Organometallics 1991, *10*, 2781-2794 2781

Synthesis and Reaction Chemistry of New η^5-Cyclopentadienylruthenium(II) Amine and Amide Complexes

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Received February 11, 1991

The complex η^5-cpRuCl($Cy_2PCH_2CH_2PCy_2$) has been prepared from the reaction of ruthenium trichloride, cyclopentadiene, and $Cy_2PCH_2CH_2PCy_2$. Treating η^5-cpRuCl($Cy_2PCH_2CH_2PCy_2$) with silver triflate in THF solvent gives [η^5-cpRu($Cy_2PCH_2CH_2PCy_2$]CF_3SO_3. Treating η^5-cpRuClLL′ with silver trilfate in THF solvent followed by ammonia gives the ammine complexes [η^5-cpRu(NH_3)LL′]CF_3SO_3 (L = L′ = PPh_3; L = PPh_3, L′ = $P(OMe)_3$; LL′ = $Cy_2PCH_2CH_2PCy_2$). The analogous procedure using amines in place of ammonia gives the amine complexes [η^5-cpRu(NH_2R)LL′]CF_3SO_3 (R = Me: L = L′ = PPh_3; L = PPh_3, L′ = $P(OMe)_3$; LL′ = $Cy_2PCH_2CH_2PCy_2$. R = CMe_3: L = PPh_3, L′ = $P(OMe)_3$. R = 1-C_8H_{17}: LL′ = $Cy_2PCH_2CH_2PCy_2$). Metathetical replacement of the chloride ion in η^5-cpRuCl($Cy_2PCH_2CH_2PCy_2$) by hydride or isocyanate ion gives η^5-cpRuX($Cy_2PCH_2CH_2PCy_2$) (X = H, NCO). Treating [η^5-cpRu(NH_3)($Cy_2PCH_2CH_2PCy_2$)]$^+$ with potassium hydride gives the amide complex η^5-cpRu(NH_2)($Cy_2PCH_2CH_2PCy_2$). This amide complex reacts with Me_4N^+ to give [η^5-cpRu(NH_2Me)($Cy_2PCH_2CH_2PCy_2$)]$^+$. Passing CO through a solution of η^5-cpRu(NH_2)($Cy_2PCH_2CH_2PCy_2$) gives the carbamoyl complex η^5-cpRu(C(O)NH_2)($Cy_2PCH_2CH_2PCy_2$). Passing CO_2 through a solution of η^5-cpRu(NH_2)($Cy_2PCH_2CH_2PCy_2$) gives the carbamate complex η^5-cpRu($OCONH_2$)($Cy_2PCH_2CH_2PCy_2$). In anhydrous solution this carbamate complex loses water to give the isocyanate complex η^5-cpRu(NCO)($Cy_2PCH_2CH_2PCy_2$). Treating [η^5-cpRu(NH_2Me)($Cy_2PCH_2CH_2PCy_2$)]$^+$ with potassium hydride gives a mixture of η^5-cpRu(NH_2)($Cy_2PCH_2CH_2PCy_2$), η^5-cpRuH($Cy_2PCH_2CH_2PCy_2$), and η^5-$cpRu_2H$(μ-$Cy_2PCH_2CH_2PCy$)$_2$. Treating [η^5-cpRu($NH_2C_8H_{17}$-1)($Cy_2PCH_2CH_2PCy_2$)]$^+$ with potassium hydride gives η^5-cpRu(NH_2)($Cy_2PCH_2CH_2PCy_2$) and η^5-cpRuH($Cy_2PCH_2CH_2PCy_2$). The organic product is 1-octanenitrile. The compound [η^5-cpRu(NH_3)(PPh_3)$_2$]CF_3SO_3 crystallizes in the monoclinic space group $P2_1/n$ with a = 12.667 (1) Å, b = 14.356 (3) Å, c = 21.457 (4) Å, β = 96.58 (1)°, and Z = 4. The structure was refined to R = 0.034 and R_w = 0.046 on the basis of 4815 unique reflections with $I \geq 3.0\sigma(I)$ and 479 variables. The compound [η^5-cpRu(NH_2CMe_3)(PPh_3)($P(OMe)_3$)]CF_3SO_3 crystallizes in the monoclinic space group $P2_1/n$ with a = 10.366 (2) Å, b = 21.862 (2) Å, c = 15.371 (2) Å, β = 92.33 (1)°, and Z = 4. The structure was refined to R = 0.041 and R_w = 0.063 on the basis of 4778 unique reflections with $I \geq 3.0\sigma(I)$ and 415 variables. The compound [η^5-cpRu($NH_2C_8H_{17}$-1)($Cy_2PCH_2CH_2PCy_2$)]CF_3SO_3 crystallizes in the rhombohedral space group $R\bar{3}$ with a = 40.907 (3) Å, c = 13.621 (2) Å, and Z = 18. The structure was refined to R = 0.048 and R_w = 0.066 on the basis of 4111 unique reflections with $I \geq 3.0\sigma(I)$ and 435 variables. The compound [η^5-cpRu(CO)($Cy_2PCH_2CH_2PCy_2$)]CF_3SO_3 crystallizes in the monoclinic space group $P2_1/n$ with a = 14.940 (5) Å, b = 15.394 (10) Å, c = 18.242 (4) Å, β = 97.63 (2)°, and Z = 4. The structure defined to R = 0.054 and R_w = 0.078 on the basis of 4657 unique reflections with $I \geq 3.0\sigma(I)$ and 411 variables.

An area of organotransition-metal chemistry which has received relatively limited attention is the synthesis and reaction chemistry of metal-heteroatom bonds. In particular there have been few published studies on the synthesis and reaction chemistry of organotransition-metal complexes having metal-nitrogen bonds between a late transition metal and an amide ligand. A basic reason for the scarcity has been the general belief that the bond between a hard nitrogen ligand and a late-transition-metal center will be relatively weak.[1] Amide complexes of high-valent early transition metals are, however, quite common. The situation results from the fact that these metal centers in the complex are not electron precise, and hence in such complexes the lone electron pair formally on the amide nitrogen ligand is partially donated to the metal center to give a partial multiple metal-nitrogen bond.[2] In many instances transition-metal amide complexes are oligomeric. These oligomers result from the lone electron pair on nitrogen in the initially formed monomeric complex acting as a ligand to a second transition-metal center. Subsequent intermolecular substitution of a support ligand between the pair of complexes results in a bimetallic complex that has one or more amide bridges joining the metal centers.[3]

Recently, we have synthesized a series of coordinately unsaturated complexes of platinum(II) having an unsubstituted amide (NH_2) ligand. Both bimetallic and monomeric complexes have been isolated. The monomeric complexes have been stabilized by the use of a bulky tricyclohexylphosphine ligand, which precludes substitution dimerization to give bridging amide complexes. These thermally stable complexes are considered to have a platinum-nitrogen single bond because multiple bonding would require the lone electron pair on nitrogen to be donated into a high-energy $d_{x^2-y^2}$ orbital on platinum(II).[4]

In this paper we report the use of a sterically bulky ligand in the directed synthesis of a monomeric ruthenium(II) complex having an unsubstituted amide (NH_2) ligand. The complexes have a "piano stool" configuration where the coordination positions are occupied by a cyclopentadienyl and a bulky chelating 1,2-bis(dicyclohexylphosphino)ethane ligand. The complexes are electron precise at ruthenium; therefore it is plausible that the ruthenium-nitrogen bond is essentially a single bond and

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[3] Park, S.; Roundhill, D. M.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 3972-4.

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0276-7333/91/2310-2781$02.50/0

that the lone electron pair is localized on nitrogen.[5]

Experimental Section

All solvents were reagent grade and dried by standard procedures prior to use. Hydrated ruthenium trichloride was supplied by Johnson Matthey, Inc. 1,2-Bis(dicyclohexylphosphino)ethane (dcpe) was purchased from Strem Chemicals. Triphenylphosphine and trimethyl phosphite were commercial samples, as were ammonia and the amines. The compounds η^5-cpRuCl(PPh_3)$_2$, η^5-cpRuCl(PPh_3)(P(OMe)$_3$), and Na[N(SiMe$_3$)$_2$] were prepared according to literature procedures.[6] Microanalyses were carried out by Galbraith Inc., Knoxville, TN. All NMR spectra were obtained on a Bruker AC 200 NMR spectrometer at the following frequencies (MHz): ^{1}H, 200.132; ^{13}C, 50.323; ^{31}P, 81.015. The solvent used, unless otherwise specified, was C_6D_6. In those samples containing triphenylphosphine, phenyl resonances were observed in the ^{1}H NMR spectrum in the range δ 6.9–7.6 and in the ^{13}C{^{1}H} NMR spectrum in the range δ 130–134. In those samples containing $Cy_2PCH_2CH_2PCy_2$, cyclohexyl resonances were observed in the ^{1}H NMR spectrum in the range δ 0.8–2.0 and in the ^{13}C{^{1}H} NMR spectrum in the range δ 26–31. All IR spectra were obtained on a KBr disk on a Mattson Cygnus 100 spectrometer unless otherwise indicated. FAB spectra were obtained on a VG70EHF mass spectrometer using *m*-nitrobenzyl alcohol as matrix.

[η^5-cpRu(NH_3)(PPh_3)$_2$]CF_3SO_3 (1). η^5-cpRuCl(PPh_3)$_2$ (0.255 g, 3.52 × 10^{-4} mol) was dissolved in tetrahydrofuran (10 mL), affording a clear orange solution. Silver triflate (1 equiv in THF) was added to the stirred solution, causing the immediate formation of a precipitate and darkening of the color of the solution. Generally, 2–3 equiv of $AgCF_3SO_3$ was weighed into a vial in a glovebox and then dissolved in THF (10.0 mL) in a Schlenk tube. The appropriate volume of this solution corresponding to 1 equiv of $AgCF_3SO_3$ was then determined and added to the stirred ruthenium complex. In the above reaction 0.1964 g of $AgCF_3SO_3$ was dissolved in THF (10.0 mL) and 4.6 mL of this solution used. The mixture was stirred for 30 s, and the solid was then allowed to settle for ca. 5 m. The supernatant was then removed by syringe and filtered through a glass wool plug to give a clear dark orange solution. Anhydrous NH_3 was bubbled through this solution for ca. 30 s, giving an immediate color change from orange to bright yellow. Removal of the solvent in vacuo resulted in the formation of a fine yellow powder. Yield: 0.284 g (94%). ^{31}P{^{1}H} NMR: δ 45.9 (s). ^{1}H NMR: δ 2.51 (b, 3 H, NH_3), 4.41 (s, 5 H, C_5H_5). ^{13}C{^{1}H} NMR (acetone-d_6): δ 82.3 (s, C_5H_5). IR: $\nu(NH_3)$ 3190, 3273, 3323, 3356 cm^{-1}. Anal. Calcd for $C_{42}H_{38}F_3NO_3P_2RuS$: C, 58.9; H, 4.47; N, 1.63. Found: C, 58.9, H, 4.56; N, 1.63.

[η^5-cpRu($MeNH_2$)(PPh_3)$_2$]CF_3SO_3 (2). In an fashion analogous to the synthesis of 1, η^5-cpRuCl(PPh_3)$_2$ (0.20 g, 2.76 × 10^{-4} mol) was dissolved in THF (10 mL) and the solution was treated with silver triflate (1 equiv in THF). The supernatant was removed and filtered, and the filtrate was treated with anhydrous H_2NMe for 30 s. The color change from orange to yellow was immediate, and removal of solvent in vacuo resulted in the formation of a fine yellow solid. Yield: 0.228 g (95%). ^{31}P{^{1}H} NMR: δ 43.7 (s). ^{1}H NMR: δ 2.44 (t, 3 H, NCH_3, $^3J(HH)$ = 6.1 Hz), 3.27 (b, 2 H, NH_2), 4.38 (s, 5 H, C_5H_5). ^{13}C{^{1}H} NMR (acetone-d_6): δ 41.1 (s, NCH_3), 82.3 (s, C_5H_5). IR: $\nu(NH_2)$ 3267, 3308 cm^{-1}. Anal. Calcd for $C_{43}H_{40}F_3NO_3P_2RuS$: C, 59.3; H, 4.63; N, 1.61. Found: C, 59.3; H, 4.88; N, 1.59.

[η^5-cpRu(NH_3)(PPh_3)(P(OMe)$_3$)]CF_3SO_3 (3). In a manner similar to the synthesis of 1, η^5-cpRuCl(PPh_3)(P(OMe)$_3$) (0.225 g, 3.83 × 10^{-4} mol) was dissolved in THF (10 mL) and the solution was treated with silver triflate (1 equiv in THF). It was necessary to stir the sample for 30 min to allow complete reaction. Removal of the supernatant and filtration yielded a clear orange solution. Treatment with anhydrous NH_3 for 30 s rapidly caused a color change to yellow. Removal of the solvent in vacuo afforded the formation of a fine yellow solid. Yield: 0.253 g (92%). ^{31}P{^{1}H} NMR: δ 56.3 (d, PPh_3), 151.5 (d, P(OMe)$_3$, $^2J(PP)$ = 68 Hz). ^{1}H NMR: δ 2.49 (b, 3 H, NH_3), 3.15 (d, 9 H, OCH_3, $^3J(PH)$ = 10.8 Hz), 4.74 (s, 5 H, C_5H_5). ^{13}C{^{1}H} NMR: δ 52.0 (d, OCH_3, $^2J(PC)$ = 7.5 Hz), 81.7 (d, C_5H_5, $^2J(PC)$ = 2.4 Hz). IR: $\nu(NH_3)$ 3199, 3273, 3328, 3362 cm^{-1}. Anal. Calcd for $C_{26}H_{32}F_3NO_6P_2RuS$: C, 45.1; H, 4.45; N, 1.95. Found: C, 44.9; H, 4.52; N, 1.86.

[η^5-cpRu($MeNH_2$)(PPh_3)(P(OMe)$_3$)]CF_3SO_3 (4). In a manner similar to the synthesis of 3, η^5-cpRuCl(PPh_3)(P(OMe)$_3$) (0.278 g, 4.74 × 10^{-4} mol) was dissolved in THF (10 mL), silver triflate (1 equiv in THF) was added, and the solution was stirred for 30 min. Treatment of the filtered supernatant with anhydrous H_2NMe for 30 s resulted in an immediate color change to yellow. Removal of the solvent in vacuo resulted in the formation of a fine yellow solid. Yield: 0.334 g (96%). ^{31}P{^{1}H} NMR: δ 55.9 (d, PPh_3), 149.7 (d, P(OMe)$_3$, $^2J(PP)$ = 68 Hz). ^{1}H NMR: δ 2.37 (d, 3 H, NCH_3, $^3J(HH)$ = 6.3 Hz), 3.1 (b, 2 H, NH_2), 3.12 (d, 9 H, OCH_3, $^3J(PH)$ = 11 Hz), 4.68 (d, 5 H, C_5H_5, $^3J(HH)$ = 0.7 Hz). ^{13}C{^{1}H} NMR (acetone-d_6): δ 41.3 (s, NCH_3), 53.0 (d, OCH_3, $^2J(PC)$ = 8.2 Hz), 82.4 (s, C_5H_5). IR: $\nu(NH_2)$ 3269, 3321 cm^{-1}. Anal. Calcd for $C_{28}H_{34}F_3N_3O_6P_2RuS$: C, 45.9; H, 4.68; N, 1.91. Found: C, 45.4; H, 4.62; N, 1.74.

[η^5-cpRu(Me_3CNH_2)(PPh_3)(P(OMe)$_3$)]CF_3SO_3 (5). In a manner similar to the synthesis of 3, η^5-cpRuCl(PPh_3)(P(OMe)$_3$) (0.300 g, 5.10 × 10^{-4} mol) was dissolved in THF (10 mL) and the solution was treated with silver triflate (1 equiv in THF) and stirred for 30 min. The resulting supernatant was filtered, and the filtrate was treated with Me_3CNH_2 (1 mL). No reaction was immediately obvious, but after 45 min the color had changed from orange to bright yellow. Removal of the solvent in vacuo resulted in a sticky yellow solid. This was extracted with benzene (2 × 5 mL) to yield, upon removal of solvent, a fine yellow solid. Yield: 0.32 g (81%). ^{31}P{^{1}H} NMR: δ 56.0 (d, PPh_3), 147.1 (d, P(OMe)$_3$, $^2J(PP)$ = 68.1 Hz). ^{1}H NMR: δ 1.08 (s, 9 H, CH_3), 2.4 (d, 1 H, NH, $^2J(HH)$ = 11 Hz), 2.7 (d, ^{1}H, NH), 3.65 (d, 9 H, OCH_3, $^3J(PH)$ = 10.8 Hz), 4.97 (s, 5 H, C_5H_5). ^{13}C{^{1}H} NMR: δ 31.0 (s, $NCCH_3$), 50.7 (s, NC), 53.4 (d, OCH_3, $^2J(PC)$ = 6.4 Hz), 81.3 (s, C_5H_5). IR: $\nu(NH_2)$ 3263, 3305 cm^{-1}. Anal. Calcd for $C_{31}H_{40}F_3N_3O_6P_2RuS$: C, 48.1; H, 5.20; N, 1.81. Found: C, 48.3; H, 5.27; N, 1.87.

η^5-cpRuCl($Cy_2PCH_2CH_2PCy_2$) (6). η^5-cpRuCl(PPh_3)$_2$ (1.165 g, 1.61 × 10^{-3} mol) was placed in a Schlenk tube and benzene (10 mL) added to give a red/brown suspension. $Cy_2PCH_2CH_2PCy_2$ (0.685 g, 1.62 × 10^{-3} mol) was added to the stirred mixture in benzene (5 mL). The sample was heated at reflux for 1 h. After 15 min the solid had dissolved to give a dark orange/red solution. Removal of the solvent in vacuo resulted in a dark red oil. This was dissolved in hexanes (3 × 5 mL), and the resulting solution was filtered through glass wool. At this point the sample is not air sensitive. The hexane solution was placed onto a dry alumina column (ca. 1 cm × 20 cm) and eluted with additional hexanes. The metal complex appeared to adsorb irreversibly to the column in hexanes, moving down 80% of the length of the column, but no further, even with additional elution with hexanes. This elution was continued until all the PPh_3 had been removed from the column. Subsequent elution with THF affords rapid stripping of the complex to give an orange/red solution. Removal of the solvent in vacuo resulted in the formation of a fluffy orange solid. Yield: 0.945 g (94%). Crystals were obtained from evaporation of a diethyl ether solution of the complex in air. ^{31}P{^{1}H} NMR: δ 8.63 (s). ^{1}H NMR: δ 2.4 (b, 4 H, PCH_2), 4.71 (s, 5 H, C_5H_5). ^{13}C{^{1}H} NMR: δ 21.6 (m, PCH_2), 36.5 (m, PCH), 41.6 (m, PCH), 76.6 (t, C_5H_5, $^3J(PC)$ = 2.3 Hz). Anal. Calcd for $C_{31}H_{53}ClP_2Ru\cdot C_4H_{10}O$: C, 60.1; H, 9.08. Found: C, 60.1; H, 8.77.

[η^5-cpRu($Cy_2PCH_2CH_2PCy_2$)]CF_3SO_3 (7). η^5-cpRuCl(dcpe) (0.10 g, 1.60 × 10^{-4} mol) was dissolved in THF (10 mL), and the solution was treated with silver triflate (1 equiv in THF). The sample was stirred for 30 s and the solid allowed to settle. The orange supernatant was removed and filtered through glass wool. Removal of the solvent in vacuo afforded a fluffy orange powder. This solid was dissolved in diethyl ether (3 × 5 mL) and the solvent removed in vacuo each time to give the complex as a fluffy orange solid. Yield: 0.114 g (96%). ^{31}P{^{1}H} NMR: δ 83.9 (s). ^{1}H NMR: δ 4.63 (s, C_5H_5). ^{13}C{^{1}H} NMR: δ 20.7 (t, PCH_2, $|^1J(PC) + {}^2J(PC)|$ = 18.7 Hz), 26.6 (s, Cy, C(4)), 27.7 (t, Cy, C(2), $|^2J(PC) + {}^4J(PC)|$ = 5.3 Hz), 27.8 (t, Cy, C(6), $|^2J(PC) + {}^4J(PC)|$ = 4.7 Hz), 29.8 (s, Cy, C(3)), 29.9 (s, Cy, C(5)), 38–40 (vb, Cy, C(1)), 74.2 (s, C_5H_5). Anal. Calcd for $C_{32}H_{53}F_3O_3P_2RuS$: C, 52.1; H, 7.2. Found: C, 51.6; H, 6.8.

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[5] For a preliminary communication see: Joslin, F. L.; Johnson, M. P.; Mague, J. T.; Roundhill, D. M. *Organometallics* **1991**, *10*, 41–3.

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$[\eta^5\text{-cpRu}(NH_3)(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3$ (8). Similar to the synthesis of 1, η^5-cpRuCl(dcpe) (0.291 g, 4.66 × 10^{-4} mol) was dissolved in THF (10 mL) and silver triflate (1 equiv in THF) added to the stirred solution. A suspension formed immediately, and the color of the mixture darkened significantly. The suspension was stirred for 30 s and the solid allowed to settle. The orange supernatant was filtered through a glass wool plug, affording a dark orange solution. Anhydrous NH_3 was bubbled through the solution for 30 s, causing an immediate color change to yellow. Removal of the solvent in vacuo afforded the complex as a bright yellow solid. Yield: 0.305 g (87%). Crystals were obtained from a diethyl ether solution at −20 °C. $^{31}P\{^1H\}$ NMR: δ 86.7 (s). ^1H NMR: δ 1.0–0.0 (b, 3 H, $N\mathit{H}_3$), 4.62 (s, 5 H, $C_5\mathit{H}_5$). $^{13}C\{^1H\}$ NMR: δ 22.2 (t, $P\mathit{C}H_2$, $|^1J(PC) + {}^3J(PC)| = 19.9$ Hz), 37.0 (m, $P\mathit{C}H$), 41.5 (m, $P\mathit{C}H$), 77.1 (s, C_5H_5). IR: $\nu(NH_3)$ 3206, 3280, 3330, 3361 cm^{-1}. Anal. Calcd for $C_{32}H_{56}F_3NO_3P_2RuS\cdot C_4H_{10}O$: C, 52.2; H, 8.02; N, 1.68. Found: C, 52.3; H, 7.54; N, 1.68.

$[\eta^5\text{-cpRu}(MeNH_2)(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3$ (9). Similar to the synthesis of 1, η^5-cpRuCl(dcpe) (0.10 g, 1.60 × 10^{-4} mol) was dissolved in THF (10 mL) and silver triflate (1 equiv in THF) added. The sample was stirred for 30 s, the solid was allowed to settle, and the supernatant was removed and filtered. Methylamine was bubbled through this clear orange solution for 2 min, causing an immediate color change to yellow. Removal of the solvent in vacuo resulted in the formation of a fine yellow powder. Yield: 0.115 g (93%). $^{31}P\{^1H\}$ NMR: δ 85.1 (s). ^1H NMR: δ 2.34 (t, 3 H, $NC\mathit{H}_3$, $^3J(HH) = 5.8$ Hz), 2.7 (b, 2 H, $N\mathit{H}_2$), 4.35 (s, $C_5\mathit{H}_5$). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 21.7 (m, $P\mathit{C}H_2$), 37.8 (m, $P\mathit{C}H$), 40.3 (s, $N\mathit{C}H_3$), 42.7 (m, $P\mathit{C}H$), 78.0 (s, C_5H_5). IR: $\nu(NH_2)$ 3267, 3329 cm^{-1}. Anal. Calcd for $C_{33}H_{54}F_3NO_3P_2RuS$: C, 51.8; H, 7.21; N, 1.83. Found: C, 51.7; H, 7.22; N, 1.70.

$[\eta^5\text{-cpRu}(1\text{-}C_8H_{17}NH_2)(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3$ (10). With a procedure similar to the synthesis of complex 1, η^5-cpRuCl(dcpe) (0.10 g, 1.60 × 10^{-4} mol) was dissolved in THF and silver triflate (1 equiv in THF) added. A solid formed immediately and, after stirring for 30 s, was allowed to settle. The supernatant was removed and filtered through glass wool and 1-octylamine (2 drops) added. The color of the solution rapidly changed from orange to yellow. Removal of the solvent in vacuo followed by extraction with diethyl ether (5 mL) afforded the complex as a sticky yellow solid. Yield: 0.125 g (90%). Crystals were obtained from a diethyl ether solution at −20 °C. $^{31}P\{^1H\}$ NMR: δ 86.5 (s). ^1H NMR: δ 0.8–2.5 (bm, Cy and 1-Oct), 4.36 (s, $C_5\mathit{H}_5$). $^{13}C\{^1H\}$ NMR: δ 21.6 (t, $P\mathit{C}H_2$, $|^1J(PC) + {}^3J(PC)| = 19.7$ Hz), 36.8 (t, $P\mathit{C}H$, $|^1J(PC) + {}^3J(PC)| = 9.6$ Hz), 42.2 (t, $P\mathit{C}H$, $|^1J(PC) + {}^3J(PC)| = 11.6$ Hz), 76.5 (s, C_5H_5), 55.5 (s, 1-Oct, $\mathit{C}(1)$), 33.0 (s, 1-Oct, $\mathit{C}(2)$), 32.2 (s, 1-Oct, $\mathit{C}(3)$), 23.0 (s, 1-Oct, $\mathit{C}(7)$), 14.3 (s, 1-Oct, $\mathit{C}(8)$). IR: $\nu(NH_2)$ 3255, 3317 cm^{-1}. Anal. Calcd for $C_{40}H_{72}F_3NO_3P_2RuS$: C, 55.4; H, 8.4; N, 1.6. Found: C, 55.5; H, 8.6; N, 1.6.

Reaction of $[\eta^5\text{-cpRu}(NH_3)(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3$ with Hydride Ion (11). $[\eta^5\text{-cpRu}(NH_3)(dcpe)]CF_3SO_3$ (0.155 g, 2.06 × 10^{-4} mol) was dissolved in THF (5 mL distilled from sodium benzophenone and then dried over KH). To this yellow solution was added a suspension of KH in THF (ca. 1 mL). The color of the mixture darkened to give a black/green suspension. This mixture was stirred for an additional 10 min and the solvent removed in vacuo. The resulting green/black solid was extracted with benzene (2 × 5 mL distilled from sodium benzophenone and dried over KH), and the extract was filtered through a glass wool plug. This procedure afforded a clear dark orange solution, which upon removal of the solvent in vacuo gave a dark orange film containing η^5-cpRu(NH_2)($Cy_2PCH_2CH_2PCy_2$) (11) and KCF_3SO_3. Yield: 0.106 g (85.%). $^{31}P\{^1H\}$ NMR: δ 92.5 (s). ^1H NMR: δ 0.0–3.0 (b, 2 H, $N\mathit{H}_2$), 2.2 (b, 4 H, PCH_2), 4.74 (s, 5 H, $C_5\mathit{H}_5$). $^{13}C\{^1H\}$ NMR: 22.0 (t, $P\mathit{C}H_2$, $|^1J(PC) + {}^2J(PC)| = 19.4$ Hz), 36.0 (m, $P\mathit{C}H$), 41.5 (m, $P\mathit{C}H$), 77.4 (s, C_5H_5).

$\eta^5\text{-cpRuH}(Cy_2PCH_2CH_2PCy_2)$ (12). η^5-cpRuCl(dcpe) (0.10 g, 1.60 × 10^{-4} mol) was dissolved in THF (5 mL) and $LiAlH_4$ (20 mg, excess) added. The sample changed from an orange solution to a green/orange suspension. The mixture was stirred for an additional 30 min and the solvent removed in vacuo. The resulting solid was extracted with benzene (2 × 5 mL), and the benzene extracts were eluted through a silica plug (5 mm × 2 cm) on glass wool to remove excess $LiAlH_4$. Removal of the solvent in vacuo resulted in the formation of the compound as an off-white sticky solid. Yield: 0.0765 g (81%). The FAB mass spectrum exhibits an envelope of peaks with m/z 586–592, which have relative intensities characteristic of cpRu(dcpe). $^{31}P\{^1H\}$ NMR: δ 110.2 (s). ^1H NMR: δ 14.7 (t, 1 H, $Ru\mathit{H}$, $^2J(PH) = 34.2$ Hz), 2.1 (b, 4 H, $PC\mathit{H}_2$), 4.94 (s, 5 H, $C_5\mathit{H}_5$). $^{13}C\{^1H\}$ NMR: δ 23.6 (m, $P\mathit{C}H_2$), 39.1 (m, $P\mathit{C}H_2$), 40.5 (m, $P\mathit{C}H$), 76.9 (s, C_5H_5). IR: $\nu(RuH)$ 2003 cm^{-1}. Anal. Calcd for $C_{31}H_{34}P_2Ru$: C, 63.3; H, 9.23. Found: C, 62.9; H, 9.11.

Reaction of $\eta^5\text{-cpRu}(NH_2)(Cy_2PCH_2CH_2PCy_2)$ with CO (13). η^5-cpRu(NH_2)(dcpe) (0.883 g, 1.46 × 10^{-4} mol) was dissolved in THF (10 mL dried as above) to give a dark orange solution. Carbon monoxide was bubbled through the solution for 5 min, resulting in a darkening of the color to orange/brown. Removal of the solvent in vacuo resulted in the formation of a dark brown solid containing $[\eta^5\text{-cpRu}(CONH_2)(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3$ (13). Yield: 0.0883 g (96%). $^{31}P\{^1H\}$ NMR: δ 89.6 (s). ^1H NMR: δ 2.8 (b, 2 H, $N\mathit{H}_2$), 4.85 (s, 5 H, $C_5\mathit{H}_5$). $^{13}C\{^1H\}$ NMR: δ 22.2 (t, $P\mathit{C}H_2$, $|^1J(PC) + {}^2J(PC)| = 24.6$ Hz), 36.6 (m, $P\mathit{C}H$), 41.6 (t, $P\mathit{C}H$, $J = 6.1$ Hz), 77.3 (s, C_5H_5), 167.3 (t, $\mathit{C}O$, $^2J(PC) = 70$ Hz). IR: $\nu(CO)$ 1597 cm^{-1}; $\nu(NH_2)$ 3077, 3091, 3100 cm^{-1}.

$[\eta^5\text{-cpRu}(CO)(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3$ (14). η^5-cpRuCl(dcpe) (0.050 g, 8.01 × 10^{-4} mol) was dissolved in THF (4 mL) and silver triflate (1 equiv in THF) added. After stirring for 30 s and settling of the solid, the supernatant was removed and filtered. Carbon monoxide gas was bubbled through the orange solution for 5 min, causing the color to change to yellow/green. Removal of the solvent in vacuo afforded a fine yellow solid. Yield: 0.0556 g (92%). Crystals were obtained from slow diffusion of diethyl ether into a benzene solution. $^{31}P\{^1H\}$ NMR: δ 84.3 (s). ^1H NMR: δ 2.4 (b, 4 H, $PC\mathit{H}_2$), 5.07 (s, 5 H, $C_5\mathit{H}_5$). $^{13}C\{^1H\}$ NMR: δ 23.0 (m, $P\mathit{C}H_2$), 38.6 (m, $P\mathit{C}H$), 41.1 (m, $P\mathit{C}H$), 86.1 (s, C_5H_5), 203.8 (t, $^{13}\mathit{C}O$, $^2J(PC) = 15.5$ Hz). IR: $\nu(CO)$ 1940 cm^{-1}. Anal. Calcd for $C_{33}H_{53}F_3O_4P_2RuS\cdot C_6H_6$: C, 55.1; H, 6.97. Found: C, 54.7; H, 6.93.

$\eta^5\text{-cpRu}(OC(O)NH_2)(Cy_2PCH_2CH_2PCy_2)$ (15). η^5-cpRu(NH_2)(dcpe) (0.1388 g, 2.30 × 10^{-4} mol) was dissolved in THF (10 mL distilled from sodium/benzophenone and dried over KH) to give a dark orange solution. Carbon dioxide was bubbled through the solution for 10 min, causing a darkening of the color to brown. The solvent was removed in vacuo affording a light brown solid. Yield: 0.135 g (90%). $^{31}P\{^1H\}$ NMR: δ 89.8 (s). ^1H NMR: δ 2.2 (b, 2 H, $N\mathit{H}_2$), 4.56 (s, 5 H, $C_5\mathit{H}_5$). $^{13}C\{^1H\}$ NMR: δ 22.56 (t, $P\mathit{C}H_2$, $|^1J(PC) + {}^2J(PC)| = 19.2$ Hz), 37.18 (t, $P\mathit{C}H$, $|^1J(PC) + {}^3J(PC)| = 5.6$ Hz), 40.76 (t, $P\mathit{C}H_2$, $|^1J(PC) + {}^3J(PC)| = 6.45$ Hz), 76.86 (s, C_5H_5), 131.3 (b, $\mathit{C}O$). IR: $\nu(NH_2)$ 3091, 3102 cm^{-1}; $\nu(CO)$ 1615 cm^{-1}. Anal. Calcd for $C_{32}H_{55}NO_2P_2Ru$: C, 59.2; H, 8.6; N, 2.2. Found: C, 57.6; H, 8.8; N, 2.4.

$\eta^5\text{-cpRu}(NCO)(Cy_2PCH_2CH_2PCy_2)$ (16). η^5-cpRuCl(dcpe) (0.0974 g, 1.56 × 10^{-4} mol) was dissolved in THF (10 mL) and treated with silver triflate (1 equiv in THF). After stirring for 30 s and settling of the solid, the resulting supernatant was removed and filtered. KOCN (30 mg, excess) was added to the stirred orange solution with no immediate reaction. After the suspension was stirred for 20 min, the color had darkened to brown. The sample was stirred for an additional 40 min and the solid allowed to settle. The supernatant was removed and filtered through a glass wool plug, affording a brown solution. Removal of the solvent in vacuo yielded the complex as a brown solid. Yield: 79 mg (80%). $^{31}P\{^1H\}$ NMR: δ 83.9 (s). ^1H NMR: δ 2.3 (b, 4 H, $PC\mathit{H}_2$), 4.69 (s, 5 H, $C_5\mathit{H}_5$). IR: $\nu(NCO)$ 2238, 1260 cm^{-1}. Anal. Calcd for $C_{32}H_{53}NOP_2Ru$: C, 60.9; H, 8.47; N, 2.22. Found: C, 60.5; H, 8.67; N, 2.07.

Reaction between $\eta^5\text{-cpRu}(NH_2)(Cy_2PCH_2CH_2PCy_2)$ and the Tetramethylammonium Ion. A solution of the complex was prepared by the standard procedure from $[\eta^5\text{-cpRu}(NH_3)(dcpe)]CF_3SO_3$ (0.133 g, 1.76 × 10^{-3} mol). A solution of tetramethylammonium tetrafluoroborate was synthesized in situ by treating a solution of trimethyloxonium tetrafluoroborate (0.1514 g, 1.02 × 10^{-3} mol) in THF (10 mL) with anhydrous trimethylamine for 10 min. An aliquot (1.7 mL) of this solution of $[NMe_4]BF_4$, which represented the molar equivalent of η^5-cpRu(NH_2)(dcpe), was added to this orange solid. The color of the complex changed to yellow, and removal of the solvent in vacuo gave the solid product containing the cation $[\eta^5\text{-cpRu}(NH_2Me)(dcpe)]^+$.

Reactions between $[\eta^5\text{-cpRu}(THF)(PPh_3)_2]CF_3SO_3$ and Dimethylamine, *N*-Deuteriodimethylamine, and Piperidine.

Table I. Details of Crystallographic Data Collections

	3	5	10	14
formula	$C_{42}H_{38}F_3NO_3P_2RuS$	$C_{31}H_{40}F_3NO_6P_2RuS$	$C_{40}H_{72}NO_3F_3P_2RuS$	$C_{39}H_{53}D_6O_4F_3P_2RuS$
fw	858.19	673.69	867.10	849.93
cryst dimens, mm	0.4 × 0.3 × 0.3	0.36 × 0.59 × 0.50	0.35 × 0.35 × 0.35	0.53 × 0.53 × 0.43
color	yellow	yellow	amber	amber
cryst syst	monoclinic	monoclinic	rhombohedral	monoclinic
space group	$P2_1/n$	$P2_1/n$	$R\bar{3}$ (No. 148)	$P2_1/n$
a, Å	12.667 (1)	10.366 (2)	40.907 (3)	14.940 (5)
b, Å	14.356 (3)	21.862 (2)		15.394 (10)
c, Å	21.457 (4)	15.371 (2)	13.621 (2)	18.242 (4)
β, deg	96.58 (1)	92.33 (1)		97.63 (2)
V, A^3	3876 (2)	3481	19740 (5)	4158
Z	4	4	18	4
ρ(calcd), g cm^{-3}	1.448	1.48	1.313	1.36
λ(Mo Kα radiation, graphite monochromated), Å	0.71073	0.71073	0.71073	0.71073
θ range for unit cell detn, deg	8–14	11.87–14.92	10.4–14.4	10.7–14.8
obsd decay in intensity monitors, %			6.3	3
χ range for abs corr refls (no. of refls), deg	85–89 (4)	82.87 (6)		82.89 (4)
agreement on F for averaged data	0.02	0.02	0.024	0.012
temp, °C	25	25	24	24
linear abs coeff, cm^{-1}	5.8	6.4	5.14	5.3
range of trans factor	0.97–1.00	0.96–1.00		0.983–1.000
θ range, deg	0.5–26.5	0.5–25.0	1.5–20.0	1.5–24.0
scan type	ω–2θ	ω–2θ	ω–2θ	ω–2θ
scan width, deg	0.80 + 0.20 tan θ	0.80 + 0.20 tan θ	0.80 + 0.20 tan θ	0.80 + 0.20 tan θ
scan rate, deg min^{-1}	1.3–16.5	1.2–16.5	1.3–16.5	1.27–16.5
attn factor	11.87	11.87	11.87	11.87
diffractometer used	Enraf-Nonius CAD 4	Enraf-Nonius CAD 4	Enraf-Nonius CAD 4	Enraf-Nonius CAD 4
programs used	Enraf-Nonius SDP	Enraf-Nonius SDP	Enraf-Nonius MolEN	Enraf-Nonius SDP
unique data	7990	6109	4111	6513
data $I \geq 3.0\sigma(I)$	4815	4778	2493	4657
no. of variables	479	415	435	411
largest shift/esd in final cycle	0.11[e]	0.06	0.34	0.13
R[a]	0.034	0.041	0.048	0.054
R_w[b,c]	0.046	0.063	0.066	0.078
p factor in weight[d]	0.04	0.04	0.04	0.04
GOF[c]	1.376	2.249	1.98	2.70

[a] $R = \sum|F_o - |F_c||/\sum F_o$. [b] $[\sum w(|F_o - F_c|)^2/\sum w(F_o)^2]^{1/2}$. [c] GOF = $]\sum w(|F_o - F_c|)^2/(N_o - N_v)^{1/2}$, where N_o and N_v are respectively the number of observations and variables. [d] The weighting scheme used in the final refinement was $w = 1/\sigma^2_F$ where $\sigma_F = \sigma(F^2)/2F$ and $\sigma(F^2) = [(\sigma_I)^2 + (pF^2)^2]^{1/2}$. [e] Excluding atoms C(62)–C(64) affected by possible disorder.

In each case η^5-cpRuCl(PPh$_3$)$_2$ (0.1 g, 1.38 × 10^{-4} mol) was dissolved in THF (10 mL) and silver triflate (1 equiv in THF) added. The solid was allowed to settle and the supernatant liquid removed and filtered. This resulting orange solution was used for the reactions. For the case of dimethylamine the compound was bubbled through the solution for 30 min. For the case of piperidine, the liquid (1 mL) was added. For the case of NDMe$_2$, the compound was prepared by adding D$_2$O (1.0 g, 99.996% D) to lithium dimethylamide (4.0 g). For reaction with the orange solution of [η^5-cpRu(THF)(PPh$_3$)$_2$]CF$_3$SO$_3$, approximately 2.3 g of NDMe$_2$ was used. In each case the yield of η^5-cpRuH(PPh$_3$)$_2$ was 95% based on the NMR spectra.

Reactions of [η^5-cpRu(NH$_2$R)LL′]CF$_3$SO$_3$ with Strong Bases. The ruthenium complexes (ca. 0.05–0.10 g) were dissolved in THF (ca. 10 mL) and treated with 1 equiv of the soluble bases. The bases used were butyllithium (1.6 M in hexanes), Na[N(SiMe$_3$)$_2$] (1.0 M in THF), and excess potassium hydride in THF. Reactions were carried out at either ambient temperature or at -78 C.

Reaction of [η^5-cpRu(NH$_2$R)(dcpe)]CF$_3$SO$_3$ (R = Me, 1-C$_8$H$_{17}$) with Potassium Hydride. The complex [η^5-cpRu(NH$_2$R)(dcpe)]CF$_3$SO$_3$ (0.10 g; R = Me, 1.31 × 10^{-4} mol; R = 1-C$_8$H$_{17}$, 1.15 × 10^{-4} mol) was dissolved in THF (10 mL dried over KH) and KH (1 mL of a suspension in THF) added. The color of the solution darkened. After the solution was magnetically stirred for 30 min, the solid was allowed to settle and the supernatant filtered through glass wool. This solution was analyzed by GC/MS. Removal of the solvent in vacuo afforded the product complexes as an orange film.

Crystal Structure Determinations. All crystals were mounted on thin glass fibers and coated with epoxy cement. General procedures for unit cell determination and data collection on the Enraf-Nonius CAD-4 diffractometer have been published.[7] Details specific to each structure are presented in Table I. Scattering factors were taken from ref 8 and include the real and imaginary parts of the correction for anomalous dispersion. All data were corrected for Lorentz and polarization effects and for absorption employing ψ scans of reflections with χ near 90°. All calculations were performed on a Vax station 3100 computer with the Enraf-Nonius SDP and MolEN program packages.[8]

[η^5-cpRu(NH$_3$)(PPh$_3$)$_2$]CF$_3$SO$_3$. The crystal was obtained by slow diffusion of diethyl ether into an acetone solution of the complex. The structure was solved by direct methods. In the final stages of refinement all hydrogen atoms were observed in difference maps. These were included in the positions obtained from these maps and allowed to ride on the attached carbon atoms with isotropic thermal parameters 1.3 times those of the attached carbon atoms. Three phenyl carbon atoms (C(62)–C(64)) refined poorly and developed unusually large thermal parameters, suggesting possible disorder, but no convincing evidence for alternate positions could be discerned in difference maps. Parameter shifts for these atoms tended to oscillate even when the remainder of the structure had converged, and it was deemed not profitable to continue the refinement since these atoms constitute a small and unessential portion. Final positional parameters are given in Table II.

[η^5-cpRu(NH$_2$CMe$_3$)(PPh$_3$)(P(OMe)$_3$)]CF$_3$SO$_3$. The crystal was obtained by slow diffusion of diethyl ether into a solution

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(7) Mague, J. T.; Lloyd, C. L. *Organometallics* **1988**, *7*, 983–93.

(8) *Enraf-Nonius Structure Determination Package*, B. A. Frenz & Associates Inc.: Delft, Holland, 1985. *MolEN, An Interactive Structure Solution Procedure*; Enraf-Nonius: Delft, The Netherlands, 1990. Scattering factors, including corrections for anomalous dispersion, are taken from: *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.

Table II. Positional Parameters (Esd) for $[cpRu(NH_3)(PPh_3)_2]CF_3SO_3$

atom	x	y	z	B, Å^{2a}
Ru	0.91167 (2)	0.17693 (2)	0.74658 (1)	2.349 (5)
S	1.2517 (1)	0.06316 (9)	0.87365 (6)	4.57 (3)
P(1)	0.93457 (8)	0.11931 (7)	0.64634 (5)	2.70 (2)
P(2)	0.73425 (8)	0.13793 (8)	0.7558 (5)	2.79 (2)
F(1)	1.4405 (3)	0.0574 (4)	0.9351 (2)	11.1 (1)
F(2)	1.3398 (4)	0.1598 (3)	0.9663 (2)	10.8 (1)
F(3)	1.3169 (4)	0.0168 (4)	0.9884 (2)	11.6 (1)
O(1)	1.2892 (3)	0.1332 (3)	0.8329 (2)	7.1 (1)
O(2)	1.1499 (3)	0.0830 (3)	0.8930 (2)	6.8 (1)
O(3)	1.2637 (4)	−0.0306 (3)	0.8555 (2)	7.7 (1)
N	0.9620 (3)	0.0440 (2)	0.7883 (2)	3.33 (7)
C(1)	0.9231 (3)	0.3276 (3)	0.7290 (2)	3.71 (9)
C(2)	0.8872 (3)	0.3126 (3)	0.7880 (2)	4.15 (9)
C(3)	0.9666 (4)	0.2654 (3)	0.8271 (2)	4.4 (1)
C(4)	1.0527 (3)	0.2507 (3)	0.7924 (2)	3.82 (9)
C(5)	1.0268 (3)	0.2888 (3)	0.7326 (2)	3.64 (9)
C(6)	1.3415 (5)	0.0738 (4)	0.9449 (3)	6.7 (2)
C(11)	1.0595 (3)	0.0538 (3)	0.6446 (2)	3.22 (8)
C(12)	1.1433 (3)	0.0687 (3)	0.6906 (2)	3.78 (9)
C(13)	1.2424 (4)	0.0292 (4)	0.6868 (2)	4.5 (1)
C(14)	1.2567 (4)	−0.0266 (4)	0.6367 (3)	5.3 (1)
C(15)	1.1750 (4)	−0.0439 (4)	0.5901 (2)	4.7 (1)
C(16)	1.0768 (4)	−0.0031 (4)	0.5935 (2)	4.3 (1)
C(21)	0.8377 (3)	0.0404 (3)	0.6036 (2)	3.08 (8)
C(22)	0.8484 (4)	−0.0561 (3)	0.6120 (2)	4.1 (1)
C(23)	0.7723 (4)	−0.1166 (4)	0.5834 (2)	4.9 (1)
C(24)	0.6860 (4)	−0.0819 (4)	0.5467 (2)	5.3 (1)
C(25)	0.6716 (4)	0.0135 (4)	0.5382 (2)	4.6 (1)
C(26)	0.7479 (3)	0.0735 (3)	0.5668 (2)	3.53 (9)
C(31)	0.9544 (3)	0.2119 (3)	0.5883 (2)	3.24 (8)
C(32)	0.8838 (4)	0.2848 (3)	0.5787 (2)	3.9 (1)
C(33)	0.9006 (4)	0.3582 (4)	0.5392 (2)	5.0 (1)
C(34)	0.9874 (5)	0.3572 (4)	0.5062 (2)	5.7 (1)
C(35)	1.0585 (5)	0.2853 (4)	0.5136 (3)	6.1 (1)
C(36)	1.0417 (4)	0.2129 (4)	0.5550 (1)	5.1 (1)
C(41)	0.6353 (3)	0.1663 (3)	0.6893 (2)	3.04 (8)
C(42)	0.6451 (3)	0.2516 (3)	0.6608 (2)	3.9 (1)
C(43)	0.5734 (4)	0.2801 (4)	0.6114 (2)	4.6 (1)
C(44)	0.4898 (4)	0.2233 (4)	0.5895 (2)	4.7 (1)
C(45)	0.4779 (4)	0.1386 (4)	0.6180 (2)	4.4 (1)
C(46)	0.5497 (3)	0.1099 (3)	0.6686 (2)	3.74 (9)
C(51)	0.6779 (3)	0.1971 (3)	0.8206 (2)	3.27 (9)
C(52)	0.7333 (4)	0.1973 (3)	0.8797 (2)	3.9 (1)
C(53)	0.6888 (4)	0.2332 (4)	0.9310 (2)	4.7 (1)
C(54)	0.5906 (4)	0.2715 (4)	0.9228 (2)	5.1 (1)
C(55)	0.5343 (4)	0.2739 (5)	0.8651 (2)	6.8 (2)
C(56)	0.5787 (3)	0.2361 (4)	0.8137 (2)	5.5 (1)
C(61)	0.7066 (4)	0.0155 (4)	0.7750 (2)	4.2 (1)
C(62)	0.6915 (8)	−0.0130 (5)	0.8331 (4)	15.1 (3)
C(63)	0.687 (1)	−0.1084 (6)	0.8481 (4)	15.8 (3)
C(64)	0.6850 (6)	−0.1750 (5)	0.8021 (4)	8.7 (2)
C(65)	0.6996 (4)	−0.1459 (4)	0.7454 (3)	5.2 (1)
C(66)	0.7136 (4)	−0.0534 (3)	0.7328 (2)	4.7 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)(B_{12}) + ac(\cos\beta)(B_{13}) + bc(\cos\alpha)(B_{23})]$.

of the complex in acetone. The structure was solved by direct methods. In the final stages of refinement most of the hydrogen atoms were observed on difference maps (except those on C(51)). These atoms were included as fixed contributions in calculated positions riding on their attached carbon atoms with $B = 1.3$ times that of the carbon atom. At this stage of refinement it was apparent that the temperature factors for the atoms of the CF_3SO_3 ion were quite large and that a single peak having significant electron density was still present in this region of a difference map. Given the mode of preparation of this complex it was concluded that incomplete removal of chloride had occurred and from relative peak heights it was determined that ca. 14% chloride remained. Final refinement was therefore carried out with anion occupancies of 0.86 for CF_3SO_3 and 0.14 for Cl. Final positional parameters are given in Table III.

Table III. Positional Parameters (Esd) for $[cpRu(CMe_3NH_2)(PPh_3)(P(OMe)_3)]CF_3SO_3$

atom	x	y	z	B, Å^{2a}
Ru	0.12276 (3)	0.17757 (1)	0.27333 (2)	2.936 (6)
Cl	0.4224 (6)	0.6915 (4)	0.7713 (4)	4.1 (1)
S	0.3892 (2)	0.68148 (8)	0.8232 (1)	6.21 (4)
P(1)	0.07878 (9)	0.10762 (4)	0.16269 (6)	2.70 (2)
P(2)	0.3005 (1)	0.12771 (5)	0.32354 (8)	4.09 (2)
F(1)	0.4049 (4)	0.5787 (2)	0.7413 (3)	10.1 (1)
F(2)	0.5338 (5)	0.6503 (3)	0.7026 (3)	15.5 (1)
F(3)	0.5719 (5)	0.6025 (2)	0.8194 (4)	12.4 (2)
O(1)	0.3792 (3)	0.0883 (2)	0.2569 (2)	5.84 (8)
O(2)	0.2707 (4)	0.0783 (2)	0.3960 (2)	6.21 (8)
O(3)	0.4191 (4)	0.1660 (2)	0.3648 (3)	7.39 (9)
O(4)	0.4825 (4)	0.7246 (2)	0.8522 (3)	5.76 (9)
O(5)	0.2923 (5)	0.6971 (3)	0.7660 (5)	12.0 (2)
O(6)	0.3392 (6)	0.6436 (4)	0.8930 (3)	15.9 (2)
N	0.0075 (4)	0.1191 (2)	0.3587 (2)	4.57 (8)
C(1)	0.1162 (6)	0.2523 (2)	0.1791 (3)	5.3 (1)
C(2)	0.0107 (5)	0.2599 (2)	0.2311 (4)	5.4 (1)
C(3)	0.0617 (6)	0.2704 (2)	0.3153 (4)	6.9 (1)
C(4)	0.1928 (6)	0.2699 (2)	0.3143 (4)	6.8 (1)
C(5)	0.2271 (5)	0.2575 (2)	0.2289 (4)	5.9 (1)
C(6)	0.4758 (7)	0.6218 (3)	0.7757 (6)	7.8 (2)
C(11)	−0.0516 (4)	0.1306 (2)	0.0841 (2)	2.92 (7)
C(12)	−0.1618 (4)	0.1587 (2)	0.1149 (3)	3.73 (8)
C(13)	−0.2635 (4)	0.1746 (2)	0.0587 (3)	4.4 (1)
C(14)	−0.2566 (4)	0.1632 (2)	−0.0295 (3)	4.21 (9)
C(15)	−0.1496 (4)	0.1356 (2)	−0.0602 (3)	4.06 (9)
C(16)	−0.0470 (4)	0.1192 (2)	−0.0038 (3)	3.42 (8)
C(21)	0.2007 (4)	0.0884 (2)	0.0885 (3)	3.43 (8)
C(22)	0.2213 (4)	0.0311 (2)	0.0545 (3)	4.38 (9)
C(23)	0.3146 (5)	0.0190 (2)	−0.0045 (3)	5.3 (1)
C(24)	0.3936 (5)	0.0656 (3)	−0.0310 (3)	6.1 (1)
C(25)	0.3794 (5)	0.1229 (3)	0.0008 (4)	6.0 (1)
C(26)	0.2886 (4)	0.1350 (2)	0.0626 (3)	4.7 (1)
C(31)	0.0219 (4)	0.0326 (2)	0.1991 (2)	3.09 (7)
C(32)	−0.1076 (4)	0.0160 (2)	0.1909 (3)	4.6 (1)
C(33)	−0.1495 (5)	−0.0377 (2)	0.2267 (4)	5.8 (1)
C(34)	−0.0641 (5)	−0.0761 (2)	0.2709 (3)	5.5 (1)
(C35)	0.0656 (5)	−0.0604 (2)	0.2795 (2)	4.7 (1)
C(36)	0.1072 (4)	−0.0066 (2)	0.2446 (3)	3.89 (9)
C(41)	−0.0851 (5)	0.1351 (2)	0.4250 (3)	4.8 (1)
C(42)	−0.1359 (6)	0.0751 (3)	0.4640 (4)	7.5 (1)
C(43)	−0.0207 (8)	0.1740 (3)	0.4950 (4)	7.9 (2)
C(44)	−0.1958 (7)	0.1700 (4)	0.3817 (5)	8.9 (2)
C(51)	0.5085 (7)	0.0966 (6)	0.2306 (6)	11.7 (3)
C(52)	0.3678 (7)	0.0397 (3)	0.4358 (4)	9.0 (2)
C(53)	0.4172 (9)	0.1928 (4)	0.4472 (5)	11.0 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B_{11} + b^2{}_{B22} + c^2B_{33} + ab(\cos\gamma)(B_{12}) + ac(\cos\beta)(B_{13}) + bc(\cos\alpha)(B_{23})]$.

[η^5-cpRu($NH_2C_8H_{17}$-1)($Cy_2PCH_2CH_2PCy_2$)]CF_3SO_3. The crystal was obtained by cooling a diethyl ether solution of the complex at −5 °C. Initially, the standard search and indexing procedures provided a triclinic cell with $a = 24.037$ Å, $b = 24.077$ Å, $c = 13.632$ Å, $\alpha = 101.0°$, $\beta = 100.9°$, $\gamma = 116.5°$, and no indication of viable higher symmetry. Therefore a full hemisphere of data ($h,\pm k,\pm l$) was collected, yielding 12665 reflections, of which 8559 had $I \geq 3\sigma(I)$. Although initially solved in space group $P\bar{1}$ with $Z = 6$ (Patterson methods), it soon became clear that higher symmetry was in fact present. This was confirmed with the use of an updated version of the CAD-4 software as well as with the TRACER cell reduction program (using DEL = 2.0), which indicated a rhombohedral cell. Transformation of the original cell to the hexagonal setting of the new cell, reindexing of the data, and averaging of equivalent reflections yielded 4111 independent data that obeyed the condition $-h,+k,+l = 3n$, consistent with the space groups $R\bar{3}$, $R32$, and $R3m$. The first was considered the most likely, and the choice was confirmed by successful refinement. In the final stages of refinement, hydrogen atoms were included in calculated positions as fixed contributions with isotropic thermal parameters 1.2 times those of the attached carbon atoms. These positions were updated every two cycles. Because the central portion of the 1-octyl group (C(9)–C(12)) appeared to be disordered, hydrogen atoms were not placed on these carbon atoms. Considerable effort was expended to model the disorder but to no avail. Alternate locations of these carbon atoms could not be

Table IV. Positional Parameters (Esd) for $[cpRu(NH_2C_8H_{17}\text{-}1)(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3$

atom	*x*	*y*	*z*	*B*, Å^{2a}
Ru	0.22202 (2)	0.18699 (2)	0.22380 (5)	3.91 (2)
P(1)	0.28322 (6)	0.21183 (6)	0.2799 (2)	4.57 (6)
P(2)	0.23289 (6)	0.14271 (6)	0.1492 (2)	4.56 (6)
N	0.2012 (2)	0.1529 (2)	0.3561 (6)	5.2 (2)
C(1)	0.2286 (2)	0.2357 (2)	0.1405 (7)	5.5 (3)
C(2)	0.2019 (2)	0.2028 (2)	0.0934 (7)	6.0 (2)
C(3)	0.1703 (2)	0.1822 (2)	0.1523 (8)	6.5 (3)
C(4)	0.1781 (2)	0.2044 (2)	0.2385 (8)	6.4 (3)
C(5)	0.2129 (2)	0.2360 (2)	0.2310 (9)	6.5 (3)
C(6)	0.1610 (3)	0.1274 (3)	0.3689 (8)	7.0 (3)
C(7)	0.1460 (4)	0.0985 (4)	0.453 (1)	12.1 (5)
C(8)	0.1571 (6)	0.1152 (6)	0.535 (2)	18.7 (8)*
C(9)	0.1478 (6)	0.0853 (6)	0.639 (2)	21.1 (9)*
C(10)	0.1064 (5)	0.0660 (5)	0.644 (2)	16.2 (6)*
C(11)	0.1032 (7)	0.0479 (7)	0.762 (2)	23 (1)*
C(12)	0.0687 (6)	0.0227 (6)	0.767 (2)	20.9 (9)*
C(13)	0.0721 (5)	0.0124 (5)	0.896 (1)	16.8 (8)
C(14)	0.2772 (3)	0.1485 (3)	0.195 (1)	8.9 (3)
C(15)	0.3016 (2)	0.1810 (3)	0.237 (1)	8.4 (3)
C(21)	0.2891 (2)	0.2115 (2)	0.4163 (7)	5.3 (3)
C(22)	0.3293 (3)	0.2244 (3)	0.4544 (8)	7.0 (3)
C(23)	0.3284 (3)	0.2159 (3)	0.5628 (9)	7.6 (3)
C(24)	0.3104 (3)	0.2342 (3)	0.6189 (8)	8.5 (4)
C(25)	0.2707 (3)	0.2226 (3)	0.5833 (7)	7.5 (4)
C(26)	0.2722 (2)	0.2313 (3)	0.4738 (7)	6.1 (3)
C(31)	0.3188 (3)	0.2596 (3)	0.2362 (8)	6.7 (3)
C(32)	0.3148 (3)	0.2915 (2)	0.2744 (8)	6.6 (3)
C(33)	0.3397 (4)	0.3288 (3)	0.225 (1)	12.7 (6)
C(34)	0.3732 (3)	0.3363 (4)	0.195 (2)	17.2 (7)
C(35)	0.3780 (3)	0.3047 (3)	0.150 (1)	11.8 (5)
C(36)	0.3534 (4)	0.2687 (4)	0.205 (2)	19.0 (6)
C(41)	0.2370 (2)	0.1455 (2)	0.0140 (7)	5.2 (3)
C(42)	0.2666 (3)	0.1830 (3)	−0.0218 (8)	6.9 (3)
C(43)	0.2641 (3)	0.1876 (3)	−0.1327 (9)	9.4 (4)
C(44)	0.2682 (4)	0.1567 (3)	−0.1862 (9)	9.4 (4)
C(45)	0.2399 (3)	0.1189 (3)	−0.1514 (8)	8.7 (4)
C(46)	0.2415 (3)	0.1155 (3)	−0.0399 (9)	7.7 (4)
C(51)	0.1991 (3)	0.0924 (2)	0.1774 (7)	5.8 (3)
C(52)	0.2132 (3)	0.0643 (3)	0.1709 (9)	8.2 (3)
C(53)	0.1829 (4)	0.0253 (3)	0.206 (1)	11.3 (4)
C(54)	0.1461 (4)	0.0124 (3)	0.151 (1)	12.1 (5)
C(55)	0.1314 (3)	0.0389 (3)	0.161 (1)	9.9 (4)
C(56)	0.1619 (3)	0.0783 (3)	0.125 (1)	8.0 (4)
S	0.17989 (9)	0.43130 (9)	0.1615 (3)	10.0 (1)
O(1)	0.2036 (2)	0.4345 (3)	0.0839 (6)	11.1 (3)
O(2)	0.1701 (3)	0.4586 (2)	0.1762 (9)	14.4 (4)
O(3)	0.1871 (4)	0.4163 (4)	0.2569 (9)	25.2 (6)
C(16)	0.1382 (4)	0.3903 (4)	0.138 (1)	12.3 (5)
F(1)	0.1425 (3)	0.2622 (2)	0.120 (1)	20.8 (5)
F(2)	0.1108 (2)	0.3818 (2)	0.1997 (7)	15.5 (3)
F(3)	0.1242 (3)	0.3952 (5)	0.0529 (9)	23.9 (7)

[a] Starred values refer to atoms that were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)(B_{12}) + ac(\cos\beta)(B_{13}) + bc(\cos\alpha)(B_{23})]$.

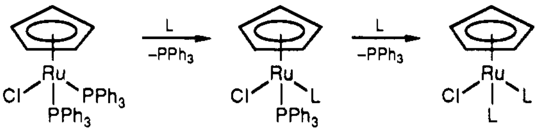
resolved in difference Fourier maps and attempts to carry out a refinement using C–C distances and C–C–C angles restrained to be close to expected values failed. The refinement was therefore completed by placing these atoms in positions that gave reasonable bond distances and interbond angles based on a difference map and alternately refining the positional and isotropic thermal parameters with considerable damping of their shifts. The resulting geometry is clearly not particularly satisfactory but does not appear to seriously affect the geometry of the remainder of the molecule. It is also apparent that the triflate ion is affected by positional disorder but again extensive consideration of difference maps did not provide well-defined alternate positions. Evidently, two or more slightly different positions are adopted for which the only feasible model is one with large thermal parameters for the constituent atoms. Final positional parameters are given in Table IV.

$[\eta^5\text{-}cpRu(CO)(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3$. The crystal was obtained by slow diffusion of diethyl ether into a solution of the complex in deuteriobenzene. The position of the ruthenium atom was obtained from an origin-removed Patterson map, and the remaining non-hydrogen atoms were located by successive cycles of full-matrix least-squares refinement and difference Fourier syntheses.

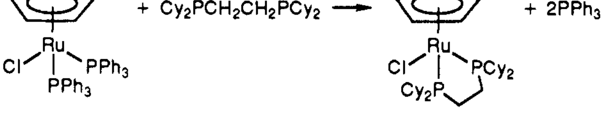
In the final stages of refinement, a molecule of deuteriobenzene of solvation was found, which was disordered over two orientations. Disorder was also noted for the triflate anion and for the cyclohexyl group built on C(28). The two orientations for the solvent molecule were assigned occupancies of 0.7 and 0.3 on the basis of relative peak heights observed in difference maps. The disorder for the triflate ion appears to involve two slightly different orientations having the carbon (C(7)) and one oxygen atom (O(2)) common to both. Alternate positions for the other two oxygens could be discerned in a difference map, but this was not possible for the sulfur and fluorine atoms. Although we cannot conclusively rule out an "end-to-end" disorder of the triflate ion, the thermal parameters for sulfur and carbon (C(7)) suggest that this is not present. The disorder in the cyclohexyl ring appears to involve its adopting two or more conformations, all of which have the positions of the 1 and 4 carbon atoms in common. Separate sites for the remaining carbons could not be distinguished, so these atoms were refined anisotropically. The disorder is therefore apparent in unusually large thermal ellipsoids for these atoms and in the resulting geometry of the cyclohexyl group. The two orientations for the other disordered groups were refined alternately. While the resulting geometries are not entirely satisfactory here either, the models used to treat the disorder are reasonable given the data available. Hydrogen atoms were included in calculated positions with isotropic thermal parameters 1.3 times that of the attached carbon atom. These positions were updated periodically during the final cycles of refinement. The final difference map was essentially featureless. Final positional parameters are given in Table V.

Results and Discussion

Complexes of stoichiometry η^5-cpRuClLL′ (L and L′ are a tertiary phosphine or phosphite, or LL′ is a ditertiary phosphine) can be prepared by treating hydrated ruthenium trichloride with cyclopentadiene and the phosphine or phosphite. Alternately, the complex η^5-cpRuCl(PPh$_3$)$_2$ can be used as the synthetic precursor, since it undergoes substitution reactions with a series of tertiary phosphines and phosphites L to give η^5-cpRu(PPh$_3$)L then η^5-cpRuL$_2$ (eq 1). For chelating diphosphines, the reaction can be used to prepare the complex η^5-cpRuCl(dppe), where dppe is $Ph_2PCH_2CH_2PPh_2$.[6,9] We now find that this reaction can be used to prepare the complex η^5-RuCl(dcpe), where dcpe is the bulky chelating phosphine ligand $Cy_2PCH_2CH_2PCy_2$ (eq 2). The orange complex is characterized by the presence of a single resonance in the $^{31}P\{^1H\}$ NMR spectrum at δ 86.3.



(1)



(2)

Cationic Complexes. The complexes η^5-cpRuClL$_2$ react with silver salts of noncoordinating anions in a coordinating solvent such as tetrahydrofuran to give the sol-

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(9) Consiglio, G.; Morandini, F. *Chem. Rev.* **1987**, *87*, 761–78. Davies, S. G.; McNally, J. P.; Smallridge, A. J. *Adv. Organomet. Chem.* **1990**, *30*, 1–76.

Table V. Positional Parameters (Esd) for $[cpRu(CO)(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3$

atom	*x*	*y*	*z*	*B*, Å^{2a}
Ru	0.31161 (3)	0.10363 (3)	0.02348 (2)	4.148 (9)
S	0.4255 (1)	0.2994 (2)	0.3945 (1)	7.72 (5)
P(1)	0.2838 (1)	0.09294 (9)	0.14610 (8)	4.08 (3)
P(2)	0.3408 (1)	0.24788 (9)	0.05374 (8)	4.29 (3)
F(1)	0.3171 (7)	0.1776 (5)	0.4014 (5)	25.8 (3)
F(2)	0.2961 (5)	0.2830 (6)	0.4694 (5)	19.8 (3)
F(3)	0.3904 (7)	0.1996 (5)	0.4992 (4)	19.2 (3)
O(1)	0.5111 (3)	0.0771 (3)	0.0527 (3)	7.7 (1)
O(2)	0.3674 (5)	0.3281 (5)	0.3304 (4)	12.3 (2)
O(3)	0.4464 (7)	0.3746 (6)	0.4389 (5)	11.6 (3)*
O(3A)	0.5066 (8)	0.2895 (7)	0.4491 (7)	6.1 (3)*
O(4)	0.4903 (9)	0.2547 (9)	0.3748 (7)	15.9 (4)*
O(4A)	0.4496 (9)	0.2079 (9)	0.3493 (8)	6.9 (4)*
C(1)	0.4343 (4)	0.0869 (4)	0.0460 (3)	5.4 (1)
C(2)	0.3105 (5)	0.0424 (4)	0.0881 (3)	6.1 (2)
C(3)	0.2746 (5)	−0.0155 (4)	−0.0434 (4)	6.4 (2)
C(4)	0.1955 (5)	0.0196 (6)	−0.0232 (4)	7.9 (2)
C(5)	0.1856 (5)	0.1038 (5)	−0.0581 (4)	7.3 (2)
C(6)	0.2587 (5)	0.1145 (5)	−0.0971 (3)	6.4 (2)
C(7)	0.3546 (7)	0.2343 (6)	0.4408 (5)	10.2 (3)
C(8)	0.3059 (4)	0.1977 (4)	0.1930 (3)	4.7 (1)
C(9)	0.3711 (4)	0.2514 (4)	0.1547 (3)	5.0 (1)
C(10)	0.3528 (4)	0.0144 (4)	0.2054 (3)	4.8 (1)
C(11)	0.4516 (5)	0.0378 (5)	0.2231 (4)	6.6 (2)
C(12)	0.5035 (5)	−0.0320 (5)	0.2744 (4)	7.6 (2)
C(13)	0.4894 (5)	−0.1215 (5)	0.2441 (5)	7.7 (2)
C(14)	0.3905 (5)	−0.1434 (5)	0.2281 (4)	6.9 (2)
C(15)	0.3407 (4)	−0.0773 (4)	0.1752 (4)	5.7 (1)
C(16)	0.1661 (4)	0.0649 (4)	0.1597 (3)	4.5 (1)
C(17)	0.1498 (4)	0.0512 (5)	0.2402 (4)	6.0 (2)
C(18)	0.0555 (5)	0.0214 (5)	0.2452 (4)	7.1 (2)
C(19)	−0.0150 (5)	0.0839 (6)	0.2050 (4)	7.9 (2)
C(20)	0.0024 (5)	0.0981 (5)	0.1267 (5)	7.5 (2)
C(21)	0.0968 (4)	0.1301 (4)	0.1230 (4)	5.7 (2)
C(22)	0.2452 (5)	0.3252 (4)	0.0330 (4)	6.6 (2)
C(23)	0.2436 (7)	0.4003 (5)	0.0818 (5)	8.8 (2)
C(24)	0.1542 (7)	0.4527 (6)	0.0619 (5)	11.0 (3)
C(25)	0.1403 (8)	0.4750 (6)	−0.0205 (6)	11.9 (3)
C(26)	0.144 (1)	0.4060 (7)	−0.0654 (7)	15.8 (4)
C(27)	0.2306 (7)	0.3492 (5)	−0.0489 (4)	9.6 (2)
C(28)	0.4414 (5)	0.2951 (5)	0.0197 (4)	8.7 (2)
C(29)	0.4926 (6)	0.357 (1)	0.0541 (5)	19.1 (3)
C(30)	0.5753 (6)	0.3894 (7)	0.0282 (6)	11.1 (3)
C(31)	0.5822 (6)	0.363 (1)	−0.0533 (6)	14.8 (4)
C(32)	0.5370 (8)	0.3062 (8)	−0.0835 (7)	26.8 (3)
C(33)	0.4478 (6)	0.2750 (6)	−0.0613 (4)	9.3 (2)
C(1S)	0.6347 (9)	0.3205 (9)	0.2418 (7)	8.8 (3)*
C(2S)	0.6357 (9)	0.2373 (9)	0.2464 (7)	9.3 (3)*
C(3S)	0.697 (1)	0.188 (1)	0.215 (1)	12.5 (5)*
C(4S)	0.760 (1)	0.231 (1)	0.1808 (9)	12.3 (5)*
C(5S)	0.761 (1)	0.324 (1)	0.1777 (8)	10.5 (4)*
C(6S)	0.689 (1)	0.364 (1)	0.2147 (9)	11.0 (4)*
C(1SA)	0.649 (1)	0.374 (1)	0.233 (1)	9.2 (4)*
C(2SA)	0.633 (1)	0.280 (1)	0.247 (1)	8.0 (4)*
C(3SA)	0.660 (1)	0.194 (1)	0.242 (1)	10.3 (5)*
C(4SA)	0.744 (1)	0.187 (1)	0.186 (1)	11.0 (6)*
C(5SA)	0.774 (1)	0.279 (1)	0.178 (1)	7.9 (4)*
C(6SA)	0.741 (1)	0.369 (1)	0.194 (1)	9.0 (4)*

[a] Starred values refer to atoms that were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos \tau)(B_{12}) + ac(\cos \beta)(B_{13}) + bc(\cos \alpha)(B_{23})]$.

vated cationic complexes resulting from the replacement of the chloride ion by solvent.[10] We have chosen to use tetrahydrofuran as the coordinating solvent and silver triflate as the reagent of choice for the removal of chloride ion. For the case of the ligand dcpe, we find that a reaction occurs between η^5-cpRuCl(dcpe) and silver triflate in tetrahydrofuran solvent. The product complex shows no evidence in the ^1H NMR spectrum for the presence of complexed tetrahydrofuran. Instead, the product is the 16-electron complex $[\eta^5\text{-cpRu(dcpe)}]CF_3SO_3$ (eq 3). The

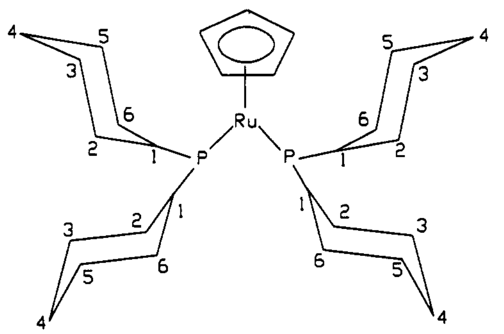


Figure 1. Structure of the complex cation $[\eta^5\text{-cpRu(dcpe)}]^+$ showing the C_{2v} symmetry.

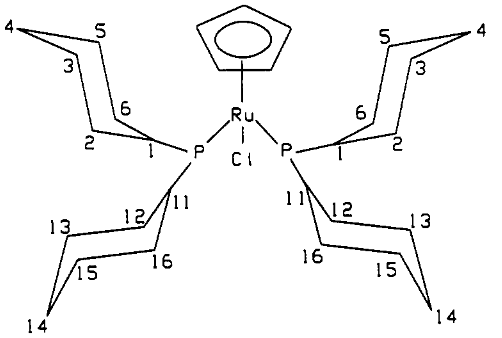
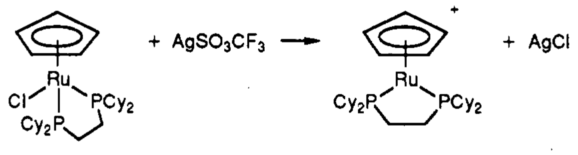


Figure 2. Structure of the complex η^5-cpRuCl(dcpe) showing the Cσ symmetry.



(3)

complex is characterized by the presence of a single resonance in the $^{31}P\{^1H\}$ NMR spectrum at δ 83.9. The $^{13}C\{^1H\}$ NMR spectrum of this complex has been obtained in C_6D_6 solution, and the simplicity of the spectrum is indicative of a cationic complex that has C_{2v} symmetry (Figure 1). In this symmetry, with two orthogonal mirror planes, all four cyclohexyl groups are equivalent. There is no symmetry that relates carbons 2 to 6 or carbons 3 to 5. Thus the four cyclohexyl rings in the cation give rise to six resonances in the spectrum. The carbon bonded to phosphorus (C(1)) is observed as a broad resonance covering the range δ 38–40. The resonance for C(2) is observed as a virtually coupled "triplet" at δ 27.7 ($|^2J(PC) + {}^4J(PC)|$ = 5.3 Hz, the absolute value of the two couplings). The resonance for C(6) is also a virtually coupled "triplet" at δ 27.8 ($|^2J(PC) + {}^4J(PC)|$ = 4.7 Hz). The resonances for C(3), C(4), and C(5) are observed as singlets at δ 29.8, 26.6, and 29.9, although no definitive assignment can be made to the individual peaks. The backbone carbons of the ethane group are observed as a virtually coupled "triplet" at δ 20.7 ($|^1J(PC) + {}^2J(PC)|$ = 18.7 Hz). The cyclopentadienyl carbons are observed as a singlet at δ 74.2.

By contrast, the $^{13}C\{^1H\}$ NMR spectrum of η^5-cpRuCl(dcpe) which has C_σ symmetry, shows 12 individual carbon-13 resonances for the cyclohexyl carbons (Figure 2). This structure has a single mirror plane that bisects the two phosphorus atoms. Thus there is no symmetry element that relates the positions in a given cyclohexyl group

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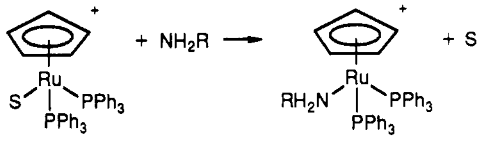
[10] Treichel, P. M.; Komar, D. A. *Synth. React. Inorg. Met.—Org. Chem.* **1980**, *10*, 205–18. Treichel, P. M.; Komar, D. A.; Vincenti, P. J. *Ibid.* **1984**, *14*, 383–400. Haines, R. J.; DuPreez, A. L. *J. Organomet. Chem.* **1975**, *84*, 357–67. Davies, S. G.; Scott, F. *Ibid.* **1980**, *188*, C41–2. Treichel, P. M.; Komar, D. A. *Inorg. Chim. Acta* **1980**, *42*, 277–80.

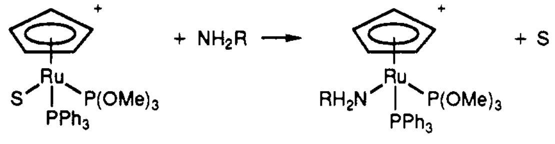
nor the two cyclohexyl groups on any given phosphorus atom.

Cationic Amine and Amide Complexes. The cationic complexes [η^5-cpRu(THF)LL′]$^+$ (LL′ is a tertiary phosphine or phosphite) and [η^5-cpRu(dcpe)]$^+$ are potential precursors of ammine or amine complexes, if ammonia or an amine will replace the complexed tetrahydrofuran in [η^5-cpRu(THF)LL′]$^+$ or if they will complex into the vacant coordination position in [η^5-cpRu(dcpe)]$^+$. We find that [η^5-cpRu(THF)LL′]$^+$ and [η^5-cpRu(dcpe)]$^+$ readily react with ammonia and amines to give cationic complexes with these ligands bonded to ruthenium via the nitrogen heteroatom. Thus the complex [η^5-cpRu(THF)(PPh$_3$)$_2$]$^+$ reacts with ammonia or methylamine to give [η^5-cpRu(NH$_2$R)(PPh$_3$)$_2$]$^+$ (R = H, Me) (eq 4). Triphenylphosphine is not displaced. For the mixed-ligand complex [η^5-cpRu(THF)(PPh$_3$)(P(OMe)$_3$)]$^+$, which has the sterically less demanding trimethyl phosphite ligand, we find that, in addition to ammonia and methylamine, the sterically bulky tertiary *tert*-butylamine ligand will coordinate to the ruthenium center (eq 5).



(4)

S = THF



(5)

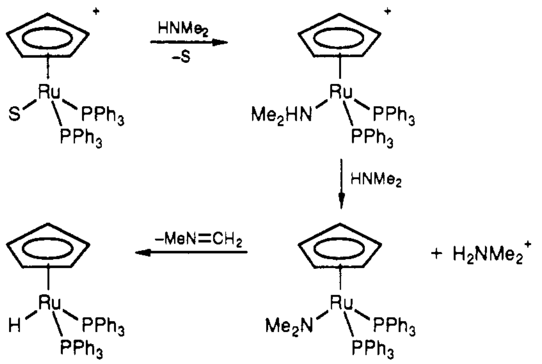
S = THF, R = CMe$_3$

The ammine (NH$_3$) complexes show broad resonances in the ^{1}H NMR spectrum in the region of δ 2.5 due to the hydrogens of the coordinated ammonia. These hydrogens are not exchanged to any appreciable extent with the deuteriums of added D$_2$O. The infrared spectra of these ammine complexes show four peaks due to the ν(NH) in the 3190–3350-cm^{-1} range. For the analogous methylamine complexes, the ^{1}H NMR spectrum again shows broad resonances in the region of δ 3.2 due to the amine hydrogens of the coordinated methylamine. Again these hydrogens do not exchange with the deuteriums of D$_2$O. The methyl hydrogens of the coordinated methylamine are observed in the region of δ 2.4, and in each case the resonances are triplets due to coupling with the amine hydrogens (^3J(HH) ~ 6 Hz). Homonuclear proton-decoupling experiments verify this assignment. The infrared spectra of the cationic amine complexes show two peaks due to ν(NH) in the vicinity of 3270 and 3310 cm^{-1}.

For the mixed-ligand complexes [η^5-cpRu(amine) LL′]$^+$ the ruthenium(II) center is chiral. As a consequence the hydrogens on the amine are diastereotopic. For the complex [η^5-cpRu(NH$_2$CMe$_3$)(PPh$_3$)(P(OMe)$_3$)]$^+$ we observe the amine hydrogens as an AB pair at δ 2.4 and 2.7, with a coupling constant between them (^2J(HH)) of 11 Hz. Homonuclear spin decoupling of either signal results in the collapse of the other to a broad singlet. The clear observation of this splitting likely results from the restricted rotation of the bulky *tert*-butylamine ligand in the coordination sphere of the ruthenium.

Attempts to prepare the dimethylamine complex [η^5-cpRu(NHMe$_2$)(PPh$_3$)$_2$]$^+$ by treating the complex [η^5-cpRu(THF)(PPh$_3$)$_2$]$^+$ with dimethylamine was unsuccessful; instead the hydride complex η^5-cpRuH(PPh$_3$)$_2$ is formed. Apparently, the initially formed complex [η^5-cpRu(NHMe$_2$)(PPh$_3$)$_2$]$^+$ reacts with the stronger base, dimethylamine, to give the amide complex η^5-cpRu(NMe$_2$)(PPh$_3$)$_2$. A subsequent β-hydrogen transfer from the *N*-methyl group to ruthenium leads to formation of the hydride (Scheme I). No intermediates are detected, but the formation of the cation [NH$_2$Me$_2$]$^+$ is verified by comparison of the ^{1}H NMR spectrum of the solution with that of [NH$_2$Me$_2$]Cl.[11] The hydride complex η^5-cpRuH(PPh$_3$)$_2$ is also formed exclusively from the deuterated amine NDMe$_2$, supporting the premise that the hydride ligand comes directly from the methyl group. A similar result is observed when a cyclic secondary amine is used instead of dimethylamine. Thus treating a solution of [η^5-cpRu(THF)(PPh$_3$)$_2$)]$^+$ with piperidine gives a high yield of the hydride η^5-cpRuH(PPh$_3$)$_2$. This result shows that β-hydrogen transfer will occur with a cyclic amide complex where conformational effects are more restrictive for the ligand to achieve the coplanar transition state necessary for such a reaction.[12]

Scheme I. Proposed Pathway for the Conversion of [η^5-cpRu(THF)(PPh$_3$)$_2$]$^+$ into η^5-cpRuH(PPh$_3$)$_2$ with Dimethylamine



S = THF

Table VI. Selected Bond Distances (Å) and Interbond Angles (deg) for [η^5-cpRu(NH$_3$)(PPh$_3$)$_2$]CF$_3$SO$_3$

	Bond Distances[a]		
Ru–P(1)	2.3533 (9)	Ru–N	2.172 (3)
Ru–P(2)	2.3463 (9)	Ru–C′[b]	1.844 (4)
	Interbond Angles[a]		
P(1)–Ru–P(2)	102.29 (3)	P(1)–Ru–C′[b]	120.5 (1)
P(1)–Ru–N	90.41 (8)	P(2)–Ru–C′[b]	122.9 (1)
P(2)–Ru–N	89.67 (8)	N–Ru–C′[b]	123.1 (3)

[a] Numbers in parentheses are the estimated standard deviation in the least significant digit(s). [b] C′ is the centroid of the cyclopentadienyl ring.

Crystal Structure of [η^5-cpRu(NH$_3$)(PPh$_3$)$_2$]CF$_3$SO$_3$. The structure of the cation [η^5-cpRu(NH$_3$)(PPh$_3$)$_2$]$^+$ confirms the "piano stool" configuration with ammonia bonded directly to ruthenium via nitrogen. The distances Ru–P(1) and Ru–P(2) are 2.3533 (9) and 2.3463 (9) Å, respectively, with a P(1)–Ru–P(2) angle of 102.29 (3)°. This obtuse angle is a consequence of the bulky triphenylphosphines having a larger steric requirement than the ammonia ligand. As a result, the P(1)–Ru–N and P(2)–Ru–N angles are 90.41 (8) and 89.67 (8)°, respectively, significantly less than the P(1)–Ru–P(2) angle. The Ru–N distance is 2.172 (3) Å, which is not unusual when compared with other ruthenium complexes.[13] Other selected

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(11) A commercial sample (Aldrich) was dissolved in C$_6$D$_6$ for comparison purposes.

(12) Hackett, M.; Whitesides, G. *J. Am. Chem. Soc.* **1988**, *110*, 1449–62. Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 1988; pp 154–5.

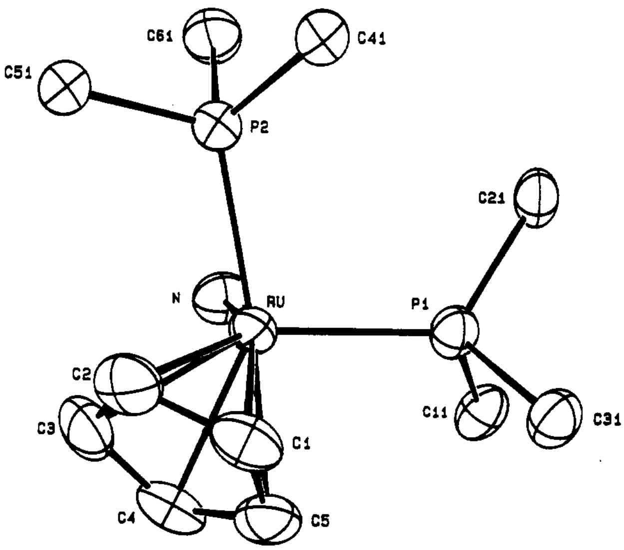

Figure 3. Perspective view of the inner coordination sphere of the $[\eta^5\text{-cpRu(NH}_3\text{)(PPh}_3\text{)}_2]^+$ cation. Thermal ellipsoids are drawn at the 30% probability level. Only the ipso carbon atoms of the phenyl rings are shown. For these rings, the carbon atoms are numbered by using the second digit as the running index (1–6).

Table VII. Selected Bond Distances (Å) and Interbond Angles (deg) for $[\eta^5\text{-cpRu(CMe}_3\text{NH}_3\text{)(PPh}_3\text{)(P(OMe)}_3\text{)]CF}_3\text{SO}_3$

	Bond Distances[a]		
Ru-P(1)	2.3183 (7)	Ru-N	2.216 (2)
Ru-P(2)	2.2501 (8)	Ru-C′[b]	1.870 (3)
	Interbond Angles[a]		
P(1)-Ru-P(2)	93.77 (3)	P(2)-Ru-N	88.35 (8)
P(1)-Ru-N	87.65 (7)	P(2)-Ru-C′[b]	122.2 (1)
P(1)-Ru-C′[b]	122.2 (1)	N-Ru-C′[b]	131.7 (3)
Ru-N-C(41)	131.0 (2)		

[a] Numbers in parentheses are the estimated standard deviation in the least significant digit(s). [b] C′ is the centroid of the cyclopentadienyl ring.

bond distances and angles are collected in Table VI. An ORTEP representation is shown in Figure 3.

Crystal Structure of $[\eta^5\text{-cpRu(NH}_2\text{CMe}_3\text{)(PPh}_3\text{)(P(OMe)}_3\text{)]CF}_3\text{SO}_3$. The structure of the cation $[\eta^5\text{-cpRu(NH}_2\text{CMe}_3\text{)(PPh}_3\text{)(P(OMe)}_3\text{)]}^+$ again shows the "piano stool" configuration with the *tert*-butylamine bonded directly to ruthenium via nitrogen. The distances Ru-P(1) and Ru-P(2) are 2.3183 (7) and 2.2501 (8) Å, respectively. The shorter Ru-P(2) distance for the bond to $P(OMe)_3$ is a consequence of the lesser steric requirements and the greater π-acceptor ability of this ligand than for PPh_3. The P(1)-Ru-P(2) angle is 93.77 (3)°, and the P(1)-Ru-N and P(2)-Ru-N angles are 87.65 (7) and 88.35 (8)°, respectively. By comparison with the structure of $[\eta^5\text{-cpRu(NH}_3\text{)(PPh}_3\text{)}_2]^+$, the P(1)-Ru-P(2) angle is significantly smaller in this *tert*-butylamine complex (a decrease of 8.52 (5)°). This change is due to a combination of the smaller size of $P(OMe)_3$ as compared to PPh_3, and the larger size of NH_2CMe_3 as compared to NH_3. The Ru-N distance is 2.216 (2) Å, which is slightly longer than the Ru-N distance of 2.172 (3) Å in $[\eta^5\text{-cpRu(NH}_3\text{)(PPh}_3\text{)}_2]^+$. We again ascribe this small lengthening to the greater steric bulk of the *tert*-butylamine ligand. Other selected bond distances and angles are collected in Table VII. An ORTEP representation is shown in Figure 4.

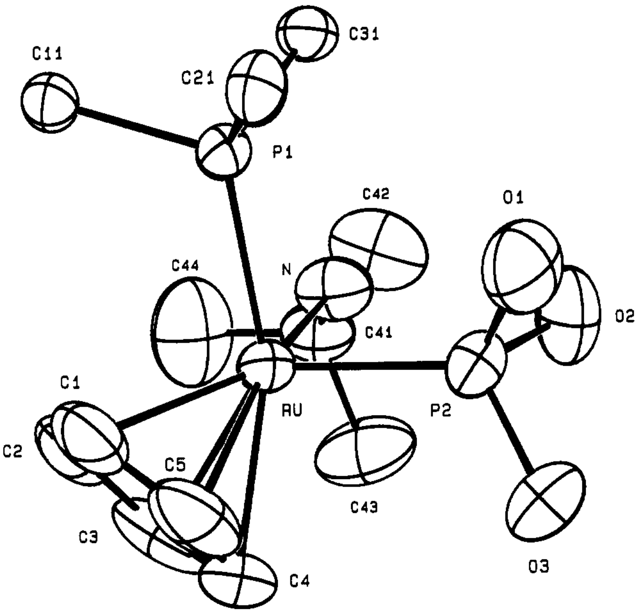

Figure 4. Perspective view of the inner coordination sphere of the $[\eta^5\text{-cpRu(NH}_2\text{CMe}_3\text{)(PPh}_3\text{)(P(OMe)}_3\text{)]}^+$ cation. Thermal ellipsoids are drawn at the 30% probability level. Only the ipso carbon atoms of the phenyl rings are shown. For these rings, the carbon atoms are numbered by using the second digit as the running index. Only the oxygens of the trimethyl phosphite are shown.

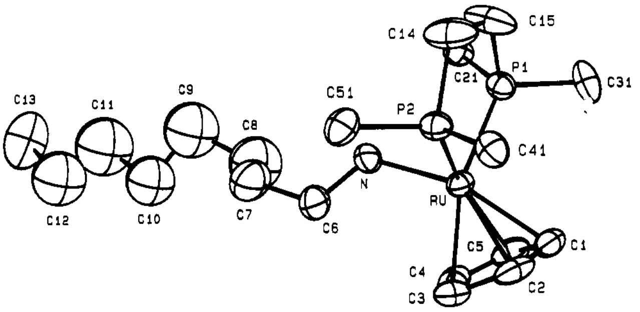

Figure 5. Perspective view of the inner coordination sphere of the $[\eta^5\text{-cpRu(NH}_2\text{C}_8\text{H}_{17}\text{-1)(Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2\text{)]}^+$ cation. Thermal ellipsoids are drawn at the 30% probability level. Only the ipso carbon atoms of the cyclohexyl rings are shown. For these rings the carbon atoms are numbered by using the second digit as the running index (1–6).

Table VIII. Selected Bond Distances (Å) and Interbond Angles (deg) for $[\eta^5\text{-cpRu(NH}_2\text{C}_8\text{H}_{17}\text{-1)(Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2\text{)]CF}_3\text{SO}_3$

	Bond Distances[a]		
Ru-P(1)	2.311 (3)	Ru-N	2.174 (8)
Ru-P(2)	2.306 (3)	Ru-C′[b]	1.87 (1)
	Interbond Angles[a]		
P(1)-Ru-P(2)	84.21 (9)	N-Ru-C′[b]	121.7 (4)
P(1)-Ru-N	89.9 (2)	P(2)-Ru-N	91.7 (2)
P(2)-Ru-C′[b]	128.2 (4)	P(1)-Ru-C′[b]	128.9 (4)
Ru-N-C(6)	120.1 (7)		

[a] Numbers in parentheses are the estimated standard deviation in the least significant digit(s). [b] C′ is the centroid of the cyclopentadienyl ring.

Crystal Structure of $[\eta^5\text{-cpRu(NH}_2\text{C}_8\text{H}_{17}\text{-1)(Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2\text{)]CF}_3\text{SO}_3$. The structure of the cation $[\eta^5\text{-cpRu(NH}_2\text{C}_8\text{H}_{17}\text{-1)(Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2\text{)]}^+$ again shows the "piano stool" configuration with the amine bonded via nitrogen. The distances Ru-P(1) and Ru-P(2) are 2.311

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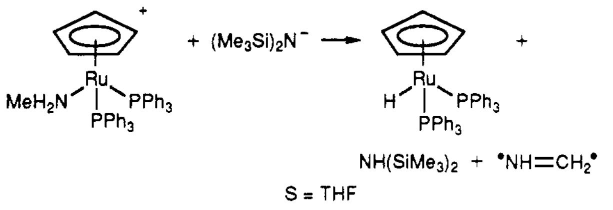
(13) Gress, M. E.; Creutz, C.; Quicksall, C. D. *Inorg. Chem.* **1981**, *20*, 1522–8. The closest analogue structure is that of $[\eta^5\text{-cpRu(NH}_3\text{)(PPh}_3\text{)}_2\text{]PF}_6$ (Conroy-Lewis, F. M.; Simpson, S. J. *J. Organomet. Chem.* **1990**, *396*, 83–94). The structural features of this cation are essentially the same as those of the CF_3SO_3 salt. The Ru-N distance in the PF_6 salt is 2.190 (6) Å, and the respective angles for P(1)-Ru-P(2), P(1)-Ru-N, and P(2)-Ru-N are 104.4 (1), 87.1 (2), and 90.3 (2)°.

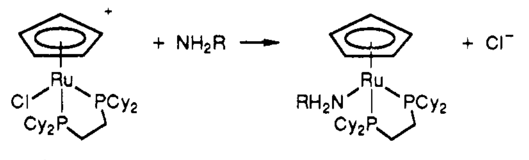
(3) and 2.306 (3) Å, respectively. The P(1)–Ru–P(2) angle is 84.21 (9)°, and the P(1)–Ru–N and P(2)–Ru–N angles are 89.9 (2) and 91.7 (2)°, respectively. The Ru–N distance is 2.174 (8) Å. This distance is close to that of 2.172 (3) Å in $[\eta^5\text{-cpRu(NH}_3\text{)(PPh}_3\text{)}_2]^+$, showing that the bulky cyclohexyl groups of the dcpe do not restrict the approach of 1-octylamine to the ruthenium center. Other selected bond distances and angles are collected in Table VIII. An ORTEP representation is shown in Figure 5. Inspection of the packing diagram shows that the molecules in the unit cell are associated together by weak van der Waals forces between 1-octyl and cyclohexyl groups.

Reactions of Cationic Ammine and Amine Complexes with Base. As a means to prepare neutral amide complexes of these cyclopentadienylruthenium(II) "piano stool" complexes, we have reacted the cationic amine and amide complexes with strong base.[3] Using a variety of reaction conditions, we have reacted the complexes $[\eta^5\text{-cpRu(NH}_3\text{)(PPh}_3\text{)}_2]^+$, $[\eta^5\text{-cpRu(NH}_2\text{Me)(PPh}_3\text{)}_2]^+$, and $[\eta^5\text{-cpRu(NH}_2\text{CMe}_3\text{)(PPh}_3\text{)(P(OMe)}_3\text{)}]^+$ with the strong bases LiBu, $\text{LiN(SiMe}_3\text{)}_2$, NaNH_2, and KH. In no case did we observe formation of the desired amide product; instead, in the examples where reaction was observed (eq 6), hydride products were detected. For the case of $[\eta^5\text{-cpRu(NH}_3\text{)(PPh}_3\text{)}_2]^+$, the solution $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum with added KH shows the presence of several compounds, including free triphenylphosphine (δ −5.5). These observations are consistent with a reaction that involves the initial formation of an intermediate amide, which then undergoes oligomerization to a variety of products by pathways involving substitution of triphenylphosphine. This postulate is consistent with recent published work which has demonstrated that the presence of ligands such as amides, which have electron pairs localized on them, has the effect of labilizing the supporting phosphine ligand.[14]



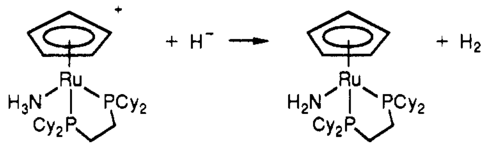
(6)

Reaction of Cationic Ammine and Amine Complexes Containing dcpe with Base. In order to suppress the dissociation of a phosphine molecule from the initially formed amide complex, we decided to use derivatives that have the sterically bulky dcpe ligand in place of the two monodentate triphenylphosphines. We decided against the use of the complex η^5-cpRuCl(dppe) for this work because of its low solubility in organic solvents. Instead, we have chosen the complex η^5-cpRuCl(dcpe) because of its high solubility in all organic solvents. Treating η^5-cpRuCl(dcpe) with silver triflate, followed by ammonia or amine, gives the cationic complexes $[\eta^5\text{-cpRu(NH}_2\text{R)(dcpe)]CF}_3\text{SO}_3$ (R = H, Me, 1-C_8H_{17}) (eq 7). The complexes $[\eta^5\text{-cpRu(NH}_2\text{R)(dcpe)}]^+$ are characterized by singlet resonances in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. These resonances are found at δ 86.7, 85.1, and 86.5 for the derivatives with R = H, Me, and 1-C_8H_{17}, respectively. In each case we observe bands in the IR spectrum due to ν(NH). For the complex having R = H, we observe these bands at 3206, 3280, 3330, and 3361 cm^{-1}; for R = Me these bands are at 3267 and 3329 cm^{-1}; and for R = 1-C_8H_{17} these bands are at 3255 and 3317 cm^{-1}. The isolation of a stable complex with 1-octylamine is noteworthy because, in general, amine complexes have low stability when there is a long alkyl chain attached to the amine nitrogen.[15]



(7)

Treating the cationic ammine complex $[\eta^5\text{-cpRu(NH}_3\text{)(dcpe)}]^+$ with potassium hydride results in its conversion to the neutral amide complex $\eta^5\text{-cpRu(NH}_2\text{)(dcpe)}$ (eq 8). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a singlet resonance at δ 92.5, which represents a downfield shift of 5.8 ppm from the position of the resonance in $[\eta^5\text{-cpRu(NH}_3\text{)(dcpe)}]^+$. The ^{1}H NMR spectrum of $\eta^5\text{-cpRu(NH}_2\text{)(dcpe)}$ shows the N*H* resonance upfield of the TMS shift position. The chemical shift position in C_6D_6 solvent is concentration dependent, and we have observed this broad resonance ranging from δ 0 up to 3 ppm upfield of this position. This upfield shift of an amide (NH_2) ligand is diagnostic of such a functional group.[4] The concentration dependence of the chemical shift position of the amide hydrogen is also expected. Early ^{1}H NMR studies of alcohols and amines demonstrated that the O*H* and N*H* shift positions were concentration dependent because of its effect on the degree of hydrogen bonding in the solute.[16] Apparently, the complex $\eta^5\text{-cpRu(NH}_2\text{)(dcpe)}$ is sufficiently unhindered sterically for associative interactions to occur between molecules. This new amide complex is exceedingly sensitive to water and is soluble in all organic solvents. Although the ^{1}H, $^{31}\text{P}\{^1\text{H}\}$, and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of $\eta^5\text{-cpRu(NH}_2\text{)(dcpe)}$ verify the absence of any other ruthenium-containing compound in solutions of the complex, the solubility and sensitivity characteristics of the complex have precluded its isolation in a pure state.[17]



(8)

Treating the cationic complex $[\eta^5\text{-cpRu(NH}_2\text{Me)(dcpe)}]^+$, with potassium hydride in dry THF affords predominantly three complexes in approximately 30% yield each. These complexes are the amide, $\eta^5\text{-cpRu(NH}_2\text{)(dcpe)}$, the monomeric hydride, η^5-cpRuH(dcpe), and a complex that has been spectroscopically characterized as the bimetallic hydride, $\eta^5\text{-cpRu}_2\text{H(dcpe)}_2$. The complex $\eta^5\text{-cpRu(NH}_2\text{)(dcpe)}$ has been formed via a pathway that involves cleavage of a carbon–nitrogen bond. Such a cleavage can arise from the attack of hydride ion at the methyl carbon of the complexed methylamine ligand (eq 9). The formation of the hydride complex η^5-cpRuH(dcpe)

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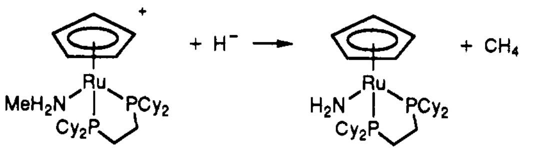
(14) Bryndza, H. E.; Domaille, P. J.; Paciello, R. A.; Beraw, J. E. *Organometallics* **1989**, *8*, 379–85.

(15) Douglas, B. E.; McDaniel, D. H.; Alexander, J. J. *Concepts and Models of Inorganic Chemistry*, 2nd ed.; Wiley: New York, 1983; pp 266–7.

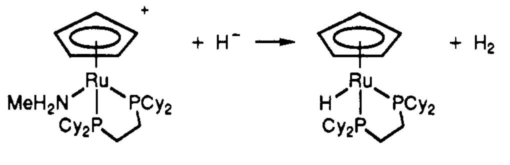
(16) Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. *High Resolution Nuclear Magnetic Resonance Spectroscopy*; Pergamon: Oxford, England, 1967; Vol. 1, p 548.

(17) In addition to those amide complexes included in ref 3, other amide complexes of late transition metals are included in the following references: Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *J. Am. Chem. Soc.* **1988**, *110*, 6738–44. Schaad, D. R.; Landis, C. R. *J. Am. Chem. Soc.* **1990**, *112*, 1628–9. Martin, G. C.; Palenik, G. J.; Boncella, J. M. *Inorg. Chem.* **1990**, *29*, 2027–30. Curtis, N. J.; Hagen, K. S.; Sargeson, A. M. *Inorg. Chem.* **1984**, *23*, 1571–3. Rotzinger, F. P.; Marty, W. *Inorg. Chem.* **1983**, *22*, 3593–602. Kretschmer, M.; Heck, L. *Z. Anorg. Allg. Chem.* **1982**, *490*, 215–29. Alcock, N. W.; Bergamini, P.; Kemp, T. J.; Pringle, P. G. *J. Chem. Soc., Chem. Commun.* **1987**, 235–6.

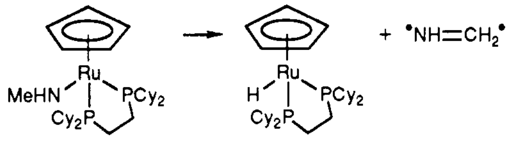


(9)

from the reaction between $[\eta^5\text{-cpRu(NH}_2\text{Me)(dcpe)}]^+$ and KH results from a pathway involving deprotonation of the amine ligand followed by β-hydrogen transfer from the methyl group of the neutral methylamide intermediate (eqs 10 and 11). The hydride complex η^5-cpRuH(dcpe) is characterized by a single $^{31}P\{^1H\}$ NMR resonance at δ 110.2 and by a triplet resonance in the ^1H NMR spectrum at δ −14.7 ($^2J(PH)$ = 34.2 Hz) due to the hydride ligand. As final confirmation of the identity of this complex, we have independently synthesized it by treating η^5-cpRuCl(dcpe) with lithium aluminum hydride in THF solution (eq 12).



(10)



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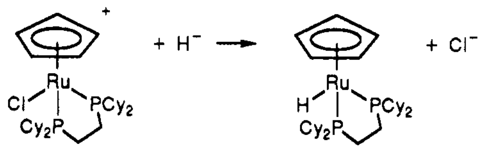


(12)

The formation of a second hydride is quite unexpected. Also, because these complexes have similar solubility and chromatographic characteristics, we have been unable to isolate the material in pure form. On the basis of spectroscopic considerations, we propose that the structure of the complex corresponds to that shown in Figure 6. The structure has the dcpe ligands spanning the pair of bnded rutheniums, with the axial positions being occupied by a cyclopentadienyl and a hydride ligand. The ^1H NMR spectrum of η^5-cpRu$_2$H(dcpe)$_2$ shows a triplet resonance at δ −13.6 ($^2J(PH)$ = 34.4 Hz) for the hydride, and a singlet resonance at δ 5.07 for the cyclopentadienyl ligand. Integration confirms the 1:1 ratio for the cyclopentadienyl and hydride ligands. The $^{31}P\{^1H\}$ NMR spectrum shows two singlet resonances a δ 92.6 and 106.0. The peak at δ 106.0 is assigned to the phosphorus that is two bonds away from the hydride ligand. This assignment is based on off-resonance decoupling experiments where the partially decoupled hydride resonance causes a broadening of this phosphorus resonance at δ 106.0. The resonance at δ 92.6 remains sharp. This hydride complex η^5-cpRu$_2$H(dcpe)$_2$ can be obtained in 70% yield in solution (the hydride complex η^5-cpRuH(dcpe) is formed in 30% yield in the reaction) by treating η^5-cpRuCl(dcpe) in benzene solution with a dispersion of sodium under ultrasound conditions. This observation suggests a pathway for the formation of this diruthenium(I) hydride. We propose that the complex η^5-cpRu$_2$H(dcpe)$_2$ can be formed by a sequence of reactions whereby the hydride complex η^5-cpRuH(dcpe) undergoes reductive elimination of cyclopentadiene to give Ru(dcpe), which then inserts into the Ru–H bond of η^5-cpRu(dcpe) (Scheme II).

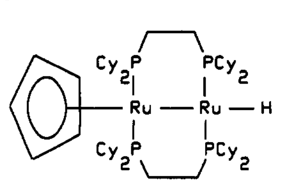
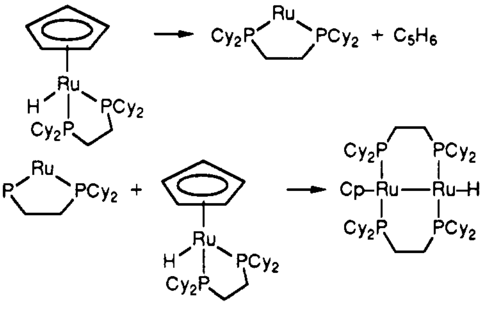
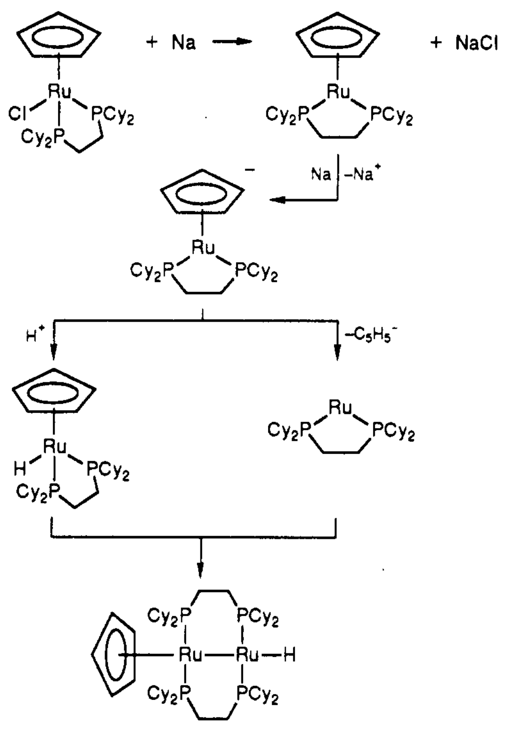


Figure 6. Structure of η^5-CpRu$_2$H(dcpe)$_2$.

Scheme II. Proposed Pathway for the Conversion of η^5-cpRuH(dcpe) into η^5-cpRu$_2$H(dcpe)$_2$



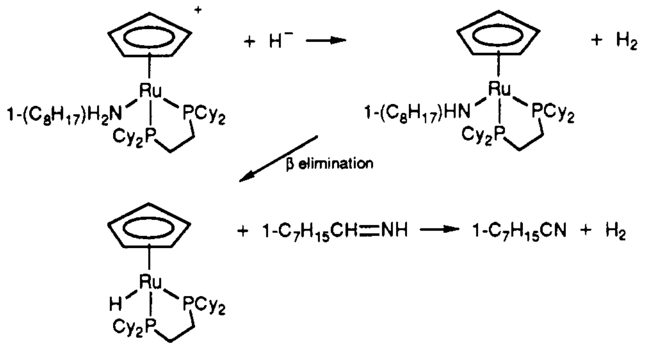
Scheme III. Proposed Pathway for the Conversion of η^5-cpRuCl(dcpe) into η^5-cpRu$_2$H(dcpe)$_2$ with Sodium



An alternate pathway is possible where the hydride ion acts as a one-electron reducing agent. Such a pathway also explains the formation of η^5-cpRu$_2$H(dcpe)$_2$ from η^5-cpRuCl(dcpe) (Scheme III). The intermediate anion $[\eta^5\text{-cpRu(dcpe)}]^-$ can either lose the cyclopentadienyl anion or be protonated by traces of water in the solvent to give Ru(dcpe) or η^5-cpRuH(dcpe), respectively. Reaction between these two intermediates can yield η^5-cpRu$_2$H(dcpe)$_2$. Using this method, we have obtained this diruthenium hydride in yield of up to 70% from η^5-cpRuCl(dcpe). These yields are, however, quite variable, which is to be expected from such a pathway where a quantitative yield can only be obtained under conditions where the intermediates η^5-cpRuH(dcpe) and Ru(dcpe) are formed in equal amounts.

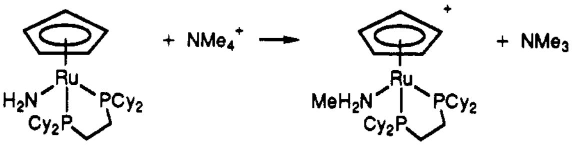
The complex $[\eta^5\text{-cpRu(NH}_2\text{C}_8\text{H}_{17}\text{-1)(dcpe)}]^+$ also reacts with potassium hydride to give two predominant products. These are η^5-cpRu(NH$_2$)(dcpe) and η^5-cpRuH(dcpe). None

Scheme IV. Proposed Pathway for the Conversion of $[\eta^5\text{-cpRu}(NH_2C_8H_{17}\text{-}1)(dcpe)]^+$ into η^5-cpRuH(dcpe) with Hydride Ion



of the trace impurities in the solution can be characterized as the amide complex η^5-cpRu(NHC_8H_{17}-1)(dcpe). The organic products from the reaction have been analyzed by GC/MS spectroscopy. We observe the formation of 1-octanenitrile but not octane. The formation of 1-octanenitrile can be explained by a sequence of reactions involving the conversion of $[\eta^5\text{-cpRu}(NH_2C_8H_{17}\text{-}1)(dcpe)]^+$ into η^5-cpRu(NHC_8H_{17}-1)(dcpe) then into η^5-cpRuH(dcpe). This second β-hydrogen abstraction step involves the elimination of the imine 1-$C_7H_{15}CH{=}NH$. Subsequent dehydrogenation of this imine gives the 1-octanenitrile (Scheme IV). The failure to detect 1-octane under reaction conditions where η^5-cpRu(NH_2)(dcpe) is formed from $[\eta^5\text{-cpRu}(NH_2C_8H_{17}\text{-}1)(dcpe)]^+$ is difficult to explain. Our proposal is that hydride ion acts as a one-electron reductant and that an octyl radical is subsequently formed. Such a radical can be transformed into a variety of products, none of which is 1-octane.

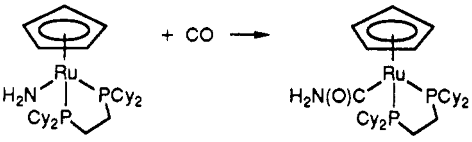
Reaction with Electrophiles. One purpose for synthesizing electron-rich amide complexes is to use them for the formation of carbon–nitrogen bonds. The complex η^5-cpRu(NH_2)(dcpe) has an 18-electron metal center when the amide (NH_2) ligand acts as a two-electron donor. It is to be expected, therefore, that there will be a lone electron pair located on the amide nitrogen. With an additional contribution to the electron density from the electron-rich dcpe ligand, it is reasonable to expect that the amide nitrogen will be nucleophilic. In agreement with this concept, we find that the complex η^5-cpRu(NH_2)(dcpe) reacts with the tetramethylammonium ion to give the cationic methylamine complex $[\eta^5\text{-cpRu}(NH_2Me)(dcpe)]^+$ (eq 13). Thus the amide ligand in η^5-cpRu(NH_2)(dcpe), like that in η^5-cpRe(NH_2)NO(PPh_3), is preferentially alkylated over the nitrogen in trimethylamine.[18]



(13)

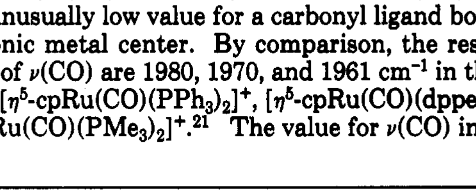
Insertion of CO into the Ruthenium–Amide Bond. A further reason for synthesizing complexes having a ruthenium–amide bond is to investigate the insertion of unsaturated small molecules into this bond. We find that η^5-cpRu(NH_2)(dcpe) reacts with carbon monoxide and that the resulting product is one derived from insertion of this compound into the Ru–N bond.

When CO is bubbled through a THF solution of η^5-cpRu(NH_2)(dcpe), the color darkens to orange/brown. Removal of the solvent in vacuo gives the product carbamoyl complex η^5-cpRu(C(O)NH_2)(dcpe) (eq 14). The complex is characterized by the presence of a single resonance in the $^{31}P\{^1H\}$ NMR spectrum at δ 89.6, a broad resonance in the ^1H NMR spectrum at δ 2.8 due to the C(O)NH_2 group, and a triplet resonance in the $^{13}C\{^1H\}$ NMR spectrum at δ 167.3 (^2J(PC) = 70 Hz) due to the acyl carbon. Again, the position of the proton chemical shift due to the amide hydrogens is dependent on the concentration of the complex in the solution. The IR spectrum of this carbamoyl complex shows a band at 1597 cm^{-1} due to ν(CO), and bands due to ν(NH) at 3077, 3091, and 3100 cm^{-1}. This carbamoyl complex resembles similar ones of structure η^5-cpRu(C(O)NH_2)L(CO) formed by reaction of the cationic carbonyl complex $[\eta^5\text{-cpRu}(CO)_2L]^+$ with ammonia.[19]



(14)

Carbonyl Complex. The formation of the carbamoyl complex by reaction between CO and an amide complex is noteworthy because in previous studies such a reaction is not observed. For example, the reaction of CO with the amide complex *trans*-PtH(NHPh)(PEt_3)$_2$ does not lead to insertion; instead, reductive elimination of aniline occurs, resulting in the formation of $Pt(CO)_2(PEt_3)_2$.[20] In our system the reductive elimination of aminocyclopentadiene is somewhat unlikely; however the displacement of the amide ligand by CO to give the cationic carbonyl complex is realistically possible. In order to synthesize this carbonyl complex by a designed procedure, we have bubbled CO through a solution of $[\eta^5\text{-cpRu(THF)(dcpe)}]^+$ for 5 min. The color of the solution changes from orange to yellow, and the carbonyl complex $[\eta^5\text{-cpRu(CO)(dcpe)}]^+$ is formed (eq 15). The complex shows a band in the IR spectrum at 1940 cm^{-1} due to ν(CO) and a triplet in the $^{13}C\{^1H\}$ NMR spectrum for the carbonyl ligand in $[\eta^5\text{-cpRu}(^{13}CO)(dcpe)]^+$ at δ 203.8 (^2J(PC) = 15.5 Hz). The value of ν(CO) is found at an unusually low value for a carbonyl ligand bonded to a cationic metal center. By comparison, the respective values of ν(CO) are 1980, 1970, and 1961 cm^{-1} in the complexes $[\eta^5\text{-cpRu(CO)}(PPh_3)_2]^+$, $[\eta^5\text{-cpRu(CO)(dppe)}]^+$, and $[\eta^5\text{-cpRu(CO)}(PMe_3)_2]^+$.[21] The value for ν(CO) in the bis



(15)

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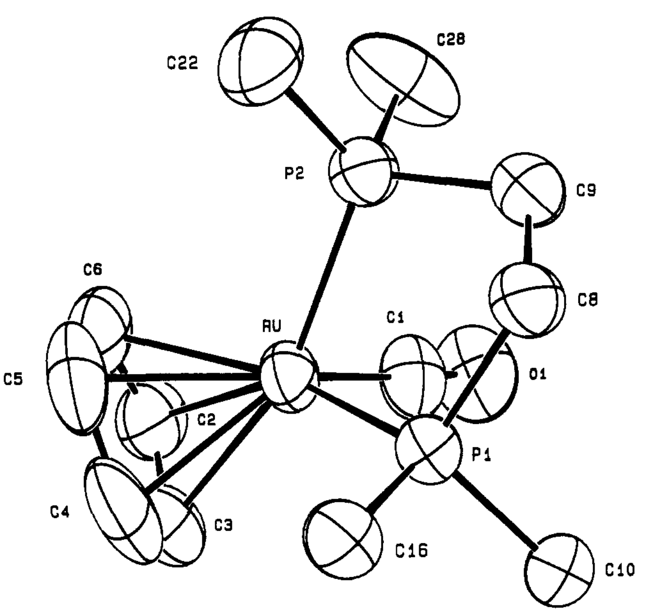


Figure 7. Perspective view of the inner coordination sphere of the [η^5-cpRu(CO)(Cy$_2$PCH$_2$CH$_2$PCy$_2$)]$^+$ cation. Thermal ellipsoids are drawn at the 30% probability level. Only the ipso carbon atoms (C(10), C(16), C(22), C(28)) of the cyclohexyl rings are shown.

Table IX. Selected Bond Distances (Å) and Interbond Angles (deg) for [η^5-cpRu(CO)(Cy$_2$PCH$_2$CH$_2$PCy$_2$)]CF$_3$SO$_3$

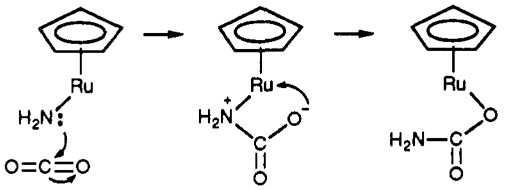
	Bond Distances[a]		
Ru-P(1)	2.3346 (9)	Ru-C′[b]	1.902 (4)
Ru-P(2)	2.318 (1)	C(1)-O(1)	1.148 (5)
Ru-C(1)	1.844 (4)		
	Interbond Angles[a]		
P(1)-Ru-P(2)	83.77 (2)	P(2)-Ru-C′[b]	130.6 (2)
P(1)-Ru-C(1)	94.3 (1)	C(1)-Ru-C′[b]	121.4 (3)
P(1)-Ru-C′[b]	128.0 (2)	Ru-C(1)-O(1)	173.3 (4)
P(2)-Ru-C(1)	86.1 (1)		

[a] Numbers in parentheses are the estimated standard deviation in the least significant digit(s). [b] C′ is the centroid of the cyclopentadienyl ring.

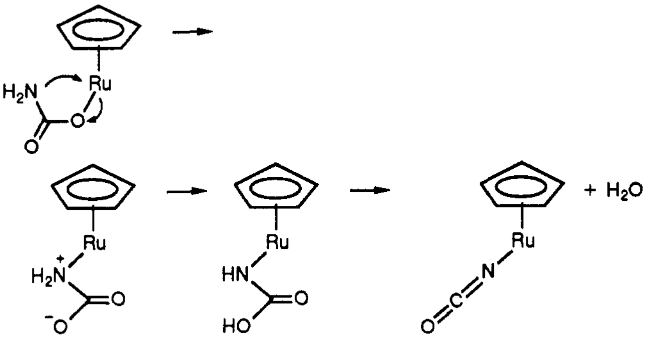
chelate complex [RuCl(CO)(dcpe)$_2$]$^+$ is found at 1940 cm^{-1}.[22]

Crystal Structure of [η^5-cpRu(CO)(Cy$_2$PCH$_2$CH$_2$PCy$_2$)]CF$_3$SO$_3$. The structure of the cation [η^5-cpRu(CO)(Cy$_2$PCH$_2$CH$_2$PCy$_2$)]$^+$ has the ligating *P*,*P*′-chelate and the carbonyl ligand in the trigonal plane of the "piano stool". The distances Ru-P(1) and Ru-P(2) are 2.3346 (9) and 2.318 (1) Å. The P(1)-Ru-P(2) angle is 83.77 (2)°, and the P(1)-Ru-C(1) and P(2)-Ru-C(2) angles are 94.3 (1) and 86.1 (1)°, respectively. The Ru-C(1) distance is 1.844 (4) Å, and the C(1)-O(1) carbonyl distance 1.148 (5) Å. This ruthenium carbonyl distance is shorter than that found in the complex [η^5-cpRu(CO)(PPh$_3$)$_2$]$^+$, where the Ru-C(O) distance is 1.869 (2) Å. The carbon-oxygen carbonyl distance in the triphenylphosphine analogue complex is 1.144 (3) Å, the same as that found in our chelate complex. In each case the Ru-C-O angle is slightly distorted from linearity; in [η^5-cpRu(CO)(Cy$_2$PCH$_2$CH$_2$PCy$_2$)]$^+$ the angle is 173.3 (4)°, whereas in [η^5-cpRu(CO)(PPh$_3$)$_2$]$^+$ the angle is 174.2 (2)°.[23] Other selected bond distances and angles are collected in Table IX. An ORTEP representation is shown in Figure 7.

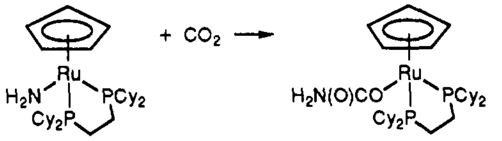
Scheme V. Insertion of CO$_2$ into the Ru-N Bond of η^5-cpRu(NH$_2$)(dcpe)



Scheme VI. Dehydration Reaction for the Conversion of η^5-cpRu(OC(O)NH$_2$)(dcpe) into η^5-cpRu(NCO)(dcpe)



Insertion of CO$_2$ into the Ruthenium-Amide Bond. When CO$_2$ is bubbled through a THF solution of η^5-cpRu(NH$_2$)(dcpe), the solution progressively darkens and the carbamato complex [η^5-cpRu(OC(O)NH$_2$)(dcpe)]$^+$ is formed (eq 16). The complex, which is very soluble in organic solvents, is characterized by the presence of a single resonance in the ^{31}P{^{1}H} NMR spectrum at δ 89.8. The ^{1}H NMR spectrum shows a broad resonance for the carbamate (OC(O)N*H*$_2$) moiety at δ 2.2. The carbamate carbon in the complex is observed as a singlet in the ^{13}C{^{1}H} NMR spectrum at δ 131.3. The absence of any observed ^3J(PC) coupling is supportive of the O-bonded structure. The IR spectrum of the complex shows ν(CO) at 1615 cm^{-1} and bands due to ν(NH$_2$) at 3091 and 3102 cm^{-1}.



(16)

The formation of a carbamate complex from an amide complex and carbon dioxide is not unexpected, since ammonia itself reacts with carbon dioxide to give ammonium carbamate (eq 17).[24] The occurrence of such a reaction

$$2NH_3 + CO_2 \rightleftharpoons NH_4[OC(O)NH_2] \qquad (17)$$

shows that the "insertion" reaction between CO$_2$ and η^5-cpRu(NH$_2$)(dcpe) does not require prior complexation of the molecule to be inserted.[25] Instead, the reaction can occur by attack of the electrophilic carbon of carbon dioxide at the lone electron pair on the complexed amide, followed by intramolecular rearrangement to the O-bonded carbamate structure (Scheme V).

The ruthenium carbamate complex η^5-cpRu(OC(O)NH$_2$)(dcpe) cannot be isolated in pure form because of its slow decomposition under the anhydrous reaction conditions used in its synthesis.[26] We observe that solutions

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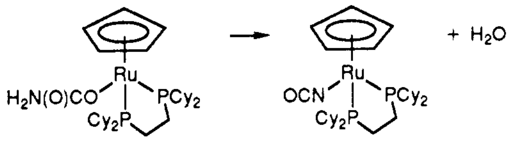
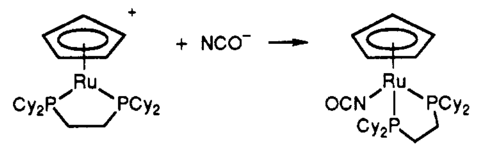
of the carbamate complex slowly convert to a second complex, which is characterized by a single $^{31}P\{^1H\}$ NMR resonance at δ 83.9 and by IR bands at 2238 and 1260 cm^{-1}. These spectral data show that the carbamate complex has been converted to the isocyanate complex via a dehydration reaction (eq 18).[27] The proposed pathway for this



(18)

transformation is shown in Scheme VI. As final confirmation of the stoichiometry of this isocyanate complex, we have independently synthesized it by treating [η^5-cpRu(dcpe)]$^+$ with the isocyanate ion (eq 19).



(19)

Acknowledgment. We thank the Louisiana Educational Quality Support Fund, administered by the Louisiana Board of Regents, for financial support. We thank the Office of Naval Research for a grant to purchase the FTIR spectrometer. We thank Johnson Matthey, Inc., for a loan of hydrated ruthenium trichloride. We thank C. J. Fritchie, E. Stevens, and F. R. Fronczek for helpful discussions. FAB spectra were provided by Dr. G. Goodloe at Auburn University.

Supplementary Material Available: Tables of positional parameters, bond distances and angles, general displacement parameter expressions, and root-mean-square amplitudes of anisotropic displacement for 14 (14 pages); a table of observed and calculated structure factors for 14 (74 pages). Ordering information is given on any current masthead page.

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(26) Stable complexes are readily obtained by the insertion of carbon dioxide into the metal–nitrogen bond of complexes of substituted amides. For examples see: Chetcuti, M. J.; Chisholm, M. H.; Folting, K.; Haitko, D. A.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 2138–46. Tsuda, T.; Watanabe, K.; Miyata, K.; Yamamoto, H.; Saegusa, T. *Inorg. Chem.* **1981**, *20*, 2728–30.

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Laser Desorption Fourier Transform Mass Spectrometric Analysis of Organoactinides: Uranium and Thorium Polypyrazolylborates

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Received January 23, 1991

In this work, we report a study of the analytical capabilities of laser desorption Fourier transform ion cyclotron resonance mass spectrometry for the characterization of several air- and moisture-sensitive organoactinide compounds: polypyrazolylborates of uranium and thorium, $AnCl_3[HB(3,5\text{-}Me_2Pz)_3]\cdot THF$, $UCl_2(HBPz_3)_2$, and $\{UCl_2[HB(3,5\text{-}Me_2Pz)_3]\}_x$ (An = Th, U; Pz = pyrazolyl; $x = 1, 2, ...$). Although the main focus of this paper is to demonstrate the analytical capability of the technique for detecting intact molecular ions of air-sensitive actinide compounds, some additional structural information can be obtained directly from the positive and negative ion mass spectra. Several interesting new species (for example, dinuclear species of the type $An_2Cl_9^-$ (An = Th, U)) were identified from reactions of laser-formed ions with desorbed neutrals and fragments. Correlations can be made between gas-phase ion-molecule reactions and their counterparts in the condensed phase. In particular, we find that the ionic size of the central metal atom can determine the fragmentation and ion-molecule reaction products.

Introduction

Structural characterization of organic molecules, coordination compounds, and organometallic complexes has recently been greatly facilitated by use of laser desorption/ionization techniques: *l*aser *m*icroprobe *m*ass *s*pectrometry (LMMS)[1] based on time-of-flight mass analysis and *l*aser *d*esorption Fourier transform ion cyclotron resonance *m*ass *s*pectrometry (LD/MS).[2,3] Of the two mass analysis methods, FT/ICR mass spectrometry offers vastly higher mass resolving power (e.g., factor of ~1000

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