Synthesis of a Configurationally Stable Three-Legged Piano-Stool Complex

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Summary: Anchoring a phosphine and an enantiopure camphorpyrazole tether to an arene (PArN) yields, after η^6:η^1:η^1 coordination to ruthenium, $[\{\eta^6:\eta^1:\eta^1\text{-(PArN*)}\}\text{-RuL}]^{2+}$ as a 1:1 mixture of diastereomers. These were separated and characterized by X-ray crystallography. The structure of the R,R_P,S_{Ru} diastereomer is depicted.*

Introduction

With the advent of electronically asymmetric bidentate ligands, the C_2 dogma that had guided chemists in the design of chiral ligands for enantioselective catalysis for two decades was seriously questioned.[1] Introducing electronic asymmetry at the metal helps to desymmetrize an incoming prochiral substrate not only by steric factors but also through the electronic factors imposed by the bidentate ligand.[2] In this context, the role of *metal-based chirality* resulting from coordination of a C_1-symmetric bidentate ligand to a metal template has received little attention. We wish to report our preliminary results on the design, the synthesis, and the characterization of configurationally stable, diastereomerically pure piano-stool complexes.

Results and Discussion

To address the question of the role of chirality at the metal in enantioselective catalysis, we focus on pseudo-tetrahedral three-legged piano-stool complexes. The presence of an arene and a bidentate ligand leaves one free site for substrate activation and functionalization. Ever since the pioneering work of Brunner on chiral-at-metal piano-stool complexes, many examples of synthesis, resolution, and enantioselective *stoichiometric* applications of chiral piano-stool complexes, devoid of ligand-based chirality, have been published.[3−15]

Theoretical studies on the configurational stability of coordinatively unsaturated two-legged piano-stool complexes of the type $[(\eta^n\text{-}C_nH_n)ML^1L^2]$ ($n = 5-7$) suggest that, although some of these indeed possess pyramidal (and thus chiral-at-metal) ground-state geometries, the computed inversion barriers are low, i.e., <15 kcal mol^{-1}, thus hampering their use as enantioselective catalysts.[16]

In analogy to Tröger's base, we reasoned that incorporation of the metal in a "bicyclic" framework would significantly raise the inversion barriers of the resulting complexes. Tethering a phosphine and a pyrazole to an arene yields a potential 10-electron donor (abbreviated PArN*) with a pronounced electronic asymmetry. Upon η^6:η^1:η^1 coordination to Ru(II), a three-legged piano-stool complex is formed: $[\{\eta^6:\eta^1:\eta^1\text{-(PArN*)}\}\text{RuL}]^{2+}$ (L = weakly bound solvent). For the preliminary studies reported herein, an enantiopure auxiliary was incorporated in the PArN* ligand, facilitating analysis and diastereomer separation. Related complexes, devoid of ligand-based chirality (i.e. camphorpyrazole replaced by achiral pyrazole derivatives), are currently being studied in our laboratories as well.[19]

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(18) Crystal structure analysis of (R,R_P,S_{Ru})-**7a** and (R,S_P,R_{Ru})-**7b**: Siemens SMART CCD diffractometer,[20] $T = 293$ K, Mo Kα radiation (0.710 73 Å). A complete hemisphere of data was scanned on ω (0.30) with a run time of 60 s, at a detector resolution of 512 × 512 pixels and a detector distance of 5.18 cm. A total of 1271 frames were collected for each data set; the collected frames were processed with the SAINT program,[21] which automatically performs Lorentz and polarization corrections. The structure was solved by direct methods, and the refinement was done by full-matrix least squares of F^2 using SHELXL96[22] (β-test version). (R,R_P,S_{Ru})-**7a**, $C_{34}H_{37}F_6N_2O_7PRuS_2$ (fw = 895.82): orthorhombic, space group $P2_12_12_1$, $a = 9.9095(4)$ Å, $b = 18.3768(7)$ Å, $c = 20.7991(8)$ Å, $V = 3787.6(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.571$ g cm^{-3}, $F(000) = 1824$, $\mu = 0.645$ mm^{-1}, crystal size 0.06 × 0.11 × 0.32 mm; 19 118 measured reflections ($-12 \le h \le 12$, $-22 \le k \le 18$, $-23 \le l \le 24$), 7137 unique reflections. Refinement of 556 variables with anisotropic thermal parameters for all non-hydrogen atoms gave $R = 0.0546$, $R_w = 0.1368$, and $S = 1.164$; residual electron density 1.793, −0.442 e Å^{-3}. (R,S_P,R_{Ru})-**7b**, $C_{34}H_{37}F_6N_2O_7PRuS_2$ (fw = 895.82): monoclinic, space group $P2_1$; $a = 8.2085(1)$ Å, $b = 21.5806(4)$ Å, $c = 11.372(6)$ Å, $\beta = 110.95(2)°$, $V = 1881.34(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.581$ g cm^{-3}, $F(000) = 912$, $\mu = 0.649$ mm^{-1}, crystal size (0.10 × 0.18 × 0.27 mm); 9525 measured reflections ($-8 \le h \le 10$, $-24 \le k \le 27$, $-14 \le l \le 13$), 5998 unique reflections. Refinement of 494 variables with anisotropic thermal parameters for all non-hydrogen atoms gave $R = 0.0465$, $R_w = 0.1001$, and $S = 1.103$; residual electron density 0.618, −0.385 e Å^{-3}.

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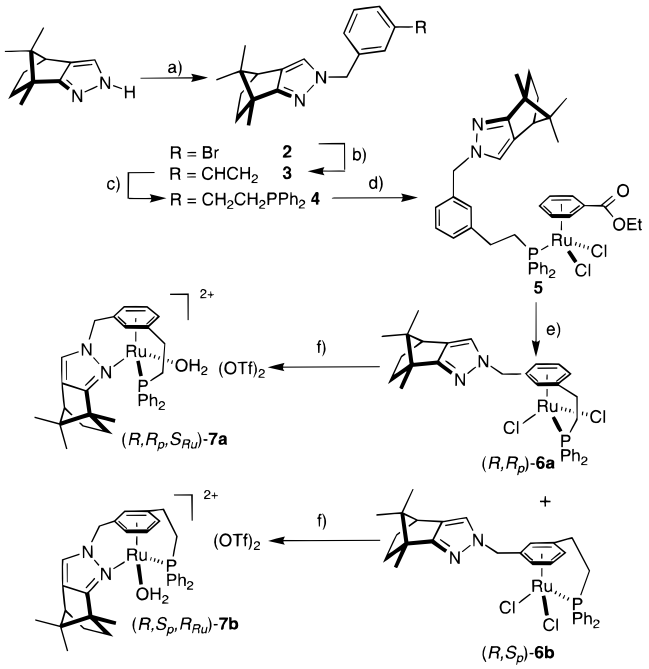

Figure 1. Preparation of diastereopure complexes **7**. Legend: (a) NaH, DMF, 60 °C, 3 h then 3-bromobenzyl bromide, 60 °C 20 h (58%); (b) $[Pd(PPh_3)_4]$, $Bu_3Sn(CHCH_2)$, toluene, 100 °C, 16 h (81%); (c) $HPPh_2$, AIBN, CH_2Cl_2, $h\nu$ (63%); (d) 0.5 equiv of $[(\eta^6\text{-}C_6H_5CO_2Et)RuCl_2]_2$, CH_2Cl_2, room temperature, 0.5 h (96%); (e) CH_2Cl_2, 110 °C, 24 h (63%); (f) excess CF_3SO_3Tl, THF/H_2O (91%).

The ligand synthesis is outlined in Figure 1. Nucleophilic substitution with enantiopure camphorpyrazole **1** on 3-bromobenzyl bromide yields exclusively the regioisomer **2** (by ^1H NMR). The phosphine donor was incorporated in two steps: a Stille coupling between bromoarene **2** and $Bu_3SnCH{=}CH_2$ yields the styrene derivative **3**, which regioselectively adds $HPPh_2$ to afford PArN* (**4**) in 30% overall yield. Phosphine coordination to the labile $[(\eta^6\text{-}C_6H_5CO_2Et)RuCl_2]_2$[17] cleaves the dimer, yielding $[(\eta^6\text{-}C_6H_5CO_2Et)Ru\{\eta^1\text{-}(PArN^*)\}RuCl_2]$ (**5**). Thermal arene displacement cleanly affords $[\{\eta^6{:}\eta^1\text{-}(PArN^*)\}RuCl_2]$ (**6**). Upon η^6-coordination of the prochiral arene, a planar chiral complex results. Despite the presence of a bulky chiral auxiliary, complex **6** is formed as a 1/1 mixture of diastereomers (by ^{31}P NMR). Flash chromatography on silica gel with a 5/1 CH_2Cl_2/acetone solvent mixture affords both (R,R_P)-$[\{\eta^6{:}\eta^1\text{-}(PArN^*)\}RuCl_2]$ (**6a**) and (R,S_P)-$[\{\eta^6{:}\eta^1\text{-}(PArN^*)\}RuCl_2]$ (**6b)** in diastereomerically pure form. Treating complex **6a** or **6b** with excess TlOTf in THF/H_2O displaces both chlorides to afford the aquo complex $[\{\eta^6{:}\eta^1{:}\eta^1\text{-}(PArN^*)\}Ru(OH_2)]^{2+}$ (**7a** or **7b**, respectively). Upon pyrazole coordination, the metal center becomes chiral. The presence of a single ^{31}P NMR resonance for complexes **7a** and **7b** suggests that the chiral center is formed diastereoselectively. Inspection of molecular models led us to suggest that the absolute configuration of the chirality at ruthenium is opposite to that of the planar chirality. Thus (R,R_P)-**6a** and (R,S_P)-**6b** should yield (R,R_P,S_{Ru})-$[\{\eta^6{:}\eta^1{:}\eta^1\text{-}(PArN^*)\}Ru(OH_2)]^{2+}$ (**7a**) and (R,S_P,R_{Ru})-$[\{\eta^6{:}\eta^1{:}\eta^1\text{-}(PArN^*)\}Ru(OH_2)]^{2+}$ (**7b**), respectively.

Suitable crystals for X-ray analysis were obtained for both diastereomers **7a** and **7b** from $CHCl_3$.[18] The molecular structures of both diastereomers (R,R_P,S_{Ru})-$[\{\eta^6{:}\eta^1{:}\eta^1\text{-}(PArN^*)\}Ru(OH_2)]^{2+}$ (**7a**) and (R,S_P,R_{Ru})-$[\{\eta^6{:}\eta^1{:}\eta^1\text{-}(PArN^*)\}Ru(OH_2)]^{2+}$ (**7b**) are presented in parts a and b, respectively, of Figure 2. The quasi-enantiomer relationship between **7a** and **7b** is emphasized. Relevant bond lengths and angles for complexes **7** are collected in Table 1. The bond lengths for both complexes **7** are very similar to those reported for related, less strained ruthenium piano-stool complexes.[17,19] In particular, we recently reported the structural characterization of *rac*-$[\{\eta^6{:}\eta^1{:}\eta^1\text{-}(PArN)\}Ru(OH_2)]^{2+}$ **(A),** where the camphorpyrazole (of PArN*) is replaced by the electron-deficient 3,5-bis(trifluoromethyl)pyrazole.[19] For comparison, metrical data for this complex are included in Table 1.

On the basis of molecular models, we anticipated that pyrazole coordination for the sterically loaded diastereomer **7a** ($C(CH_3)_2$-bridge and CH_3 of bridgehead of camphor clashing with the phenyl group of the phosphine vs the CH_2CH_2 bridge of camphor for **7b**) may be problematic. The steric clash is reflected in the angles around the ruthenium. For **7a** both N(1)−Ru(1)−P(1) and O(1)−Ru(1)−P(1) bite angles (101.1(2) and 94.0(1)°) are significantly larger that for **7b** (99.4(1) and 90.4(1)°). The 1,3-substitution pattern of the phosphine−imine tethers on the arene imposes rather large N(1)−Ru(1)−P(1) bite angles (101.1(2) and 99.4(1)°). Although the η^6-coordinated arene remains essentially planar (greatest out-of-plane deviation: 0.0337 Å for C(3) of **7a** and 0.0393 Å for C(3) of **7b**), the out-of-plane deviations of C(7) and C(19) from the best plane defined by the η^6-coordinated arene are noteworthy: 0.228 and 0.4161 Å for **7a** and 0.179 and 0.432 for **7b**.

Conclusion

Tethering two electronically asymmetric donors on an arene affords the 10-electron donor ligand PArN* adapted for piano-stool coordination geometries. Incorporation of an enantiopure camphor moiety in the PArN* skeleton allows chromatographic separation of the diastereomers resulting from η^6: η^1 coordination of PArN* to Ru(II). Coordination of the pyrazole occurs diastereoselectively to afford the chiral-at-metal $[\{\eta^6{:}\eta^1{:}\eta^1\text{-}(PArN^*)\}Ru(OH_2)](OTf)_2$ (**7**). Both diastereomers (R,R_P,S_{Ru})-**7a** and (R,S_P,R_{Ru})-**7b** were structurally characterized. It appears that the chirality at the metal is encoded by the planar chirality. All attempts to epimerize the complex by either heating or irradiation have yielded decomposition products rather than epimerization products (by ^{31}P NMR). We are currently testing these complexes as Lewis acid catalysts for Diels−Alder and Mukaiyama aldol reactions.

Experimental Section

Synthesis of 2-(3-Bromobenzyl)-7,8,8-trimethyl-4,5,6,7-tetrahydro-2*H*-4,7-methanoindazole (2). To a NaH suspen-

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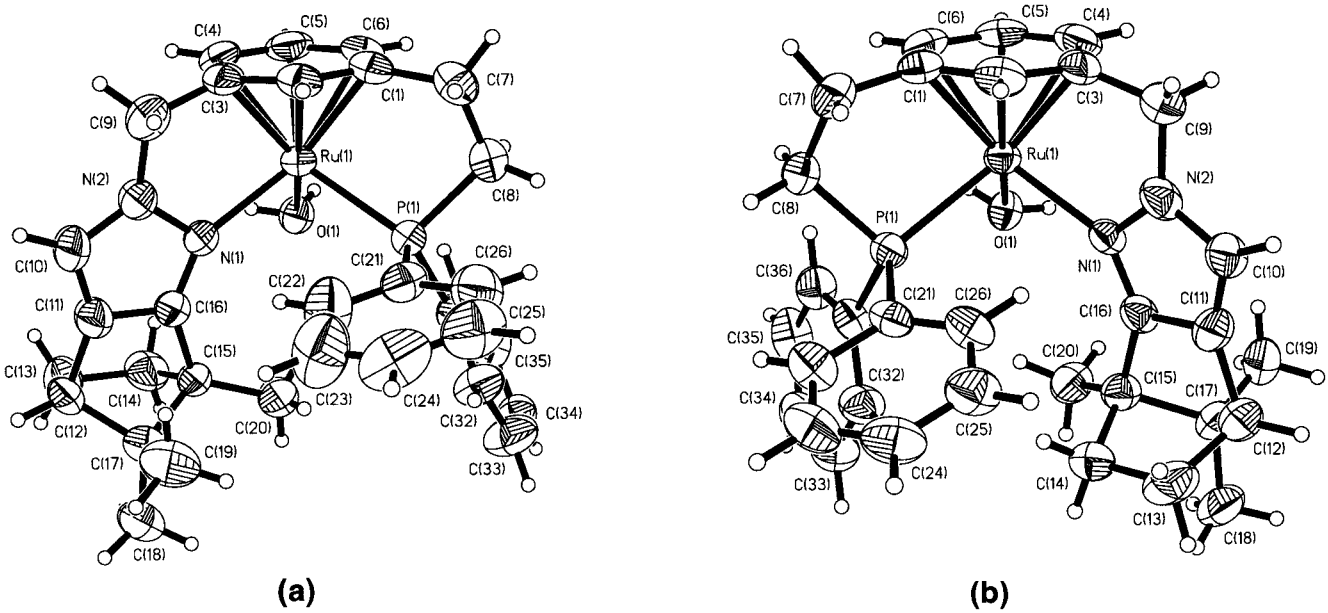

Figure 2. Molecular structures of $[\{\eta^6{:}\eta^1{:}\eta^1\text{-(PArN*)}\}Ru(OH_2)]^{2+}$ (**7**): (a) (R,R_P,S_{Ru})-**7a**; (b) (R,S_P,R_{Ru})-**7b.** Thermal ellipsoids are at the 50% probability level.

Table 1. Selected Interatomic Distances (Å), Angles (deg), and Torsion Angles (deg) for (R,R_P,S_{Ru})-$[\{\eta^6{:}\eta^1{:}\eta^1\text{-(PArN*)}\}Ru(OH_2)]^{2+}$ (7a) and (R,S_P,R_{Ru})-$[\{\eta^6{:}\eta^1{:}\eta^1\text{-(PArN*)}\}Ru(OH_2)]^{2+}$ (7b) as Well as *rac*-$[\{\eta^6{:}\eta^1{:}\eta^1\text{-(PArN)}\}Ru(OH_2)]^{2+}$ (A)[19]

	7a	7b	A
Ru(1)−P(1)	2.380(2)	2.379(2)	2.387(2)
Ru(1)−N(1)	2.144(5)	2.145(5)	2.163(4)
Ru(1)−O(1)	2.155(5)	2.132(4)	2.134(4)
Ru(1)−C_{arene}(mean)	2.197(7)	2.192(7)	2.186(5)
N(1)−Ru(1)−O(1)	85.2(2)	89.2(2)	88.8(2)
O(1)−Ru(1)−P(1)	94.0(1)	90.4(1)	88.6(1)
N(1)−Ru(1)-P(1)	101.1(2)	99.4(1)	102.2(1)
N(1)−N(2)−C(9)−C(3)	22.9(9)	21.3(10)	2.0(8)
C(1)−C(7)−C(8)−P(1)	47.1(7)	−45.1(8)	−46.4(7)

sion (75 mmol) in DMF (150 mL) was cautiously added camphorpyrazole (**1**;[23] 26 g, 68 mmol) portionwise at 0 °C. The mixture was subsequently stirred for 3 h at 60 °C. 3-Bromobenzyl bromide (17 g, 68 mmol) was then added and the solution heated at 60 °C for 20 h. After evaporation of the volatile material, the product was purified by flash chromatography (hexane/Et_2O 5/1), affording bromocamphorpyrazole (**2**; 13.5 g, 58% yield). ^{1}H NMR ($CDCl_3$): δ 7.32 (ddd, $^3J_{H-H}$ = 7.7 Hz, $^4J_{H-H}$ = 1.1 Hz, and $^4J_{H-H}$ = 0.7 Hz, 1H, CH_{ar}), 7.15 (dd, $^4J_{H-H}$ = 0.7 Hz, 1H, CH_{ar}), 7.12 (dd, 1H, CH_{ar}), 6.98 (ddd, 1H, CH_{ar}), 6.88 (s, 1H, CH_{pyr}), 5.18 (dd, $^2J_{H-H}$ = 16.0 Hz, 2H, CH_2N), 2.73 (d, $^3J_{H-H}$ = 4.0 Hz, 1H, CH_{camp}), 2.04 (m, 1H, CH_{2-camp}), 1.82 (ddd, 1H, CH_{2-camp}), 1.29 (s, 3H, CH_{3-camp}), 1.28 (m, 1H, CH_{2-camp}), 1.14 (m, 1H, CH_{2-camp}), 0.93 (s, 3H, CH_{3-anti}), 0.68 (s, 3H, CH_{3-syn}). ^{13}C NMR ($CDCl_3$): δ 167.7 (C_{pyr}), 141.7 (C_{pyr}), 131.5 (CH_{ar}), 131.1 (CH_{ar}), 130.9 (CH_{ar}), 128.6 (C_{ar}), 126.4 (CH_{ar}), 123.7 (CBr), 122.8 (CH_{pyr}), 61.6 (C_{camp}), 55.4 (CH_2N), 51.3 (C_{camp}), 48.3 (CH_{camp}), 34.8 (CH_{2-camp}), 28.8 (CH_{2-camp}), 21.5 (CH_{3-syn}), 20.2 (CH_{3-anti}), 11.7 (CH_{3-camp}). Anal. Calcd for $C_{18}H_{21}BrN_2$: C, 62.6; H, 6.1; N, 8.1. Found: C, 62.8; H, 6.1; N, 8.0.

Synthesis of 7,8,8-Trimethyl-2-(3-vinylbenzyl)-4,5,6,7-tetrahydro-2*H*-4,7-methanoindazole (3). The bromoarene **2** (5.5 g, 16 mmol), $Bu_3Sn(CH{=}CH_2)$ (5.3 g, 16.7 mmol), and $Pd(PPh_3)_4$ (370 mg, 0.32 mmol) were dissolved in toluene (80 mL) and heated at 100 °C for 16 h. After solvent removal in vacuo, the product was purified by flash chromatography (hexane/ethyl acetate 5/2) to afford vinylcamphorpyrazole (**3**; 3.8 g, 81% yield). ^{1}H NMR ($CDCl_3$): δ 7.26 (d, $^3J_{H-H}$ = 7.7 Hz, 1H, CH_{ar}), 7.22 (dd, $^3J_{H-H}$ = 7.0 Hz, 1H, CH_{ar}), 7.10 (s, 1H, CH_{ar}), 6.99 (d, 1H, CH_{ar}), 6.88 (s, 1H, CH_{pyr}), 6.63 (dd, $^3J_{H-H}$ = 17.7 Hz and $^3J_{H-H}$ = 11.0 Hz, 1H, CH_{vinyl}), 5.64 (dd, $^2J_{H-H}$ = 0.7 Hz, 1H, $CH_{2-vinyl}$), 5.22 (dd, $^2J_{H-H}$ = 16.0 Hz, 2H, CH_2N), 5.18 (dd, 1H, $CH_{2-vinyl}$), 2.73 (d, $^3J_{H-H}$ = 4.1 Hz, 1H, CH_{camp}), 2.05 (m, 1H, CH_{2-camp}), 1.84 (ddd, 1H, CH_{2-camp}), 1.32 (s, 3H, CH_{3-camp}), 1.30 (ddd, 1H, CH_{2-camp}), 1.17 (ddd, 1H, CH_{2-camp}), 0.94 (s, 3H, CH_{3-anti}), 0.71 (s, 3H, CH_{3-syn}). ^{13}C NMR ($CDCl_3$): δ 166.7 (C_{pyr}), 139.0 (C_{pyr}), 138.3 (C_{ar}), 137.0 (CH_{vinyl}), 129.2 (CH_{ar}), 127.8 (C_{ar}), 126.8 (CH_{ar}), 125.9 (CH_{ar}), 125.2 (CH_{ar}), 122.2 (CH_{pyr}), 114.5 ($CH_{2-vinyl}$), 61.0 (C_{camp}), 55.4 (CH_2N), 50.7 (C_{camp}), 47.8 (CH_{camp}), 34.3 (CH_{2-camp}), 28.3 (CH_{2-camp}), 21.0 (CH_{3-syn}), 19.7 (CH_{3-anti}), 11.3 (H_{3-camp}). Anal. Calcd for $C_{20}H_{24}N_2$: C, 82.1; H, 8.3; N, 9.6. Found: C, 80.2; H, 8.2; N, 9.2.

Synthesis of 2-[3-(2-(Diphenylphosphany)ethyl)benzyl]-7,8,8-trimethyl-4,5,6,7-tetrahydro-2*H*-4,7-methanoindazole (4). The styrene derivative **3** (3.8 g, 13 mmol) and AIBN (64 mg, 0.4 mmol) were dissolved in Et_2O (15 mL). The solution was degassed with three freeze−pump−thaw cycles, and $HPPh_2$ (2.9 g, 15.6 mmol, 1.1 equiv) was added. The mixture was irradiated (Hg low-pressure lamp) in a sealed Schlenk flask for 38 h. After evaporation of the volatiles in vacuo, the product was purified by flash chromatography on silica gel (hexane/ethyl acetate 5/1) to afford the phosphino−pyrazole PArN* (**4**; 3.9 g, 63% yield). ^{1}H NMR ($CDCl_3$): δ 7.43 (m, 4H, CH_{Ph}), 7.34 (m, 6H, CH_{Ph}), 7.21 (dd, $^3J_{H-H}$ = 7.7 Hz and $^3J_{H-H}$ = 7.4 Hz, 1H, CH_{ar}), 7.06 (d, 1H, CH_{ar}), 6.95 (d, 1H, CH_{ar}), 6.91 (m, 1H, CH_{ar}), 6.88 (s, 1H, CH_{pyr}), 5.17 (dd, $^2J_{H-H}$ = 16.0 Hz, 2H, CH_2N), 2.73 (d, $^3J_{H-H}$ = 4.0 Hz, 1H, CH_{camp}), 2.68 (m, 2H, C**H**$_2$$CH_2P$), 2.30 (m, 2H, CH_2C**H**$_2$P), 2.05 (m, 1H, CH_{2-camp}), 1.83 (m, 1H, CH_{2-camp}), 1.31 (s, 3H, CH_{3-camp}), 1.30 (m, 1H, CH_{2-camp}), 1.16 (m, 1H, CH_{2-camp}), 0.95 (s, 3H, CH_{3-anti}), 0.67 (s, 3H, CH_{3-syn}). ^{13}C NMR ($CDCl_3$): δ 166.7 (C_{pyr}), 140.7 (C_{pyr}), 133.5 (CH_{Ph}), 133.3 (CH_{Ph}), 129.3 (CH_{Ph}), 129.2 (CH_{ar}), 128.1 (CH_{ar}), 127.5 (CH_{ar}), 127.8 (C_{ar}), 125.5 (CH_{ar}), 122.7 (C_{ar}), 122.4 (CH_{pyr}), 61.3 (C_{camp}), 55.8 (CH_2N), 51.0 (C_{camp}), 48.1 (CH_{camp}), 34.6 (CH_{2-camp}), 32.9 (**C**H_2CH_2P), 30.6 (CH_2**C**H_2P), 28.6 (CH_{2-camp}), 21.3 (CH_{3-syn}), 19.9 (CH_{3-anti}), 11.5 (CH_{3-camp}). ^{31}P NMR (acetone-d_6): δ −16.5 ppm. Mass (FAB): *m*/*z* 478.8 (L). Anal. Calcd for $C_{32}H_{35}N_2P$: C, 80.3; H, 7.4; N, 5.9. Found: C, 79.2; H, 7.7; N, 5.8.

Synthesis of [(η^6-$C_6H_5CO_2Et$)Ru{η^1-(PArN*)}Cl_2] (5). The dimer [(η^6-$C_6H_5CO_2Et$)$RuCl_2$]$_2$ (2.35 g, 3.7 mmol) was suspended in CH_2Cl_2 (25 mL), and phosphino−pyrazole **4** (3.5 g, 7.3 mmol) was added. The mixture was stirred for 30 min at room temperature. The volume was reduced to 10 mL and the product precipitated with hexane to afford [(η^6-$C_6H_5CO_2$-Et)Ru{η^1-(PArN*)}Cl_2] (**5:** 5.6 g, 96% yield). ^{1}H NMR ($CDCl_3$): δ 7.88−7.82 (m, 4H, CH_{Ph}), 7.52−7.41 (m, 6H, CH_{Ph}), 7.04 (dd, $^3J_{H-H}$ = 7.7 Hz, $^3J_{H-H}$ = 7.7 Hz, 1H, CH_{ar}), 6.85 (d, 1H, CH_{ar}), 6.80 (d, 1H, CH_{ar}), 6.79 (s, 1H, CH_{pyr}), 6.70 (s, 1H, CH_{ar}), 6.33 (d, $^3J_{H-H}$ = 6.3 Hz, 2H, CH_{ester}), 5.44 (m, 1H, CH_{ester}), 5.08 (s, 2H, CH_2N), 5.06 (m, 2H, CH_{ester}), 4.28 (q, $^3J_{H-H}$ = 7.0 Hz, 2H, $CH_{2-ester}$), 2.83 (m, 2H, CH_2CH_2P), 2.68 (d, $^3J_{H-H}$ = 3.7 Hz, 1H, CH_{camp}), 2.36 (m, 2H, CH_2CH_2P), 2.00 (m, 1H, CH_{2-camp}), 1.78 (m, 1H, CH_{2-camp}), 1.33 (t, 3H, $CH_{3-ester}$), 1.24 (s, 3H, CH_{3-camp}), 1.24 (m, 1H, CH_{2-camp}), 1.08 (m, 1H, CH_{2-camp}), 0.89 (s, 3H, CH_{3-anti}), 0.60 (s, 3H, CH_{3-syn}). ^{13}C NMR ($CDCl_3$): δ 166.0 (CO), 163.9 (C_{pyr}), 141.9 (C_{pyr}), 138.1 (C_{Ph}), 133−128 (C_{Ar}, CH_{ar} and CH_{Ph}), 121.7 (CH_{pyr}), 94.7 (CH_{ester}), 89.5 (CH_{ester}), 86.2 (C_{ester}), 84.7 (CH_{ester}), 62.4 ($CH_{2-ester}$), 60.5 (C_{camp}), 55.0 (CH_2N), 50.2 (C_{camp}), 47.3 (CH_{camp}), 33.8 (CH_{2-camp}), 29.6 (d, $^3J_{C-P}$ = 5.5 Hz, **C**H_2CH_2P), 27.8 (CH_{2-camp}), 26.6 (d, $^2J_{C-P}$ = 27.4 Hz, CH_2**C**H_2P), 22.6 (CH_{3-syn}), 20.6 (CH_{3-anti}), 14.5 ($CH_{3-ester}$), 10.8 (CH_{3-camp}). ^{31}P NMR ($CDCl_3$): δ 23.0 ppm. Mass (FAB): *m/z* 800.7 ($RuCl_2$(PArN*)(η^6-ester)), 764.7 (RuCl-(PArN*)(η^6-ester), 730.7 (Ru(PArN*)(η^6-ester)), 649.7 ($RuCl_2$-(PArN*)), 614.7 (RuCl(PArN*)), 579.7 (Ru(PArN*)), 478.8 (PArN*). Anal. Calcd for $C_{41}H_{45}Cl_2N_2O_2PRu$: C, 61.5; H, 5.7; N, 3.5. Found: C, 61.2; H, 6.0; N, 3.3.

Synthesis of [Ru{η^6:η^1-(PArN*)}Cl_2] (6). In a Schlenk pressure vessel, the piano-stool complex [(η^6-$C_6H_5CO_2Et$)Ru-{η^1-(PArN*)}Cl_2] (**5**; 1.36 g, 1.7 mmol) was dissolved in CH_2-Cl_2 (15 mL). After three freeze−thaw−pump cycles, the orange solution was heated to 120 °C for 24 h and cooled to room temperature and the product was purified on silica gel (CH_2-Cl_2/acetone 5/1) to afford diastereomerically pure (R,R_P)-[{η^6:η^1-(PArN*)}$RuCl_2$] (**6a**) and (R,S_P)-[{η^6:η^1-(PArN*)}$RuCl_2$] (**6b**) (0.32 and 0.38 g, 28.9% and 34.3% yields, respectively). **6a:** ^{1}H NMR ($CDCl_3$) δ 7.73−7.64 (m, 4H, CH_{Ph}), 7.52 (s, 1H, CH_{pyr}), 7.40−7.33 (m, 6H, CH_{Ph}), 5.91 (dd, $^3J_{H-H}$ = 6.3 Hz, $^3J_{H-H}$ = 5.5 Hz, 1H, CH_{ar}), 5.58 (d, 1H, CH_{ar}), 5.39 (d, $^2J_{H-H}$ = 16.9 Hz, 1H, CH_2N), 5.26 (d, 1H, CH_2N), 5.01 (d, 1H, CH_{ar}), 4.46 (s, 1H, CH_{ar}), 3.47 (m, 1H, CH_2C**H**$_2$P), 3.40 (m, 1H, CH_2C**H**$_2$P), 2.81 (d, $^3J_{H-H}$ = 3.7 Hz, 1H, CH_{camp}), 2.58 (m, 2H, CH_2CH_2P), 2.06 (m, 1H, CH_{2-camp}), 1.85 (m, 1H, CH_{2-camp}), 1.24 (s, 3H, CH_{3-camp}), 1.25 (m, 1H, CH_{2-camp}), 1.12 (m, 1H, CH_{2-camp}), 0.96 (s, 3H, CH_{3-anti}), 0.71 (s, 3H, CH_{3-syn}); ^{13}C NMR ($CDCl_3$) δ 168.6 (C_{pyr}), 134−129 (C_{Ar} and CH_{Ph}), 125.0 (CH_{pyr}), 112.0 (C), 97.8 (CH_{ar}), 86.1 (CH_{ar}), 78.8 (CH_{ar}), 76.9 (CH_{ar}), 51.4 (CH_2N), 47.9 (CH_{camp}), 44.5 (d, $^2J_{C-P}$ = 33.0 Hz, CH_2**C**H_2P), 34.5 (**C**H_{2-camp}), 28.6 (d, $^3J_{C-P}$ = 5.5 Hz, **C**H_2CH_2P), 28.5 (CH_{2-camp}), 21.4 (CH_{3-syn}), 19.8 (CH_{3-anti}), 11.5 (CH_{3-camp}); ^{31}P NMR ($CDCl_3$) δ 46.4 ppm. **6b:** ^{1}H NMR ($CDCl_3$) δ 7.8−7.6 (m, 4H, CH_{Ph}), 7.51 (s, 1H, CH_{pyr}), 7.40−7.35 (m, 6H, CH_{Ph}), 5.97 (dd, $^3J_{H-H}$ = 5.9 Hz, $^3J_{H-H}$ = 5.9 Hz, 1H, CH_{ar}), 5.75 (d, 1H, CH_{ar}), 5.44 (d, $^2J_{H-H}$ = 16.9 Hz, 1H, CH_2N), 5.24 (d, 1H, CH_2N), 4.98 (d, 1H, CH_{ar}), 4.25 (s, 1H, CH_{ar}), 3.53 (m, 1H, CH_2C**H**$_2$P), 3.40 (m, 1H, CH_2C**H**$_2$P), 2.82 (d, $^3J_{H-H}$ = 3.7 Hz, 1H, CH_{camp}), 2.54 (m, 1H, CH_2CH_2P), 2.50 (m, 1H, CH_2CH_2P), 2.06 (m, 1H, CH_{2-camp}), 1.83 (m, 1H, CH_{2-camp}), 1.27 (s, 3H, CH_{3-camp}), 1.25 (m, 1H, CH_{2-camp}), 1.12 (m, 1H, CH_{2-camp}), 0.96 (s, 3H, CH_{3-anti}), 0.62 (s, 3H, CH_{3-syn}); ^{13}C NMR ($CDCl_3$) δ 134−129 (C_{Ar} and CH_{Ph}), 124.9 (CH_{pyr}), 97.8 (CH_{ar}), 86.1 (CH_{ar}), 78.8 (CH_{ar}), 76.9 (CH_{ar}), 51.4 (CH_2N), 47.9 (CH_{camp}), 44.5 (d, $^2J_{C-P}$ = 33.0 Hz, CH_2**C**H_2P), 34.5 (CH_{2-camp}), 28.6 (d, $^3J_{C-P}$ = 5.5 Hz, **C**H_2CH_2P), 28.5 (CH_{2-camp}), 21.4 (CH_{3-syn}), 19.8 (CH_{3-anti}), 11.5 (CH_{3-camp}); ^{31}P NMR ($CDCl_3$) δ 46.9 ppm; mass (FAB) *m/z* 650.9 (Ru-(PArN*)Cl_2), 614.9 (Ru(PArN*)Cl), 580.0 (Ru(PArN*)), 495.1 (P(O)ArN*), 479.5 (PArN*) Anal. Calcd for $C_{32}H_{35}Cl_2N_2PRu$: C, 59.1; H, 5.4; N, 4.3. Found: C, 56.7; H, 5.4; N, 3.9.

Synthesis of [Ru(η^6:η^1:η^1-(PArN*)(OH_2)]$(CF_3SO_3)_2$ (7a or 7b). The complex **6a** or **6b** (210 mg, 0.32 mmol) and $TlCF_3$-SO_3 (285 mg, 0.81 mmol) was dissolved in THF (5 mL). The mixture was stirred for 24 h, filtered on Celite, and evaporated to dryness; then the solid was dissolved in water, and after evaporation, **7a** or **7b** was obtained (260 mg, 0.29 mmol, 91% yield). Crystals of (R,R_P,S_{Ru})-**7a** and (R,S_P,R_{Ru})-**7b** were obtained independently by slow evaporation of a $CHCl_3$ solution. **7a**: ^{1}H NMR ($CDCl_3$) δ 7.67 (m, 2H, CH_{Ph}), 7.52 (m, 4H, CH_{Ph}), 7.42 (m, 4H, CH_{Ph}), 6.99 (s, 1H, CH_{pyr}), 6.47 (s, 1H, CH_{ar}), 6.35 (dd, $^3J_{H-H}$ = 6.1 Hz, $^3J_{H-H}$ = 6.1 Hz, 1H, CH_{ar}), 6.14 (dd, $^4J_{H-H}$ = 2.7 Hz, 1H, CH_{ar}), 5.21 (m, 1H, CH_2N and 1H, CH_{ar}), 5.05 (d, $^2J_{H-H}$ = 14.7 Hz, 1H, CH_2N), 3.72 (m, 1H, CH_2C**H**$_2$P), 3.50 (m, 1H, CH_2C**H**$_2$P), 2.80 (m, 1H, CH_2CH_2P), 2.68 (d, $^3J_{H-H}$ = 3.7 Hz, 1H, CH_{camp}), 2.55 (m, 1H, CH_2CH_2P), 1.92 (m, 1H, CH_{2-camp}), 1.44 (m, 1H, CH_{2-camp}), 1.34 (s, 3H, CH_{3-camp}), 1.25 (m, 1H, CH_{2-camp}), 1.05 (m, 1H, CH_{2-camp}), 0.72 (s, 3H, CH_{3-anti}), 0.40 (s, 3H, CH_{3-syn}); ^{13}C NMR ($CDCl_3$) δ 170.0 (C_{camp}), 134.4−125.7 (C_{ph} and CH_{Ph}), 119.2 (CH_{pyr}), 107.1 (CH_{ar}), 104.0 (C_{ar}), 88.8 (CH_{ar}), 84.6 (C_{ar}), 85.8 (CH_{ar}), 73.8 (CH_{ar}), 70.5 (CH_2N), 61.5 (C_{ar}), 54.4 (CH_2C**H**$_2$P), 49.4 (**C**H_2CH_2P), 46.7 (CH_{camp}), 32.5 (CH_{2-camp}), 27.7 (CH_{2-camp}), 21.2 (CH_{3-syn}), 19.6 (CH_{3-anti}), 12.2 (CH_{3-camp}); ^{31}P NMR ($CDCl_3$) δ 50.4 ppm. **7b**: ^{1}H NMR ($CDCl_3$) δ 7.80−7.63 (m, 4H, CH_{Ph}), 7.51 (s, 1H, CH_{pyr}), 7.40−7.37 (m, 6H, CH_{Ph}), 5.90 (dd, $^3J_{H-H}$ = 5.9 Hz, $^3J_{H-H}$ = 5.9 Hz, 1H, CH_{ar}), 5.57 (d, 1H, CH_{ar}), 5.32 (system AA′, 2H, CH_2N), 5.00 (d, 1H, CH_{ar}), 4.45 (s, 1H, CH_{ar}), 3.60−3.30 (m, 2H, CH_2C**H**$_2$P), 2.81 (d, $^3J_{H-H}$ = 4.0 Hz, 1H, CH_{camp}), 2.63−2.50 (m, 2H, C**H**$_2CH_2P$ and 1H, CH_{2-camp}), 2.05 (m, 1H, CH_{2-camp}), 1.83 (m, 1H, CH_{2-camp}), 1.27 (s, 3H, CH_{3-camp}), 1.25 (m, 1H, CH_{2-camp}), 1.21 (m, 1H, CH_{2-camp}), 0.95 (s, 3H, CH_{3-anti}), 0.71 (s, 3H, CH_{3-syn}); ^{13}C NMR ($CDCl_3$) δ 135−129 (C_{Ph} and CH_{Ph}), 126.4 (CH_{pyr}), 118.9 (C_{ar}), 107.5 (CH_{ar}), 89.7 (CH_{ar}), 84.6 (C_{ar}), 77.9 (CH_{ar}), 74.2 (CH_{ar}), 61.1 (CH_2N), 46.8 (CH_{camp}), 44.5 (d, $^2J_{C-P}$ = 33.0 Hz, CH_2**C**H_2P), 33.6 (CH_{2-camp}), 32.4 (**C**H_2CH_2P), 27.4 (CH_{2-camp}), 21.8 (CH_{3-syn}), 19.7 (CH_{3-anti}), 14.9 (CH_{3-camp}); ^{31}P NMR ($CDCl_3$) δ 45.9 ppmm; mass (FAB) *m/z* 728.8 (Ru(PArN*)-(OTf)), 597.8 (Ru(PArN*)(H_2O)), 579.8 (Ru(PArN*)), 494.9 (P(O)ArN*). Anal. Calcd for $C_{34}H_{37}F_6N_2O_7PRuS_2$: C, 45.6; H, 4.2; N, 3.1. Found: C, 45.2; H, 4.3; N, 2.9.

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Supporting Information Available: Tables of crystal data, atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles of compounds **7a** and **7b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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