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Diastereospecific and Diastereoselective Syntheses of Ruthenium(II) Complexes Using N,N′ Bidentate Ligands Aryl-pyridin-2-ylmethyl-amine ArNH-CH_2-2-C_5H_4N and Their Oxidation to Imine Ligands

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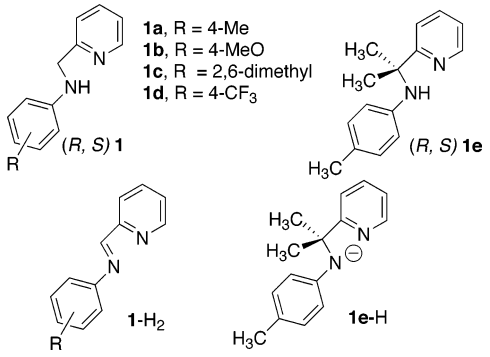
Coordination of N,N′ bidentate ligands aryl-pyridin-2-ylmethyl-amine ArNH-CH_2-2-C_5H_4N **1** (Ar = 4-CH_3-C_6H_4, **1a**; 4-CH_3O-C_6H_4, **1b**; 2,6-$(CH_3)_2$-C_6H_3, **1c**; 4-CF_3-C_6H_4, **1d**) to the moieties $[Ru(bipy)_2]^{2+}$, $[Ru(\eta^5\text{-}C_5H_5)L]^+$ (L = CH_3CN, CO), or $[Ru(\eta^6\text{-arene})Cl]^{2+}$ (arene = benzene, *p*-cymene) occurs under diastereoselective or diastereospecific conditions. Detailed stereochemical analysis of the new complexes is included. The coordination of these secondary amine ligands activates their oxidation to imines by molecular oxygen in a base-catalyzed reaction and hydrogen peroxide was detected as byproduct. The amine-to-imine oxidation was also observed under the experimental conditions of cyclic voltammetry measurements. Deprotonation of the coordinated amine ligands afforded isolatable amido complexes only for the ligand (1-methyl-1-pyridin-2-yl-ethyl)-*p*-tolyl-amine, **1e**, which doesn't contain hydrogen atoms in a β position relative to the N–H bond. The structures of $[Ru(2,2'\text{-bipyridine})_2(1b)](PF_6)_2$, **2b**; $[Ru(2,2'\text{-bipyridine})_2(1c)](PF_6)_2$, **2c**; *trans*-$[RuCl_2(COD)(1a)]$, **3**; and $[RuCl_2(\eta^6\text{-}C_6H_6)(1a)]PF_6$, **4a**, have been confirmed by X-ray diffraction studies.

Introduction

The state of the art in stereoselective synthesis in coordination chemistry was reviewed by Knof and von Zelewsky in 1999.[1] They pointed out its relevance to such important subjects as enantioselective catalysis, supramolecular chemistry, and bioinorganic chemistry. To achieve stereoselectivity at the metal center, one must modify the ligands to introduce an element of chirality. Thus, for instance, diastereospecificity has been reported, and qualified as surprising, for 5,5′-(L-valine) amino acid substituted 2,2′-bipyridyl ligands in the tris-chelated octahedral complexes $[M(NN)_3]^{2+}$ (M = Fe^{II} and Co^{II}) with Δ and Λ helical structures.[2] Diastereoselectivity has also been reported in the reaction of the octahedral complexes (Δ,Λ)-$[Ru(2,2'\text{-bipyridine})_2Cl_2]$ with (*R*)-(+)-methyl-*p*-tolylsulfoxide to give $[Ru(2,2'\text{-bipyridine})_2(\text{methyl-}p\text{-tolylsulfoxide})Cl]^+$, in which the Δ,*R* isomer formed with a diastereomeric excess of nearly 50% over the Λ,*R* isomer.[3,4] This represented the first process by which a ligand occupying only a single coordination site has had such an important influence on the stereochemical outcome of ruthenium bis(bipyridine) complex formation.

Chart 1



In the foregoing examples, stereoselectivity was achieved by using enantiomerically pure ligands. The results reported here show that diastereoselectivity and diastereospecificity can be observed using ligands **1** (see Chart 1). Once

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(1) Knof, U.; von Zelewsky, A. *Angew. Chem., Int. Ed.* **1999**, *38*, 303−322.
(2) Telfer, S. G.; Bernardinelli, G.; Williams, A. F. *Chem. Commun.* **2001**, 1498−1499.

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coordinated to a metal in a chelating fashion, this kind of ligand has two sources of chirality. One is the amine nitrogen atom that is bonded to four different substituents (i.e., *R* or *S* configuration) and the other is the δ,λ conformation of the nonplanar five-membered chelate ring formed upon coordination. Although facile inversion at the amino nitrogen atom precludes separation of the enantiomers of the ligands, the coordination to the octahedral or tetrahedral ruthenium(II) metal complexes turned out to be diastereospecific or diastereoselective as discussed below.

Dehydrogenation of secondary amines to imines,[5−11] along with the reverse process,[12] is a subject of current interest.[13,14] Herein we report that the amino complexes we have prepared can be oxidized to imines by molecular oxygen in a base-catalyzed reaction. This could be relevant to the subject of oxidation of amines under green and sustainable chemistry conditions and supports the mechanism proposed for the oxidation of primary amines to imines and further to nitriles in the presence of molecular oxygen.[15,16] This mechanism supplies an alternative pathway to that proposed by Keene for the oxidative dehydrogenation of coordinated amines.[17]

As previously reported,[18] amido complexes are intermediate in the oxidation of metal-coordinated amines to imines. The amino−amido conversion is of great importance in the catalyzed hydrogen-transfer reactions through the ruthenium−nitrogen ligand bifunctional mechanism in which β hydrogen atoms are present in the N-donor ligand and the use of chiral amine effects asymmetric transformations.[19,20] Nevertheless, stable ruthenium complexes with terminal (nonbridging) amido ligands containing β hydrogen atoms are not very common.[21] Deprotonation of amine complexes has been explored as a means of obtaining amido complexes. Stable amido complexes of ruthenium(II) have been obtained only when β hydrogen atoms were avoided.

Experimental Section

Unless otherwise stated, all manipulations were carried out under nitrogen using standard Schlenk techniques. Solvents were dried and stored under nitrogen. Amine ligands **1a**−**d** and dehydrogenated imines (**1**-H_2)**a**−**d** were prepared as described elsewhere.[22] The starting compounds *cis*-[Ru(2,2′-bipyridine)$_2$Cl$_2$]·2H$_2$O,[23] [RuCl$_2$(η^4-1,5-cyclooctadiene)]$_n$,[24] [RuCl$_2$(CH$_3$CN)(η^6-C$_6$H$_6$)],[25] [RuCl$_2$(η^6-C$_6$H$_6$)]$_2$,[26] [RuCl$_2$(η^6-*p*-cymene)]$_2$,[26] [Ru(η^5-C$_5$H$_5$)(CH$_3$CN)$_3$]PF$_6$,[27] and [Ru(η^5-C$_5$H$_5$)(CO)(CH$_3$CN)$_2$]PF$_6$[27] were prepared according to the literature. All other starting reagents were used as commercially obtained.

^{1}H NMR spectra were recorded on Varian VXR200S, Bruker ARX 300, and Varian Unity Inova-400 spectrometers. Chemicals shifts are in ppm relative to $SiMe_4$ (TMS) as the external standard. The IR spectra were recorded as KBr disks on a Nicolet Impact 410, and elemental analyses were made on a Leco CHNS 932. Cyclic voltammetry was carried out using an EG&G VersaStat potentiostat in conjunction with a three-electrode cell using 0.1 M [NBu_4^n][PF_6] solutions in CH_2Cl_2, a Pt bead electrode, and the saturated calomel electrode (SCE) as reference. Under the conditions used, $E^{0'}$ for the one-electron oxidation of [Fe(η^5-C$_5$H$_5$)$_2$], added to the test solutions as an internal calibrant, is 0.47 V.

Syntheses

(1-methyl-1-pyridin-2-yl-ethyl)-*p*-tolyl-amine (1e). A 250 mL flask equipped with a stir bar and Dean−Stark glassware was charged with 2-acetylpyridine (5.7 g, 43.7 mmol), *p*-toluidine (*p*-methylaniline; 4.68 g, 43.7 mmol), and a catalytic amount of *p*-toluenesulfonic acid in toluene (125 mL). It was refluxed for 3 h. The solution was evaporated to dryness. The precipitate was recrystallized in hexane and dried in vacuo, yielding a white solid product identified as the product of condensation, (1-pyridin-2-yl-ethylidene)-*p*-tolyl-amine[28] (9.0 g, 98%). ^{1}H NMR ($CDCl_3$): δ 8.66 (1 H, m, py), 8.27 (1 H, dd, py H^5), 7.76 (1 H, tt, py H^4), 7.34 (1 H, m, py), 7.18 (2 H, d, Ar), 6.74 (2 H, d, Ar), 2.37 (6 H, s, Me_{im} + Me_{Ar}). Anal. Calcd. for $C_{14}H_{14}N_2$: C, 79.97; H, 6.71; N, 13.32. Found: C, 80.12; H, 6.65; N, 13.09.

To a stirred and cooled (at −50 °C) solution of (1-pyridin-2-yl-ethylidene)-*p*-tolyl-amine (2.0 g, 9,52 mmol) in tetrahydrofuran (10 mL) was slowly added 20 mL of a solution of 1.4 M LiMe (28 mmol). The solution was then stirred for 36 h at −50 °C and, after warming to room temperature, water (15 mL) was added. The tetrahydrofuran was removed in a rota-vapor. The organic residue was extracted with diethyl ether (3 × 20 mL) and dried over anhydrous $MgSO_4$. The filtered solution was evaporated to dryness. The residue was distilled in vacuo. Yield: 2.65 g, 85%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.61 (m, 1H, py H^6), 7.59 (m, 2H, py H$^{3-5}$), 7.13 (m, 1H, H^4), 6.55 (m, 4H, Ar), 2.17 (s, 3H, *Me*-Ar), 1.67 (s,

(3) Pezet, F.; Daran, J. C.; Sasaki, I.; Ait-Haddou, H.; Balavoine, G. G. A. *Organometallics* **2000**, *19*, 4008−4015.
(4) Hesek, D.; Inoue, Y.; Everitt, S. R. L.; Ishida, H.; Kunieda, M.; Drew, M. G. B. *Inorg. Chem.* **2000**, *39*, 317−324.
(5) Gu, X. Q.; Chen, W.; Morales-Morales, D.; Jensen, C. M. *J. Mol. Catal. A: Chem.* **2002**, *189*, 119−124.
(6) Aidyn, A.; Medzhidov, A. A.; Fatullaeva, P. A.; Tashchioglu, S.; Yalchin, B.; Saiyn, S. *Russ. J. Coord. Chem.* **2001**, *27*, 486-492.
(7) Coalter, J. N.; Huffman, J. C.; Caulton, K. G. *Organometallics* **2000**, *19*, 3569−3578.
(8) El-Hendawy, A. M.; Alqaradawi, S. Y.; Al-Madfa, H. A. *Transition Met. Chem.* **2000**, *25*, 572−578.
(9) Ell, A. H.; Samec, J. S. M.; Brasse, C.; Backvall, J. E. *Chem. Commun.* **2002**, 1144−1145.
(10) Weeks, C. L.; Turner, P.; Fenton, R. R.; Lay, P. A. *J. Chem. Soc., Dalton Trans.* **2002**, 931−940.
(11) Mukaiyama, T.; Kawana, A.; Fukuda, Y.; Matsuo, J. *Chem. Lett.* **2001**, 390−391.
(12) Samec, J. S. M.; Backvall, J. E. *Chem.*−*Eur. J.* **2002**, *8*, 2955−2961.
(13) Kamiguchi, S.; Nakamura, A.; Suzuki, A.; Kodomari, M.; Nomura, M.; Iwasawa, Y.; Chihara, T. *J. Catal.* **2005**, *230*, 204−213.
(14) Cabort, A.; Therrien, B.; Stoeckli-Evans, H.; Bernauer, K.; Suss-Fink, G. *Inorg. Chem. Commun.* **2002**, *5*, 787−790.
(15) Mori, K.; Yamaguchi, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Chem. Commun.* **2001**, 461−462.
(16) Yamaguchi, K.; Mizuno, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 1480−1483.
(17) Keene, F. R. *Coord. Chem. Rev.* **1999**, *187*, 121−149.
(18) Gunnoe, T. B.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 6916−6923.
(19) Yamakawa, M.; Ito, H.; Noyori, R. *J. Am. Chem. Soc.* **2000**, *122*, 1466−1478.
(20) Abbel, R.; Abdur-Rashid, K.; Faatz, M.; Hadzovic, A.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2005**, *127*, 1870−1882.
(21) Gao, J. X.; Wan, H. L.; Wong, W. K.; Tse, M. C.; Wong, W. T. *Polyhedron* **1996**, *15*, 1241−1251.
(22) Cuevas, J. V.; Garcia-Herbosa, G.; Munoz, A.; Garcia-Granda, S.; Miguel, D. *Organometallics* **1997**, *16*, 2220−2222.
(23) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334−3341.
(24) Albers, M. O.; Ashworth, T. V.; Oosthuisen, H. E.; Singleton, E. *Inorg. Synth.* **1989**, *26*, 69.
(25) Takahashi, H.; Kobayashi, K.; Osawa, M. **2000**, *16*, 777−779.
(26) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233−241.
(27) Gill, T. P.; Mann, K. R. *Organometallics* **1982**, *1*, 485−488.
(28) Dieck, H. T.; Bruder, H.; Kuhl, E.; Junghans, D.; Hellfeldt, K. *New J. Chem.* **1989**, *13*, 259−268.

6H, *Me*$_2$-C). Anal. Calcd for $C_{15}H_{18}N_2$: C, 79.61; H, 8.02; N, 12.38. Found: C, 79.21; H, 7.86; N, 12.24.

[Ru(2,2′-bipyridine)$_2$(1)](PF$_6$)$_2$ (2). Compounds **2a**−**c** were prepared in the same way. The procedure for the synthesis of **2a** is described here. To a solution of *cis*-[Ru(2,2′-bipyridine)$_2$Cl$_2$]·2H$_2$O (0.1 g, 0.22 mmol) in ethanol (20 mL) was added **1a** (44 mg, 0.22 mmol). The mixture was refluxed for 4 h. After the solution was cooled to room temperature, glacial acetic acid (three drops) and NH_4PF_6 (300 mg, 1.84 mmol) dissolved in water (10 mL) were added. The solution was boiled and partially concentrated. The solution was cooled overnight in the fridge. The precipitate was collected, washed with ether (10 mL), and dried in vacuo. The product was dissolved in acetone (10 mL), and hexane (10 mL) was added to induce precipitation. Yield: 170 mg, 85%. ^{1}H NMR (400 MHz, acetone-d_6): δ 9.77 (d,1H), 8.87 (d, 1H), 8.76 (d, 1H), 8.54 (d, 1H), 8.44 (d, 1H), 8.33 (td, 2H), 8.06 (td, 2H), 7.99 (td, 2H), 7.96−7.83 (m, 5H), 7.79 (d, 1H), 7.75 (m, 1H), 7.58 (d, 1H), 7.40 (m, 1H), 7.32 (m, 2H), 6.44 (m, 4H, Ar), 5.04 (dd, 1H, $^2J_{Ha-Hb}$ = 15.1 Hz, $^3J_{Ha-NH}$ = 5.0 Hz, C*H*aHb), 4.95 (dd, 1H, $^2J_{Ha-Hb}$ = 15.1 Hz, $^3J_{Hb-NH}$ = 6.0 Hz, CHa*Hb*), 2.08 (s, 3H, Me).^{13}C NMR (100 MHz, acetone-d_6): δ 162.7, 158.7, 158.6 157.8, 157.7, 152.8, 152.5, 152.3, 152.1, 150.9, 141.4, 138.3 138.1, 137.9, 137.3, 136.9, 134.9, 129.4, 128.3, 128.0, 127.5, 126.8, 125.6, 124.9, 124.8, 124.2, 123.7, 123.2, 118.2, 56.1, 19.9. IR (KBr, cm^{-1}): 3287 ($\nu_{(NH)}$), 856−828 ($\nu_{(P-F)}$). Anal. Calcd for $C_{33}H_{30}F_{12}N_6P_2Ru$: C, 43.96; H, 3.35; N, 9.32. Found: C, 43.74; H, 3.31; N, 9.21.

2b. Yield: 89%. ^{1}H NMR (400 MHz, acetone-d_6): δ 9.69 (d, 1H), 8.85 (d, 1H), 8.73 (d, 1H), 8.54 (d, 1H), 8.46 (d, 1H), 8.31 (td, 1H), 8.22 (m, 2H), 8.04 (td, 1H), 7.97 (td, 1H), 7.91−7.72 (m, 6H), 7.56 (d, 1H), 7.38 (tc, 1H), 7.30 (tc, 1H), 6.34 (m, 4H, Ar), 4.99 (dd, 1H, $^2J_{Ha-Hb}$ = 16.4 Hz, $^3J_{Ha-NH}$ = 8.3 Hz C*H*aHb), 4.91 (dd, 1H, $^2J_{Ha-Hb}$ = 16.4 Hz, $^3J_{Hb-NH}$ = 5.7 Hz CHa*Hb*), 3.61 (s, 3H, CH_3). ^{13}C NMR (100 MHz, acetone-d_6): δ 162.6, 158.6, 158.5, 157.9, 157.7, 157.1, 152.8, 152.3, 152.2, 152.1, 150.9, 138.3, 138.0, 137.9, 137.2, 136.9, 136.7, 128.3, 128.0, 127.5, 126.8, 125.6, 124.9, 124.8, 124.2, 123.6, 123.2, 119.4, 114.1, 56.4, 55.2. IR (KBr, cm^{-1}): 3294 ($\nu_{(NH)}$), 846−842 ($\nu_{(P-F)}$). Anal. Calcd for $C_{33}H_{30}F_{12}N_6OP_2Ru$: C, 43.19; H: 3.29; N, 9.16. Found: C, 42.85; H, 3.12; N, 9.21.

2c. Yield: 90%. ^{1}H NMR (400 MHz, acetone-d_6): δ: 9.62 (d, 1H), 8.76 (d, 1H), 8.68 (d, 1H), 8.58 (d, 1H), 8.25 (m, 2H), 8.16 (d, 1H), 8.01 (t, 2H), 7.94−7.84 (m, 3H), 7.80 (d, 1H), 7.64 (d, 1H), 7.59 (t, 1H), 7.51 (d, 1H), 7.45 (d, 1H), 7.36 (t, 2H), 7.25 (dd, 1H, N*H*), 7.04 (d, 1H), 6.69 (t, 1H), 6.54 (d, 1H), 6.37 (d, 1H), 5.62 (dd, 1H, $^2J_{Ha-Hb}$ = 19.6 Hz, $^3J_{Ha-NH}$ = 9.6 Hz, C*H*aHb), 5.19 (dd, 1H, $^2J_{Ha-Hb}$ = 19.6 Hz, $^3J_{Hb-NH}$ = 2.5 Hz, CHa*Hb*), 1.72 (s, 3H, CH_3), 1.69 (s, 3H, CH_3). ^{13}C NMR (100 MHz, acetone-d_6): δ 165.3, 158.7, 158.5, 158.1, 157.9, 153.4, 152.9, 152.7, 152.4, 151.1, 142.1, 138.6, 138.2, 138.0, 137.7, 137.5, 132.0, 129.2, 128.7, 128.5, 127.8, 127.3, 127.2, 126.7, 125.9, 125.5, 125.0, 124.8, 123.9, 123.5, 122.2, 58.1, 23.1, 16.8. IR (KBr, cm^{-1}): 3330 ($\nu_{(NH)}$), 853−830 ($\nu_{(P-F)}$). Anal. Calcd for $C_{34}H_{32}F_{12}N_6P_2Ru$: C, 44.60; H: 3.52; N, 9.18. Found: C, 44.37; H, 3.51; N, 9.21.

***trans*-[Ru(1,5-cyclooctadiene)(1a)Cl$_2$] (3).** To a suspension of [RuCl$_2$(η^4-1,5-cyclooctadiene)]$_n$ (201.7 mg, 0.72 mmol) in ethanol (20 mL) was added **1a** (150 mg, 0.72 mmol). The mixture was refluxed for 1 h. After being cooled overnight at −20 °C, the yellow solid was collected and washed with ethanol (10 mL) and diethyl ether (10 mL). The product was dissolved in chloroform (10 mL). The addition of *n*-hexane and concentration to induce precipitation afforded the complex (245 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (m, 1H, py H^6), 7.74 (td, 1H, py), 7.27 (t, 1H, py), 7.26 (m, 4H, Ar), 7.17 (m, 1H, py), 6.83 (dd, 1H, $^3J_{Hb-NH}$ = 11.9 Hz, $^3J_{Ha-NH}$ = 4.3 Hz, N−H), 5.64 (dd, 1H, $^2J_{Hb-Ha}$ = 15.5 Hz, $^3J_{Hb-NH}$ = 11.9 Hz, CHa*Hb*), 4.42 (m, 1H, −CH-cod), 4.66 (m, 1H, −CH-cod), 4.38 (dd, 1H, $^2J_{Hb-Ha}$ = 15.5 Hz, $^3J_{Ha-NH}$ = 4.3 Hz, C*H*aHb), 3.92 (m, 1H, −CH-cod), 3.59 (m, 1H, −CH-cod), 2.80 (m, 1H, −$CH_{2(exo)}$-cod), 2.69 (m, 1H, −$CH_{2(exo)}$-cod), 2.50 (m, 1H, −$CH_{2(exo)}$-cod), 2.34 (m, 1H, −$CH_{2(exo)}$-cod), 2.29 (s, 1H, Me), 2.21 (m, 1H, −$CH_{2(endo)}$-cod), 2.07 (m, 1H, −$CH_{2(endo)}$-cod), 1.93 (m, 1H, −$CH_{2(endo)}$-cod), 1.74 (m, 1H, −$CH_{2(endo)}$-cod). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4, 149.8, 142.6, 137.9, 135.9, 129.9, 124.4, 122.2, 120.1, 92.2, 91.8, 88.1, 87.9, 60.1, 59.2, 30.3, 29.2, 28.6, 21.1. Anal. Calcd for $C_{21}H_{26}Cl_2N_2Ru$: C, 52.72; H, 5.48; N, 5.86. Found: C, 52.51; H, 5.38; N, 5.49.

[Ru(η^6-C$_6$H$_6$)(1)Cl]PF$_6$ (4). Compounds **4a**−**e** were prepared in the same way. The synthesis of **4a** is described here. To a suspension of [RuCl$_2$(η^6-C$_6$H$_6$)]$_2$ (145 mg, 0.29 mmol) in acetonitrile (10 mL) was added **1a** (115 mg, 0.58 mmol). The mixture was stirred at room temperature for 1 h. The mixture was evaporated to dryness, and the solid was treated with ethanol (5 mL) and $NaPF_6$ (164 mg, 1 mmol). The addition of water (10 mL) led to a yellow solid that was collected by filtration, washed with water followed by diethyl ether, and dried in vacuo. Yield: 232 mg, 72%. ^{1}H NMR (200 MHz, acetone-d_6): δ 9.22 (m, 1H, py H6), 8.11 (td, 1H, py), 7.78 (m, 1H, py), 7.63 (m, 1H, py), 7.51 (m, 4H, Ar), 6.47 (br, 1H, NH), 5.70 (s, 6H, C_6H_6), 5.47 (dd, 1H, $^2J_{Hb-Ha}$ = 15.1 Hz, $^3J_{Hb-NH}$ = 10.6 Hz, CHa*Hb*), 4.70 (dd, 1H, $^2J_{Hb-Ha}$ = 15.1 Hz, $^3J_{Ha-NH}$ = 3.2 Hz, C*H*aHb), 2.41 (s, 3H, Me). IR (KBr, cm^{-1}): 3184 ($\nu_{(NH)}$), 850 ($\nu_{(P-F)}$). Anal. Calcd for $C_{19}H_{20}ClN_2PF_6Ru$: C, 40.91; H, 3.61; N, 5.02. Found: C, 41.29; H, 3.80; N, 4.92.

4b. Yield: 82%. ^{1}H NMR (200 MHz, acetone-d_6): δ 9.22 (m, 1H, py H^6), 8.11 (td, 1H, py), 7.78 (m, 1H, py), 7.67 (m, 1H, py), 7.52 (m, 4H, Ar), 6.43 (br, 1H, NH), 5.72 (s, 6H, C_6H_6), 5.45 (dd, 1H, $^2J_{Hb-Ha}$ = 14.8 Hz, $^3J_{Hb-NH}$ = 11.2 Hz, CHa*Hb*), 4.69 (dd, 1H, $^2J_{Hb-Ha}$ = 14.8 Hz, $^3J_{Ha-NH}$ = 11.2 Hz, C*H*aHb), 3.88 (s, 3H, MeO). IR (KBr, cm^{-1}): 3182 ($\nu_{(NH)}$), 849 ($\nu_{(P-F)}$). Anal. Calcd for $C_{19}H_{20}ClN_2OPF_6Ru$: C, 39.76; H, 3.52; N, 4.88. Found: C, 39.20; H, 3.30; N, 4.90.

4c. Yield: 80%. ^{1}H NMR (200 MHz, acetone-d_6): δ 9.62 (m, 1H, py H^6), 8.12 (td, 1H, py), 7.64 (m, 1H, py), 7.29 (m, 1H, py), 7.20 (m, 4H, Ar), 6.74 (br, 1H, NH), 5.79 (s, 6H, C_6H_6), 4.95 (dd, 1H, $^2J_{Hb-Ha}$ = 19 Hz, $^3J_{Hb-NH}$ = 9.6 Hz, CHa*Hb*), 4.62 (dd, 1H, $^2J_{Hb-Ha}$ = 19 Hz, $^3J_{Ha-NH}$ = 3.8 Hz, C*H*aHb), 2.64 (s, 3H, Me), 2.31 (s, 3H, Me). IR (KBr, cm^{-1}): 3184 ($\nu_{(NH)}$), 849 ($\nu_{(P-F)}$). Anal. Calcd for $C_{20}H_{22}ClN_2PF_6Ru$: C, 42.00; H, 3.88; N, 4.90. Found: C, 41.75; H, 3.67; N, 5.15.

4d. Yield: 76%. ^{1}H NMR (200 MHz, acetone-d_6): δ 9.22 (m, 1H, py H^6), 8.12 (td, 1H, py), 7.93 (m, 4H, Ar), 7.80 (m, 1H, py), 7.65 (m, 1H, py), 6.72 (br, 1H, NH), 5.76 (s, 6H, C_6H_6), 5.57 (dd, 1H, $^2J_{Hb-Ha}$ = 15.0 Hz, $^3J_{Hb-NH}$ = 11.4 Hz, CHa*Hb*), 4.77 (dd, 1H, $^2J_{Hb-Ha}$ = 15.0 Hz, $^3J_{Ha-NH}$ = 3.0 Hz, C*H*aHb). IR (KBr, cm^{-1}): 3186, ($\nu_{(NH)}$), 852 ($\nu_{(P-F)}$). Anal. Calcd for $C_{19}H_{17}ClN_2PF_9Ru$: C, 37.30; H, 2.80; N, 4.58. Found: C, 36.70; H, 2.61; N, 4.63.

4e. Yield: 78%. ^{1}H NMR (200 MHz, acetone-d_6): δ 9.35 (d, 1H, py H6), 8.17 (t, 1H, py), 7.76 (d, 1H, py), 7.64 (t, 1H, py), 7.41 (s, 4H, Ar), 6.02 (s, 6H, C_6H_6), 5.56 (br, 1H, NH), 2.43 (s, 3H, *Me*-Ar), 1.95 (s, 3H, Me), 1.59 (s, 3H, Me). IR (KBr, cm^{-1}): 3169 ($\nu_{(NH)}$), 846 ($\nu_{(P-F)}$). Anal. Calcd for $C_{21}H_{23}ClN_2PF_6Ru$: C, 43.05; H, 4.13; N, 4.88. Found: C, 43.27; H, 3.99; N, 5.01.

[Ru(η^6-*p*-cymene)(1)Cl]PF$_6$ (5). Compounds **5d**,**e** were prepared in the same way. The procedure for the synthesis of **5d** is described here. To a solution of [RuCl$_2$(η^6-*p*-cymene)]$_2$ (100 mg, 0.163 mmol) in dichloromethane (10 mL) was added **1d** (89 mg, 0.35 mmol). After being stirred for 1.5 h at room temperature, the mixture was evaporated to dryness. Ethanol (5 mL) was added to the residue,

and the solution was treated with $NaPF_6$ (200 mg, 1.2 mmol) and water (30 mL). The solid was collected and dried in vacuo. Yield: 138 mg, 76%. ^{1}H NMR (200 MHz, acetone-d_6): δ 9.18 (m, 1H, py H6), 8.16 (td, 1H, py), 7.94 (m, 4H, Ar), 7.84 (m, 1H, py), 7.71 (m, 1H, py), 6.59 (br, 1H, NH), 5.74 (m, 2H, Ar *p*-cymene), 5.52 (dd, 1H, $^2J_{Hb-Ha}$ = 15.0 Hz, $^3J_{Hb-NH}$ = 12.0 Hz, CHa*Hb*), 5.33 (d, 1H, Ar *p*-cymene), 5.12 (d, 1H, Ar *p*-cymene), 4.77 (dd, 1H, $^2J_{Hb-Ha}$ = 15.0 Hz, $^3J_{Ha-NH}$ = 3.0 Hz, C*Ha*Hb), 2.69 (hept, 1H, C*H*(Me)$_2$), 2.00 (s, 3H, *p-Me* cymene), 1.15 (d, 3H, CH-*Me*Me), 1.01 (d, 3H, CH-Me*Me*). IR (KBr, cm^{-1}): 3285 ($\nu_{(NH)}$), 846 ($\nu_{(P-F)}$). Anal. Calcd for $C_{22}H_{26}ClN_2PF_6Ru$: C, 40.35; H, 3.69; N, 4.28. Found: C, 40.70; H, 3.49; N, 4.37.

5e. Yield: 71%.^{1}H NMR (200 MHz, acetone-d_6): δ 9.30 (m, 1H, py H^6), 8.21 (m, 1H, py), 7.98 (m, 1H, Ar), 7.79 (d, 1H, py), 7.70 (m, 1H, py), 7.52 (m, 1H, Ar), 7.28 (m, 1H, Ar), 7.05 (m, 1H, Ar), 6.37 (m, 1H, Ar *p*-cymene), 6.03 (m, 1H, Ar *p*-cymene), 5.82 (m, 1H, Ar *p*-cymene), 5.48 (br, 1H, NH), 5.04 (m, 1H, Ar *p*-cymene), 2.81 (hept, 1H, C*H*(Me)$_2$), 2.42 (s, 3H, *p-Me* Ar), 2.04 (s, 3H, Me *p*-cymene), 2.00 (s, 3H, N−C*Me*Me), 1.95 (d, 3H, CH-*Me*Me), 1.59 (s, 3H, N−CMe*Me*), 1.13 (d, 3H, CH-Me*Me*.) IR (KBr, cm^{-1}): 3285 ($\nu_{(NH)}$), 846 ($\nu_{(P-F)}$). Anal. Calcd for $C_{22}H_{26}ClN_2PF_6Ru$: C, 40.35; H, 3.69; N, 4.28. Found: C, 40.70; H, 3.49; N, 4.37.

[Ru(η^5-C_5H_5)(1a)(CH_3CN)]PF_6 (6). To a solution of [Ru(η^5-C_5H_5)(CH_3CN)$_3$]PF_6 (45 mg, 0.104 mmol) in dichloromethane (10 mL) was added **1a** (22 mg, 0.111 mmol). After being stirred for 2 h at room temperature, the mixture was evaporated to dryness. Diethyl ether (5 mL) was added to the residue, and the solid was collected and dried in vacuo. Yield: 25.6 mg, 45%. ^{1}H NMR (400 MHz, acetone-d_6, major diastereomer): δ 9.36 (d, 1H, py), 9.25 (d, 1H, py), 8.55 (br, 1H, py), 7.98 (t, 1H, py), 7.33 (m, 4H, Ar), 4.45−4.97 (m, 2H, CH_2), 3.88 (s, 5H, Cp), 2.32 (s, 3H, MeCN), 2.28 (s, 3H, Me). ^{1}H NMR (400 MHz, acetone-d_6, minor diastereomer): 9.36 (d, 1H, py), 9.25 (d, 1H, py), 8.55 (br, 1H, py), 7.98 (t, 1H, py), 7.33 (m, 4H, Ar), 4.45−4.97 (m, 2H, CH_2), 4.26 (s, 5H, Cp), 2.46 (s, 3H, MeCN), 2.08 (s, 3H, Me). Anal. Calcd for $C_{20}H_{18}N_3PF_6Ru$: C, 43.96; H, 3.32; N, 7.69. Found: C, 43.70; H, 3.49; N, 7.37.

[Ru(η^5-C_5H_5)(1)(CO)]PF_6 (7). Compounds **7a**,**e** were prepared in the same way. The synthesis of **7a** is described here. To a solution of [Ru(η^5-C_5H_5)(CO)(CH_3CN)$_2$]PF_6 (40 mg, 0.095 mmol) in dichloromethane (20 mL) was added **1a** (20 mg, 0.1 mmol). After being refluxed for 6 h, the mixture was evaporated to dryness. Yield: 40 mg, 80%. ^{1}H NMR (400 MHz, acetone-d_6, major diastereomer): δ 9.24 (m, 1H, py H^6), 8.98 (m, 1H, py), 8.06 (m, 1H, py), 7.43 (t, 1H, py), 7.12 (m, 4H, Ar), 5.18 (s, 5H, Cp), 4.75 (dd, 1H, $^2J_{Ha-Hb}$ = 16.0 Hz, $^3J_{Hb-NH}$ = 7.4 Hz, CHa*Hb*), 4.61 (dd, 1H, $^2J_{Ha-Hb}$ = 16.0 Hz,$^3J_{Ha-NH}$ = 4.4 Hz, C*Ha*Hb), 2.25 (s, 3H, Me). ^{1}H NMR (400 MHz, acetone-d_6, minor diastereomer): δ 9.24 (m, ^{1}H, py H^6), 8.98 (m, 1H, py), 8.06 (m, 1H, py), 7.43 (t, 1H, py), 7.12 (m, 4H, Ar), 4.85 (s, 5H, Cp), 4.95 (dd, 1H, $^2J_{Ha-Hb}$ = 15.3 Hz, $^3J_{Hb-NH}$ = 6.3 Hz, CHa*Hb*), 4.46 (dd, 1H, $^2J_{Ha-Hb}$ = 15.3 Hz,$^3J_{Ha-NH}$ = 4.0 Hz, C*Ha*Hb), 2.25 (s, 3H, Me). IR (KBr, cm^{-1}): 3294 and 3270 ($\nu_{(NH)}$), 1969 ($\nu_{(CO)}$), 846 ($\nu_{(P-F)}$). Anal. Calcd for $C_{19}H_{19}N_2OPF_6Ru$: C, 42.47; H, 3.56; N, 5.21. Found: C, 42.21; H, 3.39; N, 5.46.

7e. Yield: 71%. ^{1}H NMR (400 MHz, acetone-d_6, major diastereomer): δ 9.13 (m, 1H, py H^6), 8.20 (m, 1H, py), 7.74 (m, 1H, py), 7.54 (t, 1H, py), 7.14 (m, 4H, Ar), 5.00 (s, 5H, Cp), 2.25 (s, 3H, Me), 1.75 (s, 3H, C(*Me*Me)), 1.75 (s, 3H, C(Me*Me*). ^{1}H NMR (400 MHz, acetone-d_6, minor diastereomer): δ 9.13 (m, 1H, py H6), 8.20 (m, 1H, py), 7.74 (m, 1H, py), 7.54 (t, 1H, py), 7.14 (m, 4H, Ar), 4.97 and 4.87 (s, 5H, Cp), 2.25 (s, 3H, Me), 1.68 (d, 3H, C(*Me*Me)), 1.58 (s, 3H, C(Me*Me*)). IR (KBr, cm^{-1}): 1975 ($\nu_{(CO)}$), 844 ($\nu_{(P-F)}$). Anal. Calcd for $C_{21}H_{23}N_2OPF_6Ru$: C, 44.61; H, 4.10; N, 4.95. Found: C, 44.51; H, 3.89; N, 4.75.

[Ru(2,2′-bipyridine)$_2$(1-H_2)](PF$_6$)$_2$ (8). (a) Imine derivatives **8a**−**d** were prepared as described for amine-related compounds **2** but using the imine ligands (**1**-H_2)**a**−**d**.

8a. Yield: 82%. ^{1}H NMR (400 MHz, acetone-d_6): δ 9.36 (s, 1H, HC═N), 8.88 (dc, 1H), 8.84 (m, 2H), 8.54 (m, 2H), 8.34 (dd, 1H), 8.30−8.18 (m, 4H), 8.12 (d, 1H), 8.06 (dc, 1H), 7.99 (dc, 1H), 7.96−7.91 (m, 2H), 7.74 (tc, 1H), 7.69 (tc, 1H), 7.63 (tc, 1H), 7.55 (tc, 1H), 7.40 (tc, 1H), 6.78 (m, 4H, Ar), 2.16 (s, 3H, Me). ^{13}C NMR: δ 168.7, 157.7, 157.3, 157.2, 157.1, 156.9, 153.4, 152.4, 152.3, 152.1, 152.0, 147.0, 138.8, 138.6, 138.5, 138.4, 138.1, 137.9, 130.8, 129.7, 129.2, 128.4, 128.3, 128.0, 127.6, 124.8, 124.7, 123.9, 123.7, 121.4, 20.2. IR (KBr, cm^{-1}): 846−842 ($\nu_{(P-F)}$). Anal. Calcd for $C_{33}H_{28}F_{12}N_6P_2Ru$: C, 43.89; H, 3.17; N, 9.09. Found: C, 44.01; H, 3.24; N, 9.23.

Salt **8a** was the resulting product when the reaction used to prepare **2a** was carried out in air. Yield: 78%.

8b. Yield: 85%. ^{1}H NMR (400 MHz, acetone-d_6): δ 9.32 (s, 1H, HC═N), 8.87−8.80 (m, 3H), 8.52 (dd, 2H), 8.36 (m, 1H), 8.26 (td, 1H), 8.20 (m, 3H), 8.09 (d, 1H), 8.06 (d, 1H), 7.98−7.93 (m, 3H), 7.72 (tt, 1H), 7.67 (tt, 1H), 7.61 (tt, 1H), 7.41 (tt, 1H), 6.68 (m, 4H, Ar), 3.67 (s, 3H, OMe). ^{13}C NMR (100 MHz, acetone-d_6): δ 167.9, 160.0, 157.7, 157.3, 157.2, 157.1, 157.0, 153.4, 152.3, 152.2, 152.1, 151.9, 142.5, 138.6, 138.5, 138.0, 137.9, 130.6, 129.0, 128.4, 128.3, 128.0, 127.6, 124.8, 124.7, 123.8, 123.7, 123.0, 114.4, 55.3. IR (KBr, cm^{-1}): 854−830 ($\nu_{(P-F)}$). Anal. Calcd for $C_{33}H_{28}F_{12}N_6OP_2Ru$: C, 43.28; H, 3.08; N, 9.18. Found: C, 43.05; H, 3.10; N, 9.26.

8c. Yield: 88%. ^{1}H NMR (400 MHz, acetone-d_6): δ 9.33 (s, 1H, HC═N), 8.82−8.76 (m, 3H), 8.82 (dc, 1H), 8.56 (dc, 1H), 8.46 (d, 1H), 8.43 (d, 1H), 8.30−8.20 (m, 3H), 8.15 (m, 3H), 7.92 (dc, 1H), 7.88 (td, 1H), 7.73 (tc, 1H), 7.67−7.60 (m, 2H), 7.48 (tc, 1H), 7.35 (tc, 1H), 6.90 (t, 1H), 6.82 (d, 1H), 6.63 (d, 1H), 2.22 (s, 3H, Me), 1.17 (s, 3H, Me). ^{13}C NMR (100 MHz, acetone-d_6): δ 172.7, 158.2, 157.4, 157.3, 156.4, 154.3, 152.9, 152.6, 152.0, 151.5, 146.9, 139.2, 138.8, 138.4, 138.2, 138.0, 131.4, 130.6, 129.6, 129.5, 129.0, 128.6, 128.3, 127.8, 127.7, 127.1, 126.6, 124.7, 124.6, 124.3, 122.7, 20.9, 16.5. IR (KBr, cm^{-1}): 854−827 (ν_{P-F}). Anal. Calcd for $C_{34}H_{28}F_{15}N_6P_2Ru$: C, 41.56; H, 2.64; N, 8.81. Found: C, 41.32; H, 2.72; N, 8.69.

8d. Yield: 80%. ^{1}H NMR (400 MHz, acetone-d_6): δ 9.48 (s, 1H, HC═N), 8.94 (d, 1H), 8.83 (c, 2H), 8.59 (d, 1H), 8.55 (d, 1H), 8.35−8.17 (m, 6H), 8.05 (c, 2H), 7.92 (m, 2H), 7.76−7.65 (m, 3H), 7.56 (t, 1H), 7.40 (t, 1H), 7.25 (m, 4H, Ar). ^{13}C NMR (100 MHz, acetone-d_6): δ 170.9, 157.3, 157.1, 157.0, 156.8, 153.4, 152.7, 152.5, 152.2, 152.1, 151.9, 138.9, 138.7, 138.6, 138.2, 137.9, 131.6, 129.7, 128.7, 128.4, 128.1, 127.9, 126.5, 126.4, 124.9, 124.8, 124.0, 123.7, 122.6. IR (KBr, cm^{-1}): 854−827 (ν_{P-F}). Anal. Calcd for $C_{33}H_{33}F_{12}N_6P_2Ru$: C, 44.70; H, 3.31; N, 9.20. Found: C, 44.34; H, 3.41; N, 9.33.

***trans*-[Ru(1,5-cyclooctadiene)(1a-H_2)Cl_2] (9).** Complex **9** was prepared as described above for complex **3** but using the imine ligand (**1a**-H_2). Yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 1H, HC═N), 8.20 (d, 1H, py H^6), 7.92 (m, 2H, py), 7.51 (m, 1H, py), 7.23 (m, 4H, Ar), 4.70 (m, 2H, −CH-cod), 4.12 (m, 2H, −CH-cod), 2.62 (m, 4H, −$CH_{2(exo)}$-cod), 2.34 (s, 3H, Me), 2.13 (m, 2H, −$CH_{2(endo)}$-cod), 1.99 (m, 2H, −$CH_{2(endo)}$-cod). ^{13}C NMR (400 MHz, $CDCl_3$): δ 168.2, 156.9, 147.3, 140.8, 138.3, 137.9, 129.7, 129.2, 128.0, 120.8, 92.5, 92.1, 29.9, 29.4, 21.3. Anal. Calcd for $C_{21}H_{24}Cl_2N_2Ru$: C, 52.94; H, 5.08; N, 5.88. Found: C, 52.48; H, 4.89; N, 5.70.

Table 1. Crystal Data for Compounds **2b**·CH_2Cl_2, **2c**·$2CH_2Cl_2$, **3**, and **4a**·$Me_2C{=}O$

	2b·CH_2Cl_2	**2c**·$2CH_2Cl_2$	**3**	**4a**·$Me_2C{=}O$
formula	$C_{34}H_{32}Cl_2F_{12}N_6OP_2Ru$	$C_{36}H_{36}Cl_4F_{12}N_6P_2Ru$	$C_{21}H_{26}Cl_2N_2Ru$	$C_{22}H_{26}ClF_6N_2OPRu$
fw	1002.57	1085.52	478.41	615.94
a (Å)	18.573(4)	14.2588(3)	9.052(6)	8.3919(16)
b (Å)	13.703(18)	21.5216(9)	22.714(4)	11.6702(14)
c (Å)	16.916(6)	28.1859(8)	9.890(6)	13.5049(12)
α (deg)	90	90	90	80.353(10)
β (deg)	102.80(2)	90	105.81(6)	82.684(9)
γ (deg)	90	90	90	72.537(10)
V (Å^3)	4198.4(15)	8649.5(15)	1956.5(18)	1239.6(3)
space group	$P2_1/c$ (No. 14)	*Pbca* (No. 61)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
Z	4	8	4	2
D_{calcd} (g cm^{-3})	1.586	1.667	1.624	1.650
T (°C)	26(2)	−100(2)	−123(1)	−10(1)
λ (Å)	0.71073			
μ (mm^{-1})	0.666	0.772	1.082	0.868
R values [$I > 2\sigma(I)$][a,b]	R1 = 0.1418	R1 = 0.0714	R1 = 0.0624	R1 = 0.0496
	wR2 = 0.3421	wR2 = 0.1758	wR2 = 0.1410	wR2 = 0.1182
R values (all data)[a,b]	R1 = 0.4112	R1 = 0.0838	R1 = 0.1081	R1 = 0.0657
	wR2 = 0.4649	wR2 = 0.1834	wR2 = 0.1631	wR2 = 0.1286
quality-of-fit[c]	1.032	1.061	1.039	1.016

[a] $R1 = \sum||F_{obs}| - |F_{calcd}||/\sum|F_{obs}|$. [b] $wR2 = [\sum w(F_{obs}^2 - F_{calcd}^2)^2/\sum w(F_{obs}^2)^2]^{1/2}$. [c] Quality-of-fit $= [\sum w(F_{obs}^2 - F_{calcd}^2)^2/(N_{obs} - N_{param})]^{1/2}$.

[Ru(η^6-C_6H_6)(1-H_2)Cl]PF_6 (10). Salts **10a**−**d** were prepared as described above for salts **4** but using the imine ligands (**1**-H_2).

10a. Yield: 87%. ^{1}H NMR (200 MHz, acetone-d_6): δ 9.70 (m, 1H, py H^6), 8.84 (s, 1H, HC═N), 8.35 (m, 2H, py), 7.89 (m, 1H, py), 7.56 (m, 4H, Ar), 6.04 (s, 6H, C_6H_6), 2.47 (s, 3H, Me). IR (KBr, cm^{-1}): 849 ($\nu_{(P-F)}$). Anal. Calcd for $C_{19}H_{18}ClN_2PF_6Ru$: C, 41.05; H, 3.26; N, 5.04. Found: C, 41.10; H, 3.04; N, 5.28.

10b. Yield: 85%. ^{1}H NMR (200 MHz, acetone-d_6): δ 9.68 (m, 1H, py H^6), 8.82 (s, 1H, HC═N), 8.33 (m, 2H, py), 7.89 (m, 1H, py), 7.50 (m, 4H, Ar), 6.05 (s, 6H, C_6H_6), 3.93 (s, 3H, MeO). IR (KBr, cm^{-1}): 852 ($\nu_{(P-F)}$). Anal. Calcd for $C_{19}H_{18}ClN_2OPF_6Ru$: C, 39.91; H, 3.17; N, 4.90. Found: C, 40.10; H, 3.07; N, 5.10.

10c. Yield: 87% ^{1}H NMR (200 MHz, acetone-d_6): δ 9.71 (m, 1H, py H^6), 8.67 (s, 1H, HC═N), 8.34 (m, 2H, py), 7.90 (m, 1H, py), 7.31 (m, 3H, Ar), 5.98 (s, 6H, C_6H_6), 2.44 (s, 3H, Me), 2.29 (s, 3H, Me). IR (KBr, cm^{-1}): 849 ($\nu_{(P-F)}$). Anal. Calcd for $C_{20}H_{20}ClN_2PF_6Ru$: C, 42.15; H, 3.54; N, 4.92. Found: C, 42.10; H, 3.44; N, 5.08.

10d. Yield: 85% ^{1}H NMR (200 MHz, acetone-d_6): δ 9.73 (m, 1H, py H^6), 8.97 (s, 1H, HC═N), 8.40 (m, 2H, py), 8.36 (m, 1H, py), 8.04 (m, 4H, Ar), 6.08 (s, 6H, C_6H_6). IR (KBr, cm^{-1}): 852 ($\nu_{(P-F)}$). Anal. Calcd for $C_{19}H_{14}ClN_2PF_9Ru$: C, 37.42; H, 2.48; N, 4.59. Found: C, 37.22; H, 2.38; N, 4.67.

[Ru(η^6-*p*-cymene)(1d-H_2)Cl]PF_6 (11). Salt **11** was prepared as described above for salt **5** but using the imine ligand (**1d**-H_2). Yield: 78%. ^{1}H NMR (400 MHz, acetone-d_6): δ 9.58 (d, 1H, py H^6), 8.96 (s, 1H, HC═N), 8.30 (m, 2H, py), 7.99 (m, 4H, Ar), 7.89 (d, 1H, py), 6.09 (d, 1H, Ar *p*-cymene), 5.77 (m, 1H, Ar *p*-cymene), 5.71 (d, 1H, Ar *p*-cymene), 5.56 (d, 1H, Ar *p*-cymene), 2.47 (hept, 1H, C*H*(Me)$_2$), 2.14 (s, 3H, *p*-Me cymene), 0.95 (d, 6H, CH(*Me*)$_2$). IR (KBr, cm^{-1}): 848 (ν_{P-F}). Anal. Calcd for $C_{23}H_{22}ClN_2PF_9Ru$: C, 41.48; H, 3.48; N, 4.2. Found: C, 41.70; H, 3.49; N, 4.37.

[Ru(η^5-C_5H_5)(1a-H_2)(CH_3CN)]PF_6 (12). Salt **12** was prepared as described above for salt **6** but using the imine ligand (**1a**-H_2). Yield: 77%. ^{1}H NMR (400 MHz, acetone-d_6): δ 9.66 (d, 1H, py H^6), 9.08 (s, 1H, HC═N), 8.29 (m, 1H, py), 8.15 (td, 1H, py), 7.70 (m, 1H, py), 7.60 (m, 4H, Ar), 4.46 (s, 5H, Cp), 2.45 (s, 3H, MeCN), 2.37 (s, 3H, Me). Anal. Calcd for $C_{20}H_{20}N_3PF_6Ru$: C, 43.80; H, 3.68; N, 7.66. Found: C, 43.70; H, 3.49; N, 7.47.

[Ru(η^5-C_5H_5)(1a-H_2)(CO)]PF_6 (13). Salt **13** was prepared as described above for salts **7** but using the imine ligand (**1a**-H_2). Yield: 79%. ^{1}H NMR (400 MHz, acetone-d_6): δ 9.35 (d, 1H, py H^6), 9.14 (s, 1H, HC═N), 8.49 (d, 1H, py), 8.34 (t, 1H, py), 7.76 (t, 1H, py), 7.54 (m, 4H, Ar), 5.32 (s, 5H, Cp), 2.43 (s, 3H, Me). IR (KBr, cm^{-1}): 1982 (ν_{CO}), 850 (ν_{P-F}). Anal. Calcd for $C_{19}H_{17}N_2OPF_6Ru$: C, 42.63; H, 3.20; N, 5.23. Found: C, 42.70; H, 3.39; N, 5.37.

[Ru(η^6-*p*-C_6H_6)(1e-H)]PF_6 (14). A suspension of **4e** (50 mg, 0.085 mmol) in tetrahydrofuran (10 mL) was treated with a solution 0.5 M sodium methoxide (0.18 mL, 0.09 mmol) in methanol. The mixture was evaporated to dryness. The solid was dissolved in tetrahydrofuran (10 mL), and the resulting solution was filtered and evaporated to dryness to afford a red solid. Yield: 87%. ^{1}H NMR (200 MHz, acetone-d_6): δ 9.89 (d, 1H, py H^6), 8.14 (t, 1H, py), 7.82 (d, 1H, py), 7.68 (t, 1H, py), 7.28 (s, 4H, Ar), 5.81(s, 6H, C_6H_6), 2.43 (s, 3H, *Me*-Ar), 1.42 (s, 6H, Me_2). IR (KBr, cm^{-1}): 842 ($\nu_{(P-F)}$). Anal. Calcd for $C_{21}H_{23}N_2PF_6Ru$: C, 45.91; H, 4.22; N, 5.10. Found: C, 45.67; H, 4.09; N, 5.31.

[Ru(η^6-*p*-cymene)(1e-H)]PF_6 (15). A suspension of **5e** (60 mg, 0.094 mmol) in tetrahydrofuran (10 mL) was treated with a solution 0.63 M sodium methoxide (0.15 mL, 0.095 mmol) in methanol. The mixture was evaporated to dryness. The solid was dissolved in tetrahydrofuran (10 mL), and the resulting solution was filtered and evaporated to dryness to afford a red solid. Yield: 87%. ^{1}H NMR (200 MHz, acetone-d_6): δ 9.89 (d, 1H, py H^6), 8.15 (t, 1H, py), 7.83 (d, 1H, py), 7.71 (m, 1H, py), 7.28 (m, 4H, Ar), 5.84 (m, 1H, Ar *p*-cymene), 5.73 (m, 1H, Ar *p*-cymene), 5.41 (m, 2H, Ar *p*-cymene), 2.81 (hept, 1H, C*H*Me_2), 2.45 (s, 3H, *Me*-Ar), 2.29 (s, 3H, Me *p*-cymene), 1.40 (s, 6H, N−CMe_2), 1.32 (d, 6H, CH*Me*$_2$). IR (KBr, cm^{-1}): 3168 (ν_{N-H}), 843 ($\nu_{(P-F)}$). Anal. Calcd for $C_{25}H_{31}N_2PF_6Ru$: C, 49.59; H, 5.16; N, 4.63. Found: C, 49.67; H, 5.04; N, 4.73.

Molecular Mechanics Calculations. Quantum chemical calculations were performed using the MacSpartan Pro 1.0.2 program suite implemented on an Apple Macintosh G4 1.25 GHz dual.[29] Nongeometrical restrictions were imposed. The calculations were carried out at the semiempirical model PM3.[30]

X-ray Crystallography. General crystallographic data and refinement indicators are presented in Table 1 for the structures of **2b**·CH_2Cl_2, **2c**·$2CH_2Cl_2$, **3**, and **4a**·$Me_2C{=}O$. Crystals were grown from dichloromethane/diethyl ether (**2b** and **2c**), from acetone/

(29) *Wavefunction*, version 1.0.2; Wavefunction, Inc.: Irvine, CA, 1999−2000.
(30) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209−220.

diethyl ether (**4a**), and from chloroform/ethanol (**3**). X-ray diffraction data were measured using a Nonius KappaCCD diffractometer with a rotating anode source for **2c** and with a Nonius CAD-4 equipped with a sealed tube for the other structures.[31] Multiscan absorption corrections were used in all cases (with absorption data obtained in the case of the CAD-4 by ψ-scans of a group of scattering vectors spanning a wide range of Eulerian-equivalent χ values in their respective bisecting positions). The structures were solved by direct methods and refined to F^2 using full-matrix least squares. [32] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included at calculated positions (derived from a local difference Fourier map for methyl groups) with isotropic U constrained to values of 1.2× the equivalent isotropic displacement parameters of their respective parent atoms. The one exception was the H atom bonded to N2 in the structure of **4a**; this hydrogen atom is a H-bond donor to the neighboring chlorine atom and was refined freely. For **2b**, a total of 1 formula equiv of CH_2Cl_2 was included in the model and distributed over two sites, one of which was disordered. No hydrogen atoms were included for this moiety. The PF_6^- groups in **2b**, **2c**, and **4a** showed signs of varying degrees of disorder; similarity restraints were used where deemed appropriate.

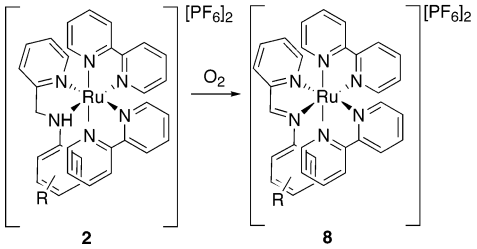
Crystals of **2b**·CH_2Cl_2 presented special problems, which are reflected in the poor quality of the results obtained from them. The crystals diffracted very weakly at room temperature, but the diffraction pattern became entirely unobservable when the temperature was lowered to any value that might have been expected to produce an improvement in the diffraction, e.g., −100 °C, probably as the result of a first-order structural transformation. The results that we report, obtained at room temperature, establish the connectivity and general structural features, especially the relative stereochemistries of the three possible sources of chirality (see Results and Discussion); but we would advise against using bond distances and angles from this structure determination in an analysis of fine structural features or in a comparative geometrical study.

Crystallographic data in the form of a crystallographic information file are included in the Supporting Information.

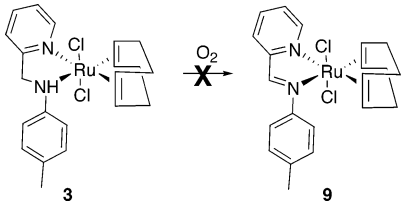
Results and Discussion

Synthesis of [Ru(2,2′-bipyridine)$_2$(1)](PF$_6$)$_2$ (2). Compounds **2a**, **2b**, and **2c** were prepared by the reaction of (Δ,Λ)-*cis*-[Ru(2,2′-bipyridine)$_2$Cl$_2$] with amine ligands **1a**, **1b**, or **1c** under nitrogen. The presence of small amounts of adventitious oxygen led to small amounts of the oxidized imine compounds **8a**, **8b**, and **8c** following the reaction shown in Scheme 1. Such β-oxidation reactions are known to take place on amines coordinated to ruthenium upon reaction with O_2,[33−35] and a possible mechanism has been proposed.[15,16] We failed to prepare compound **2d**. The reaction of (Δ,Λ)-*cis*-[Ru(2,2′-bipyridine)$_2$Cl$_2$] with ligand **1d** (under the same conditions as those indicated for **1a**, **1b**, or **1c**) afforded **8d**. The acidity of the N−H bond after the coordination of ligands **1** to ruthenium seems to control the oxidation reaction as discussed below. The CF_3 group in the para position induces the strongest acidity, and compound **2d** is elusive.

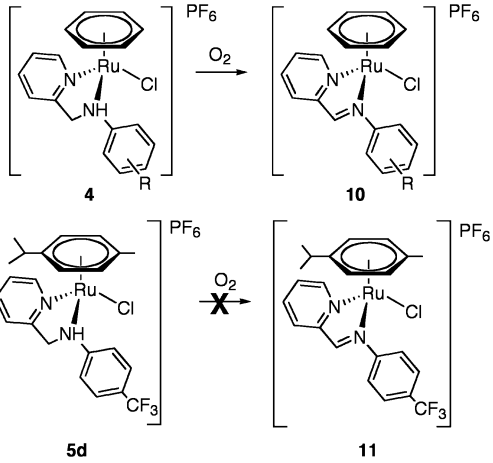
Scheme 1



Scheme 2



Scheme 3



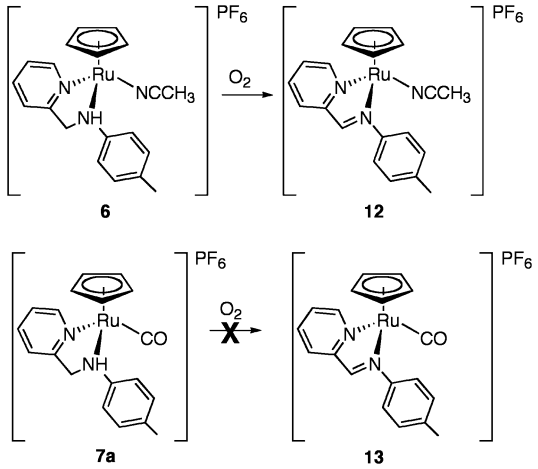
Synthesis of *trans*-[Ru(1,5-cyclooctadiene)(1a)Cl$_2$] (3). Complex **3** was prepared by the reaction of [RuCl$_2$(1,5-cyclooctadiene)]$_n$ with ligand **1a**. The reaction conditions were the same as those for compounds **2**; the formation of the imine derivative **9** was not observed (Scheme 2). Thus, in addition to the substituents in the para position mentioned for compounds **2**, the nature of the ancillary ligands coordinated to ruthenium also affects the oxidation reaction of amine to imine.

Synthesis of [Ru(η^6-arene)(1)Cl]PF$_6$ (arene = C$_6$H$_6$, 4; *p*-cymene, 5). Salts **4a**, **4b**, **4c**, **4d**, and **4e** were prepared by the reaction of [RuCl$_2$(CH$_3$CN)(η^6-C$_6$H$_6$)] with the appropriate ligand **1a**−**e**. Salts **5d**,**e** were prepared by the reaction of [RuCl$_2$(η^6-*p*-cymene)]$_2$ with corresponding ligand **1d** or **1e**. As indicated for compounds **2**, small amounts of imine derivatives **10** were formed (Scheme 3) if oxygen was not rigorously excluded from the reaction in the synthesis of salts **4a**−**d**. However, compound **5d** was synthesized under the

(31) (a) *KappaCCD, COLLECT*; Nonius BV: Delft, The Netherlands, 1999. (b) *DENZO, see:* Otwinowski, Z.; Minor, W. In *Methods in Enzymology, Vol. 276A: Macromolecular Crystallography*; Carter, C. W., Sweet, R. M., Eds.; Academic Press: New York, 1997; pp 307−326. (c) *SORTAV*, see: Blessing, R. H. *Acta Crystallogr., Sect. A*, **1995**, *51*, 33−38. (d) *CAD-4: Instrument Control, CAD4/PC*, version 2.0; Nonius BV: Delft, The Netherlands, 1996. (e) Harms, K. University of Marburg, Germany. Private communication on data reduction using XCAD4B, 1996. (f) *SHELXTL*, release 5.05/VMS; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1996.

(32) (a) Sheldrick, G. M. *SHELXS-97: Fortran Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997. Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467. (b) Sheldrick, G. M. *SHELXL-97: Fortran Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

Scheme 4



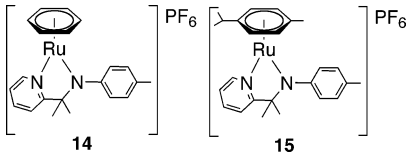
same conditions without the formation (Scheme 3) of the imine derivative **11**. This indicates that the electronic effects induced by substituents on the η^6-arene ligands account for the different behavior toward molecular oxygen. The synthesis and characterization of stable compounds **4d** and **5d** (we mentioned above that attempts to prepare **2d** failed) again support the notion that the oxidation of amine complexes to imine complexes by molecular oxygen is strongly dependent on the ancillary ligands coordinated to ruthenium.

Synthesis of [RuCp(L)(1)]PF_6 (L= CH_3CN, 6; CO, 7). Salt **6** was prepared as a mixture of diastereomers (3:2, d.e. 20%) by the reaction of [Ru(η^5-C_5H_5)(CH_3CN)$_3$]PF_6 with **1a**. This mixture is very sensitive in solution to molecular oxygen, leading to the imine derivative **12** (Scheme 4). Salts **7a**,**e** were also prepared as mixtures of diastereomers (2:1, d.e. 33%) by simple substitution reactions of [Ru(η^5-C_5H_5)(CO)(CH_3CN)$_2$]PF_6 with the appropriate amine ligand **1a** or **1e**. In contrast to compound **6**, compound **7a** is stable to air in solution (Scheme 4). The difference in the donor−acceptor properties of ligands CO and CH_3CN accounts for such a different behavior.

Synthesis of Derivatives with Imine Ligands 1-H_2. The imine derivatives **8**−**13** were prepared for comparison purposes. They are the products of oxidation of amine derivatives **2**−**7** and differ only by one molecule of hydrogen. As already indicated, they appear occasionally as impurities if molecular oxygen is present in the experimental procedures to synthesize the amine derivatives. In all cases, the synthetic procedures consisted of the reaction of the appropriate precursor with the corresponding imine ligand under the same conditions as those used for the preparation of the amine derivatives. Imine derivative **8a** was also prepared in high yield by the reaction of (Δ,Λ)-*cis*-[Ru(2,2′-bipyridine)$_2$$Cl_2$] with amine ligand **1a** in air; the reaction required 4 h in refluxing methanol.

Deprotonation of Amine Complexes. **Synthesis of Amido Complexes [Ru(η^6-C_6H_6)(1e-H)]PF_6 (14) and [Ru-(η^6-*p*-cymene)(1e-H)]PF_6 (15).** Our interest in amido complexes led us to explore deprotonation reactions of the amine complexes containing ligands **1a**−**d** (NaOMe, KOBu^t, and K-Selectride were used as deprotonating agents). We were unable to characterize any amido complexes in these reactions, and imine complexes were the only identified products. The synthesis of ligand **1e** (without β hydrogen atoms, see Scheme 1) allowed for preparation of compounds **4e** and **5e**. We also attempted to prepare **2e** but did not succeed, likely because of the higher steric requirements of the [Ru(bipy)$_2$] moiety compared with those of [Ru(arene)Cl]. Amido complexes **14** and **15** were prepared by simple deprotonation of amine complexes **4e** or **5e** with a stoichiometric amount of NaOMe.

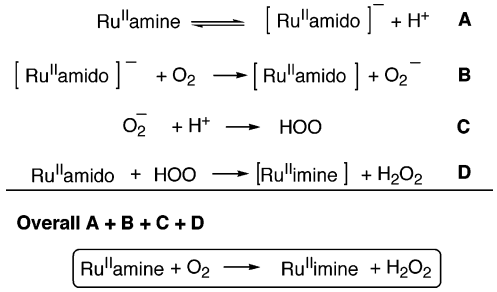
Chart 2



Base-Catalyzed Oxidative Dehydrogenation of Amine to Imine Complexes. The results described above indicate that amido complexes, although elusive, play an important role in the oxidation of the coordinated amine ligand to the corresponding imine by air. In fact, the results presented here suggest that the oxidation of amine complexes to imine complexes takes place only if the amido complex is formed in situ by deprotonation of the precursor amine complex. The highest concentration of amido complex in solution should lead to the fastest oxidation to imine complex. This is strongly supported by our failure in attempting to prepare **2d**, which should be the more acidic of complexes **2** thus leading to the highest concentrations of amido complex in solution. Complexes **2** and **4** were suspended or dissolved in tetrahydrofuran and treated with different amounts of base (NaMeO in MeOH) in air at room temperature. The formation of imine derivatives **8** or **10** was monitored by ^{1}H NMR. The best yields of imine derivatives (yields greater than 75% after 5 h at room temperature) were obtained when 10% of the amount of NaMeO required for a 1:1 base:Ru molar ratio was used. This shows that the oxidation of amine complex to imine complex is base-catalyzed. Thus, small amounts of base made the oxidation reaction to imine faster, whereas an excess of base led to lower yields and less-clean reactions, likely because of the further reaction of imine complexes with the excess of base. The presence of H_2O_2 in the reaction (>10 mg L^{-1}) was unequivocally proved in a peroxide test (Quantofix test stick; detection range = 0.5−25 mg L^{-1} H_2O_2). Further oxidation of the imine ligand to amide, as described for the reaction of [Ru(II)(diimine)$_2$$Cl_2$] complexes with H_2O_2,[36] was not observed. Whereas hydrogen peroxide is an end product of the amine oxidation in biological systems and the mechanism of the dioxygen activation by oxidase enzymes is of current interest,[37] this is, to the best of our knowledge, the first report of hydrogen

(33) Bailey, A. J.; James, B. R. *Chem. Commun.* **1996**, 2343−2344.
(34) Naota, T.; Takaya, H.; Murahashi, S. I. *Chem. Rev.* **1998**, *98*, 2599−2660.
(35) Gemel, C.; Folting, K.; Caulton, K. G. *Inorg. Chem.* **2000**, *39*, 1593−1597.
(36) Menon, M.; Pramanik, A.; Chakravorty, A. *Inorg. Chem.* **1995**, *34*, 3310−3316.

Scheme 5. Proposed Steps for the Oxidation of Ruthenium(II) Amine Complexes with Air



peroxide formation in the reaction between a coordination compound and dioxygen. This could be used as a model to understand the more complicated biological systems.

Mechanism for Amine Oxidation. Scheme 5 shows the proposed mechanism for the oxidation of ruthenium(II) amine complexes on the basis of the experimental results reported above. The first step explains that a higher concentration of amido complex leads to a faster oxidation reaction to imine. A higher N−H bond acidity leads to an easier (faster) oxidation to imine. Electron-withdrawing substituents, such as CF_3 on the aryl group, increase the acidity, and oxidation becomes easier. This explains our failure in trying to prepare complex **2d**. However, the electronic effect of the ancillary ligands on the acidity of the N−H bond is less evident, although good π-acceptor ligands such as CO make oxidation more difficult (compare the behaviors of **6** and **7a** as shown in Scheme 4). Step B is a one-electron transfer reaction and the rate-determining step. Step D is in partial agreement with the proposed mechanism for the ruthenium-catalyzed aerobic oxidation (by molecular oxygen) of amines.[15,16,38] However, our results do not support the notion that the formation of Ru−H species is always required. Thus, for instance, in the case of the coordinatively saturated tris-chelate cationic complexes $\mathbf{2}^{2+}$, we would have to accept seven-coordinated Ru(II) or decoordination of a chelate ligand to create a vacant coordination site for the hydrido ligand. Furthermore, direct hydride removal from the methylene unit of a coordinatively saturated tungsten benzylamido complex under oxidizing conditions has been reported.[18] Attempts to detect radicals by the ESR spin−trap technique using 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) failed.

Stereochemical Considerations and Structural Characterization of Complexes in Solid and in Solution. Complex **3** has two sources of chirality. The stereogenic amino nitrogen of the coordinated ligand **1a** could have either *R* or *S* configuration, and the puckered nonplanar five-membered chelate ring of coordinated ligands **1** is also a chiral entity identified as δ or λ.[39] Two diastereomers can be anticipated for complex **3** (see Figure 1). Although the ^{1}H NMR could be assigned to the isomer (λ,*R*) and its enantiomer (δ,*S*), which allow a hydrogen bond interaction

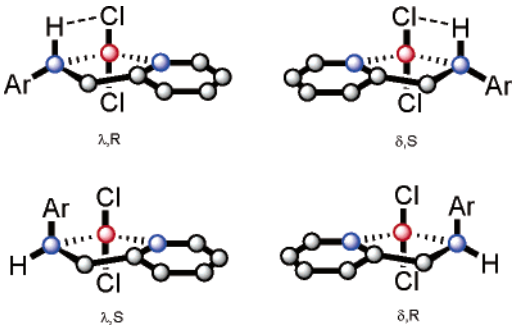


Figure 1. Four possible geometrical isomers of the octahedral complex **3**. Chelating 1,5-cyclooctadiene ligands have been omitted for clarity.

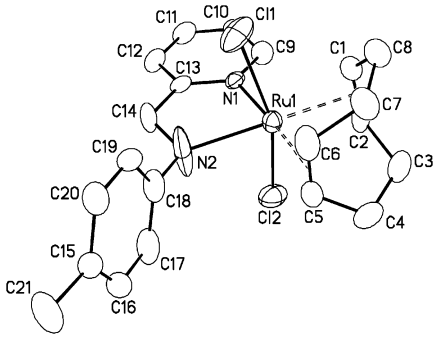


Figure 2. Crystal structure of **3**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ru1−N1, 2.102(6); Ru1−N2, 2.169(8); Ru1−Cl1, 2.404(3); Ru1−Cl2, 2.438(3); Ru1−C1, 2.187(8); Ru1−C2, 2.196(8); Ru1−C5, 2.212(7); Ru1−C6, 2.212(7); Cl1−Ru1−Cl2, 159.42(9); N1−Ru1−N2, 78.0(3); N1−Ru1−Cl1, 82.52(18); N2−Ru1−Cl1, 85.0(4); N1−Ru1−Cl2, 81.34(18); N2−Ru1−Cl2, 79.3(4).

with the chloro ligand, a rapid equilibrium exchange between both diastereomers cannot be ruled out. The energy barrier for the λ,δ conversion is, in general, expected to be very low, in the range 2−4 kcal mol^{-1}. Quantum chemical calculations performed at the PM3 level indicate that the more stable conformation is (λ,*R*) or (δ,*S*). At this level of theory, the other diastereomer (λ,*S*) or (δ,*R*) is not a minimum in the potential energy surface. ^{1}H NMR variable temperature experiments in the range 193−300 K in d^6-acetone showed no signals of dynamic behavior.

The anisotropic displacement parameters of atom N(2) in the structure of complex 3 (see Figure 2) reveal what appears to be disorder of this atom in a direction roughly perpendicular to the plane of the other four atoms of the five-membered chelate ring. Given that the diffraction data were less than ideal in this case, we cannot rule out the possibility that the anomalous elongation of the ellipsoid for N(2) is an artifact of the refinement. However, the elongation also has a plausible chemical and structural interpretation, which is supported by the finer numerical analysis of the displacement parameters of N(2) and the atoms around it. (Details of this analysis are available from the authors.) Taking into account that the complex has two origins of chirality (the asymmetric N(2), which can have either an *R*- or *S*-configuration, and the five-membered chelate ring, which can be in either the λ or δ conformation), and noting also that N(2) is the "flap" atom of the envelope formed by the chelate ring, we can consider two possibilities for explaining such disorder. First, fluxionality based on the movement of N(2) in the direction

(37) Prabhakar, R.; Siegbahn, P. E. M.; Minaev, B. F. *Biochim. Biophys. Acta* **2003**, *1647*, 173−178.
(38) Diamond, S. E.; Mares, F. *J. Organomet. Chem.* **1977**, *142*, c55.
(39) Petra, D. G. I.; Reek, J. N. H.; Handgraaf, J. W.; Meijer, E. J.; Dierkes, P.; Kamer, P. C. J.; Brussee, J.; Schoemaker, H. E.; van Leeuwen, P. *Chem.—Eur. J.* **2000**, *6*, 2818−2829.

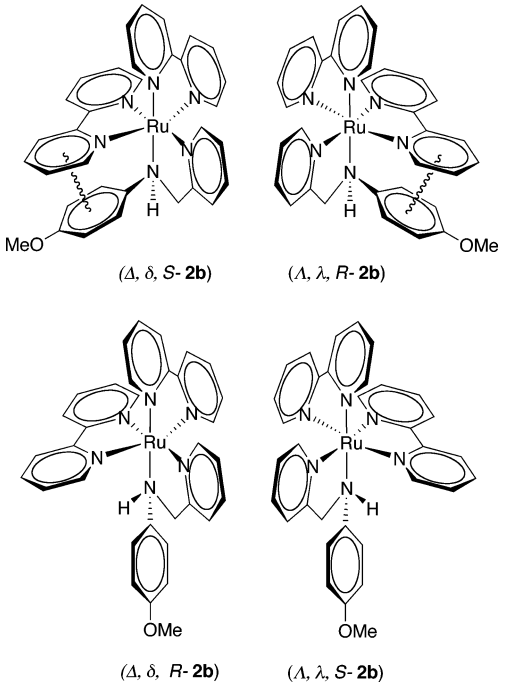


Figure 3. Top: π-interaction allowed, diastereomer is formed. Down: π-interaction is not allowed, diastereomer is not formed.

indicated by the displacement ellipsoid would give rise to two diastereomers, for example, (δ,*S*) and (λ,*S*). This would mean that the hydrogen bond N(2)−H(2A)···Cl(1) favored in diastereomer (δ,*S*) would be a longer contact after fluxional motion to (λ,*S*). Second, a static model on the basis of configurational disorder about N(2)-*R/S,* with hydrogen pointing toward either Cl(1) or Cl(2) and with concomitant stabilization of one five-membered ring conformation or the other, would yield a disorder of the enantiomers (δ,*S*) and (λ,*R*) and would lead to the same results from the structure analysis. In either case, the crystal is racemic on the whole, as the centric space group indicates, although either of the models considered could give rise to local deviations from stereochemical parity. Because the shape and topology of the molecule are such that neither the conformation of the chelate ring nor the stereochemistry about N(2) is expected to influence crystal packing significantly, it is possible that both conformational fluxionality and configurational disorder about N(2) are in play.

The cationic complexes $\mathbf{2}^{2+}$, $\mathbf{4}^{+}$, $\mathbf{5}^{+}$, $\mathbf{6}^{+}$, and $\mathbf{7}^{+}$ have three sources of chirality. In addition to those described for complex **3**, cationic complexes $\mathbf{2}^{2+}$ have helical structures with Δ and Λ descriptors for a right or left helix.[1] The cationic complexes $\mathbf{4}^{+}$−$\mathbf{7}^{+}$ have instead R_{Ru}, S_{Ru} configurations for the stereogenic ruthenium-metal center (R_N and S_N refer to the configuration of the chiral nitrogen atom). Eight geometrical isomers (four chiral diastereomers and their four enantiomers) can be anticipated for complexes with three sources of chirality.

The ^{1}H NMR spectra of compounds **2** again show that only one diastereomer is specifically formed. Molecular models indicate that only the combination Λ,λ,*R* (or its enantiomer Δ,δ,*S*) is sterically acceptable. It is interesting to note that the combination is the same as that found in

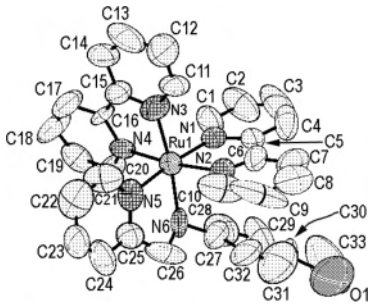


Figure 4. Crystal structure of Λ,λ,*R*-[**2b**]$^{2+}$. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ru1−N1, 2.01(3); Ru1−N2, 2.08(2); Ru1−N3, 2.06(2); Ru1−N4, 2.03(2); Ru1−N5, 2.08(2); Ru1−N6, 2.09(3); N1−Ru1−N5, 173.8(11); N2−Ru1−N4, 172.9(10); N3−Ru1−N6, 172.3(9). These values are provided as a general guide to the coordination geometry; see the Experimental Section for a caveat regarding the quality of this structure determination.

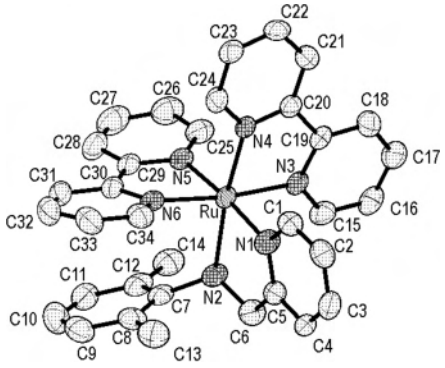


Figure 5. Crystal structure of Δ,δ,*S*-[**2c**]$^{2+}$. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ru−N1, 2.079(5); Ru−N2, 2.200(5); Ru−N3, 2.075(5); Ru−N4, 2.039(5); Ru−N5, 2.054(5); Ru−N6, 2.062(6); N1−Ru−N5, 174.9(2); N2−Ru−N4, 173.1(2); N3−Ru−N6, 172.2(2).

complex **3** that allows the aryl group to be arranged in a less-crowded equatorial position in the five-membered chelate ring (see Figure 1). The diastereomer Λ,λ,*R* allows π-interactions between one of the 2,2′-bipyridine rings and the aryl group (see Figure 3). NOE 1D experiments carried out for compound **2a** showed interaction between the *o*-hydrogens of the aryl group and the hydrogen atoms H^4, H^5, and H^6 of one of the bipyridine rings. For compound **2c**, NOE interactions were observed between the hydrogen atoms of the 2,6-dimethyl groups and the hydrogen atoms H,^{4} H^5, and H^6 of one of the bipyridine rings. Also in compound **2c**, anisotropic shifts were observed for the 2,6-dimethyl groups that appear nonequivalent below 2 ppm in the spectrum, indicating that free rotation of the aryl group is not allowed.

The solid-state structure determination of **2b** (Figure 4) confirms that both enantiomers Λ,λ,*R* and Δ,δ,*S* are present in the unit cell. The angle between the planes of the rings that allow π-interactions is 31.4(10)° and the distance between centroids is 4.12 Å, so although it no doubt contributes to the stability of the molecule, this interaction is significantly "slipped."

A thermal ellipsoid plot of **2c** is shown in Figure 5.

The cation is a six-coordinate Ru(II) tris chelato complex containing two 2,2′-bipyridine ligands and the chelating amine−pyridine ligand 2,6-(CH$_3$)$_2$C$_6$H$_3$NH-CH$_2$-2-C$_5$H$_4$N.

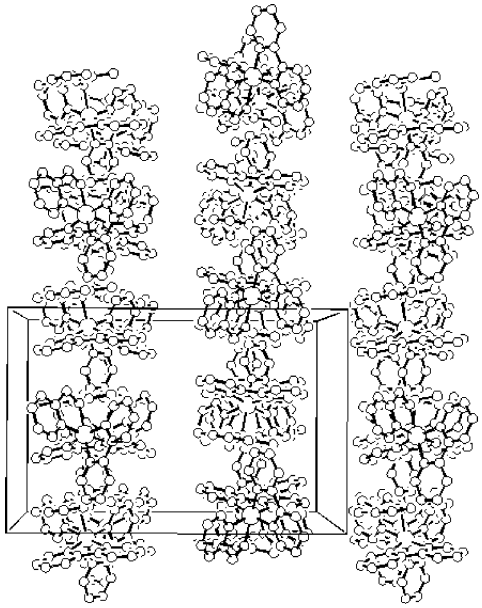


Figure 6. Perspective drawing of the extended structure of **2c** showing the columnar stacking arrangement. Hydrogen atoms have been omitted for clarity.

The asymmetric unit of the crystal structure comprises a single cation of $[\mathbf{2c}]^{2+}$, along with PF_6^- anions and interstitial solvent sites; because the space group (*Pbca*) is centric, both enantiomers Λ,λ,R and Δ,δ,S of the ruthenium complex are present in equal numbers in the unit cell. The aryl (2,6-dimethylphenyl) ring of the amine−pyridine moiety is oriented so as to be nearly parallel to, and partially eclipsed with, the plane of a coordinated bipyridine (atoms C(30)−C(34) and N(6)) of the same molecule. The intramolecular distance between the rings is 3.43 Å, calculated as the distance between the two ring centroids, projected onto the cell edge *a*. The two rings are not quite parallel to each other, with a dihedral angle of 14.91 (17)°. The same aryl ring is also nearly eclipsed with a symmetrically equivalent bipyridine entity (also C(30)−C(34) and N(6)) of the neighboring molecule, a mirror image of the first, at $(0.5 + x, y, 0.5 - z)$, to give an unbounded ring-stacking pattern propagated in a direction parallel to the crystallographic *x*-axis. The intermolecular distance between the rings, calculated as before, is 3.70 Å, and the dihedral angle is 13.57(17)°. The stacking gives an overall columnar appearance to the extended crystal structure when viewed along the crystallographic *c*-axis, as shown in Figure 6. In fact, the columns are further packed into slabs that extend in the z-direction. The maximal radius of the columns, or thickness of the extended slabs, is roughly 6.5 Å; and the space between them, which is occupied by the anions and interstitial solvent, is about 4.3 Å thick. The bond distances and angles in the structures of **2b**,**c** fall into the expected ranges of values for the bond types involved.

Table 2. Anodic Peak and Half-Wave Potentials[a]

	2a	2b	2c[b]	8a	8b	8c	8d
E_{pk} (V)	1.32	1.31	1.28				
$E_{1/2}$ (V)	1.46	1.45	1.42	1.47	1.48	1.46	1.51

[a] Scan rate = 100 mV s^{-1}. Potentials vs SCE; Pt bead electrode; in dichloromethane and tetrabutylammonium hexafluorophosphate as the supporting electrolyte. [b] In the reverse scan, a new reversible wave appears at $E_{1/2} = +0.8$ V.

The geometry of cationic complexes $\mathbf{4}^+$ could lead to eight different geometric isomers, as shown in Figure 7. Once again, only one diastereoisomer (as an enantiomeric pair) is specifically formed in solution.

The ^{1}H NMR spectra for compounds **4** and **5** are assigned to the diastereomer R_{Ru},δ,S_N and its enantiomer S_{Ru},λ,R_N, the only stereochemistry that allows intramolecular hydrogen bonding between the N−H bond and the chloro ligand. This assignment is in agreement with the X-ray structural characterization of **4a** (See Figure 8), in which the distance N(2)−H···Cl(1) is 2.603 Å, which is in the accepted range for such interactions.[19,40] The stereochemical analysis of the crystal structure of **4a** unequivocally shows that both enantiomers are present in the unit cell and form a noncovalent dimer through intermolecular hydrogen bonding with an N−H···Cl distance of 2.629 Å. As already mentioned for compounds **3**, **2b**, and **2c**, the chelating ligand **1a** arranges in **4a** in such a way as to permit the aryl group to occupy an equatorial position of the chelate ring.

In contrast to compounds **4** and **5**, compounds **6** and **7**, which allow the same stereochemical analysis shown in Figure 7, were synthesized as mixtures of two diastereomers. As the main difference is the change of the chloro ligand in **4** and **5** for a neutral (CO or CH_3CN) ligand in **6** and **7**, we suggest that the driving force for the diastereospecificity in the synthesis of complexes **4** and **5** is the possibility of forming a hydrogen bond. In the absence of this stabilizing factor, two diastereoisomers appeared for **6** and **7** (likely those two containing the aryl group in the equatorial position).

Electrochemistry. Cyclic voltammetry of compounds **2** in dichloromethane shows two anodic peaks and a cathodic

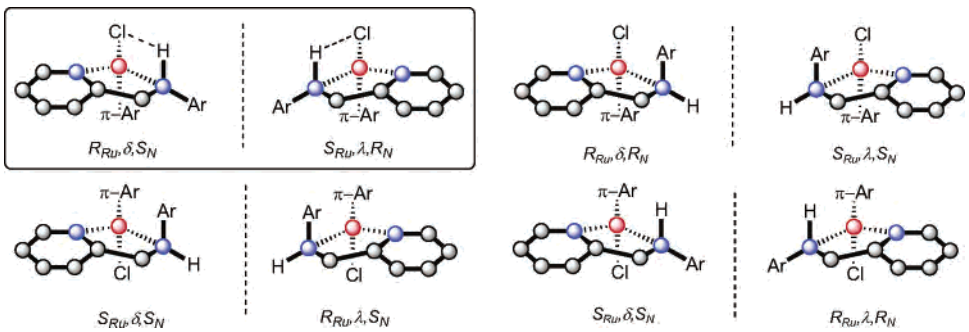


Figure 7. Eight possible geometric isomers for cationic complexes $\mathbf{4}^+$ and $\mathbf{5}^+$. Only the framed couple of enantiomers R_{Ru}, δ, S_N and S_{Ru}, λ, R_N is actually formed.

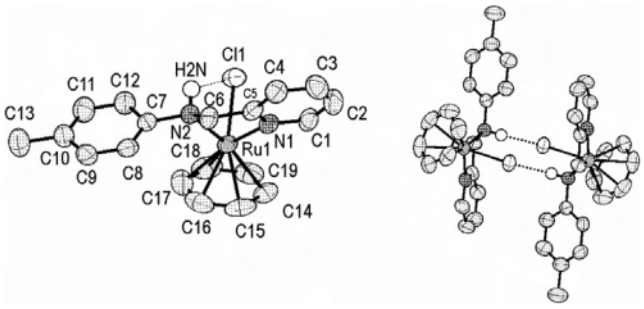


Figure 8. Left: Crystal structure of S_{Ru},λ,R_N-**4a**. Right: Assembly of pairs of enantiomers R_{Ru},δ,S_N and S_{Ru},λ,R_N. Hydrogen atoms have been omitted for clarity (hydrogen atoms involved in hydrogen bonding interactions are shown). Selected bond distances (Å) and angles (deg): Ru1−Cl1, 2.403(14); Ru1−N1, 2.093(5); Ru1−N2, 2.139(4); Ru1−C14, 2.182(6); Ru1−C15, 2.166(6); Ru1−C16, 2.159(6); Ru1−C17, 2.175(7); Ru1−C18, 2.192(6); Ru1−C19, 2.168(6); N1−Ru1−Cl1, 84.83(12); N2−Ru1−Cl1, 83.34(13); N1−Ru1−N2, 76.86(16).

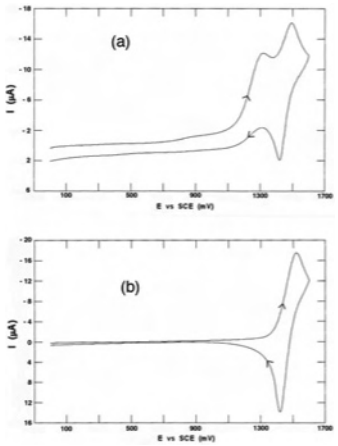


Figure 9. Cyclic voltammograms of **2a** (a) and **8a** (b). In dichloromethane, 0.1 M [NBu_4^n][PF_6] at a Pt bead electrode. Scan rate = 100 mV s^{-1}.

peak as shown in Figure 9a for **2a**. In the reverse scan, **2c** shows an additional small wave at $E_{1/2} = +0.8$ V that is apparently reversible under successive scans. Imine derivatives show a reversible wave, as shown in Figure 9b for **8a**. The data are collected in Table 2.

Similar voltammograms have been reported for related cationic complexes [Ru(bipy)$_2${2-(aminomethyl)pyridine}]$^{2+}$,[41] [Ru(bipy)$_2$(α-iminoacidato)]$^+$, and [Ru(bipy)$_2$(α-iminoacidato)]$^+$.[42] By analogy with previous reported data, the irreversible anodic peak is considered to be a one-electron oxidation of **2** to **2**$^+$. The apparently reversible couple in the voltammograms of salts **2** is attributed to the transformation of **2**$^+$ into **8**. The reversible couple was unequivocally assigned by recording the cyclic voltammograms of **8**, as shown in Figure 9b for **8a**.

The additional wave shown by **2c** can be attributed to a chemical reaction on the para position of the aryl ring, as reported in complexes containing such arylamino groups.[43,44]

Conclusions

Coordination of chiral N, N′ bidentate ligands 2-(arylaminomethyl)pyridine ArNH-CH_2-2-C_5H_4N **1** (Ar = 4-CH_3-C_6H_4, **1a**; 4-CH_3O-C_6H_4, **1b**; 2,6-$(CH_3)_2$-C_6H_4, **1c**; 4-CF_3-C_6H_4, **1d**) to the moieties [Ru(bipy)$_2$]$^{2+}$, [$RuCl_2$(COD)], (COD = 1,5-cyclooctadiene), [Ru(η^5-C_5H_5)L]$^+$ (L = CH_3CN, CO), or [Ru(η^6-arene)Cl]$^{2+}$ (arene = benzene, *p*-cymene) occurs under diastereoselective or diastereospecific conditions. Coordination of these secondary amine ligands activates their oxidation to imines by molecular oxygen, which is reduced to hydrogen peroxide. The oxidation of amine complexes to imine complexes by molecular oxygen is strongly dependent not only on the ancillary ligands coordinated to ruthenium but also on the substituents of the aryl group. Electrochemical oxidation of the amine complexes, under cyclic voltammetric conditions, resulted in the formation of imine complexes. Deprotonation of the coordinated amine ligands afforded isolatable amido complexes only when the β hydrogen atoms were excluded. The structures of complexes [Ru(2,2′-bipyridine)$_2$(1b)](PF_6)$_2$, **2b**; [Ru(2,2′-bipyridine)$_2$(1c)](PF_6)$_2$, **2c**; *trans*-[$RuCl_2$(COD)(1a)], **3**; and [$RuCl_2$(η^6-C_6H_6)(1a)]PF_6, **4a**, have been confirmed by X-ray diffraction studies.

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Supporting Information Available: Supplementary X-ray data submitted in CIF format for complexes **2b**,**c**, **3**, and **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(40) Soleimannejad, J.; Sisson, A.; White, C. *Inorg. Chim. Acta* **2003**, *352*, 121−128.
(41) Ridd, M. J.; Keene, F. R. *J. Am. Chem. Soc.* **1981**, *103*, 5733−5740.
(42) Yamaguchi, M.; Machiguchi, K.; Mori, T.; Kikuchi, K.; Ikemoto, I.; Yamagishi, T. *Inorg. Chem.* **1996**, *35*, 143−148.
(43) Espinet, P.; Alonso, M. Y.; García-Herbosa, G.; Ramos, J. M.; Jeannin, Y.; Philochelevisalles, M. *Inorg. Chem.* **1992**, *31*, 2501−2507.
(44) Albeniz, A. C.; Calle, V.; Espinet, P.; Gomez, S. *Chem. Commun.* **2002**, 610−611.