally, the double alkylation of the pinene moieties in (-)-**L1** provokes a further increase of the steric hindrance clearly destabilizing the *cis,fac* isomers **C1b** and **C1b'** by 12.9 and 16.9 kcal/mol over *trans,fac*-**C1a** respectively (Figure 4(a)), that is the more stable in the present case. Strong repulsive steric interactions between the bpy ligand and one of the bulky Me-pinene groups of (-)-**L1**, both occupying the equatorial plane, are responsible for this energy increase. As a consequence of this, **C1b**/**C1b'** isomers present a large distortion of the octahedral geometry (see Figure 4(a) and Table S1 in the Supporting Information). An indication of the degree of this octahedral distortion is offered by the dihedral angles between the two pyridyl rings of (-)-**L1**. For **C1b**, this angle is 68.4° whereas for **C1b'** is 71.4° while for an ideal geometry these rings should be almost coplanar. This highly disfavored steric situation explains why these *cis,fac* isomers are not observed experimentally. In sharp contrast, the steric constrains clearly decrease when (-)-**L1** coordinates meridionally to the Ru metal center. Now the *anti,mer*-**C1c** and *syn,mer* **C1d** are only 1.3 and 2.6 kcal/mol above the more stable *trans,fac*-**C1a** isomer**.** This enhanced stability of the *mer* isomers with regard to the *cis,fac* ones is due to the reduced steric hindrance between the bpy ligand and the pinene groups in this new geometry, as can be clearly observed in Figure 4. Nevertheless, there is still some remaining hindrance between the bpy pyridyl group *trans* to the chlorido ligand and (-)-**L1,** as can be inferred from the increased Ru-N_{bpy} distance from the typical 2.05 Å up to the 2.10 Å calculated for this isomer (see for instance Ru-N4/N5 in Table S1). Finally the *trans,fac* disposition of (-)-**L1** has the lowest steric hindrance between the bpy and the pinene groups and thus becomes the most stable isomer. This is in total agreement with the fact that is by far the major isomer obtained experimentally.

In conclusion, we have prepared a new chiral dialkylated pyridyl-pineno-fused aldehyde building block, (-)-**4**, which has been employed in the preparation of a new enantiopure derivative of the bpea ligand, (-)-**L1**. Combination of the latter with a $[RuCl(bpy)]^+$ subunit afforded *trans,fac*-**C1a** as major product together with *anti,mer*-**C1c** in much lesser amounts. The reduced isomeric mixture here obtained (when compared with the one previously reported for Ru-Cl complexes bearing a non-alkylated pineno-fused bpea ligand, **C2**) arises from the strong destabilization of *cis,fac* **C1b**/**C1b'** isomers. As shown by their highly distorted DFT calculated structures, the large steric repulsions between one of the bulky Me-pinene groups and a bpy pyridyl moiety occupying the equatorial plane produce the observed energy increase. Furthermore, the calculated thermodynamic instability of the *anti,mer* isomer vs. its *trans,fac* counterpart is experimentally confirmed by the **C1c→C1a** thermo and photo-isomerization process observed. Here again, for the thermal case, steric arguments (lower ligand reorganization energies) support the initial dissociation of a bpea pyridylic arm as described by DFT instead of a Ru-Cl decoordination pathway.

ASSOCIATED CONTENT

Supporting Information. Computational details and spectroscopic (1D and 2D NMR) and electrochemical measurements for the reported complexes. UV-vis spectra of the **C1c** to **C1a** isomerization process. CD spectrum of **C1a.** This material is available free of charge via the Internet at http://pubs.acs.org."

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