Synthesis of Ruthenium Amide Complexes by Nucleophilic Attack on Ortho-Metalated Imine Ligands

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The cationic ortho-metalated imine complexes, $(\eta^6\text{-}C_6R_6)\overline{Ru(R')N{=}C(R'')}C_6H_4(L)$ (R = Me, H; R' = Ph, Et, Me; R'' = H, Me; L + PMe_3, CO), **1**, are formed in the reaction of $(C_6R_6)RuCl_2(L)$ with 2 equiv of imine and 2 equiv of $AgBF_4$. These complexes react with powerful nucleophiles $[Li(Bu^tO)_3AlH,RLi]$ via attack at the imine carbon atom, giving the neutral ortho-metalated amide complexes $C_6R_6\overline{Ru(R')\text{-}NC(R'')(Nu)}C_6H_4(L)$. The nucleophilic attack occurs with high (>98%) diastereoselectivity when the nucleophile differs from the substituent on the imine carbon. The molecular structures of $[(\eta^6\text{-}C_6Me_6)\overline{Ru(Ph)N{=}(CH)}C_6H_4(PMe_3)][BF_4]$, **1a**, and $(\eta^6\text{-}C_6Me_6)\overline{Ru(Ph)NC(H)(Me)}C_6H_4(PMe_3)$, **2a**, were determined by X-ray diffraction. Complex **1a** crystallizes in space group $P2_1/c$ (No. 14) with cell parameters a = 10.893 (2) Å, b = 14.507 (1) Å, c = 17.568 (3) Å, β = 100.40 (1)°, Z = 4, R = 0.025, and R_w = 0.028. Compound **2a** crystallizes in space group $P2_1/c$ (No. 14) with cell parameters a = 16.803 (3) Å, b = 9.306 (2) Å, c = 18.077 (3) Å, β = 109.65 (1)°, Z = 4, R = 0.061, and R_w = 0.060.

Introduction

There has been much recent interest in the reaction chemistry of late-transition-metal (group 8–10) amide complexes.[3] This interest arises from the possibility of using such compounds in carbon–nitrogen bond-forming reactions in chemistry similar to that of isoelectronic metal alkyl complexes.[4] There is also a desire to understand the fundamental bonding and thermodynamic properties of such compounds.[5] These efforts have been hampered by difficulties in the synthesis of such compounds and by their relative scarcity. We have been interested in nontraditional approaches to the synthesis of this interesting class of compounds and report our results on one such method. Some of the work reported here has been the subject of a preliminary communication.[6]

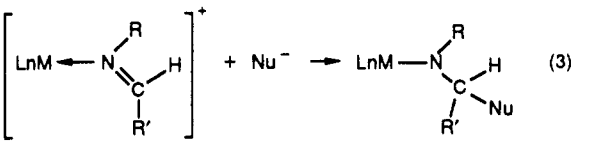
The usual method for the synthesis of transition-metal amide complexes involves nucleophilic displacement of a halide or other leaving group from a transition-metal precursor with an alkali-metal amide reagent (eq 1).[4,5a,7]

$$\text{LnM–X} + \text{M'NR}_2 \rightarrow \text{LnM–NR}_2 + \text{M'X} \qquad (1)$$

We have been interested in alternatives to this synthetic method since side reactions such as deprotonation of an ancillary ligand or reduction of the metal center often compete with the desired chemistry, thereby rendering eq 1 useless as a synthetic tool. One alternative that has been explored by us as well as others involves deprotonation of primary or secondary amine cations as shown in eq 2.[3,8]

$$[\text{LnM}{\leftarrow}\text{NHR}_2]^+ + \text{B}^- \rightarrow \text{LnM–NR}_2 + \text{B–H} \qquad (2)$$

A second alternative that we have been pursuing utilizes nucleophilic attack at the carbon atom of an N-bound imine cation as shown in eq 3. Activation of unsaturated organic ligands such as carbonyl groups toward nucleophilic attack by coordination to transition metals is well-known,[9] and the chemistry in eq 3 takes advantage of the same effect in the isoelectronic imine complexes. Recently, Gladysz has demonstrated that this method is useful for the synthesis of rhenium alkoxide complexes from coordinated ketones and aldehydes,[10] while Templeton has shown that amides of tungsten are accessible through eq 3.[11] This paper reports the synthesis of ortho-metalated amide complexes of ruthenium by nucleophilic attack on the corresponding ortho-metalated imine complexes.



(3)

Experimental Section

All manipulations were performed by using glovebox or standard Schlenk line techniques. Deuterated solvents were

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purchased from MSD Isotopes and were dried with 4-Å molecular sieves. CH_2Cl_2 was purified by distillation from CaH_2. Diethyl ether, THF, and pentane were all purified by distillation from sodium benzophenone. All NMR spectra were recorded on a JEOL FX-100, a G.E. QE-300, or a Varian XL-200 or VXR-300 spectrometer. Chemical shifts are reported in ppm downfield of TMS or H_3PO_4. IR data were obtained by using a Nicolet FT-IR spectrometer. Elemental analyses were obtained from either Atlantic Microlabs or the analytical services of this department. The $(\eta^6\text{-}C_6R_6)Ru(L)(Cl)_2$ complexes as well as all imines were prepared by published methods.[12,13]

Preparation of $[(\eta^6\text{-}C_6Me_6)\overline{Ru(Ph)N{=}C(H)C_6H_4}(PMe_3)][BF_4]$, 1a. To a stirred solution of $(\eta^6\text{-}C_6Me_6)Ru(PMe)_3Cl_2$ (0.277 g, 0.675 mmol) was added benzylideneaniline (0.262 g 1.35 mmol) and $AgBF_4$ (0.263 g 1.35 mmol) as a mixture in 50 mL of dichloromethane. An immediate color change from red to yellow was accompanied by the formation of a white precipitate. The reaction was stirred for 6 h and allowed to settle for 1 h. Filtration of the yellow solution followed by solvent removal under reduced pressure gave a yellow foamy material that was washed with pentane (3 × 10 mL) and Et_2O (3 × 10 mL). The material was scraped from the sides of the flask and the solid extracted with THF (3 × 10 mL). The resultant bright yellow solid was isolated as the crude product (0.287 g, 0.473 mmol), 70% yield. Crystals suitable for elemental analysis may be obtained from a CH_2Cl_2/pentane layer. Anal. Calcd for $C_{28}H_{37}BF_4NPRu$: C, 55.4; H, 6.15; N, 2.31. Found: C, 55.2; H, 6.25; N, 2.29. Mp: 280–282 °C (dec.). ^1H NMR (300 MHz, $CDCl_3$, 22 °C): 8.33 (d, J_{P-H} = 2.9 Hz, 1 H, imine H), 7.66 (d, J_{H-H} = 8.4 Hz, 1 H, ring), 7.52 (d, J_{H-H} = 8.1 Hz, 1 H, ring), 7.46 (t, J_{H-H} = 8.4 Hz, 2 H, aniline), 7.33 (t, J_{H-H} = 7.2 Hz, 1 H, aniline), 7.25 (d, J_{H-H} = 8.1 Hz, 2 H, aniline), 7.19 (t, J_{H-H} = 8.1 Hz, 1 H, ring), 7.04 (t, J_{H-H} = 7.8 Hz, 1 H, ring), 1.80 (s, 18 H, C_6Me_6), 1.07 (d, J_{P-H} = 9.1 Hz, 9 H, PMe_3). $^{13}C\{^1H\}$ NMR (74.4 MHz, $CDCl_3$, 22 °C): 187.0 (d, J_{P-C} = 21.7 Hz, imine C), 175.3, 151.3, 146.5, 137.7, 131.2, 130.5, 129.9, 128.6, 123.2, 121.9 (aniline or ring), 102.8 (d, J_{P-C} = 2.4 Hz, C_6Me_6), 15.72 (C_6Me_6), 14.80, (d, J_{P-C} = 32.9 Hz, PMe_3). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 22 °C): 7.60.

Preparation of $[(\eta^6\text{-}C_6Me_6)\overline{Ru(Ph)N{=}C(Me)C_6H_4}(PMe_3)][BF_4]$, 1b. To a stirred solution of $(\eta^6\text{-}C_6Me_6)Ru(PMe)_3Cl_2$ (0.505 g, 0.814 mmol) in dichloromethane (50 mL) was added $AgBF_4$ (0.317 g, 1.63 mmol) and methylbenzylideneaniline (0.318 g, 1.63 mmol). The mixture was stirred for 4 h and allowed to settle. The solution was filtered and the solvent removed under reduced pressure. The remaining yellow foamy solid was washed with pentane (3 × 10 mL) and diethyl ether (3 × 10 mL). Addition of CH_2Cl_2 to dissolve the solid followed by layering with pentane gave crystalline product (0.267 g, 0.430 mmol), 53% yield. Anal. Calcd for $C_{29}H_{39}BF_4NPRu$: C, 56.1; H, 6.34; N, 2.26. Found: C, 55.9; H, 6.40; N, 2.22. Mp: 271–273 °C (dec.). ^1H NMR (300 MHz, $CDCl_3$, 22 °C): 7.58–7.50 (m, 4 H, ring and aniline), 7.32 (t, J_{H-H} = 6.5 Hz, 1 H, ring or aniline), 7.25 (t, J_{H-H} = 7.8 Hz, 2 H, aniline), 7.12 (t, J_{H-H} = 7.4 Hz, 1 H, ring or aniline), 7.01 (d, J_{H-H} = 7.9 Hz, 2 H, aniline), 2.39 (d, J_{P-H} = 1.5 Hz, 3 H, imine, Me), 1.81 (s, 18 H, C_6Me_6), 1.11 (d, J_{P-H} = 9.23 Hz, 9 H, PMe_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 22 °C): 184.7 (d, J_{P-C} = 22 Hz, imine C), 180.4, 150.3, 147.8, 137.8, 130.5, 129.5, 129.1, 127.7, 123.6, 122.9 (ring or aniline), 103.0 (C_6Me_6), 18.2 (imine Me), 15.7 (C_6Me_6), 14.9 (d, J_{P-C} = 32.7 Hz, PMe_3). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 22 °C): 2.70.

Preparation of $[(\eta^6\text{-}C_6Me_6)\overline{Ru(p\text{-}MePh)N{=}C(H)C_6H_4}(PMe_3)][BF_4]$, 1c. A flask was charged with $(\eta^6\text{-}C_6Me_6)Ru(PMe_3)Cl_2$ (0.192 g, 0.468 mmol), $AgBF_4$ (0.182 g, 0.936 mmol), (*p*-MePh)N=CHPh (0.183 g, 0.936 mmol), and CH_2Cl_2 (50 mL). This reaction mixture was stirred for 12 h, and the white precipitate was allowed to settle. The supernatant was filtered away, and the precipitate was extracted with CH_2Cl_2 (3 × 5 mL). The extract was combined with the supernatant and concentrated under reduced pressure. An alumina column ($^1/_2$-in. diameter × 1-in length, neutral, Brockman activity I) was used to filter the solution. The CH_2Cl_2 solution was loaded onto the column and eluted with CH_2Cl_2. The eluent was collected and the solvent removed under reduced pressure. The solid was then washed with H_2O (3 × 10 mL) and dissolved in CH_2Cl_2 (5 mL). The stirred solution of the product was precipitated by dropwise addition of Et_2O (40 mL). The red-yellow powder may be crystallized by layering CH_2Cl_2/pentane to give brown crystals. Anal. Calcd for $C_{29}H_{39}BF_4NPRu$: C, 56.1; H, 6.34; N, 2.27. Found: C, 56.0; H, 6.23; N, 2.21. Mp: 264–266 °C. ^1H NMR (300 MHz, $CDCl_3$, 22 °C): 8.33 (d J_{P-H} = 2.89 Hz, 1 H, imine CH), 7.67 (d of d, J_{P-H} = 1.47 Hz, J_{H-H} = 7.4 Hz, 1 H, ring), 7.57 (d, J_{H-H} = 7.63 Hz, 1 H, ring), 7.30 (d, J_{H-H} = 8.00 Hz, 2 H, N-phenyl), 7.19 (m, 3 H, ring of N-phenyl), 7.08 (t, J_{H-H} = 7.4 Hz, 1 H, ring), 2.40 (s, 3 H, N-phenyl CH_3), 1.85 (s, 18 H, C_6Me_6), 1.11 (d, J_{P-H} 9.33 Hz, 9 H, PMe_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 22 °C): 172.5 (imine C), 148.8, 146.3, 138.9, 137.7, 130.4, 130.2, 123.1, 121.5, 102.8 (ring), 102.7 (C_6Me_6), 20.9 (C_6H_4Me), 15.7 (C_6Me_6), 14.8 (d, J_{P-C} = 33 H, PMe_3). $^{31}P\{^1H\}$ NMR (121 HMz, $CDCl_3$, 22 °C): –0.44.

Preparation of $[(\eta^6\text{-}C_6H_6)\overline{Ru(Ph)N{=}C(H)C_6H_4}(PMe_3)][BF_4]$, 1d. This compound was prepared from $(\eta^6\text{-}C_6H_6)Ru(PMe_3)Cl_2$ (0.239 g, 0.734 mmol), $AgBF_4$ (0.286 g, 1.47 mmol), and PhN=CHPh (0.266 g, 1.47 mmol) according to the procedure described for 1c. The product was isolated as a bright yellow powdery solid (0.295 g, 0.570 mmol), 77% yield. Anal. Calcd for $C_{22}H_{25}BF_4NPRu$: C, 50.5; H, 5.01; N, 2.68. Found: C, 50.4; H, 4.93; N, 2.60. Mp: 202–204 °C. ^1H NMR (300 MHz, $CDCl_3$, 22 °C): 8.73 (d, J_{P-H} = 2.98 Hz, 1 H, imine H), 8.02 (m, 1 H, phenyl H), 7.90 (m, 1 H, phenyl H), 7.60 (m, 4 H, phenyl H), 7.45 (m, 1 H, phenyl H), 7.22 (m, 2 H, phenyl H), 5.94 (s, 6 H, C_6H_6), 1.40 (d, J_{P-C} = 10.42 Hz, 9 H, PMe_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 22 °C): 180.9 (imine *C*), 160.6, 147.4, 137.8, 136.9, 136.6, 136.0, 134.7, 131.1, 129.9, 128.9 (ring or aniline *C*'s), 98.9 (C_6H_6), 22.2 (d, J_{P-C} = 34.8 Hz, PMe_3). $^{31}P\{^1H\}$ NMR (121 MHz, d_6-acetone, 22 °C): 4.33.

Preparation of $[(\eta^6\text{-}C_6H_6)\overline{Ru(Ph)N{=}C(H)C_6H_4}(PEt_3)][BF_4]$, 1e. This compound was prepared from $(\eta^6\text{-}C_6H_6)Ru(PEt_3)Cl_2$ (0.135 g, 0.218 mmol), $AgBF_4$ (0.079 g, 0.436 mmol), and PhN=CHPh (0.085 g, 0.436 mmol), according to the method described for 1c. The resultant oily solid product was then triturated with Et_2O (70 mL) to yield (0.075 g, 0.13 mmol), 61% yield, a yellow powder. Anal. Calcd for $C_{25}H_{31}BF_4NPRu\cdot{}^1/_4CH_2Cl_2$: C, 51.8; H, 5.42; N, 2.39. Found: C, 52.2; H, 5.44; N, 2.31. Mp: 200–202 °C. ^1H NMR (300 MHz, $CDCl_3$, 22 °C): 8.34 (d, J_{P-H} = 2.67 Hz, 1 H, imine CH), 7.83 (d, J_{H-H} = 1.76 Hz, 1 H, ring), 7.71 (d, J_{H-H} = 1.76 Hz, 1 H, ring), 7.47 (m, 2 H, ring), 7.38 (m, 3 H, ring), 7.18 (m, 2 H, ring), 5.70 (s, 6 H, C_6H_6), 1.59 (m, 6 H, PCH_3CH_3), 1.01 (m, 9 H, PCH_2CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 22 °C): 141.0, 131.5, 131.0, 130.8, 129.7, 128.8, 123.3, 122.4, 123.0, 122.4, 123.0, 122.4 (ring C's); 92.1 (C_6H_6); 17.5 (d, J_{P-C} = 29.7 Hz, CH_2CH_3); 8.02 (PCH_2CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 22 °C): 25.3.

Preparation of $[(\eta^6\text{-}C_6H_6)\overline{Ru(Et)N{=}C(H)C_6H_4}(PMe_3)][BF_4]$, 1f. This compound was prepared according to the procedure used for 1c from $(\eta^6\text{-}C_6H_6)Ru(PMe_3)Cl_2$ (0.164 g, 0.503 mmol), $AgBF_4$ (0.196 g, 1.06 mmol), and EtN=CHPh (0.145 mL, 1.06 mmol). The resulting yellow powder was crystallized from acetone/pentane, producing yellow crystals (0.194 g, 0.407 mmol), 81% yield. Anal. Calcd for $C_{18}H_{25}BF_4NPRu$: C, 45.5; H, 5.51; N, 8.95. Found: C, 45.3; H, 5.38; N, 8.94. Mp: 233–235 °C. ^1H NMR (300 MHz, $CDCl_3$, 22 °C): 8.20 (d, J_{P-H} = 3.03 Hz, 1 H, imine CH), 7.69 (d, J_{H-H} = 7.94 Hz, 1 H, ring H), 7.56 (d, J_{H-H} = 6.84 Hz, 1 H, ring H), 7.10 (m, 2 H, ring H), 5.85 (s, 6 H, C_6H_6), 4.03 (m, 2 H, NCH_2CH_3), 1.42 (t, J_{H-H} = 7.21 Hz, NCH_2CH_3), 1.12 (d, J_{P-C} = 10.2 Hz, 9 H, PMe_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 22 °C): 179.9 (d, J_{P-H} = 27.4 Hz, imine *C*); 172.2, 146.2, 140.2, 129.6, 123.3, (phenyl C's); 91.6 (C_6H_6); 61.3 (NCH_2CH_3); 16.5 (d, J_{P-C} = 35.9 Hz, PMe_3); 15.9 (NCH_2CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 22 °C): 4.83.

Preparation of $[(\eta^6\text{-}p\text{-Cymene})\overline{Ru(Ph)N{=}C(H)C_6H_4}(PMe_3)][BF_4]$, 1g. This compound was prepared from $(\eta^6$-cymene$)Ru(PMe)_3Cl_2$ (0.578 g, 1.51 mmol), $AgBF_4$ (0.587 g, 3.02 mmol), and PhN=CHPh (0.548 g, 3.02 mmol), using the method described for 1c. The resultant oily solid was triturated with Et_2O

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(100 mL) to produce 0.640 g (1.13 mmol), 75% yield, of yellow powder. Anal. Calcd for $C_{28}H_{33}BF_4NPRu$: C, 53.0; H, 5.87; N, 2.47. Found: C, 53.1; H, 5.89; N, 2.43. Mp: 230–232 °C. ^{H} NMR (300 MHz, $CDCl_3$, 22 °C): 8.35 (d, J_{P-H} = 3.00 Hz, 1 H, imine H), 7.80 (d, J_{H-H} = 7.50 Hz, 1 H, ring), 7.68 (d, J_{H-H} = 6.60 Hz, 1 H, ring), 7.51 (t, J = 7.50 Hz, 3 H, ring), 7.40 (t, J_{H-H} = 7.50 Hz, 1 H, ring), 7.31 (d, J_{H-H} = 7.20 Hz, 2 H, ring), 7.24 (t, J_{H-H} = 7.50 Hz, 1 H, ring), 7.14 (t, J_{H-H} 7.20 Hz, 1 H, ring), 5.71 (m, br, 2 H, cymene), 5.32 (m, 2 H, cymene), 5.21 (d, J_{H-H} = 6.00 Hz, 1 H, cymene), 2.44 (m, 1 H, C*H*Me_2), 2.28 (s, 3 H, CH_3), 1.25 (d, J_{P-H} = 9.90 Hz, 9 H, PMe_3), 1.00 (d, J_{H-H} = 6.90 Hz, 3 H, CH*Me*$_2$), 0.62 (d, J_{H-H} = 6.60 Hz, 3 H, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 22 °C): 183.8 (d, J_{P-C} = 22.4 Hz, imine *C*); 172.9, 153.6, 146.5, 140.5, 130.8, 129.6, 128.4, 123.5, 121.6, 119.7 (ring C's); 119.6, 106.5, 97.1, 88.2, 87.7, 85.8 (cymene ring C's); 30.7 (cymene CH_3); 23.0 (CH*Me*$_2$); 20.8 (*C*HMe$_2$); 18.8 (CH*Me*CH_3); 15.8 (d, J_{P-C} = 34.9 Hz, PMe_3). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 22 °C): 2.04.

Preparation of [(η^6-C_6Me_6)Ru(Ph)N=C(H)C_6H_4(CO)][BF_4], 1h. The method described for **1c** was used starting with (η^6-C_6Me_6)$Ru(CO)Cl_2$ (0.200 g, 0.552 mmol), $AgBF_4$ (0.215 g, 1.10 mmol), and PhN=CHPh (0.200 g, 1.10 mmol). The resultant dark yellow oily residue was triturated with Et_2O (100 mL) to produce a yellow powder (0.242 g, 0.411 mmol), 75% yield. Anal. Calcd for $C_{26}H_{28}BF_4NPRu\cdot{}^1/_4CH_2Cl_2$: C, 54.4; H, 4.95; N, 2.42. Found: C, 54.8; H, 4.99; N, 2.30. Mp: >300 °C. ^1H NMR (300 MHz, $CDCl_3$, 22 °C): 8.45 (s, 1 H, imine H), 7.86 (d of d, J_{H-H} = 1.5 Hz, J_{H-H} = 7.2 Hz, 1 H, ring), 7.54 (m, 3 H, ring), 7.43 (M, 3 H, ring or aniline), 7.34 (t of d, J_{H-H} = 1.5 Hz, J_{H-H} = 7.8 Hz, 1 H, ring), 7.21 (t, J_{H-H} = 7.20 Hz, 1 H, ring); 2.00 (s, 18 H, C_6Me_6). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 22 °C): 194.0 (CO); 176.9 (imine); 174.1, 149.7, 146.6, 137.2, 132.4, 132.3, 129.9, 129.0, 125.2, 122.2 (ring and aniline); 111.5 (C_6Me_6); 16.1 (C_6Me_6). IR (Nujol, cm^{-1}): ν_{CO} 1986.

Preparation of (η^6-C_6Me_6)Ru(Ph)NC(H)(Me)C_6H_4(PMe$_3$), 2a. To a stirred suspension of **1a** (0.103 g, 0.171 mmol) in tetrahydrofuran (20 mL) was added 1.4 M methyllithium (0.18 mL, 0.257 mmol) at room temperature. Reaction of the yellow mixture occurred in 5 min to produce an orange solution. The solvent was then removed under reduced pressure, and the product was extracted with toluene (3 × 10mL), evaporated to dryness, and extracted again using hexanes (3 × 10mL). The orange hexane solution was then filtered, and the hexanes were removed under reduced pressure to yield the product as an orange microcrystalline solid (0.081 g, 0.162 mmol), 94% yield. Anal. Calcd for $C_{29}H_{40}NPRu$: C, 65.1; H, 7.54; N, 2.62. Found: C, 64.8; H, 7.51; N, 2.59. ^1H NMR (300 MHz, C_6D_6, 22 °C): 7.64 (t, J_{H-H} = 8.4 Hz, 1 H, ring), 7.52 (t, J_{H-H} = 7.2 Hz, 1 H, ring), 7.41–7.30 (m, 5 H, ring and aniline), 7.14 (d, J_{H-H} = 8.1 Hz, 1 H, ring), 6.82 (t, J_{H-H} = 7.5 Hz, 2 H, aniline), 5.01 (q of d, J_{H-H} = 5.87 Hz, J_{P-H} = 2.47 Hz, 1 H, C(*H*)Me), 1.78 (d, J_{H-H} = 5.7 Hz, 3 H, CH*Me*), 1.94 (s, 18 H, C_6Me_6), 0.93 (d, J_{P-H} = 9.0 Hz, 9 H, PMe_3). $^{13}C\{^1H\}$ NMR (74.4 MHz, C_6D_6, 22 °C): 158.4, 138.4, 130.8, 129.5, 124.1, 122.3, 121.1, 121.0, 112.0, 106.3, 99.5 (ring and aniline C), 68.0 (*C*HMe), 24.3 (C(H)*Me*), 16.5 (C_6Me_6), 16.0 (d, J_{P-H} = 30.0 Hz, PMe_3). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 22 °C): 8.98.

Preparation of (η^6-C_6Me_6)Ru(Ph)NC(Me)(H)C_6H_4(PMe$_3$), 3a. This compound was prepared from **1b** (0.437 g, 0.710 mmol) and $LiAl(O^tBu)_3H$ (0.271 g, 0.710 mmol) at −20 °C according to the procedure described for **2a**, giving a bright orange solid (0.318 g, 0.639 mmol), 90% yield. Mp: 132–136 °C (dec.). ^1H NMR (300 MHz, C_6D_6, 22 °C): 7.31–7.19 (m, 2 H, ring or aniline), 7.16–7.12 (m, 2 H, ring or aniline), 7.08–7.02 (m, 2 H, ring or aniline), 6.83 (d, J_{H-H} = 6.9 Hz, 1 H, ring or aniline), 6.67 (d, J_{H-H} = 5.4 Hz, 1 H, ring or aniline), 6.53 (t, J_{H-H} = 6.9 Hz, 1 H, ring or aniline), 5.15 (q, J_{H-H} = 5.7 Hz, 1 H, C(*H*)Me), 1.56 (d, J_{H-H} = 5.7 Hz, 3 H, C(H)*Me*), 1.51 (s, 18 H, C_6Me_6), 0.93 (d, J_{P-H} = 8.7 Hz, 9 H, PMe_3). $^{13}C\{H\}$ NMR (75 MHz, C_6D_6, 22 °C): 158.4, 138.4, 130.8, 129.5, 129.0, 124.1, 122.3, 121.1, 121.0, 112.0, 108.3, 99.3, 68.0, 24.3, 16.5, 16.0 (d, J_{P-C} 30.0 Hz, PMe_3). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 22 °C): 4.16.

Preparation of (η^6-C_6Me_6)Ru(Ph)NC(H)(Ph)C_6H_4(PMe$_3$), 2b. This compound was prepared from **1a** (0.360 g, 0.599 mmol) and phenyllithium (0.24 mL, 0.599 mmol) at −20 °C according to the procedure used for **2a**, giving an orange solid product (0.276 g, 0.527 mmol), 88% yield. Anal. Calcd for $C_{34}H_{42}NPRu$: C, 68.4; H, 7.09; N, 2.35. Found: C, 68.1; H, 7.13; N, 2.31. ^1H NMR (300 MHz, C_6D_6, 22 °C): 7.78–7.75 (m, 2 H, ring or aniline), 7.28–7.21 (m, 4 H, ring or aniline), 7.17–7.07 (m, 6 H, ring or aniline), 6.53 (t, J_{H-H} = 8.1 Hz, 1 H, ring or aniline), 5.97 (s, 1 H, C(*H*)(Ph)), 1.59 (s, 18 H, C_6Me_6), 0.64 (d, J_{P-H} = 9.0 Hz, 9 H, PMe_3). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 22 °C): 128.7, 127.5, 126.0, 109.5 (aromatic C); 99.5 (C_6Me_6); 16.2 (C_6Me_6); 15.9 (d, J = 29 Hz, P*Me*$_3$). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 22 °C): 7.92.

Preparation of (η^6-C_6Me_6)Ru(Ph)NC(H)(H)C_6H_4(PMe$_3$), 2c. **2c** was prepared by using the procedure for **2a** from **1a** (0.100 g, 0.182 mmol) and $LiAl(O^tBu)_3H$ (0.046 g, 0.182 mmol) at −20 °C and isolated as red crystals following crystallization from Et_2O (0.084 g, 0.172 mmol), 94% yield. Anal. Calcd for $C_{28}H_{36}NPRu$: C, 64.6; H, 7.35; N, 2.69. Found: C, 64.5; H, 7.38, N, 2.74. Mp: 132–136 °C. ^1H NMR (300 MHz, C_6D_6, 22 °C): 7.42 (t, J_{H-H} = 6.6 Hz, 1 H, ring or aniline), 7.28 (t, J_{H-H} = 8.4 Hz, 1 H, ring or aniline), 7.21 (t, J_{H-H} = 5.1 Hz, 1 H, ring or aniline), 7.18–7.08 (m, 8 H, ring or aniline), 6.76 (t, J_{H-H} = 8.7 Hz, 1 H, ring or aniline), 6.57 (t, J_{H-H} = 6.9 Hz, 1 H, ring or aniline), 6.47 (d, J_{H-H} = 8.1 Hz, 1 H, ring or aniline), 4.75 (d, J_{H-H} = 16.5 Hz, 1 H, C(*H*)(H)), 4.47 (d of d, J_{H-H} = 16.5, J_{P-H} = 3.3 Hz, 1 H, C(H)(*H*)), 1.62 (s, 18 H, C_6Me_6), 0.78 (d, J_{P-H} = 8.7 Hz, 9 H, PMe_3). $^{13}\{^1H\}$ NMR (75 MHz, C_6D_6, 22 °C): 159.0, 153.3, 129.6, 127.5, 124.2, 122.0, 121.3, 120.3, 119.6, 112.3, 108.3 (aromatic C), 99.6 (C_6Me_6), 82.8 (*C*(H)(H)), 16.4 (d, J_{P-C} = 29.4 Hz, P*Me*$_3$), 16.2 (C_6Me_6). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 22 °C): 7.54.

Preparation of (η^6-C_6Me_6)Ru(*p*-MePh)NC(H)(Me)C_6H_4(PMe$_3$), 2d. This compound was prepared from **1c** (0.147 g, 0.237 mmol) and MeLi (0.24 mmol) at −20 °C by using the procedure for **2a** and was isolated as red crystals following crystallization from Et_2O (0.120 g, 0.218 mmol), 91% yield. Anal. Calcd for $C_{30}H_{42}NPRu\cdot{}^1/_8CH_2Cl_2$: C, 64.7; H, 7.55; N, 2.50. Found: C, 64.8; H, 7.52; N, 2.72. ^1H NMR (300 MHz, $CDCl_3$, 22 °C): 7.01 (m, 8 H, ring or aniline), 4.72 (m, 1 H, C(*H*)(Me)CH), 2.40 (s, 3 H, aryl CH_3), 1.69 (s, 18 H, C_6Me_6), 1.50 (d, J_{H-H} = 6.16 Hz, ring CH_3), 0.65 (d, J_{P-H} = 9.09 Hz, PMe_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 22 °C): 159.6, 156.4, 138.5, 138.4, 128.5, 124.0, 122.2, 121.1, 121.0, 115.7 (ring); 99.5 (C_6Me_6); 68.1 (*C*(H)(Me)); 24.5 (C_6H_4Me); 20.7 (C(H)(*Me*)); 16.5 (C_6Me_6); 16.1 (d, J_{P-H} = 29.6, P*Me*$_3$). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 22 °C): 9.32.

Preparation of (η^6-C_6H_6)Ru(Ph)NC(H)(Me)C_6H_4(PMe$_3$), 5. This compound was prepared from **1d** (0.160 g, 0.310 mmol) and methyllithium (0.310 mmol) at −20 °C by using the procedure for **2a**. Recrystallization of the crude products from Et_2O gave red crystals (0.128 g, 0.284 mmol), 91% yield. Anal. Calcd for $C_{23}H_{28}NPRu$: C, 61.32; H, 6.26; N, 3.11. Found: C, 60.4; H, 6.08; N, 3.10. ^1H NMR (300 MHz, $CDCl_3$, 22 °C): 7.34 (t, J_{H-H} = 7.14 Hz, 2 H, ring), 7.09 (m, 2 H, ring), 7.00 (m, 2 H, ring), 6.80 (d, J_{H-H} = 8.10 Hz, 2 H, ring), 6.56 (t, J_{H-H} = 6.83 Hz, 1 H, ring), 4.90 (br, m, 1 H, C(*H*)(Me)), 4.70 (s, 6 H, C_6H_6), 1.43 (d, J_{H-H} = 5.97 Hz, 3 H, C(H)(*Me*)), 0.67 (d, J_{P-H} = 9.82 Hz, 9 H, PMe_3). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 22 °C): 172.0, 161.0, 159.0, 158.2, 138.8, 128.9, 124.5, 122.8, 121.3, 108.0 (ring), 89.5 (C_6H_6), 66.8 (*C*(H)(Me)), 21.6 C(H)(*Me*)), 17.2 (d, J_{P-C} = 31.5 Hz, P*Me*$_3$). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 22 °C): 10.82.

Preparation of [(η^6-C_6Me_6)Ru(Ph)N(H)C(H)(Me)C_6H_4(PMe$_3$)][BF_4], 6. To a stirred solution of **2a** (0.150 g, 0.285 mmol) in THF (20 mL) was added 1.5 mL of 0.19 M HBF_4 solution. The red color of the solution instantly disappeared, and an off-white precipitate began to form. The mixture was stirred for 1 h and allowed to settle. The supernatant was filtered away, and the solid was washed with Et_2O (3 × 15 mL). The off-white powder was crystallized from CH_2Cl_2/pentane to give colorless crystals, 0.146 g (0.235 mmol), 82% yield. Anal. Calcd for $C_{29}H_{41}BF_4NPRu\cdot{}^1/_4CH_2Cl_2$: C, 54.6; H, 6.49; N, 2.17. Found: C, 54.5; H, 6.52; N, 2.05. Mp: 249–250 °C. ^1H NMR (300 MHz, $CDCl_3$, 22 °C): 7.49 (t, J_{H-H} = 6.99 Hz, 2 H, ring), 7.83 (t, J_{H-H} = 6.97 Hz, 1 H, ring), 7.25 (m, 3 H, ring), 7.12 (t, J_{H-H} = 6.25 Hz, 1 H, ring), 7.02 (t, J_{H-H} = 7.36 Hz, 1 H, ring), 6.79 (d, J_{H-H} = 7.36 Hz, 1 H, ring), 4.58 (br, 1 H, NH), 3.83 (q, J_{H-H} = 6.25 Hz, 1 H, C(*H*)(Me)), 1.91 (s, 18 H, C_6Me_6), 1.46 (d, J_{H-H} = 6.25 Hz, 3 H, (C(H)(*Me*)), 1.29 (d, J_{P-H} = 8.45 Hz, 9 H, PMe_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 22 °C): 145.8, 137.9, 129.5, 127.9, 127.5, 124.2,

Table I. Crystal and Data Collection Parameters

	1a	2a
a, Å	10.893 (2)	16.803 (3)
b, Å	14.507 (1)	9.306 (2)
c, Å	17.568 (3)	18.077 (3)
β, deg	100.40 (1)	109.65 (1)
V, Å	2730.5 (8)	2662.0 (5)
T, °C	23 (1)	23 (1)
space group	$P2_1/c$	$P2_1/c$
μ, cm^{-1}	6.6	6.5
fw	606.45	534.69
Z	4	4
d(calcd), g/cm^3	1.48	1.33
cryst size, mm	0.40 × 0.40 × 0.44	0.12 × 0.15 × 0.15
θ range, deg	$1.5 < \theta < 25.0$	$2.0 < \theta < 22.5$
rflns measd	$+h,+k,\pm l$	$\pm h,-k,+l$
no. of unique rflns	4580	3588
no. of rflns with $I > 3\sigma(I)$	4313	2381
no. of params	350	289
R, %	2.5	6.1
R_w, %	2.8	6.0
GOF	1.01	1.11

Table II. Selected Bond Lengths (Å) and Angles (deg) in $[(\eta^6\text{-}C_6Me_6)\overline{Ru(Ph)N{=}C(H)C_6H_4(PMe_3)}][BF_4]$, 1a

Ru-P	2.316 (1)	Ru-C17	2.260 (2)
Ru-N	2.093 (3)	Ru-C18	2.267 (2)
Ru-C1	2.058 (2)	Ru-C19	2.241 (2)
Ru-C14	2.247 (2)	N-C7	1.294 (3)
Ru-C15	2.340 (2)	N-C8	1.430 (3)
Ru-C16	2.330 (3)		
P-Ru-N	89.03 (6)	N-C7-C6	116.6 (2)
P-Ru-C1	83.62 (8)	C1-C6-C7	114.8 (2)
N-Ru-C1	77.46 (9)	Ru-C1-C6	114.2 (2)
Ru-N-C7	116.5 (2)		

123.8, 122.8 (phenyl C's), 101.2 (C_6Me_4), 69.8 (C(H)(Me)), 19.6 (C(H)(*Me*)), 17.5 (d, J_{P-C} = 30.7 Hz, PMe_3), 16.2 (C_6Me_6). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 22 °C): −1.36.

X-ray Crystallography. General data collection and refinement data are listed in Table I. Refined positional parameters are given in Tables III and V. Selected bond distances and angles are listed in Tables II and IV. The supplemental material contains a listing of anisotropic thermal parameters and listings of F_o and F_c (symmetry adapted). All calculations were carried out by using SDP/Vax software (Enraf-Nonius and B. A. Frenz & Associates, Inc.).

$[(\eta^6\text{-}C_6Me_6)\overline{Ru(Ph)N{=}C(H)C_6H_4(PMe_3)}][BF_4]$, 1a. A crystal of $C_{28}H_{37}NPRuBF_4$ was cleaved from a larger obelisk-shaped crystal and glued onto the tip of a glass fiber. The crystal was then mounted in a random orientation on the diffractometer. A rotational photograph was used to locate 25 reflections ($12° < \theta < 17.5°$), which were used to determine lattice constants and crystal orientation. Data were collected by using the θ–2θ scan technique. The intensities of three standard reflections were measured every 60 min of exposure and showed a smooth 1.9% decrease. A decay correction was applied. Azimuthal scan data revealed only weak and irregular variations (1.3%) due to absorption (μ = 6.6 cm^{-1}), and no correction was applied. Lorentz and polarization corrections and rejection of systematically absent and weak [$I < 3\sigma(I)$] data left 4313 reflections for structural refinement. Systematically absent data indicated the space group $P2_1/c$, which was subsequently confirmed by the successful solution and refinement of the structure. Twenty-five reflections with $18.5 < \theta < 20.0$ were selected and used to determine the final cell constants in a restrained least-squares calculation (Table I). The positions of the Ru and P atoms were determined from a Patterson calculation. Subsequent full-matrix least-squares and difference Fourier syntheses revealed the positions of all other non-hydrogen atoms. Further refinement with anisotropic thermal parameters revealed no unusual features in the cation, but a disorder of the BF_4^- fragment was apparent. Fluorine atoms F2, F3, and F4 were each assigned three positions (e.g., F2, F2A, F2B) with occupation factors of 0.50, 0.35, and 0.15, respectively. A parameter to correct for secondary extinction was included and refined (3.16 (6) × 10^{-7}). Approximate hydrogen atom positions were located from a difference Fourier map and were used to calculate fixed hydrogen atom positions. The hydrogen atom positions were periodically recalculated. Refinement using Killean–Lawrence weights converged to R = 2.5%, R_w = 2.8%, and GOF = 1.01. The largest residual peak in the final difference Fourier map was 0.4 e$^-$/Å^3 located near the boron atom.

Table III. Positional Parameters and Their Estimated Standard Deviations for $[(\eta^6\text{-}C_6Me_6)\overline{Ru(Ph)N{=}C(H)C_6H_4(PMe_3)}][BF_4]$, 1a[a]

atom	x	y	z	B, Å^2
Ru	0.25153 (2)	0.35664 (1)	0.12242 (1)	2.160 (3)
P	0.20904 (6)	0.20713 (4)	0.15597 (4)	2.91 (1)
N	0.3884 (2)	0.3647 (1)	0.2224 (1)	2.75 (4)
C1	0.4036 (2)	0.2968 (2)	0.0877 (1)	2.79 (5)
C2	0.4136 (2)	0.2572 (2)	0.0163 (2)	3.45 (5)
C3	0.5287 (3)	0.2291 (2)	0.0007 (2)	4.18 (6)
C4	0.6362 (2)	0.2355 (2)	0.0554 (2)	4.53 (6)
C5	0.6302 (2)	0.2714 (2)	0.1270 (2)	4.35 (7)
C6	0.5144 (2)	0.3021 (2)	0.1427 (2)	3.16 (5)
C7	0.4995 (2)	0.3382 (2)	0.2161 (2)	3.37 (5)
C8	0.3675 (2)	0.4035 (2)	0.2938 (1)	2.97 (5)
C9	0.4548 (3)	0.4640 (2)	0.3350 (2)	3.87 (6)
C10	0.4279 (3)	0.5071 (2)	0.4001 (2)	4.85 (7)
C11	0.3176 (3)	0.4903 (2)	0.4251 (2)	4.86 (7)
C12	0.2323 (3)	0.4288 (2)	0.3856 (2)	4.38 (6)
C13	0.2578 (3)	0.3857 (2)	0.3193 (2)	3.57 (6)
C14	0.0567 (2)	0.3821 (2)	0.0582 (2)	3.07 (5)
C15	0.0672 (2)	0.4380 (2)	0.1260 (2)	3.09 (5)
C16	0.1671 (2)	0.5000 (2)	0.1434 (2)	2.91 (5)
C17	0.2564 (2)	0.5080 (2)	0.0928 (2)	2.90 (5)
C18	0.2398 (2)	0.4582 (2)	0.0233 (1)	2.99 (5)
C19	0.1412 (2)	0.3926 (2)	0.0059 (1)	2.98 (5)
C14M	−0.0556 (3)	0.3204 (2)	0.0348 (2)	4.73 (7)
C15M	−0.0305 (3)	0.4325 (2)	0.1775 (2)	4.84 (7)
C16M	0.1776 (3)	0.5647 (2)	0.2113 (2)	4.19 (6)
C17M	0.3652 (3)	0.5740 (2)	0.1143 (2)	4.56 (7)
C18M	0.3266 (3)	0.4748 (2)	−0.0339 (2)	4.38 (6)
C19M	0.1181 (3)	0.3407 (2)	−0.0698 (2)	4.60 (7)
C1P	0.3289 (3)	0.1516 (2)	0.2265 (2)	4.58 (7)
C2P	0.1858 (3)	0.1255 (2)	0.0770 (2)	4.68 (7)
C3P	0.0719 (3)	0.1854 (2)	0.1996 (2)	4.61 (6)
B	0.1685 (3)	0.6443 (3)	0.6424 (2)	4.70 (8)
F1	0.2139 (2)	0.5745 (2)	0.6915 (1)	7.47 (6)
F2	0.2617 (4)	0.6910 (4)	0.6182 (3)	9.0 (1)
F3	0.1037 (4)	0.7057 (3)	0.6845 (3)	7.7 (1)
F4	0.0811 (4)	0.6181 (4)	0.5821 (3)	9.2 (1)
F2A	0.2442 (6)	0.7165 (5)	0.6508 (4)	7.4 (2)*
F2B	0.252 (1)	0.623 (1)	0.5890 (9)	7.2 (3)*
F3A	0.0559 (7)	0.6704 (5)	0.6485 (4)	8.3 (2)*
F3B	0.189 (1)	0.716 (1)	0.6933 (9)	7.2 (3)*
F4A	0.1582 (7)	0.6212 (6)	0.5642 (5)	8.8 (2)*
F4B	0.061 (2)	0.594 (1)	0.618 (1)	8.9 (4)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as (4/3) [$a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)$].

Table IV. Selected Bond Lengths (Å) and Angles (deg) in $(\eta^6\text{-}C_6Me_6)\overline{Ru(Ph)NC(H)(Me)C_6H_4(PMe_3)}$, 2a

Ru-P	2.290 (2)	Ru-C18	2.25 (2)
Ru-N	2.08 (2)	Ru-C19	2.24 (2)
Ru-C1	2.20 (1)	Ru-C20	2.22 (1)
Ru-C15	2.322 (9)	N-C7	1.40 (1)
Ru-C16	2.30 (1)	N-C9	1.32 (2)
Ru-C17	2.286 (9)		
P-Ru-N	87.2 (2)	N-C7-C6	105.5 (9)
P-Ru-C1	81.4 (3)	C1-C6-C7	117 (2)
N-Ru-C1	76.4 (5)	Ru-C1-C6	116 (2)
Ru-N-C7	121.3 (9)	C6-C7-C8	110.3 (9)
		N-C7-C8	115.0 (8)

$(\eta^6\text{-}C_6Me_6)\overline{Ru(Ph)NC(H)(Me)C_6H_4(PMe_3)}$, 2a. Crystals were grown by slow evaporation of toluene solution. A small block-shaped crystal was selected and glued onto the tip of a thin

Table V. Position Parameters and Their Estimated Standard Deviations for (η^6-C_6Me_6)Ru(Ph)NC(H)(Me)C_6H_4(PMe_3), 2a[a]

atom	x	y	z	B, Å²
Ru	0.74406 (5)	0.23784 (9)	0.41731 (4)	5.07 (2)
P	0.8487 (1)	0.3300 (3)	0.5235 (1)	4.12 (6)
N	0.7847 (7)	0.379 (1)	0.3486 (5)	8.8 (3)
C1P	0.9488 (6)	0.234 (1)	0.5606 (5)	6.1 (3)
C2P	0.8244 (6)	0.351 (1)	0.6133 (5)	6.3 (3)
C3P	0.8861 (6)	0.509 (1)	0.5112 (5)	5.6 (3)
C15	0.7704 (6)	−0.006 (1)	0.4117 (5)	5.1 (2)
C15M	0.8496 (7)	−0.098 (1)	0.4302 (8)	8.1 (4)
C16	0.7251 (6)	0.041 (1)	0.3366 (6)	6.1 (3)
C16M	0.7576 (9)	0.006 (2)	0.2687 (7)	11.1 (4)
C17	0.6463 (7)	0.114 (1)	0.3188 (6)	7.2 (3)
C17M	0.598 (1)	0.154 (2)	0.2338 (8)	12.4 (5)
C18	0.6142 (7)	0.140 (1)	0.3784 (7)	7.3 (3)
C18M	0.5256 (7)	0.212 (2)	0.361 (1)	11.4 (5)
C19	0.6580 (6)	0.095 (1)	0.4558 (6)	5.7 (3)
C19M	0.6169 (7)	0.106 (1)	0.5201 (7)	8.9 (3)
C20	0.7376 (6)	0.026 (1)	0.4720 (5)	5.2 (3)
C20M	0.7802 (8)	−0.034 (1)	0.5542 (6)	7.8 (3)
C1	0.6830 (7)	0.442 (1)	0.4285 (8)	9.6 (4)
C2	0.6375 (6)	0.472 (1)	0.4785 (7)	7.5 (3)
C3	0.5976 (6)	0.599 (1)	0.4818 (7)	8.8 (4)
C4	0.6003 (7)	0.715 (1)	0.4254 (8)	9.5 (4)
C5	0.6482 (6)	0.673 (1)	0.3751 (7)	6.4 (3)
C6	0.6860 (6)	0.541 (1)	0.3820 (6)	6.5 (3)
C7	0.7434 (6)	0.511 (1)	0.3236 (6)	5.7 (3)
C8	0.6861 (7)	0.515 (1)	0.2360 (6)	7.1 (3)
C9	0.8541 (5)	0.362 (1)	0.3308 (5)	7.3 (3)
C10	0.8849 (6)	0.460 (1)	0.2843 (5)	5.5 (3)
C11	0.9569 (7)	0.429 (1)	0.2742 (6)	6.7 (3)
C12	1.0033 (8)	0.314 (1)	0.2979 (6)	9.0 (4)
C13	0.9790 (6)	0.226 (1)	0.3402 (5)	6.5 (3)
C14	0.9105 (5)	0.231 (1)	0.3597 (4)	4.7 (2)

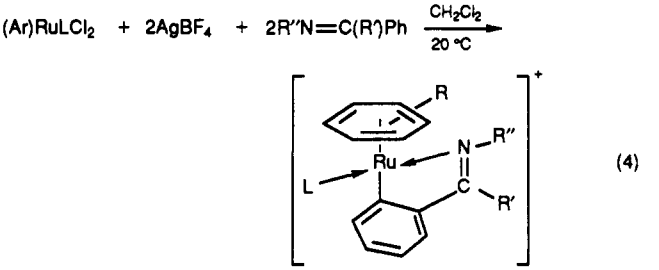
[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as (4/3) $[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

glass fiber. The crystal was mounted in a random orientation on the diffractometer. An automated search routine around $\theta = 10.0°$ was used to locate 10 reflections, which were then used to initially determine the lattice constants and orientation matrix. These values were refined by using 25 centered reflections $12.5° < \theta < 15.0°$ located in a prior structural determination. Data were collected by using the θ–2θ scan technique. The intensities of three standard reflections were measured every 60 min of exposure and showed a smooth 2.8% decrease. A decay correction was applied that also accounted for a one-time 4.4% intensity increase which occurred after data collection was interrupted. Azimuthal scan data revealed a regular 4.9% variation in intensity so an empirical absorption correction ($\mu = 6.5$ cm^{-1}) was applied. Lorentz and polarization corrections and rejection of systematically absent and weak [$I < 3\sigma(I)$] data left 2381 reflections for structural refinement. Systematically absent data indicated the space group $P2_1/c$, which was subsequently confirmed by the successful solution and refinement of the structure.

A prior attempt at structural characterization in the same space group had been solved by using direct methods. This initial attempt, however, was marred by a ca. 25% disorder of the metallocycle and phenyl rings. Accordingly, the previously determined atomic coordinates were applied to this new data set. Repeated full-matrix least-squares refinement using isotropic thermal parameters and later anisotropic thermal parameters was carried out. A parameter to correct for secondary extinction was included and fixed (3.0×10^{-9}). A difference map revealed probable locations of the hydrogen atoms. Idealized hydrogen atom positions were calculated from these data and included in the structural calculation, but the hydrogen atom parameters were not refined. Refinement using Killean–Lawrence weights converged to $R = 6.1\%$, $R_w = 6.0\%$, and GOF = 1.11. The largest peaks in the final difference map (1.4 and 1.0 e$^-$/Å^3) were located near the ruthenium and nitrogen atoms and are probably due to a disorder of the metallocycle.

Results and Discussion

The synthesis of the ortho-metalated benzylidene amine cations, **1a–h**, is accomplished by allowing the arene complexes (η^6-C_6R_6)$RuCl_2(PMe_3)$ to react with 2 equiv of imine and 2 equiv of $AgBF_4$ in CH_2Cl_2 as shown in eq 4. The



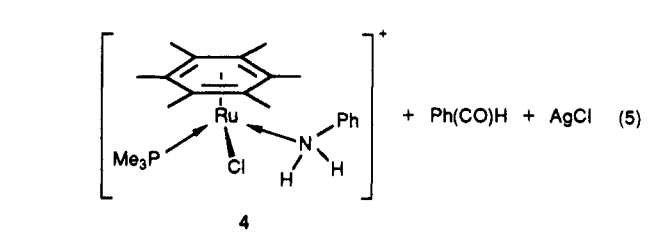
(4)

1a: R = Me, R′ = H, R″ = Ph, L = PMe_3
b: R = Me, R′ = Me, R″ = Ph, L = PMe_3
c: R = Me, R′ = H, R″ = *p*-Tol, L = PMe_3
d: R = H, R′ = H, R″ = Ph, L = PMe_3
e: R = H, R′ = H, R″ = Ph, L = PEt_3
f: R = H, R′ = H, R″ = Et, L = PMe_3
g: *p*-cymene, R′ = H, R″ = Ph, L = PMe_3
h: R = Me, R′ = H, R″ = Ph, L = CO

reaction is generally complete within 4–6 h, and the ^{1}H NMR spectra of the crude reaction mixtures show essentially complete conversion to products. The complexes, **1a–h**, are yellow, air-stable, crystalline solids and have been characterized by using ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies as well as by a single-crystal X-ray diffraction study on **1a**. The variability in the isolated yields arises from difficulties in separating the iminium salts from the Ru complexes and accounts for the somewhat extensive work-up procedures needed to obtain pure materials.

These ortho-metalation reactions (eq 4) probably proceed via an electrophilic mechanism that requires abstraction of both halide ligands from the starting material. Abstraction of the first chloride supplies a vacant site on the metal for imine coordination while abstraction of the second chloride generates a dication with a vacant site. Intramolecular coordination of the electrophilic ruthenium center with the arene ring of the imine then facilitates deprotonation of the ortho hydrogen atom by a second equivalent of imine, giving the ortho-metalated product. Similar electrophilic ortho-metalation reactions of phenyl imine ligands [RN=C(R′)Ph] occur with a variety of different transition-metal centers and are especially common in palladium(II) chemistry.[4]

Although the cationic complexes **1a–h** are air and water stable, water must be carefully excluded during their synthesis. The presence of water in the reaction mixture results in the formation of complexes having the composition [(arene)$Ru(PR_3)(NH_2R)Cl]^+[BF_4^-]$. Performing the reaction in the presence of 1 equiv of water has allowed the isolation of **4** (eq 5) which has been synthesized and



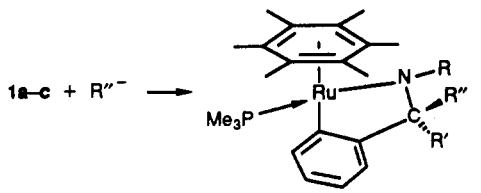
(5)

4

characterized independently.[8d] Formation of the amine cations is consistent with the reaction of water with the

monodentane imine complex intermediate as shown in eq 5. Attempts to isolate the proposed intermediate monodentane imine complex by using only 1 equiv of $AgBF_4$ and imine gave greatly reduced yields of **1** as the only tractable product. The observation that benzaldehyde is formed when water is present is also consistent with this proposal. These observations also suggest that imines which are N bound to transition-metal cations are very susceptible to nucleophilic attack.

The reaction between the ortho-metalated cations **1a–h** and strong nucleophiles proceeds in high yield as shown in eq 6. The amide complexes **2a–d** and **3a** are soluble



(6)

2a: R = Ph, R′ = H, R″ = Me
b: R = Ph, R′ = H, R″ = Ph
c: R = Ph, R′ = H, R″ = H
d: R = *p*-Tol, R′ = H, R″ = Me
3a: R = Ph, R′ = Me, R″ = H

in ether and aromatic hydrocarbons and are sparingly soluble in aliphatic hydrocarbons. They are air stable in the solid state and slightly air sensitive in solution. These compounds have been characterized by using ^1H, ^{13}C, and ^{31}P NMR spectroscopies, and a single-crystal X-ray diffraction study has been performed on **2a**, confirming the spectroscopic characterization. Reaction 6 appears to give the amide complexes only when powerful nucleophiles such as RLi or $LiAlH_4$ are used and only if the substituent on the N atom is a phenyl group or a substituted phenyl group. Although compounds with other substituents on nitrogen react with alkyllithium reagents, no tractable materials were isolated from these reactions. Weaker nucleophiles such as alkoxide did not react with any of the compounds **1a–h**. The relatively unreactive nature of **1a–h** toward nucleophiles stands in marked contrast to the metalation reaction (eq 4) from which all traces of water must be excluded to prevent nucleophilic attack of water on the imine carbon of the intermediate. Evidently, formation of the metallocyte ring significantly decreases the electrophilicity of the imine carbon atom, and only when R′ is electron withdrawing will the reaction proceed, and then only with strong nucleophiles.

X-ray Crystal Structures. The crystal structure of compound **1a** reveals discrete anion and cation entities. The anion exhibits a noncrystallographic 3-fold disorder of F2, F3, and F4, while B and F1 are not disordered and roughly define a pseudo-3-fold axis for the disorder. The bond distances and angles in the organometallic cation are in the ranges expected for such a structure. An ORTEP drawing of **1a** is found in Figure 1, while selected bond lengths and angles are found in Table II. The five-membered metallocyclic group is nearly planar (±0.05 Å) with a short N–C7 bond distance (1.294 Å) indicative of a C=N double bond. The hexamethylbenzene ring is planar (±0.03 Å), but the ruthenium atom is not centered directly below the ring. The phenyl carbon atom exerts a strong trans influence, causing C15 and C16 to be ca. 0.08 Å further from the metal atom than are the other ring carbon atoms. Such a trans influence has been identified in the crystal structures of a variety of arene complexes.[15]

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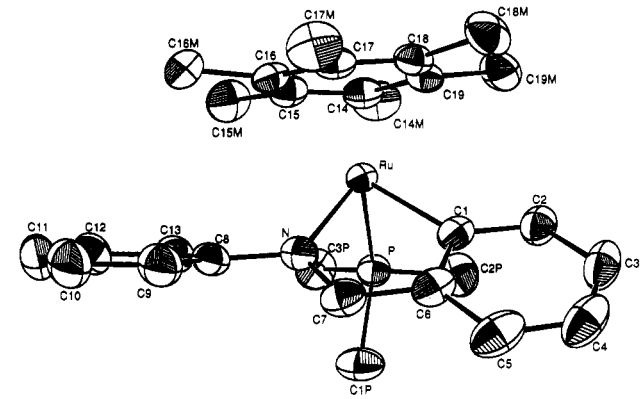


Figure 1. Molecular structure (ORTEP drawing, 50% ellipsoids) of $[(\eta^6\text{-}C_6Me_6)\overline{Ru(Ph)N{=}C(H)C_6H_4(PMe_3)}][BF_4]$, **1a**.

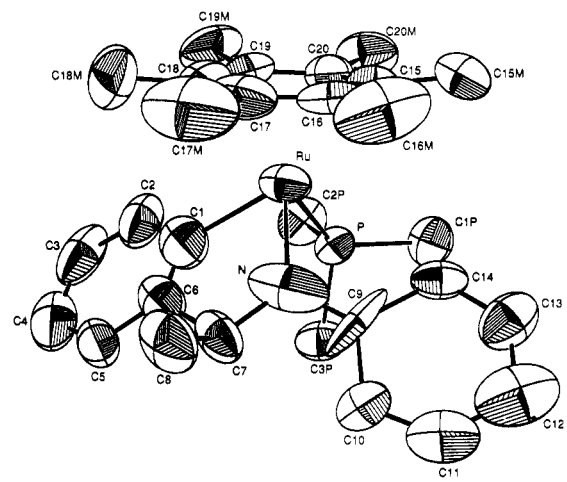


Figure 2. Molecular structure (ORTEP drawing, 50% ellipsoids) of $(\eta^6\text{-}C_6Me_6)\overline{Ru(Ph)NC(H)(Me)C_6H_4(PMe_3)}$, **2a**.

The crystallographic study of **2a** was complicated by a disorder of the metallocycle fragment. The first determination revealed that the metallocycle, with its two phenyl rings, formed a nearly planar base. This extended planar structure appeared to lie one way about 75% of the time and the other way 25%. In other words, the independent unit was ca. 75% *R* and ca. 25% *S* conformation at the Ru atom. Both configurations showed the methyl group on the metallocycle to be in the endo position pointing toward the η^6-hexamethylbenzene ring. The determination reported herein was carried out after careful optical inspection of crystals after recrystallization. Despite careful crystal selection, several large peaks in the final difference map and large thermal parameters for the metallocycle and phenyl atoms indicate that some small amount of disorder (perhaps 10%) exists. The disorder appears to concern only the relative orientation of the Ru–C1 and Ru–N linkages. In both structure determinations, the C8 methyl group lies in the endo position toward the coordinated arene.

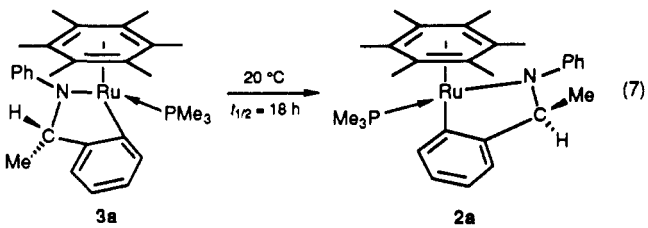
An ORTEP drawing of **2a** is found in Figure 2, while selected bond lengths and angles are found in Table III. The bond distances and angles for **2a** fall within the expected ranges. The N–C7 distance is considerably longer than in the cation, **1a**, as would be expected for a nitrogen–carbon single bond. The hexamethylbenzene ligand is planar (±0.02 Å). Coordination of the metal atom to the arene ring is not perfectly symmetric; the Ru–C15, Ru–C16, and Ru–C17 bond distances are longer than the other metal ring distances. C15 and C16 are again approximately trans to the Ru–C1 bond. The atoms of the

metallocycle and the two phenyl rings lie within 0.5 Å of their calculated least-squares plane. The exact conformation of the five-membered metallocyclic ring is difficult to discern, but the N atom does lie 0.27 Å out of the plane of the other four atoms (Ru, C1, C6, C7) away from the coordinated hexamethylbenzene. Unfortunately, the disorder in the structure does not allow definitive conclusions to be made about whether or not the N atom is pyramidal or planar; however, a pyramidal geometry would be expected since the Ru atom is already electronically saturated without π donation from the amide N atom.

Reactivity. When the identity of the attacking nucleophile differs from the substituent on the imine carbon, the carbon atom of the resultant metalated amide complex is chiral. Since the Ru atom is also a chiral center, formation of two pairs of diastereomers is possible. When alkyllithium reagents are added to complex **1a**, only one set of diastereomers is formed as detectable by 300-MHz ^{1}H NMR spectroscopy. Proton difference NOE spectroscopy has been used to assign the solution structure of **2a** as having the methyl group endo to the C_6Me_6 ring,[6] and the X-ray crystal structure of **2a** confirms this spectroscopic assignment. The geometry of **2a** suggests nucleophilic attack occurs endo to the C_6R_6 ring. Examination of the X-ray structure of **1a** reveals that the closest nonbonded contact between the imine carbon and the methyl groups of the arene ring is 4.00 Å, while the closest nonbonded distance between the imine carbon atom and the PMe_3 methyl groups is 3.32 Å. Clearly, the more exposed face of the imine functionality is the face that is endo to the C_6Me_6 ring. Thus, steric factors favor nucleophilic attack to occur at the imine face, which is endo to the C_6Me_6 group.

In order to test whether or not the nucleophilic attack occurs endo to the arene ring, the addition of hydride to **1b** was studied. When **1b** is allowed to react with Li(Bu^{t}O)$_3$AlH and the reaction mixture is rapidly worked up, the only observable product is **3a**, the product of H$^-$ attack endo to the arene ring. Compounds **2a** and **3a** represent the two possible sets of distereomers (isolated as the enantiomeric pairs *RS*, *SR* and *RR*, *SS*). These results strongly support the conclusion that the nucleophilic attack occurs at the less hindered face of the imine, endo to the C_6Me_6 ring.

If compound **3a** is dissolved in C_6D_6, a slow isomerization process occurs ($t_{1/2} \approx 18$ h, 25 °C) that converts it cleanly and completely to **2a** (eq 7). This suggests that **3a** is



3a 2a (7)

produced as the kinetic product of the reaction of **1b** with hydride, while the thermodynamically more stable isomer is **2a** (the isomer with the CH_3 group endo to the C_6Me_6 ring). Thus, nucleophiliic attack on the imine carbon atom is kinetically controlled and occurs with high >98% diastereoselectivity at the face of the imine, which is endo to the arene ring.

A kinetic study of the isomerization of **3a** to **2a** has been carried out and reveals that the reaction is first order in the Ru complex. The rate constants for this reaction have been determined at several temperatures and are found in Table VI. An Eyring plot has been used to determine

Table VI. Rate Constants for the Isomerization of 3a to 2a[a]

T, K	$10^5 k_{obs}$, s^{-1}	T, K	$10^5 k_{obs}$, s^{-1}
303	1.0 (1)	335	74 (4)
313	4.1 (6)	345	170 (4)
323	15 (5)		

[a] $\Delta H^\ddagger$ = 25 (1) kcal mol^{-1}; $\Delta S^\ddagger$ = 2.6 (5) eu.

the activation parameters of the reaction (Table VI). The $\Delta S^\ddagger$ value differs significantly from the value that was reported initially by using a limited set of data.[6] Performing the reaction in the presence of a 50-fold excess of PMe_3 has little effect on the rate of the reaction and indicates that the isomerization essentially is independent of the presence of excess ligand. When the reaction is carried out in the presence of $P(CD_3)_3$, exchange of $P(CD_3)_3$ with coordinated $P(CH_3)_3$ occurs more rapidly than the isomerization reaction.

The net reaction that occurs during the isomerization of **3a** to **2a** involves the epimerization of one of the two chiral centers in the molecule. Since the barriers to carbon epimerization are generally higher than those observed,[8c] it is reasonable to propose that it is the Ru center which epimerizes in this reaction. There are several mechanisms that are possible for this process including loss of PMe_3 followed by inversion of the 16e$^-$ Ru center and intramolecular rearrangements involving cleavage of the Ru–N bond or slippage of the arene ring fron η^6 to η^4 coordination. The observation that excess phosphine has no effect on the rate of the reaction does not rule out a dissociative mechanism. Furthermore, the fact that PMe_3 and $P(CD_3)_3$ exchange more rapidly than the isomerization occurs suggests that the rate-determining step of the isomerization may be either epimerization of the Ru center or trapping of the 16$^-$ intermediate, [(η^6-C_6Me_6)Ru(Ph)NC(H)(Me)C_6H_4], to give product. It is clear that more experiments will be necessary to understand the mechanism of this isomerization process since epimerization processes in related piano-stool complexes have been shown or proposed to proceed by both dissociative and intramolecular mechanisms.[16]

The amide complexes are readily protonated by HBF_4 and react readily with diesters of acetylenedicarboxylic acid and with CO under 3 atm of pressure. They do not appear to react with olefins, hydrogen (40 °C, 3 atm), ordinary acetylenes, or methyl iodide. The product that results from protonation of **2a** has been isolated and characterized (see Experimental Section) and is consistent with protonation of the amide nitrogen, giving an ortho-metalated benzylamine cation. It is possible that reaction with methyl iodide is prevented by the extremely hindered nature of the amide nitrogen atom in this structure, and studies with more powerful electrophiles are in progress.

It is evident from the results reported here and elsewhere[11] that the use of nucleophilic attack on cationic imine complexes has potential as a general method of synthesis of transition-metal amides. The availability of a large number of ortho-metalated imine complexes[17]

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makes this method particularly useful for the synthesis of ortho-metalated benzylamide complexes. The only potential limitation of this method of amide synthesis arises from the weak Lewis basicity of the imine nitrogen. There are only a few examples of N-bound imine ligands that are not stabilized by ortho-metalation or heteroatom coordination.[18] The generalization of this chemistry to the synthesis of monodentate amide complexes may be limited by starting material availability, which awaits further research.

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Supplementary Material Available: Tables of anisotropic thermal parameters and bond lengths and angles for **1a** and **2a** (12 pages); tables of observed and calculated structure factors for **1a** and **2a** (27 pages). Ordering information is given on any current masthead page.

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Titanocene(III) Phosphides: Trapping and Structure of Mononuclear Intermediates in the Formation of $[Cp_2Ti(\mu\text{-}PR_2)]_2$

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Intermediates in the reactions of Cp_2TiCl_2 with phosphides have been previously inferred by EPR studies. In this report two intermediates are trapped, isolated, and structurally characterized. Reaction of $LiPR_2$ (R = Et, Ph) with Cp_2TiCl_2 in the presence of PMe_3 yields the compounds $Cp_2TiPR_2(PMe_3)$ (**3**). The compound $Cp_2TiPPh_2(PMe_3)$ (**3b**) crystallizes in the space group $P2_1/c$ with a = 8.716 (3) Å, b = 25.914 (13), c = 10.225 (5) Å, Z = 4, and V = 2276 (2) Å^3. With the employment of excess phosphide and TMEDA, the compounds $[Li(TMEDA)_2][Cp_2Ti(PR_2)_2]$ (**4**) are obtained. The compound $[Li(TMEDA)_2][Cp_2Ti(PPh_2)_2]$ (**4b**) crystallizes in the space group $P2_1/c$ with a = 13.058 (5) Å, b = 19.312 (5) Å, c = 18.441 (6) Å, Z = 4, and V = 4613 (4) Å^3. The synthesis, isolation, and structural studies of these compounds serve not only to confirm the nature of the intermediates and the mechanism of formation of $[Cp_2Ti(\mu\text{-}PR_2)]_2$ but also to represent the first structural studies of mononuclear titanium phosphide complexes.

Introduction

Our interest in early-metal phosphide species has arisen from their utility as synthetic precursors for the preparation of early/late heterobimetallic (ELHB) complexes.[1] For example, we[2-6] and others[7-9] have described the use of species of the form $Cp_2M(PR_2)_2$ (R = Ph, Cy, Et; M = Zr, Hf) as metalloligands in the formation of mixed-metal, diphosphide-bridged products. The monophosphido-bridged ELHB complexes $Cp_2Zr(\mu\text{-}PR_2)(\mu\text{-}\eta^1,\eta^2\text{-}OC)M(CO)Cp$ are also accessible via redox reactions involving the zirconium(IV) phosphido precursors $Cp_2Zr(PR_2)_2$[10] or the zirconium(III) phosphido species $[Cp_2Zr(\mu\text{-}PR_2)]_2$.[11] Analogous reactions employing the Ti(III) species $[Cp_2Ti(\mu\text{-}PR_2)]_2$ afford the ELHB species $Cp_2Ti(THF)(\mu\text{-}OC)M(CO)_2Cp$.[11] While the chemistry of the derived ELHB complexes is a subject of ongoing investigations, further development in synthetic strategies to such complexes hinges on the development of new early-metal phosphide reagents.

The reactions of Cp_2TiCl_2 with phosphides affording diamagnetic Ti(III) and Zr(III) complexes were first reported in 1966 by Issleib and Hackert.[12] These species have been recently confirmed crystallographically to be the dimeric complexes $[Cp_2M(\mu\text{-}PR_2)]_2$ (a) (R = Me, M = Ti,[13] Zr;[14] R = Ph, M = Ti;[15a] R = Et, M = Ti[15b]). The preparation of the first zirconocene(IV) diphosphide species

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