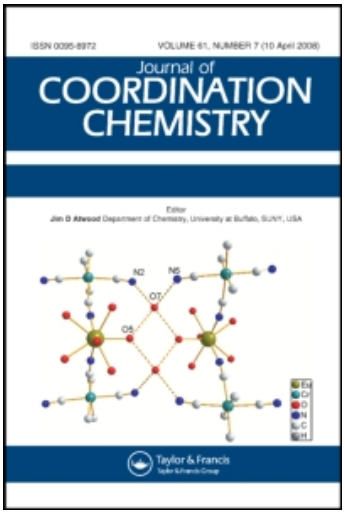

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SYNTHESIS AND REACTIVITY OF NITRIDORUTHENIUM(VI) COMPLEXES OF WEAKLY COORDINATING LIGANDS

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Neutral, trialkylruthenium complexes $Ru(N)R_3L$ ($R = CH_3$, CH_2SiMe_3; L = pyridine, 2,6-lutidine, 4-picoline, PMe_3, $CNCMe_3$) were prepared by the reaction of $[Ru(N)R_4]^-$ salts with HBF_4 and the ligand, L. The molecular structure of $Ru(N)(CH_2SiMe_3)_3(py)$ was determined by X-ray diffraction. Crystals of $Ru(N)(CH_2SiMe_3)_3(py)$ are monoclinic in space group. $P2_1/n$ with $a = 14.551(5)$ Å, $b = 9.113(4)$ Å, $c = 19.801(5)$ Å, $\alpha = \gamma = 90°$, $\beta = 109.27(2)$, $Z = 4$, $R = 0.032$ and $R_w = 0.039$. The neutral dialkyl complex, $Ru(N)R_2Cl$, is in equilibrium with the dimer and adds a variety of neutral, two-electron ligands. Cationic complexes $[Ru(N)R_2L_2][BF]_4]$ ($R = CH_3$, CH_2SiMe_3;L = $NCCH_3$, pyridine) were prepared by the reactions of $Ru(N)R_3L$ with HBF_4 and additional ligand. The addition of concentrated $HNO_{3(aq)}$ to $[Ru(NO)R_4]^-$ gave the nitrato complexes $[Ru(N)R_2(ONO_2)_2]^-$. The complexes $[Ru(N)R_2L_2][BF_4]$ react with water to form the μ-hydroxo dimers, $\{Ru(N)R_2(\mu\text{-}OH)\}_2$. The molecular structure of $\{Ru(N)(CH)_2SiMe_3)_2(\mu\text{-}OH)\}$ was determined by X-ray diffraction. Crystals of $\{Ru(N)(CH)]_2SiMe_3)_2(\mu\text{-}OH)\}$ are monoclinic in space group $P2_1/a$ with $a = 11.510(8)$ Å, $b = 20.440(8)$ Å, $c = 12.858(4)$ Å, $\alpha = \gamma = 90°$, $\beta = 109.04$, $Z = 4$, $R = 0.027$ and $R_w = 0.029$. The acetonitrile complex, $[Ru(N)(CH_2SiMe_3)_2(NCMe)_2][BF_4]$, is a catalyst for the polymerization of ethylene.

KEYWORDS: nitridoruthenium, substitution, polymerization, pyridine-complex, acetonitrile-complex, hydroxo complex.

INTRODUCTION

Transition metal complexes containing substitutionally labile ligands are of great importance as homogeneous catalysts and as precursors to new metal complexes. Ligands such as acetonitrile, tetrahydrofuran, and pyridine can be displaced to form coordinatively unsaturated complexes or substituted by stronger σ-donors.[1]

We previously prepared the first organometallic complexes of ruthenium(VI), $[NBu_4][Ru(N)R_4]$ and $Ru(O)R_4$($R = CH_3$, CH_2SiMe_3).[2,3] Although these 16-electron complexes are not coordinatively saturated, they are relatively unreactive and do not add Lewis bases. The bulky alkyl groups prevent additional molecules from coordinating *trans* to the nitrido or oxo ligands. In order to increase the reactivity of the ruthenium(VI) center, we sought to substitute one or more of the

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alkyl groups on ruthenium for more weakly bound ligands. Here we report the synthesis of a series of organometallic complexes containing acetonitrile or pyridine ligands and some reactions of these new complexes.

EXPERIMENTAL

General Experimental

Reactions were carried out under nitrogen using standard air-sensitive techniques with a Schlenk line or in a Vacuum Atmospheres glove box unless otherwise stated. Anhydrous diethyl ether, tetrahydrofuran, and n-hexane were distilled from sodium/benzophenone under nitrogen and stored over 4 Å sieves. Methylene chloride and acetonitrile were distilled from calcium hydride under nitrogen and stored over 4 Å sieves. Deuterated chloroform was distilled from calcium hydride under nitrogen, subjected to three cycles of freeze-pump-thaw degassing and stored over 4 Å sieves. Pyridine, 2-picoline and 4-picoline were fractionally distilled, degassed and stored over 4 Å sieves. The ruthenium alkyls $[Y][Ru(N)R_4]$ and $[Y][Ru(N)R_3Cl]$ ($R = CH_3$, CH_2SiMe_3; $Y = NBu_4$, PPh_4) were prepared according to published procedures.[2,4]

^1H NMR and ^{13}C NMR spectra were recorded on one of the following instruments GE GN-500, GE QE-300 or GE Unity 400 spectrometer. Chemical shifts (δ) for $CDCl_3$ solutions are reported in parts per million (ppm) relative to $CDCl_3$ ($\delta(^1H)$7.26 and $\delta(^{13}C)$ 77.0). IR spectra were recorded on a Perkin-Elmer 1600 series FTIR with 4 cm^{-1} resolution. UV and visible spectra were recorded on a Perkin-Elmer. Mass spectra were recorded on a Finnigan MAT CH—5 (EI) or 731 (FI, FD). Analyses were performed by the University of Illinois microanalytical service.

$Ru(N)(CH_2SiMe_3)_3(py)$, 1

Pyridinium tetrafluoroborate (0.005 g, 0.031 mmol) was added to a solution of $[PPh_4][Ru(N)(CH_2SiMe_3)_4]$ (0.025 g, 0.031 mmol) in 5 mL CH_2Cl_2. The pale yellow solution became a deeper yellow upon addition of the acid. After stirring for 1 h the solvent was removed under reduced pressure and the yellow crystalline residue extracted with 5 mL of hexane. The yellow solid dissolved in the hexane leaving white $[PPh_4][BF_4]$. The yellow solution was filtered through Celite and the hexane removed leaving the $Ru(N)(CH_2SiMe_3)_3(py)$ as a yellow solid (0.014 g, 0.031 mmol, 99%). UV (CH_2Cl_2, λ_{max} nm(ε)): 382 (443), 300 (3656), 264 (4489), 242(7522). IR (KBr, Cm^{-1}) 2949-2868, 1447, 1251, 1239, 1082(Ru≡N), 845, 826. ^1H NMR (300 MHz, $CDCl_3$): δ 7.86 (*m*, 1H, p-C_5H_5N), 7.82 (*m*, 2H, o-C_5H_5N), 7.44 (*m*, 2H, *m*-C_5H_5N), 1.50 (*s*, 2H, $RuCH_2$), 1.31 (*d*, 2H, J = 9.5 Hz, $RuCH^aH^b$), 0.018 (*s*, 9H, $SiMe_3$), 0.010 (*s*, 18 H, $SiMe_3$), -0.095 (*d*, 2H, J = 9.5 Hz, $RuCH^aH^b$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 150.87(*o*-C_5H_5N), 137.92 (*p*-C_5H_5N), 125.49 (*m*-C_5H_5N), 24.10 ($RuCH_2$), 9.16 ($RuCH_2$), 2.89($SiCH_3$), 1.38($SiCH_3$). *Anal.* Calcd. for $C_{17}H_{38}N_2Si_3Ru$: C, 44.79; H, 8.40; No, 6.15. Found: C, 44.81; H, 8.47; N, 6.13.

[Ru(N)[CH_2SiMe_3)$_3$(4-picoline)], 2

Solid 4-picoline·HBF_4 (0.006 g, 0.031 mmol) was added to a solution of [PPh_4][Ru(N)(CH_2SiMe_3)$_4$] (0.025 g, 0.031 mmol) as above. Yellow crystals of [Ru(N)(CH_2SiMe_3)$_3$(4-picoline)](0.014 g, 0.029 mmol, 96%) were obtained. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.98 (*d*, J = 6 Hz, 2 H, *o*-4-$CH_3C_5H_4N$), 7.24 (*d*, J = 6 Hz, 2 H, *p*-4-$CH_3C_5H_4N$), 2.49 (*s*, 3 H, 4-$CH_3C_5H_4N$), 1.48 (*s*, 2 H, *trans* $RuCH_2$), 1.27 (*d*, J = 9.6 Hz, 2 H, $RuCH^aH^b$), 0.01 (*s*, 18 H, $SiCH_3$), 0.00 (*s*, 9 H, $SiCH_3$), -0.10 (*d*, J = 9.6 Hz, 2 H, $RuCH^aH^b$). $^{13}C\{^1H\}$ (125 MHz, $CDCl_3$): δ 150.27 (*o*-4-$CH_3C_5H_4N$), 149.93 (*p*-4-$CH_3C_5H_4N$), 126.38 (*m*-4-C_5H_4N), 23.79 ($RuCH_2$), 21.14 (4-$CH_3C_5H_4N$), 8.91 ($RuCH_2$), 2.91 ($SiCH_3$), 1.37 ($SiCH_3$).

Equilibrium of [Ru(N)(CH_2SiMe_3)$_3$(4-picoline)] with L'

The 4-picoline complex *2* (14 mg, 0.30 mmol) was dissolved in approximately 1 mL of $CDCl_3$ and 5 μL CH_2Cl_2 was added as an internal standard. The initial concentration of *2* was calculated as 0.030 M from integration of the ^{1}H NMR signals. Pyridine (5 μL, 0.087 M) was added. The concentrations of *2* (0.011 M) and free picoline (0.018 M) were determined by integration of the ^{1}H NMR signals. The NMR spectrum did not change over a 24 h period. An approximate equilibrium (K_{eq} = 0.46) constant was calculated.

$$L' + \text{Ru-L} \rightleftharpoons L + \text{Ru-L}'$$

$$K_{eq} = \frac{([\text{Ru-L}]_{initial} - [\text{Ru-L}])([L])}{([L']_{initial}^{-} - [\text{Ru-L}]_{initial} + [\text{Ru-L}])([\text{Ru-L}])}$$

A solution of *2* was prepared as above and 6μL of 4-fluoropyridine was added by syringe. The initial concentration of *2* (0.030 M) and final concentrations of *2* (0.023 M) and free picoline (0.007 M) were determined by integration of NMR spectra. An approximate equilibrium constant was found to be 0.034.

[Ru(N)(CH_2SiMe_3)$_3$(2,6-lutidine)], 3

Solid 2,6-lutidine·HBF_4 (0.007 g, 0.031 mmol) was added to a solution of [PPh_4][Ru(N)(CH_2SiMe_3)$_4$] (0.025 g, 0.031 mmol) in CH_2Cl_2 as above. [Ru(N)(CH_2SiMe_3)$_3$(2,6-lutidine)](0.011 g, 0.023 mmol, 73%) was obtained as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24 (*br*, 1 H, 2,6-$Me_2C_5H_3N$), 7.00 (*m*, 2 H, 2,6$Me_2C_5H_3N$), 2.42 (*s*, 6 H, 2,6-(CH_3)$_2C_5H_3N$), 1.52 (*s*, 2 H, $RuCH_2$), 1.11 (*d*, J = 10 Hz, 2 H, $RuCH^aH^b$), 0.06 (*s*, 9 H, $SiCH_3$), 0.00 (*s*, 18H, $SiCH_3$), -0.02 (*d*, $RuCH^aH^b$, partially obscured).

[Ru(N)Me_3(py)], 4

Pyridinium tetrafluoroborate (0.016 g, 0.097 mmol) and pyridine (0.2 mL) were added to a solution of [PPh_4][ru(N)Me_4] (0.050 g, 0.097 mmol) in 5 mL CH_2Cl_2. The pale yellow solution became an intense yellow immediately upon addition of the acid and pyridine. After stirring for 1 h the solvent was removed under reduced pressure and the yellow residue extracted with hexane. The hexane solution was filtered through Celite to remove the [PPh_4][BF_4] and pyridine (0.2 mL) added to

the hexane solution. The hexane solution was concentrated to 1 mL and cooled to −30 °C. Red-orange crystals (0.016 g, 0.067 mmol, 69%) of $[Ru(N)Me_3(py)]$ were obtained. ^1H NMR (500 MHz, $CDCl_3$): δ 8.32 (*m*, 2 H, *o*-C_5H_5N), 7l.88 (*m*, 1 H, p-C_5H_5N), 7.47 (*m*, 2 H, *m*-C_5H_5N), 1.46 (*s*, 3 H, $RuCH_3$), 1.04 (*s*, 6 H, $RuCH_3$). $^{13}C\{^1H\}$ (125 MHz, $CDCl_3$): δ 151.16 (*o*-C_5H_5N), 138.06 (*p*-C_5H_5N), 125.72 (*m*-C_5H_5N), 13.20 ($RuCH_3$), 5.14 ($RuCH_3$). *Anal.* Calcd. for $C_8H_{14}N_2Ru$: C, 40.16; H, 5.90; N, 11.71. Found: C, 40.47; H, 6.07; N, 11.95.

[Ru(N)(CH$_2$SiMe$_3$)$_3$(NCCH$_3$)] and [Ru(N)(CH$_2$SiMe$_3$)$_3$(THF)].

Silver tetrafluoroborate (0.018 g, 0.092 mmol) was added to a solution of $[PPh_4][Ru(N)(CH_2SiMe_3)_3Cl]$ (0.069 g, 0.092 mmol) in 5 mL CH_3CN. The orange solution became yellow upon addition of the silver salt. After stirring for 15 min, the AgCl (0.010 g) was filtered off, the solution was concentrated under vacuum, and the product was extracted into hexane. The hexane solution was filtered through Celite and 2 mL of CH_3CN was added to the filtrate. The hexane was removed under vacuum. The yellow acetonitrile solution was stable at room temperature, but the product was not stable in the absence of excess acetonitrile and could not isolate.

Silver tetrafluoroborate (0.018 g, 0.092 mmol) was added to a solution of $[PPh_4][Ru(N)(CH_2SiMe_3)_3Cl]$ (0.069 g, 0.092 mmol) in 5 mL THF. The orange solution became yellow upon addition of the silver salt. After stirring for 15 min, the AgCl (0.012 g) was filtered off. The yellow solution was stable for days at -30° but it slowly decomposed at room temperature, leading to a brown solution with an insoluble black precipitate. Concentration of the solution under vacuum greatly increased the rate of decomposition.

Pyridine (20 μL, 0.25 mmol) was added to each solution above. Solvent was then removed under vacuum, leaving a yellow solid. A sample of the solid was dissolved in $CDCl_3$, ^1H NMR showed only one product and the spectra were identical to that of *1*.

[Ru(N)(CH$_2$SiMe$_3$)$_2$(py)$_2$][BF$_4$],5

Pyridinium tetrafluoroborate (0.010 g, 0.062 mmol) was added to a solution of *1* (0.028 g, 0.062 mmol) in 5 mL CH_2Cl_2. After stirring for 16 h the orange solution was filtered through Celite, the CH_2Cl_2 removed under vacuum and the orange residue dissolved in diethyl ether. Cooling the diethyl ether solution gave 0.010 g (0.019 mmol, 30%) of *5* as orange crystals. ^1H NMR (300 MHz, $CDCl_3$): δ 8.70 (*m*, 2H, *o*-C_5H_5N), 7.97 (*m*, 1H, *p*-C_5H_5N), 7.59 (*m*, 2H, *m*-C_5H_5N), 2.74 (d, 2H, J = 11 Hz, $RuCH^aH^b$), 1.74 (*d*, 2H, J = 11 Hz, $RuCH^aH^b$), -0.09 (*s*, 18H, $SiCH_3$). $^{13}C\{^1H\}$ (125 MHz, $CDCl_3$): δ 151.45 (*m*-C_5H_5N), 140.17 (*p*-C_5H_5N), 126.75 (*o*-C_5H_5N), 24.15 ($RuCH_2$), 0.025 ($SiCH_3$). IR (KBr pellet) 3060 (*w*, νC-H), 2944 (*m*, νC-H), 2876(*m*, νC-H), 1483 (*s*, νC = C), 1109 (*s*, δipC-H), 1080(*s*, νRu≡N), 724 (*s*, δoopC-H), 687 (*s*, δoopC-H), 527 (*s*, δoopC-H). *Anal.* Calcd. for $C_{18}H_{32}N_3Si_2BF_4Ru$: C, 40.45; H, 6.03; N, 7.86. Found: C, 40.32; H, 6.07; N, 7.65.

[Ru(N)Me$_2$(py)$_2$][BF$_4$], 6

Solid $AgBF_4 \cdot (CH_3CN)_4$ (0.037 g, 0.10 mmol) was added to a solution of $[PPh_4][Ru(N)Me_2Cl_2]$ (0.054 g, 0.097 mmol) and pyridine (16 μL, 0.19 mmol, 2

equiv) in 5 mL CH_2Cl_2. The solution remained orange in color and a white precipitate of AgCl formed immediately upon addition of the silver salt. The reaction mixture was stirred for 30 min, and filtered through Celite to remove the AgCl. Pyridine (500 μL) and $AgBF_4 \cdot (CH_3CN)_4$ (0.023 g, 0.064 mmol) were added to the CH_2Cl_2 solution and the reaction mixture stirred for 1 h. A white precipitate of AgCl formed and the color of the solution became dark orange. The AgCl was removed by filtration and the solution concentrated under reduced pressure. Hexane was added and the solution cooled to -30°C and a precipitate of $[PPh_4][BF_4]$ formed. Hexane was added until no more precipitate formed and the solution was filtered. The solvent was removed under reduced pressure. Crystallization from concentrated CH_2Cl_2 afforded 0.015 g (0.38 mmol, 40%) of *6* as orange-red blocks. ^1H NMR (500 MHz, $CDCl_3$): δ 8.71 (*m*, 2H, 0-C_5H_5N), 8.03 (*m*, 1 H, *p*-C_5H_5N), 7.60 (*m*, 2 H, *m*-C_5H_5N), 2.29 (*s*, 6 H, $RuCH_3$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 152.41 (*o*-C_5H_5N), 140.15 (*p*-C_5H_5N), 126.38 (*m*-C_5H_5N), 13.11 ($RuCH_3$). *Anal.* Calcd. for $RuC_{12}H_{16}N_3BF_4$: C, 36.94; H, 4.13; N, 10.77. Found: C, 37.07; H, 4.18; N, 10.69.

[Ru(N)(CH_2SiMe_3)$_2$($NCCH_3$)$_2$][BF_4], 7a

Excess tetrafluoroboric acid dimethyl ether complex (0.256 g, 1.9 mmol) was dissolved in 2 mL CH_3CN and added to a solution of *1* (0.028 g, 0.062 mmol) in 5 mL CH_3CN. The yellow reaction mixture became orange as the acid was added to the $[Ru(N)(CH_2SiMe_3)_3(py)]$ solution. The solvent was removed under vacuum immediately after the addition of the acid and the orange residue extracted with diethyl ether. The solution was filtered through Celite to remove the pyridinium tetrafluoroborate and then concentrated under vacuum and cooled to -30 °C. Cooling the diethyl ether solution provided 0.024 g (0.052 mmol, 84%) of *7a* as orange crystals. UV-visible (CH_2Cl_2, λ_{max}nm(ε)): 430 (144), 290 (1589), 242 (3682). ^1H NMR (300 MHz, $CDCl_3$) δ 2.64 (*d*, 2H, J = 10.9 Hz, $RuCH^aH^b$), 2.54 (*s*, 3H, CH_3CN), 1.96 (*d*, 2H, J = 10.9 Hz, $RuCH^aH^b$), 0.06 (*s*, 18H, $SiCH_3$). $^{13}C\{^1H\}$ (125 MHz, $CDCl_3$):δ 128.96 (CH_3CN), 24.42 ($RuCH_2$), 3.64 (CH_3CN), 0.10 ($SicH_3$). *Anal.* Calcd. for $C_{12}H_{28}N_3BF_4Si_2Ru$: C, 31.44; H, 6.16; N, 9.17. Found: C, 31.20; H, 6.28; N, 8.91.

[Ru(N)(CH_2SiMe_3)$_2$($NCCH_3$)$_2$][NO_3], 7b

To a solution of $[Ru(N)(CH_2SiMe_3)_3(py)]$ (0.029 g, 0.062 mmol) in 5 mL CH_3CN was added 1 mL concentrated HNO_3 and 5 mL H_2O. The reaction mixture became cloudy but appeared to be homogeneous. The color changed from yellow to yellow-orange and an orange solid began to form. The reaction mixture was stirred for 12 h, during which time the reaction mixture became homogeneous. The reaction mixture was transferred to a separatory funnel and extracted with CH_2Cl_2. The orange CH_2Cl_2 extract was filtered and the solvent removed under reduced pressure to afford 0.010 g (0.023 mmol, 37%) of *7b* as an orange solid. ^1H NMR (400 MHz, $CDCl_3$): δ 2.71 (*d*, J = 10.74 Hz, 2 H, $RuCH^aH^b$), 2.37 (*s*, 3 H, $NCCH_3$), 1.63 (*d*, J = 10.74 Hz, 2 H, $RuCH^aH^b$), 0.08 (*s*, 18 H, $SiCH_3$). IR (solution cell, $CDCl_3$): 2954 (*m*, νC-H), 2895 (*w*, νC-H), 2317 (*w*, νC≡N), 2290 (*w*, νC≡N), 1514 (*s*, νN = O), 1247 (*s*, δSi-Me_3), 1095 (*w*, νRu≡N), 835 (*s*, νSi-C).

Reaction of 7a with Ethylene

A solution of *7a* (0.013 g, 0.028 mmol) in a 50:50 mixture of toluene: CH_2Cl_2 (5 mL) was placed in a high pressure reaction vessel. The vessel was pressurized to 1000 psi with ethylene, and the mixture was stirred at 20 °C for 65 h. After release of the ethylene gas, the reaction mixture consisted of a white solid in a yellow solution. The yellow solution contained *7a* as the only organometallic material by NMR spectroscopy. The white solid was collected by vacuum filtration and exhaustively extracted with CH_3CN, then dried under vacuum. Polyethylene, 0.011 g, containing minor amounts of Ru and Cl impurities (Ru, 0.16%; Cl, 0.56%) was obtained.

[Ru(N)(CH_2SiMe_3)$_2$Cl], 8

Solid $AgBF_4$ (0.014 g, 0.072 mmol,) was added to a solution of [PPh_4][Ru(N)(CH_2SiMe_3)$_2Cl_2$] (0.043 g, 0.062 mmol) in 5 mL CH_2Cl_2. A precipitate of AgCl formed after 2 min. After 45 min the solution was a light orange color. The reaction mixture was filtered through Celite and the solvent removed under reduced pressure. The orange residue was extracted with pentane and filtered through Celite to remove the [PPh_4][BF_4] salts. Evaporation of the pentane solution afforded 0.017 g (0.052 mmol, 84%) of *8* as orange needles. ^{1}H NMR (300 MHz, $CDCl_3$, 294 K): δ 2.79 (*br*, 2 H, RuC*H*^{a}H^b), 2.05 (*v br*, 2 H, RuCH^a*H*^{b}), 0.09 (*br*, 18 H, $SiCH_3$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 294K): δ 25.53 (*br*, $RuCH_2$), 0.43 ($SiCH_3$). ^{1}H NMR (500 MHz, $CDCl_3$, 223K, two isomers in a ratio of 4:3. Integration values are relative for each isomer.): major isomer: δ 2.81 (*d*, J = 9.6 Hz, 2H, RuC*H*^{a}H^b), 2.11 (*d*, J = 9.6 Hz, 2H, RuCH^a*H*^{b}), 0.07 (*s*, $SiCH_3$); minor isomer: δ 2.67 (*d*, J = 9.8 Hz, 2H, RuCH^a*H*^{b}), 1.80 (*d*, J = 9.8 Hz, 2 H, RuCH^a*H*^{b}), 0.02 (*s*, $SiCH_3$). ^{13}C[^{1}H] NMR (125 MHz, $CDCl_3$, 213 K): δ 25.60 ($RuCH^2$), 25.33 ($RuCH_2$), 0.28 ($SiCH_3$), 0.02 ($SiCH_3$). IR (KBr pellet) 2952, 2930, 2882, 1248, 1092, 831. *Anal.* Calcd. for $RuC_8H_{22}NSi_2Cl$: C, 29.57; H, 6.82; N, 4.31. Found: C, 29.47; H, 6.95; N, 4.15.

[Ru(N)(CH_2SiMe_3)$_2$(py)Cl], 9

Solid $AgBF_4$ (25 mg, 0.12 mmol) was added to a solution of [PPh_4][Ru(N)(CH_2SiMe_3)$_2Cl_2$] (43 mg, 0.062 mmol) in CH_2Cl_2 (10 mL) and pyridine (2 equivalents). A white precipitate formed immediately upon addition of the $AgBF_4$ and the solution became a lighter orange color. The reaction mixture was allowed to stir for 45 min and filtered. The solvent was removed under reduced pressure and the residue extracted with hexane. Concentration of the hexane solution under reduced pressure and cooling to -30°C afforded 0.1015 g (0.019 mmol, 60%) of *9* as orange crystals. ^{1}H NMR (500 MHz, $CDCl_3$, 18°C): δ 8.75 (*m*, 2 H, *o*-C_5H_5N), 7.99(*m*, 1 H, p-C_5H_5N), 7.57 (*m*, 2 H, *m*-C_5H_5N), 2.30 (*br*, 2 H, RuCH), 2.20 (*br*, 1 H, RuCH), 1.69 (*br*, 1 H, RuCH), 0.10 (*br s*, 9 H, $SiCH_3$), 0.13 (*br s*, 9 H, $SiCH_3$). *Anal.* Calcd. for $RuC_{13}H_{27}NSi_3Cl$: C, 38.64; H, 6.74; N, 6.93. Found: C, 38.99; H, 6.81; N, 6.90.

[PPh_4][Ru(N)(CH_2SiMe_3)$_2$(NO_3)$_2$], 10

Solid $AgNO_3$ (21 mg, 0.062 mmol) was added to a biphasic reaction mixture

containing $[PPh_4][Ru(N)(CH_2SiMe_3)_2Cl_2]$ (48 mg, 0.062 mmol) in 5 mL CH_2Cl_2 and 5 ml H_2O. The aqueous phase was acidified with concentrated HNO_3 (1 mL). The $[PPh_4][Ru(N)(CH_2SiMe_3)_2Cl_2]$ was insoluble in the H_2O phase and remained in the CH_2Cl_2 phase. Immediately upon addition of the $AgNO_3$ a white precipitate of AgCl formed. The reaction mixture was stirred vigorously for 10 h. Hexane was added to the reaction mixture until the organic phase became less dense than the aqueous phase. The organic phase was separated from the reaction mixture and filtered. Removal of the solvent under reduced pressure afforded 0.042 mg (0.056 mmol, 90%) of *10* as analytically pure orange crystals. ^1H NMR (500 MHz, $CDCl_3$): δ 7.88 (*m*, 1H, *p*-PC_6H_5), 7.74 (*m*, 2H, *m*-C_6H_5), 7.62 (*m*, 2H, *o*-PC_6H_5), 2.30 (*d*, J = 10.9 Hz, 2H, $RuCH^aH^b$), 1.43 (*d*, J = 10.9 Hz, 2H, $RuCH^aH^b$), 0.01 (*s*, 18H, $SiCH_3$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 135.72 (*d*, J_{P-C} = 2.9 Hz, p-PC_6H_5), 134.36 (*d*, J_{P-C} = 10.3 Hz, *m*-PC_6H_5), 130.66 (*d*, J_{P-C} = 12.9 Hz, o-PC_6H_5), 117.42 (*d*, J_{P-C} = 89.6 Hz, *ipso*-PC_6H_5), 17.81 (*s*, $RuCH_2$), 0.17 (*s*, $SiCH_3$). IR (KBr pellet) 3060 (*w*, ν_{C-H}), 2951, (*m*, ν_{C-H}), 1497 (*s*, ν_{N-O}), 1478 (*s*, ν_{C-C}), 1280 (*s*, ν_{N-O}), 1243 (*m*, δ_{Si-C}), 1107 (*s*, δip_{C-H}), 1088 (*m sh*, $\nu_{Ru\equiv N}$), 832 (*s*, ν_{Si-C}), 722 (*s*, δoop_{C-H}), 526 (*s*, δoop_{C-H}). (Solution cell, $CDCl_3$) 3065 (*w*, ν_{C-H}), 2952 (*m*, ν_{C-H}), 2892 (*m*, ν_{C-H}), 1588 (w, ν_{C-C}), 1485 (*s*, ν_{N-O}), 1438 (*s*, ν_{C-C}), 1284 (*s*, ν_{N-O}), 1244 (*m*, δ_{Si-C}), 1109 (*s*, δip_{C-H}), 1090 (*m sh*, $\nu_{Ru\equiv N}$), 849 (*s*, γ_{Si-C}), 833 (*s*, ν_{Si-C}), 528 (*s*, δoop_{C-H}). *Anal.* Calcd. for $C_{32}H_{42}N_3O_6PRu$: C, 51.05; H, 5.62; N, 5.58. Found: C, 50.85; H, 5.67; N, 5.53. FAB MS positive ion *m/z* 339 $P(C_6H_5)_4$.

[Ru(N)(CHSiMe$_3$(PMe$_3$), 11

Solid $[HPMe_3][BF_4]$ (0.010 g, 0.062 mmol) was added to a solution of $[PPh_4][Ru(N)(CH_2SiMe_3)_4]$ (0.050 g, 0.062 mmol) in 5 mL CH_2Cl_2. The reaction mixture was allowed to stir for 1 h. The color of the solution changed from yellow to orange-brown. The solvent was removed under reduced pressure and the residue extracted with hexane and filtered to remove the $[PPh_4][BF_4]$. Slow evaporation of a hexane solution afforded 0.020 g (0.044 mmol, 71%) of *11* as yellow crystals. The same material can be prepared in quantitative yield by adding 1-2 equivalents of PMe_3 to solutions of *1*, *2* or *3* in CH_2Cl_2 by adding PMe_3 to $Ru(N)(CH_2SiMe_3)_3(NCMe)$ in acetonitrile, or by adding PMe_3 to $Ru(N)(CH_2SiMe_3)_3(THF)$ in THF solution. ^1H NMR (300 MHz, $CDCl_3$): δ 1.69 (*d*, J_{PH} = 5.19 Hz, 2H, $RuCH_2$), 1.54 (*d*, J_{PH} = 9.63 Hz, 9H, PCH_3), 0.77 (*dd*, J_{HH} = 9.84, J_{PH} = 4.17 Hz, 2H, $RuCH^aH^b$), 0.67 (*dd*, J_{PH} = 16.7, J_{HH} = 9.84 Hz, 2H, $RuCH^aH^b$), 0.15 (*s*, 18H, $SiCH_3$), -0.15 (*s*, 9H, $SiCH_3$). $^{13}C\{^1H\}$NMR (75 MHz, $CDCl_3$):δ 14.49 (*d*, J_{PC} = 28.2 Hz, PCH_3), 14.08 (*d*, J_{PC} = 33.9 Hz, $RuCH_2$), 11.83 (*d*, J_{PC} = 6.87 Hz, $RuCH_2$), 3.50 (*s*, $Si(CH_3)$, 1.99 (*s*, $Si(CH_3)$. IR (KBr pellet) 2949 (*s*, νC-H), 2896 (*m*, νC-H), 2876 (*m*, νC-H) 1424 (*w*, δCH_2), 1361 (*w*, δCH_3), 1241 (*s*, δSi-Me_3), 1076 (*s*, νRu≡N), 848 (*s*, γSi-Me_3), 828 (*s*, νSi-C). *Anal.* Calcd. for $RuC_{15}H_{36}NSi_3P$: C, 39.79; H, 9.35; N, 3.09; P, 6.84. Found: C, 39.98; H, 9.45; N, 3.07; P, 6.70.

[Ru(N)Me$_3$(PMe$_3$)], 12

Solid $[HPMe_3][BF_4]$ (0.013 g, 0.097 mmol) was added to a solution of $[PPh_4][Ru(N)Me_4]$ (0.050 g, 0.097 mmol) in 5 mL CH_2Cl_2. The reaction mixture was allowed to stir for 1 h. Solvent was removed under reduced pressure and the

residue extracted with hexane and filtered to removed the $[PPh_4][BF_4]$. The hexane solution was concentrated under reduced pressure. Cooling the solution to -30°C afforded 0.011 g (0.047 mmol, 48%) of *12* as yellow crystals. Complex *12* can be prepared in quantitative yield by the reaction of *4* with 1-2 equivalents of PMe_3 in CH_2Cl_2 solution. ^1H NMR (400 MHz, $CDCl_3$); δ 1.58 (*d*, J = 9.77 Hz, 9 H, PCH_3), 1.30 (*d*, J_{PH} = 2.0 Hz, 3 H, $RuCH_3$), 0.97 (*d*, J_{PH} = 8.30 Hz, 6 H, $RuCH_3$)., $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 14.47 (*d*, J_{PC} = 28.2 Hz, PCH_3), 12.73 (*d*, J_{PC} = 36.6 Hz, $RuCH_3$), 5.26 (*d*, J_{PC} = 8.4 Hz, $RuCH_3$). *Anal.* Calcd. for $RuC_6H_{18}NP$: C, 30.50; H, 7.68; N, 5.93. Found: C, 31.71; H, 7.82; N, 5.71

[Ru(N)(CH_2SiMe_3)$_3$($CNCMe_3$)], 13

A solution o f *1* (0.033 g, 0.0071 mmol) in $CDCl_3$ (0.7 mL) was placed into a 5 mm NMR tube under N_2. *tert*-Butyl isonitrile (8 μL, 0.071 mmol) added. The solution became lighter yellow in color. The ^1H NMR spectrum showed only one organometallic complex. ^1H NMR (300 MHz, $CDCl_3$): δ 1.63 (*s*, 9H, $CNC(CH_3)_3$), 1.36 (*d*, J = 9.4 Hz, 2 H, $RuCH^aH^b$), 1.29 (*s*, 2 H, $RuCH_2$), 0.83 (*d*, J = 9.4 Hz, 2 H, $RuCH^aH^b$), 0.07 (*s*, 18 H, $SiCH_3$), -0.05 (*s*, 9H, $SiCH_3$).

[Ru(N)(CH_2SiMe_3)$_2$(C_5H_5)], 14

Solid NaC_5H_5 (6 mg, 0.062 mmol) was added to a solution of *7* (0.035 mg, 0.062 mmol) in 10 mL CH_2Cl_2. The reaction mixture was allowed to stir for 12 h. The orange color of the initial solution became orange brown. The reaction mixture was filtered and the solvent removed under reduced pressure. The residue was extracted with hexane and the hexane removed under reduced pressure to give a brown oil. ^1H NMR (500 MHz, $CDCl_3$): δ 5.50 (*s*, 5 H, C_5H_5), 1.42 (*d*, J = 12 Hz, 2 H, $RuCH^aH^b$), 0.25 (*d*, J = 12 Hz, 2 H, $RuCH^aH^b$), 0.16 (*s*, 18 H, $SiCH_3$) $13C\{^1H\}$ (125 MHz, $CDCl_3$): δ 96.64 (C_5H_5), 1.20 ($SiCH_3$), -10.03 ($RuCH_2$).

[{Ru(N)(CH_2SiMe_3)$_2$(μ-OH)}$_2$], 15

Solid Ag_2O (0.015g, 0.062 mmol) was added to a solution of *7* (0.035 g, 0.062 mmol) in 10 mL CH_2Cl_2. The reaction mixture was stirred for 36 h, then filtered. The filtrate was yellow. Solvent was removed under reduced pressure. Crystallization from concentrated hexane solution afforded 0.009 g (0.015 mmol, 47%) of $[Ru(N)(CH_2SiMe_3)_2(\mu\text{-}OH)]_2$ as yellow needles. Two isomers were present in a ratio of 7:3 by ^1H NMR. ^1H NMR (300 MHz, $CDCl_3$) major isomer: δ 1.96 (*d*, J = 11.1 Hz, 8 H, $RuCH^aH^b$), 0.92 (*s*, 2 H, RuOH), 0.75 (*d*, J = 11.1 Hz, 8 H, $RuCH^aH^b$), 0.06 (*s*, $SiCH_3$); minor isomer: δ 2.19 (*d*, J = 10.9 Hz, 8 H, $RuCH^aH^b$), 1.17 (*d*, J = 10.9 Hz, 8 H, $RuCH^aH^b$), 0.94 (*s*, 2 H, RuOH), 0.06 (*s*, $SiCH_3$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) major isomer: δ 16.48 ($RuCH_2$), 0.20 ($SiCH_3$); minor isomer: δ 15.93 ($RuCH_2$), 0.26 ($SiCH_3$). IR (KBr pellet) 3626(ν_{OH} major isomer), 3616(ν_{OH} minor isomer), 2952, 2924, 2856, 1244, 1097($\nu_{Ru=N}$ minor isomer), 1091($\nu_{Ru=N}$ major isomer), 831. *Anal.* Calcd. for $Ru_2C_{16}H_{46}N_2O_2Si_4$: C, 31.35; H, 7.56; N, 4.57. Found: C, 32.89; H, 7.77; N, 4.35.

Crystallographic Data Collection and Reduction for [Ru(N)(CH_2SiMe_3)$_3$(py)], 1

A crystal of [Ru(N)(CH_2SiMe_3)$_3$(py)] suitable X-ray crystallographic study was grown by slow evaporation of hexane solution of [Ru(N)(CH_2SiMe_3)$_3$(py)]. The translucent, yellow-orange equidimensional, data crystal was cut from a much larger crystal. The crystal was mounted using oil (Paratone-N, Exxon) to a thin glass fiber and cooled to -75°C with the (-2 1 4) scattering planes roughly normal to the spindle axis. Data were collected at -75 °C. The data crystal volume was larger than ideal, but the crystal mosaic was not too broad. No change in the appearance of the sample was observed during the experiment. Data were collected on an Enraf-Nonius CAD4 automated κ-axis diffractometer equipped with a graphite crystal monochrometer (λ (Mo κ_α) = 0.71073 Å. Cell parameters and other crystallographic data are given in Table 1.

The structure was solved by Patterson methods (SHELXS-86); the correct ruthenium atom position was deduced from a Patterson map and subsequent partial-structure expansion revealed positions for the remaining non-hydrogen atoms. Hydrogen atoms were included as fixed contributors in "idealized" positions. In the final cycle of least-squares refinement, non-hydrogen atom positions were refined with anisotropic thermal coefficients, a common isotropic thermal parameter was varied for the hydrogen atoms and an empirical extinction parameter was refined. Successful convergence was indicated by the maximum shift/error for the final cycle. The highest peaks in the final difference Fourier map were in the vicinity of the ruthenium atom; there were no other significant features. A final analysis of variance between observed and calculated structure factors showed a slight dependence on sine (θ).

Crystallographic Data Collection and Reduction for [{Ru(N)(CH)]$_2$SiMe$_3$)$_2$(μ-OH)}$_2$], 15

Suitable crystals of [{Ru(N)(CH_2SiMe_3)$_2$(μ-OH)}$_2$] were grown by slow evaporation of hexane at -30°C from a concentrated hexane solution of *15*. The yellow,

Table 1 Crystal data collection and refinement parameters

Compound	1	15
Formula	$RuSi_3N_2C_{17}H_{38}$	$Ru_2Si_4O_2N_2C_{16}H_{46}$
Formula weight	455.83	613.04
Space Group	$P2_1/n$(No. 14)	$P2_1/a$(No. 14)
a, Å	14.551(5)	11.510(8)
b, Å	9.133(4)	20.440(8)
c, Å	19.801(5)	12.858(4)
α = γ, deg	90	90
β, deg	109.27(2)	109.04(5)
Formula/Unit cell, *Z*	4	4
Density calculated (ρ) gm/cm^3	1.219	1.424
Temperature, °C	-75	-75
Radiation	Mo Kα (graphite crystal monochromator)	
	$K\alpha_1$ = 0.70930, Kα = 0.71073Å	$K\alpha_2$ = 0.71359
Absorption Coeff. (μ), cm^{-1}	7.62	12.13
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.032	0.027
$R_w = (\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2)^{1/2}$	0.039	0.029

translucent, prismatic data crystal had slightly damaged faces. There were internal flaws but no crystallites or other contaminating substances were attacked to the surface of the sample and the crystal uniformly extinguished plane-polarized light. The crystal was mounted using oil (Paratone-N, Exxon) to a thin glass fiber then cooled to −75°C with the (3 0 −2) scattering planes roughly normal to the spindle axis. Data were collected on an Enraf-Nonius CAD4 automated κ-axis diffractometer at −75°C. No change in the appearance of the sample was observed during the experiment. Cell parameters and crystallographic data are given in Table 1.

The structure was solved by direct methods (SHELXS-86); the correct positions for the ruthenium atoms were deduced from an E-map. Subsequent least-squares refinement and difference Fourier syntheses revealed positions for the remaining non-hydrogen and hydrogen atoms. In the final cycle of least-squares refinement, anisotropic thermal coefficients were refined for non-hydrogen atoms and a common isotropic thermal parameter was refined for hydrogen atoms. Successful convergence was indicated by maximum shift/error for the last cycle. The final difference Fourier map had no significant features. A final analysis for variance between observed and calculated structure factors showed no systematic errors. The hydroxyl hydrogen atom positions both converged with unusually short *d*(O-H). This may be attributed to a broad mosaic spread, *i.e.*, inaccurate low angle data.

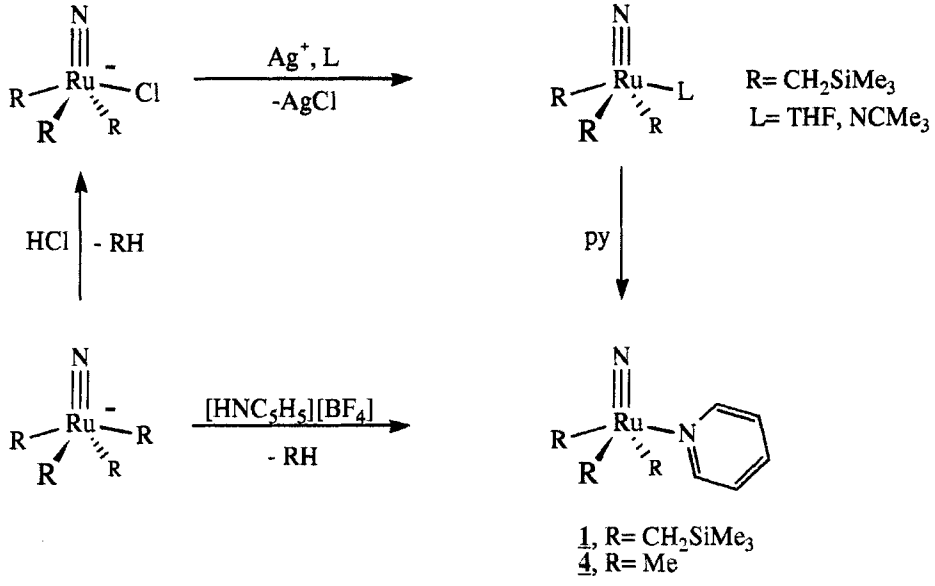
RESULTS

1. Nitridoruthenium(VI)trialkyl Complexes

The anionic nitridoruthenium complexes [Y][Ru(N)R_4] (Y = NBu_4, PPh_4; R = CH_3, CH_2SiMe_3) react rapidly with acids. Protonation with one equivalent or two equivalents of $HCl_{(g)}$ or $C_6H_5N \cdot HCl$ gives [Y][Ru(N)R_3Cl] or [Y][Ru(N)R_2Cl_2].[4] Protonation of [NBu_4][Ru(N)(CH_2SiMe_3)$_4$] with one equivalent of pyridinium tetrafluoroborate or pyridinium trifluoromethanesulfonate gives Ru(N)(CH_2SiMe_3)$_3$(py), *1*. (Scheme 1) Complex *1* does not lose the pyridine ligand under vacuum. Solutions of this complex are air stable for about 24 h, while crystalline samples are stable for several days.

Several other pyridine derivatives can be prepared in the same manner. Addition of one equivalent of 4-picoline·HBF_4 or 2,6-lutidine·HBF_4 to [NBu_4][Ru(N)(CH_2SiMe_3)$_4$] gives [Ru(N)(CH_2SiMe_3)$_3$(4-picoline)], *2*, or [Ru(N)(CH_2SiMe_3)$_3$(2,6-lutidine)]*3*. The reaction of [NBu_4][Ru(N)(CH_3)$_4$] with one equivalent of $C_5H_5N \cdot HBF_4$ or $C_5H_5N \cdot HOSO_2CF_3$ gives the neutral trimethyl complex [Ru(N)Me_3(py)], *4*. Unlike complexes *1-3, 4* loses pyridine under vacuum and the resulting nitridoruthenium trimethyl complex is unstable and decomposes rapidly. The ^{1}H NMR spectra of *1-4* have signals for two types of alkyl ligands (*cis* and *trans* to the pyridine ligands) in a 2:1 ratio.

The reaction between [NBu_4][Ru(N)(CH_2SiMe_3)$_3$Cl] and one equivalent of $AgBF_4$ in acetonitrile or THF produces AgCl and solutions of [Ru(N)(CH_2SiMe_3)$_3$L] (L = NCMe, THF). The complexes are stable at room temperature in solutions containing excess L but we have been unsuccessful in our attempts to isolate them in pure form. The ligands, L, are quite labile and addition of pyridine to [Ru(N)(CH_2SiMe_3)$_3$L] gives *1*.



The molecular structure of complex *1* was determined by single crystal X-ray diffraction. The geometry is distorted square pyramidal with an apical nitrogen atom. (Figure 1) The pyridine ring lies parallel to the Ru≡N axis with a Ru-N bond distance of 2.163(3) Å. (Table 1) The distance between the ruthenium atom and the nitrido nitrogen, 1.602(3) Å, is slightly smaller than that distance in $[NBu_4][Ru(N)Me_4]$, 1.58(1) Å. The average ruthenium-carbon bond distance (2.12Å), avereage C-Ru-C angle (84.8°), and average $N_{nitrido}$-Ru-C angle (106.4°) of $Ru(N)(CH_2SiMe_3)_3(NC_5H_5)$ are very close to those average values in $[NBu_4][Ru(N)Me_4]$ (2.14Å, 83.0°, 110.4°).

2. Nitrodoruthenium(VI)dialkyl Complexes

The neutral trialkyl complex, *1*, reacts with a second equivalent of pyridinium tetrafluoroborate to give $[Ru(N)(CH_2SiMe_3)_2(py)_2][BF_4]$*5*. (Scheme 2) Alternatively, *5* can be prepared by the reaction of $[NBu_4][Ru(N)(CH_2SiMe_3)_2Cl_2]$ with two

Table 2 Selected bond distances and angles of $Ru(N)(CH_2SiMe_3)_3(NC_5H_5)$

			Distances		
Ru1-N1	1.602(3)	Ru1-N2	2.163(3)	Ru1-C1	2.123(4)
Ru1-C5	2.125(4)	Ru1-C9	2.112(4)		
			Angles		
N1-Ru1-N2	105.7(1)	N1-Ru1-C1	108.9(2)	N1-Ru1-C5	108.8(2)
N1-Ru1-C9	101.5(2)	N2-Ru1-C1	85.5(1)	N2-Ru1-C5	87.3(1)
N2-Ru1-C9	152.8(1)	C1-Ru1-C5	142.2(2)	C1-Ru1-C9	84.8(2)
		C5-Ru1-C9	84.9(2)		

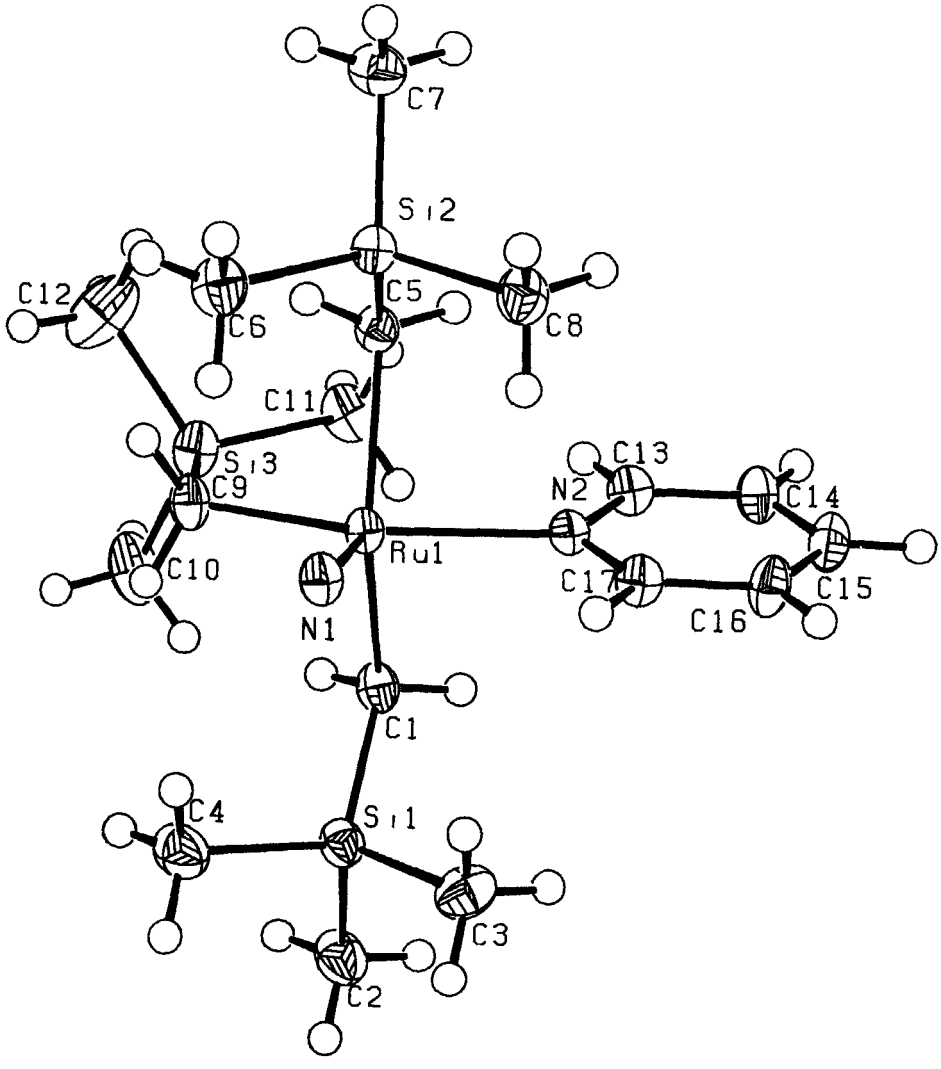
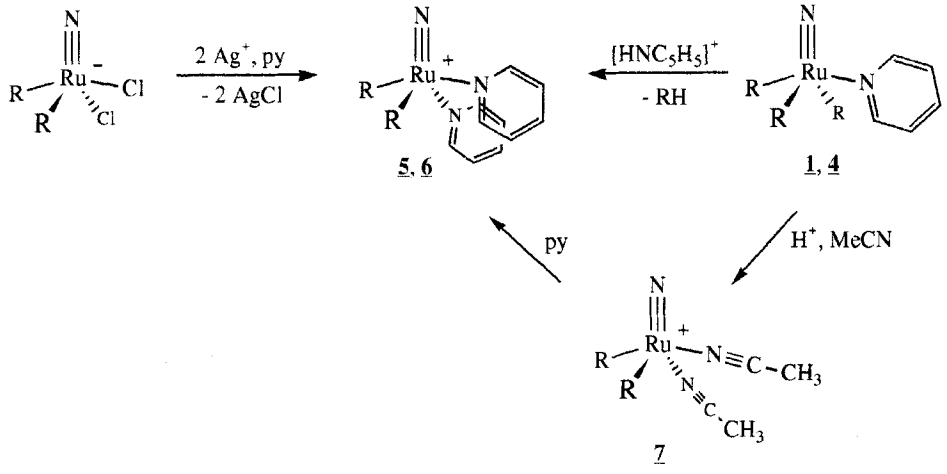


Figure 1 ORTEP diagram of $Ru(N)(CH_2SiMe_3)_3(NC_5H_5)$

equivalents of $AgBF_4$ in pyridine/dichloromethane solution. The analogous methyl complex $[Ru(N)Me_2(py)_2][BF_4]$, *6*, was prepared from the reaction of $[NBu_4][Ru(N)(CH_3)_2Cl_2]$ with two equivalents of $AgBF_4$ in the presence of pyridine.

The reaction of *1* with excess $HBF_4 \cdot Me_2O$ or HNO_3 in acetonitrile gives $[Ru(N)(CH_2SiMe_3)_2(NCCH_3)_2][Z]$, (*7a*, $Z = BF_4$; *7b*, $Z = NO_3$). The reaction of $[PPh_4][Ru(N)Me_2Cl_2]$ with $AgBF_4$ in acetonitrile gives $[Ru(N)Me_2(NCCH_3)_2][BF_4]$, which is very unstable and decomposes even in acetonitrile shortly after formation.

The alkyl groups in complexes *5-7* are in a *cis* configuration. The ^1H NMR spectra of the trimethylsilylmethyl complexes *5* and *7* include two sets of doublets for



diastereotopic methylene protons. The protons in the methyl groups are all equivalent.

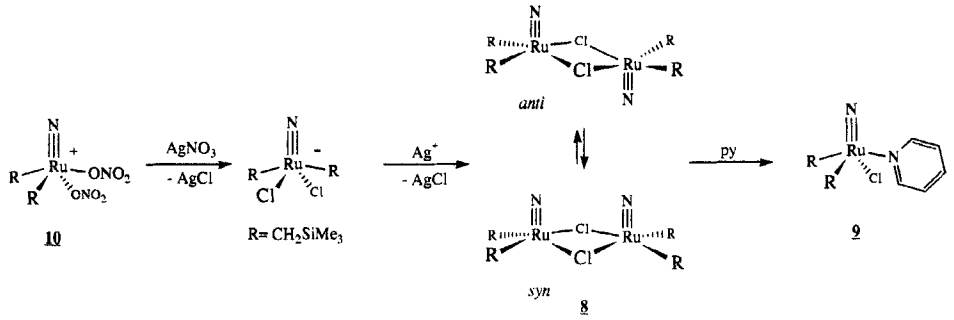
3. *Synthesis and Reactions of* $[Ru(N)R_2Cl]_2$

Abstraction of a chloride ligand from ruthenium in the presence of a neutral donor molecule, such as pyridine or acetonitrile, results in the formation of a ruthenium-donor molecule complex. In the absence of potential ligands, the reaction of $[Y][Ru(N)(CH_2SiMe_3)_2Cl_2]$ with one equivalent of $AgBF_4$ gives a chloride-bridged dimer $[Ru(N)(CH_2SiMe_3)_2Cl]_2$, *8*. It can be isolated in good yield as an orange crystalline solid. This neutral, hexane soluble complex is remarkably stable to air in the solid state and in solution. It is similar to complexes *1-4* with a chloride from another $Ru(N)(CH_2SiMe_3)_2Cl$ unit acting as a two electron donor.

^1H and ^{13}C NMR spectra indicate that a dynamic process occurs in solution. There is a single broad resonance for each of the two diastereotopic methylene protons and another broad singlet for the trimethylsilyl group in the ^1H NMR spectrum. The ^{13}C spectrum includes a broad resonance for the methylene carbons and another for the methyl carbons at room temperature. At low temperature ($< -50°C$), sharp resonance lines for two isomers are observed. The isomers are present in a 4:3 ratio. Spectroscopic data are insufficient to assign either syn or anti structures to the major isomer, but from steric considerations the anti isomer should be somewhat favoured.

The dimeric monochloro complex, *8*, reacts rapidly with neutral donors. It reacts with pyridine to give $Ru(N)(CH_2SiMe_3)_2Cl(py)$, *9*. This complex can also be prepared in one step by the reaction of $[Y][Ru(N)(CH_2SiMe_3)_2Cl_2]$ with one equivalent of $AgBF_4$ and 2 equivalents of pyridine in methylene chhloride solution. An ^1H NMR spectrum shows that the two alkyl groups in *9* are inequivalent as would be expected for a square pyramidal geometry with one alkyl *trans* to chloride and the other *trans* to pyridine.

In a related reaction, $[PPh_4][Ru(N)(CH_2SiMe_3)_2$ reacts with silver nitrate and nitric acid to give a nitrato complex $[PPh_4][Ru(N)(CH_2SiMe_3)_2(NO_3)_2]$, *10*. In the



^{1}H NMR spectrum of *10*, the methylene protons of the trimethylsilylmethyl ligands are split into a set of doublets indicating the *cis* relationship of the alkyl ligands.

4. Reactivity of the Trialkyl Complexes

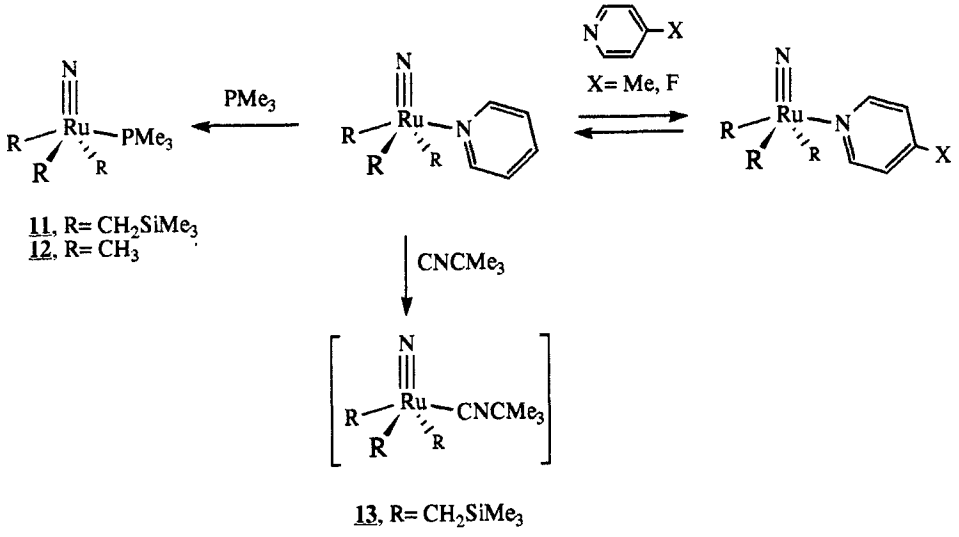
The neutral complexes $Ru(N)R_3L$ have several potential sites for reactivity. The nitrido ligand may react with electrophiles, the alkyl ligands may be susceptible to protonation, and the metal center may add other donor molecules. We have shown (above) that $Ru(N)(CH_2SiMe_3)_3(NC_5H_5)$, *1*, reacts with pyridinium salts to protonate an alkyl and give *5*.

Ligand exchange and substitution reactions of $Ru(N)R_3L$ are facile. Poor ligands, such as THF and acetonitrile, are readily and irreversibly substituted by the better donor, pyridine. The addition of pyridine to a solution of 2 in $CDCl_3$, or the addition of 4-picoline to a solution of *1* in $CDCl_3$ gives an equilibrium mixture of *1*, *2*, free pyridine, and free picoline by NMR. 4-Fluoropyridine also substitutes for the pyridine and picoline ligands in *1* and *2*, the equilibrium favors more electron-rich ligands bound to the metal. An approximate equilibrium constant for the reaction between *2* and pyridine was found to be 0.46, and for the reaction between *2* and *4*-fluoropyridine 0.034. Trimethylphosphine displaces pyridine and 4-picoline quantitatively in *1* and *2* to form the trimethylphosphine adduct *11*. The addition of PMe_3 to *4* produces $Ru(N)Me_3(PMe_3)$, *12*. The trimethylphosphine complexes can also be formed by the protonation of $[NBu_4][Ru(N)R_4]$ ($R = CH_2SiMe_3$, CH_3) with one equivalent of $[HPMe_3][BF_4]$.

Reaction of *1* with one equivalent of *t*-butyl isonitrile results in the immediate formation of $Ru(N)(CH_2SiMe_3)_3(CNCMe_3)$, *13*, which rapidly decomposes. The initial formation of the isonitrile complex can be observed by ^{1}H NMR spectroscopy at room temperature. After 10 min the color of the solution begins to change from pale yellow to brown and a multitude of new singals are observed in the t-butyl and trimethylsilyl region of the ^{1}H NMR spectrum. Upon standing an insoluble brown film is deposited on the walls of the reaction vessel.

5. Reactivity of $[Ru(N)R_2L_2]^+$

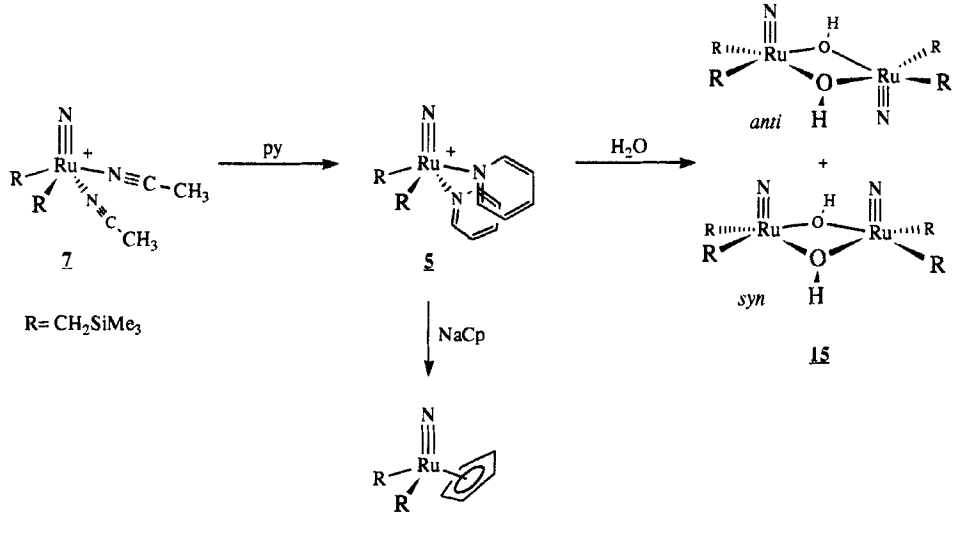
Ligand substitution reactions dominate the chemistry of complexes *5-7*. The reaction of *7* with pyridine leads to the formation of *5* with the liberation of free acetonitrile. Tetrahydrofuran does not displace acetonitrile even in THF solution



11, R= CH_2SiMe_3
12, R= CH_3

13, R= CH_2SiMe_3

and acetonitrile does not displace pyridine from *5*. Reaction of a *5* or *7* with one equivalent of NaC_5H_5 results in the formation of $[Ru(N)(CH_2SiMe_3)_2(C_5H_5)]$, *14*, as the major product. The NMR spectra of *14* are nearly identical to those of the previously osmium analog.[5] Byproducts in the reaction have the same solubility properties as *14* and the cyclopentadienyl complex has not been isolated in pure form.



7

R= CH_2SiMe_3

5

15

14

Reaction of *5* or *7* with two equivalents of Ag_2O results in the formation of a neutral, hydroxo dimer, $[Ru(N)(CH_2SiMe_3)_2(\mu\text{-}OH)]_2$, *15*. The ^1H NMR spectrum of *15* is similar to the spectrum of *8* with two isomers present in a 7:3 ratio. Four sets of doublets and two singlets are observed for the methylene protons and the methyl groups of the trimethylsilylmethyl ligands, respectively. The IR spectrum includes two sharp hydroxyl stretches and two sharp Ru≡N stretches. The pyridine complex, *5*, reacts with water much more rapidly than to give *15*.

The molecular structure of the *syn* isomer of 15 was determined by single crystal X-ray diffraction. (Figure 2). The ruthenium centers have a distorted square pyramidal geometry and are joined through the bridging hydroxyl ligands with equidistant Ru-OH bond distances. The Ru-Ru distance of 3.3407(5) shows no metal-metal interaction. Bond distances and angles are shown in Table 2. The geometry and metal-ligand distances are very similar to those of other nitridoruthenium alkyl complexes.

Solutions of *7* in non-coordinating solvents react at room temperature under 1000 psi of ethylene to give some polyethylene. When the reaction is carried out using acetonitrile as a solvent, no polyethylene is formed and the starting material is recovered.

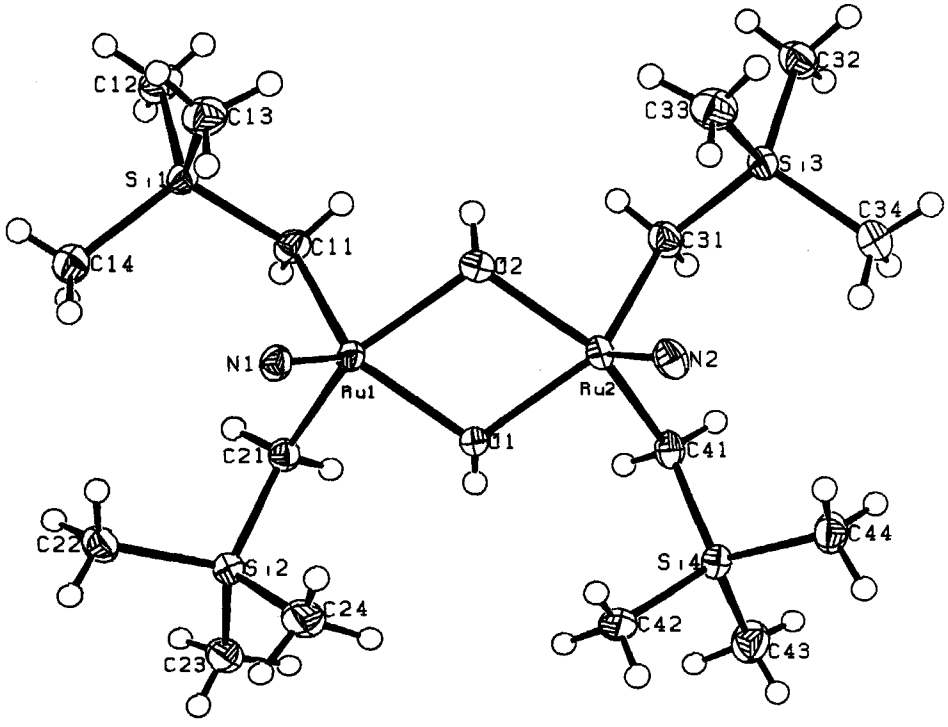


Figure 2 ORTEP diagram of $[Ru(N)(CH_2SiMe_3)_2(\mu\text{-}OH)]_2$

Table 3 Selected bond distances and angles of $[Ru(N)(CH_2SiMe_3)_2(OH)]_2$

Distances					
Ru1-O1	2.046(3)	Ru2-O1	2.048(3)	Ru1-O2	2.060(3)
Ru2-O2	2.056(3)	Ru1-N1	1.589(3)	Ru2-N2	1.585(4)
Ru1-C11	2.075(5)	Ru1-C21	2.082(5)	Ru2-C31	2.079(5)
Ru2-C41	2.097(5)	O1-H1	0.61(5)	O2-H2	0.76(5)
Angles					
O1-Ru1-O2	70.9(1)	O1-Ru1-W1	118.8(2)	O1-Ru1-C21	88.2(2)
2-Ru1-N1	115.2(2)	O2-Ru1-C11	88.3(2)	N1-Ru1-C11	103.5(2)
N1-Ru1-C21	101.4(2)	C11-Ru1-C21	87.4(2)	O1-Ru2-O2	71.0(1)
O1-Ru2-N2	116.9(2)	O1-Ru2-C41	89.8(2)	O2-Ru2-N2	114.1(2)
O2-Ru2-C31	88.7(2)	N2-Ru2-C31	103.2(2)	N2-Ru2-C41	100.3(2)
C31-Ru2-C41	88.1(2)	Ru1-O1-Ru2	109.4(1)	Ru1-O1-H1	124(5)
Ru2-O1-H1	122(5)	Ru1-O2-Ru2	108.5(1)		

DISCUSSION

All complexes described in this paper are five coordinate and have a distorted square pyramidal geometry with an apical nitrido ligand. This is shown in the crystal structures of both *1* and *15*, and in the structures of previously characterized nitridoruthenium(VI) alkyl complexes. These 16-electron complexes do not add a sixth ligand because of the strong *trans* labilizing effect of the nitrido ligand. Alkyl groups are also strong σ donors and the *trans* effect of the alkyl groups leads to a *cis* configuration of the alkyls in $[Ru(N)(CH_2SiMe_3)_2L_2]^+$ and $[Ru(N)(CH_2SiMe_3)_2(NO_3)_2]^-$.

Protonation of $[Y][Ru(N)(CH_2SiMe_3)_4]$ ($Y = PPh_4$, NBu_4) with $HBF_4 \cdot OMe_2$ at room temperature in toluene or methylene chloride leads to the formation of a black, ruthenium-containing precipitate and a mixture of organic products. The initially formed trialkyl complex, $Ru(N)(CH_2SiMe_3)_3$, is not stable and immediately decomposes under these conditions. Donor solvents, such as THF and acetonitrile, stabilize the trialkyl complex and solutions remain yellow and homogeneous for days. THF and acetonitrile probably coordinate weakly to the metal, forming $Ru(N)(CH_2SiMe_3)_3L$. Pyridine displaces the solvent molecule and forms $Ru(N)(CH_2SiMe_3)_3(py)$.

Protonation of the neutral trialkyl complexes is slower than protonation of the anionic species. The reaction gives $[Ru(N)(CH_2SiMe_3)_2(py)_2]^+$ and $[Ru(N)(CH_2SiMe_3)_2(NCMe)_2]^+$. The acetonitrile complex is quite stable and does not lose CH_3CN under vacuum. It is interesting that the nitrate salt $[Ru(N)(CH_2SiMe_3)_2(NCMe)_2][NO_3]$ is stable and the nitrate does not substitute for one of the acetonitrile ligands. Also, the nitrato complex $[PPh_4][Ru(N)(CH_2SiMe_3)_2(ONO_2)_2]$ is stable with respect to ligand substitution in acetonitrile solution.

Transition metal complexes containing the nitrate ligand are common in inorganic chemistry, and several modes of coordination are known for this ligand.[6] Although the nitrate group is capable of bidentate and bridging modes of coordination, the elemental analysis and spectroscopic data indicate that *10* almost certainly contains two nitrate ligands, each coordinated through a single oxygen atom. The signals for the methylene protons in the ^1H NMR spectrum are sharp suggesting that the

nitrato ligands are strongly coordinated and undergo rapid rotation about the Ru-O bond.

Ligand exchange reactions occur with $Ru(N)(CH_2SiMe_3)_3L$ and with $[Ru(CH_2SiMe_3)_2L_2]^+$. Based on the reactivity of these complexes in substitution reactions, the donor ability of the ligand L increases in the order THF < MeCN < 4-fluoropyridine < pyridine < picoline < PMe_3. Dissociative and associative mechanisms for the substitution reactions are possible with these complexes and we do not have sufficient data to rule out either possibility. Because the complexes $Ru(N)(CH_2SiMe_3)_3L$ lose ligand, L, under vacuum, it is reasonable to assume that these complexes are in equilibrium with a small amount of $Ru(N)(CH_2SiMe_3)_3$ in solution and other two-electron donor molecules add to this very reactive species. The cationic complexes $[Ru(CH_2SiMe_3)_2L_2]^+$ show no indication of dissociating L.

Aquo complexes cannot be formed by adding water to $Ru(N)(CH_2SiMe_3)_3L$ or $[Ru(CH_2SiMe_3)_2L_2]^+$ but pyridine, liberated by water exchange with $[Ru(CH_2SiMe_3)_2(py)_2]^+$, deprotonates bound water and a hydroxo complex is formed. The hydroxo complex is formed much more slowly from $[Ru(CH_2SiMe_3)_2(NCMe)_2]^+$ and water. The acetonitrile ligand should exchange with water more rapidly than pyridine. Presumably, water displaces pyridine or acetonitrile from the ruthenium center in a reversible reaction. Pyridine, the stronger base, deprotonates the aquo ligand and drives the reaction forward.

The dimeric complex $[Ru(N)(CH_2SiMe_3)_2Cl]_2$ is related to the dialkyl complexes above. The ruthenium center is stabilized by donation of an electron pair from a chloride on another $Ru(N)(CH_2SiMe_3)_2Cl$ unit. The dimer exists are two rapidly converting isomers. We propose that the dimer is in equilibrium with a small amount of monomer. The monomers can come together with both nitrido ligands on the same side of the Ru-Ru vector, giving the syn isomer, or they coordinate with the nitrido ligands on opposite sides, giving the anti isomer. The monomer can be trapped by the addition of pyridine to the solution.

In reactions of $Ru(N)R_3L$ and $[Ru(N)R_2L_2]^+$ with trimethyl phosphine, the phosphine adds to the metal, not to the nitrogen atom. Griffith and co-workers showed that tertiary phosphines react with inorganic nitridoruthenium complexes at nitrogen, generating phosphinimidato complexes.[7] Related reactions of other metal-nitrides with tertiary phosphines have been reported.[8] The organometallic nitridoruthenium complexes are more stable in the +6 oxidation state than are the inorganic complexes.

Isonitriles are isoelectric with carbon monoxide, however, isonitriles are better σ-donors and unlike carbon monoxide do not require a significant backbonding interaction to form stable complexes. The pyridine ligand in *1* is displaced by *t*-butylisonitrile giving a short lived trialkylisonitrile complex, *13*. Once formed, the isonitrile complex undergoes further reactions leading to decomposition. Since isonitrile ligands commonly insert into metal carbon bonds it seems likely that once formed, migration of a trimethylsilylmethyl occurs. Migration of a trimethylsilylmethyl ligand was observed in the reaction of the methylimidoosmium(VI) complex $[Os(NMe)(CH_2SiMe_3)_4]$ with *t*-butylisonitrile to give the stable isonitrile complex $[Os(NMe)(CH_2SiMe_3)_3(C(NCMe_3)CH_2SiMe_3)]$.[9]

The methyl complexes are less stable than the trimethylsilylmethyl analogs. For example, $[RuMe_2(NCMe)_2][BF_4]$ decomposes at room temperature in solution while $[Ru(CH_2SiMe_3)_2(NCMe)_2][BF_4]$ is quite stable under those conditions. Electronically, the two alkyl groups are quite similar. Steric bulk in the larger alkyl

group may prevent bimolecular decomposition pathways and lead to increased stability.

CONCLUSION

Trialkyl complexes, $Ru(N)(CH_2SiMe_3)_3L$ (L = THF, MeCN, py, picoline, lutidine, PMe_3), were synthesized by the protonation of $[Ru(N)(CH_2SiMe_3)_4]^-$ with HBF_4 in the presence of the ligand, L. The reaction of $[Ru(N)Me_4]^-$ with $[HNC_5H_5][BF_4]$ produced $Ru(N)Me_3(py)$. Protonation of a second alkyl ligand in $[Ru(N)(CH_2SiMe_3)_3(NC_5H_5)]$ with either $[HNC_5H_5][BF_4]$ or $HBF_4 \cdot OMe_2$ in CH_3CN gives $[Ru(N)(CH_2SiMe_3)_2(py)_2][BF_4]$ or $[Ru(N)(CH_2SiMe_3)_2(NCMe)_2][BF_4]$. The complexes $[Ru(N)(CH_2SiMe_3)_2Cl]_2$ and $[PPh_4][Ru(N)(CH_2SiMe_3)_2(NO_3)_2]$ were synthesized from $[Ru(N)(CH_2SiMe_3)_2Cl_2]$. All of these complexes readily undergo substitution reactions with stronger donor molecules. The stability of the complexes increases in the order L = THF<MeCN< pyridine<picoline<PMe_3.

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Supplementary Material Available

For $[Ru(N)(CH_2SiMe_3)_3(py)]$ and $\{Ru(N)(CH_2SiMe_3)_2(\mu\text{-}OH)\}_2$, tables of atomic coordinates, thermal parameters, selected distances and angles, (13 pages) are available upon request from the authors.

References

1. (a) B.J. Hathaway, D.G. Holah, A.E. Underhill, *J. Chem. Soc.*, 2444 (1962). (b) B.B. Wayland, *J. Chem. Soc., Chem. Commun.*, 898 (1968). (c) A. Sen, T.-W. Lai, *J. Am. Chem. Soc.*, **103**, 4627 (1981). (d) M.S. Wrighton, M.A. Schroeder, *J. Am. Chem. Soc.*, **95**, 5764 (1973). (e) K. Seyferth, R. Taube, *J. Organomet. Chem.* **229**, C-19 (1982). (f) J.H. Merrifield, G.-Y. Lin, W.A. Kiel, J.A. Gladysz, *J. Am. Chem. Soc.*, **105**, 5811 (1983). (g) A.W. Konradi, S.F. Pedersen, *J. Am. Chem. Soc.*, **111**, 8014 (1989). (h) R.F. Jordon, W.E. Dasher, S.F. Echols, *J. Am. Chem. Soc.*, 1718 (1986). (i) P.A. Belmonte, Z.Y. Own, *J. Am. Chem. Soc.*, **106**, 7493 (1984). (j) W.A. Hermann, R. Serrano, H. Bock, *Angew. Chem., Int. Ed. Eng.* **23**, 383 (1984).
2. P.A. Shapley, J.P. Wepsiec, *Organometallics* **5**, 1515 (1986).
3. R.W. Marshman, W.S. Bigham, S.R. Wilson, P.A. Shapley, *Organometallics* **9**, 1341 (1990).
4. P.A. Shapley, H.S. Kim, S.R. Wilson, *Organometallics* **7**, 928 (1988).
5. R.W. Marshman, J.M. Shusta, S.R. Wilson, P.A. Shapley, *Organometallics* **10**, 1671 (1991).
6. C.C. Addison, N. Logan, S.C. Wallwork, C.D. Garner, *Quarte. Rev.* **25**, 289 (1971).
7. W.P. Griffith, D. Pawson, *J. Chem. Soc., Dalton Trans.* 417 (1975).

8. (a) M. Bakir, P.S. White, A. Dovletoglou, T.J. Meyer, *Inorg. chem.* **30**, 2835 (1991). (b) I. Schmidt, U.H.J. Kynast, K. Dehnicke, *Z. Naturforsch.* **39B**, 1248 (1984). (c) V.C. Gibson, D.N. Williams, W. Clegg, *J. Chem. Soc. Chem. Commun.* 1863 (1989). (d) J. Chatt, J.R. Dilworth, *J. Indian Chem. Soc.* 13 (1977).
9. R.W. Marshman, P.A. Shapley, *J. Am. Chem. Soc.*, **112**, 8369 (1990).