bonds of transition-metal compounds could possibly be deduced from the magnitude of Δ. Similarly, differing ligand sets and metal oxidation states (even for the same transition metal) may result in greatly different relative metal-hydride and metal-alkyl bond strengths due to variations in the *effective* electronegativity of the metal center.[13] Standard values of electronegativity will not generally give accurate pictures of bond polarity and consequent relative bond strengths for transition-metal complexes, as is readily apparent from Figure 2. The most commonly cited values around 25 kcal·mol^{-1} should only be ascribed to L_nM fragments with strongly π-withdrawing ligand sets and, hence, are probably at the upper end of the range. One might also infer a strategy for designing an alkane-activating metal center: relatively strong M–C bonding should be favored by a relatively electropositive $[L_nM]$ which by inference uses much metal s character in the M–C bonding.

Acknowledgment. J.E.B. acknowledges financial support from the Shell Company Foundation. We thank W. A. Goddard for stimulating discussions.

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[13] Limited data demonstrate that this is also true for main-group compounds; e.g. for A = $SiMe_3$, $SiMe_2Cl$, and $SiMeCl_2$, Δ = 1, 2, and 7 kcal mol^{-1} respectively (calculated from data in: Pilcher, G.; Skinner, H. A. In *The Chemistry of the Metal–Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1982; Vol. 1, pp 43–90).

Syntheses of the Ruthenium(VI) Alkyl Complexes $[Ru(N)R_{4-x}Cl_x]^-$ (R = Me, CH_2SiMe_3) and the X-ray Crystal Structure of $[N\text{-}n\text{-}Bu_4][Ru(N)Me_4]$

Patricia A. Shapley,* Hoon sik Kim, and Scott R. Wilson

School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

Received September 14, 1987

Anionic nitridoruthenium(VI) alkyl complexes $[Ru(N)Me_4]^-$ and $[Ru(N)(CH_2SiMe_3)_4]^-$ have been prepared by the alkylation of $[Ru(N)(OSiMe_3)_4]^-$ with $AlMe_3$ or with $Mg(CH_2SiMe_3)_2$, respectively. The structure of one of these, $[N\text{-}n\text{-}Bu_4][Ru(N)Me_4]$, was determined by single-crystal X-ray diffraction: a = 9.359 (3) Å, b = 18.368 (4) Å, c = 15.193 (5) Å; V = 2519 (1) Å^3; Z = 4; β = 105.31 (2)°; ρ_{calcd} = 1.101 g/cm^3, monoclinic space group $P2_1/n$. Mixed alkyl-chloro complexes, $[Ru(N)R_{4-x}Cl_x]^-$ (R = CH_2SiMe_3, x = 1–2; R = Me, x = 1–3), result from the reaction of HCl(g) with the alkyl complexes. The gold(I) chloro complex $Au(PPh_3)Cl$ reacts in a manner analogous to HCl and converts $[Ru(N)Me_4]^-$ to $[Ru(N)ClMe_3]^-$ with formation of $Au(PPh_3)Me$. In contrast to the related osmium complexes, both Lewis acid adducts of the ruthenium nitrides and (alkylimido)tetraalkylruthenium complexes are thermally unstable.

Introduction

Alkyl complexes of early transition elements in high oxidation states are now well-known but only recently have similar complexes of the platinum metals in high oxidation states been prepared. The homoleptic osmium(IV) alkyl complexes $Os(c\text{-}C_6H_{11})_4$ and $Os(o\text{-}MeC_6H_4)_4$ were prepared and structurally characterized.[1] The first ruthenium(IV) alkyl complexes, (1–3:6,7:10–12-η-$C_{12}H_{18}$)RuIMe and (1–3:6,7:10–12-η-$C_{12}H_{18}$)$RuMe_2$, were reported in 1985.[2] Cyclopentadienylrhodium and -iridium alkyl complexes in the +4 and +5 oxidation states were prepared.[3,4] Series of nitrido-[5] and (alkylimido)[6]osmium(VI) alkyl complexes were synthesized and the oxoosmium(VI) alkyl complexes $Os(O)(CH_2SiMe_3)_4$,[7] $Os(O)R_4$ (R = Me, CH_2SiMe_3, CH_2Ph, and Ph),[8] and $OsO_2(2,4,6\text{-}Me_3C_6H_2)_2$[9] were also prepared. Prior to this work, however, no ruthenium(VI) alkyl complexes had been reported.

An investigation of the reaction chemistry of ruthenium(VI) alkyl complexes has implications to the catalytic oxidation and ammoxidation of organic molecules. Ruthenium tetraoxide and other complexes of ruthenium have been used as stoichiometric and catalytic oxidants.[10–14] It has been proposed that some of these oxidants form intermediate high oxidation state organometallic complexes in their reactions with unsaturated organic molecules.[15,16]

An investigation of reactions occurring at the heteroatom ligand are especially important. There is a possibility for protic acids and other electrophiles to react with nitridotetraalkylruthenium(VI) complexes at the nitrido nitrogen atom, at the d^2 metal center, or at a metal–carbon bond. There is precedent for each of these reactions. Molybdenum nitrides can be protonated[17,18] the d^0 alkyl complexes of metals of the titanium triad are directly cleaved

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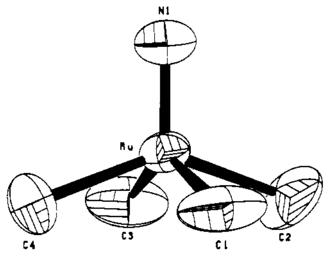

Figure 1. ORTEP diagram of $[Ru(N)Me_4]^-$.

by acids, and many anionic metal complexes can be protonated to form metal hydrides.[19] In some cases, gold(I) complexes react like protons.[20]

We report here on the synthesis of nitridotetraalkylruthenium(VI) anions as either the tetrabutylammonium or tetraphenylphosphonium salts, on the crystal structure of one of these, and on the reactions of these alkyl complexes with HCl and certain other electrophiles. Part of this work has appeared previously.[21]

Results and Discussion

Reaction of trimethylsiloxy complexes of osmium and ruthenium with magnesium or aluminum alkyls has proven to be a general method for the preparation of corresponding alkyl complexes of the transition metal.[5,6] Even high oxidation state alkyl complexes can be prepared without competing reduction of the metal. Reduction of the central metal is frequently observed in reactions of transition-metal complexes with main-group metal alkyls.[7,9]

The nitridotetrakis(trimethylsiloxy)ruthenium(VI) salts $[Y][Ru(N)(OSiMe_3)_4]$ ($Y = PPh_4$, N-*n*-Bu_4) can be readily prepared by metathesis of the chloride ligands in the nitridotetrachlororuthenium(VI) salts with sodium trimethylsiloxide. These trimethylsiloxide complexes are purple crystalline solids that are soluble in a variety of organic solvents. Although the ruthenium trimethylsiloxide complexes are thermally stable, they decompose rapidly when exposed to air or water.

The reactions of $[Y][Ru(N)(OSiMe_3)_4]$ with 4 equiv of $Mg(CH_2SiMe_3)_2$ in ether/hexane solution at room temperature produce the tetrakis(trimethylsilylmethyl) complexes $[Y][Ru(N)(CH_2SiMe_3)_4]$ in 65–75% isolated yield. Slightly higher yields are obtained when the reactions are carried out at −78 °C. With fewer than the 4 equiv of the dialkylmagnesium reagent, $[Ru(N)(CH_2SiMe_3)_2(OSiMe_3)_2]^-$ can be obtained.[21]

The nitridotetramethylruthenium(VI) salts, $[Y][Ru(N)Me_4]$, are best prepared by the reaction of $[Y][Ru(N)(OSiMe_3)_4]$ with 4 equiv of trimethylaluminum and excess tetramethylethylenediamine in toluene solution at room temperature. The color of the reaction mixture gradually changes from purple to yellow during the course of the reaction. Addition of hexane causes the precipitation of $[Y][Ru(N)Me_4]$. Without TMEDA or another Lewis base, a black, insoluble solid is the only ruthenium-containing product of this reaction. We believe that the base binds excess $AlMe_3$ and $AlMe_2(OSiMe_3)$ and prevents formation of an unstable adduct between the Lewis acidic aluminum species and the ruthenium nitride. Addition of $AlMe_3$ or $BF_3 \cdot Et_2O$ to a solution of $[Y][Ru(N)Me_4]$ leads to decomposition of the ruthenium complex. With the analogous osmium compounds, stable trimethylaluminum and boron trifluoride adducts have been isolated and fully characterized

Scheme I

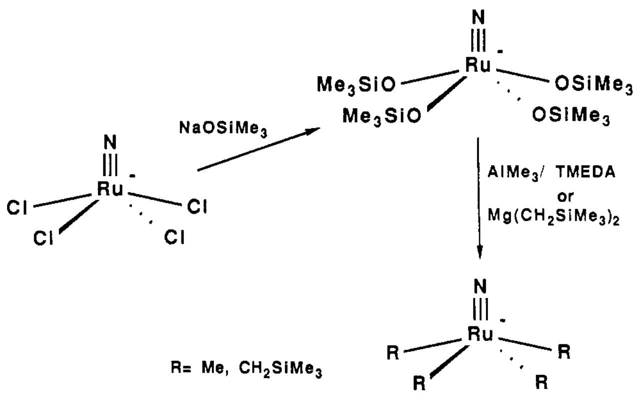

Table I. Selected Bond Distances and Angles for $[Ru(N)Me_4]^-$

	Distances (Å)		
Ru–N1	1.58 (1)	Ru–C3	2.14 (2)
Ru–C1	2.14 (2)	Ru–C4	2.16 (2)
Ru–C2	2.12 (2)		
	Angles (deg)		
N1–Ru–C1	111.2 (6)	C1–Ru–C3	137.1 (7)
N1–Ru–C2	108.6 (7)	C2–Ru–C3	78.6 (8)
N1–Ru–C3	111.2 (7)	C2–Ru–C4	141.0 (7)
N1–Ru–C4	110.4 (6)	C3–Ru–C4	86.2 (8)
C1–Ru–C2	82.5 (8)	C4–Ru–C1	84.8 (7)

The nitridoruthenium alkyl complexes are thermally stable but sensitive to oxygen and to light. All are yellow or orange crystalline solids. These d^2 ruthenium complexes are diamagnetic. The four alkyl groups of $[Y][Ru(N)R_4]$ are equivalent in the NMR spectra down to −70 °C, suggesting a square-pyramidal structure with an apical nitride. The ruthenium nitrogen stretching vibration produces a sharp band in the IR spectrum of each of these complexes.

The structure of one of the alkyl complexes, [N-*n*-Bu_4][$Ru(N)Me_4$], was determined by single-crystal X-ray diffraction. Selected bond distances and angles for the anion are shown in Table I; atomic parameters are shown in Table II.

The structure of the ruthenium anion in [N-*n*-Bu_4][$Ru(N)Me_4$] was found to be square pyramidal, with the alkyl groups bent down below the plane of the metal. A similar distortion in the structures of $[AsPh_4][Ru(N)Cl_4]$[22] and $[AsPh_4][Os(N)Cl_4]$[23] was ascribed to electronic repulsion between metal–nitrogen π-bonding electrons, located primarily on the central metal, and the σ-bonding electrons to the chloride ligands. Since methyl groups are better electron donors than chlorides, it is reasonable that the distortion in this complex is greater. The average N–Ru–C angle of 110.4° can be compared with the N–Os–C angle in [N-*n*-Bu_4][$Os(N)(CH_2SiMe_3)_4$] of 107.4°.[6] The N–M–Cl angles in $[AsPh_4][Ru(N)Cl_4]$ and $[AsPh_4][Os(N)Cl_4]$ are 104.6° and 104.5°, respectively. The structures of other tetramethylmetal complexes with π-donor ligands, $[Re(O)Me_4]_2Mg(THF)_4$ and $[W(O)Me_4]_2Mg(THF)_4$, are also distorted square pyramids.[24,25] In these molecules the oxotetramethylmetal anions are

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Table II. Fractional Atomic Parameters for $[N\text{-}n\text{-}Bu_4][Ru(N)Me_4]$

	x/a	*y/bl*	*z/c*
Ru	0.1026 (1)	0.18074 (6)	0.33343 (8)
N1	−0.018 (1)	0.2239 (6)	0.3682 (8)
C1	0.239 (2)	0.115 (1)	0.440 (1)
C2	0.298 (2)	0.245 (1)	0.358 (2)
C3	0.101 (2)	0.212 (1)	0.197 (1)
C4	0.014 (2)	0.780 (9)	0.275 (2)
N2	0.627 (1)	0.3387 (5)	0.2013 (7)
C5A	0.583 (2)	0.376 (1)	0.279 (2)
C6A	0.688 (3)	0.347 (2)	0.380 (2)
C7A	0.623 (4)	0.400 (3)	0.440 (3)
C8A	0.679 (4)	0.421 (2)	0.515 (3)
C9A	0.807 (2)	0.352 (1)	0.211 (1)
C10A	0.838 (3)	0.441 (2)	0.215 (2)
C11A	1.020 (4)	0.430 (2)	0.221 (3)
C12A	1.101 (4)	0.439 (2)	0.289 (3)
C13A	0.542 (2)	0.376 (1)	0.114 (1)
C14A	0.370 (4)	0.357 (2)	0.096 (3)
C15A	0.309 (3)	0.399 (2)	0.000 (2)
C16A	0.148 (4)	0.383 (2)	−0.017 (3)
C17A	0.612 (2)	0.259 (1)	0.208 (2)
C18A	0.643 (3)	0.221 (2)	0.113 (2)
C19A	0.611 (4)	0.141 (3)	0.101 (3)
C20A	0.605 (4)	0.089 (2)	0.056 (3)
C5B	0.731 (4)	0.391 (2)	0.195 (2)
C6B	0.873 (3)	0.402 (2)	0.245 (2)
C7B	0.962 (3)	0.461 (2)	0.209 (2)
C8B	1.103 (4)	0.487 (2)	0.259 (3)
C9B	0.447 (4)	0.360 (2)	0.155 (3)
C10B	0.411 (4)	0.364 (2)	0.067 (2)
C11B	0.253 (4)	0.373 (2)	0.029 (3)
C12B	0.187 (4)	0.390 (2)	−0.068 (3)
C13B	0.634 (3)	0.319 (2)	0.304 (3)
C14B	0.625 (3)	0.377 (2)	0.350 (3)
C15B	0.658 (3)	0.359 (2)	0.468 (2)
C16B	0.560 (5)	0.422 (3)	0.481 (4)
C17B	0.668 (3)	0.266 (2)	0.167 (3)
C18B	0.590 (4)	0.213 (2)	0.150 (3)
C19B	0.611 (3)	0.134 (2)	0.139 (2)
C20B	0.644 (4)	0.116 (2)	0.033 (3)

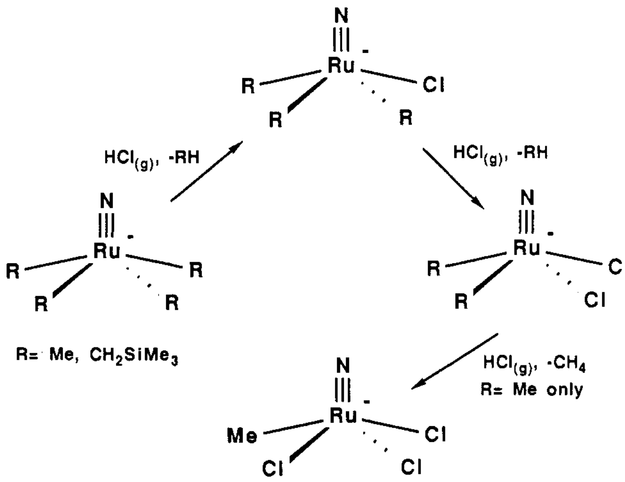
bridged by magnesium cations.

The ruthenium nitrogen distance of 1.58 (1) Å in the methyl complex and the distance of 1.570 (7) Å found for Ru–N in $[AsPh_4][Ru(N)Cl_4]$ are the same within experimental error. We can compare this to the significant difference in the length of the Os–N bonds in $[N\text{-}n\text{-}Bu_4][Os(N)(CH_2SiMe_3)_4]$ and $[AsPh_4][Os(N)Cl_4]$, of 1.631 and 1.604 Å, respectively. The average metal–carbon bond distance in $[Ru(N)Me_4]_-$ (2.14 Å) and $[Os(N)(CH_2SiMe_3)_4]^-$ (2.13 Å) are also quite similar.

We have previously shown that nitridoosmium alkyl complexes $[Os(N)R_4]^-$ react with organic electrophiles, R′X, by an S_N2 mechanism to form the imido complexes $Os(NR')R_4$.[26] A similar reaction occurs with the ruthenium alkyl complexes, but the imido products are not thermally stable. Both $[Y][Ru(N)(CH_2SiMe_3)_4]$ and $[Y][Ru(N)Me_4]$ react with MeI, $[Me_3O][BF_4]$, $MeOSO_2CF_3$, or $Me_3SiOSO_2CF_3$. In all cases, the appropriate amount of salt is produced ([Y]I, $[Y][SO_3CF_3]$, or $[Y][BF_4]$) along with a hexane-soluble orange-brown organometallic product. Only in the reaction of $[Y][Ru(N)(CH_2SiMe_3)_4]$ with $Me_3SiOSO_2CF_3$ can the product $Ru(NSiMe_3)(CH_2SiMe_3)_4$ be isolated. The steric bulk around the metal in this complex probably slows down the decomposition reactions.

The reaction of HCl(g) with the nitridotetraalkylruthenium(VI) anions produces alkyl chloro complexes of ruthenium. With $[Ru(N)(CH_2)SiMe_3)_4]^-$ and 1 or 2 equiv of HCl(g), the monochloro complex $[Ru(N)Cl(CH_2SiMe_3)_3]^-$ can be isolated in good yield. The reaction with excess HCl(g) gives *cis*-$[Ru(N)Cl_2(CH_2SiMe_3)_2]^-$. The cis arrangement of the alkyl ligands gives the characteristic double–doublet pattern for the diastereotopic methylene protons of the equivalent trimethylsilylmethyl groups in the ^1H NMR spectrum. Even bubbling HCl(g) through a toluene solution of $[Ru(N)Cl_2(CH_2SiMe_3)_2]^-$ for long reaction times does not give further reaction. The reaction of HCl(g) with $[Ru(N)Me_4]^-$ produces $[Ru(N)ClMe_3]^-$, cis-$[Ru(N)Cl_2Me_2]^-$, and $[Ru(N)Cl_3Me]^-$, depending on reaction conditions.

Scheme II



Substitution of halides for alkyl groups at the ruthenium center decreases the electron density at the metal which decreases the tendency of the complexes to react with electrophiles. This decrease in electron density is observed in the ^1H NMR spectra as a downfield shift of alkyl resonances as the number of chloride ligands increases in $[Ru(N)R_{4-x}Cl_x]^-$. The ruthenium–nitrogen triple bond becomes somewhat stronger which results in the observed shift of the Ru–N stretching vibration to higher energy.

The monochloride $[Ru(N)ClMe_3]^-$ can be synthesized more conveniently by reaction of $[Ru(N)Me_4]^-$ with HCl·TMEDA or with chloroacetic acid. The bromo complex $[Ru(N)BrMe_3]^-$ results from treatment of $[Ru(N)Me_4]^-$ with 1 equiv of bromoacetic acid. The α-haloacetic acids are not acting simply as a source of protons in these reactions since no ruthenium–haloacetate complexes can be detected in the reaction mixture. We believe that the α-carbon atom, activated by the carboxyl group, undergoes an S_N2 reaction by the nitride with displacement of halide to form an unstable imido complex, $[Ru(NCH_2COOH)Me_4]$. Loss of propionic acid and addition of halide to the metal center would generate $[Ru(N)ClMe_3]^-$ or $[Ru(N)BrMe_3]^-$.

(Triphenylphosphine)gold(I) chloride reacts with $[Ru(N)Me_4]^-$ to form $[Ru(N)ClMe_3]^-$ and $Au(PPh_3)Me$. One possible mechanism for this reactions involves initial nucleophilic substitution by the nitride on the gold center with loss of halide. We know that Lewis acids adducts of the ruthenium nitride and ruthenium alkylimido complexes are unstable. Decomposition of the intermediate in the presence of halide ion could give the observed products.

The isolobal analogy between gold(I) and protons has been used to explain the reactions between gold complexes and transition-metal species.[27] The reaction of mononuclear or polynuclear anionic transition-metal complexes

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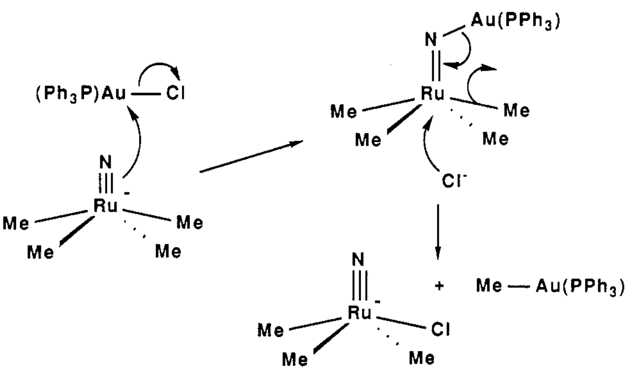
Scheme III



with Au(PPh$_3$)Cl is a common method for the formation of gold–transition-metal complexes.[28,20] A number of gold–ruthenium clusters have been synthesized with Au(PPh$_3$)Cl or other Au(I) reagents.[29-42] We have found that the reactions of Au(PPh$_3$)Cl and HCl with [Ru(N)Me$_4$]$^-$ are similar in the cleavage of the Ru–CH$_3$ bond by these electrophiles and formation of Au–CH$_3$ and H–CH$_3$ bonds, respectively.

Conclusion

We have prepared the first examples of ruthenium(VI) alkyl complexes. The anions [Ru(N)R$_{4-x}$Cl$_x$]$^-$ (R = Me, x = 0–3; R = CH$_2$SiMe$_3$, x = 0–2) can be isolated as the tetraphenylphosphonium or tetrabutylammonium salts. These are yellow to orange crystalline compounds that are thermally stable and diamagnetic but sensitive to light and oxygen. The tetramethyl complex [N-*n*-Bu$_4$][Ru(N)Me$_4$] is a distorted square-based pyramid with an axial nitrido group. Products resulting from the coordination of Lewis acids or organic electrophiles to the ruthenium nitride are unstable.

Experimental Section

All operations were carried out under nitrogen in either a Vacuum Atmosphere drybox or on a Schlenk line. Toluene, diethyl ether, hexane, benzene, and tetrahydrofuran were distilled from sodium/benzophenone under nitrogen. Methylene chloride and acetonitrile were distilled from CaH$_2$. Sodium trimethylsiloxide was prepared by hydrolysis of chlorotrimethylsilane.[5] AlMe$_3$ and Mg(CH$_2$SiMe$_3$)Cl were purchased from Aldrich and used without further purification. Mg(CH$_2$SiMe$_3$)$_2$ was prepared from Mg(CH$_2$SiMe$_3$)Cl and dioxane.[43] [RuNCl$_4$][NBu$_4$] and [RuNCl$_4$][PPh$_4$] were prepared according to Griffith.[44] Tetramethylethylenediamine was distilled under nitrogen and stored over molecular sieves. Methyl isocyanide was synthesized by the dehydration of *N*-methylformamide.[45] IR spectra were obtained on an IBM IR/32 spectrometer. NMR spectra were obtained on a Varian XL200, General Electric QE300, or General Electric GN500 FT NMR spectrometer. Chemical shifts are reported in parts per million downfield from TMS for ^{1}H and ^{13}C NMR spectra.

Preparation of [NBu$_4$][RuN(OSiMe$_3$)$_4$]. A solution of NaOSiMe$_3$ (450 mg, 4.0 mmol) in 50 mL of toluene was cooled to −30 °C and [NBu$_4$][RuNCl$_4$] (500 mg, 1.0 mmol) was added over a period of 10 min. The mixture was warmed to room temperature and stirred for 1 h. The solvent was evaporated, and the residue was extracted with 20 mL of ether. After filtration through Celite, 20 mL of hexane was added to the solution and it was cooled to −30 °C. The product [NBu$_4$][RuN(OSiMe$_3$)$_4$] (yield 590 mg, 80%) was obtained after recrystallization. IR (KBr pellet): Ru–N, 1090 cm^{-1} (s). ^{1}H NMR (C$_6$D$_6$, 300 MHz, 300 K): δ 2.45, m, 2 H, NCH_2; δ 1.1, m, 4 H, NCH$_2$CH_2CH_2CH$_3$; δ 0.83, t, 3 H, NCH$_2$CH$_2$CH$_2$CH_3; δ 0.60, s, 9 H, RuOSi(CH_3)$_3$. Anal. Calcd: C, 47.08; H, 10.16; N, 3.92. Found: C, 46.98; H, 10.14; N, 3.96.

Preparation of [PPh$_4$][RuN(OSiMe$_3$)$_4$]. To a solution of NaOSiMe$_3$ (455 mg, 4.1 mmol) in 40 mL of toluene was added [PPh$_4$][RuNCl$_4$] (600 mg, 1 mmol). The mixture was stirred for 1 h. The solution was filtered through Celite, and the solvent was removed under vacuum. The residue was dissolved in ether/hexane (25 mL/10 mL), filtered, and cooled to −30 °C. Purple crystals of the product [PPh$_4$][RuN(OSiMe$_3$)$_4$] (yield 710 mg, 87%) were obtained. IR (KBr pellet): Ru–N, 1060 cm^{-1} (s). ^{1}H NMR (CD$_2$Cl$_2$, MHz, 295 K): δ 8.0–7.5, m, 5 H, PPh; δ 0.032, s, 9 H, RuOSi(CH_3)$_3$. Anal. Calcd: C, 52.63; H, 7.11; N, 1.79. Found: C, 53.3; H, 6.93; N, 1.73.

Preparation of [NBu$_4$][RuN(CH$_2$SiMe$_3$)$_4$]. In a 100-mL flask, 160 mg (0.56 mmol) of Mg(CH$_2$SiMe$_3$)$_2$·Et$_2$O was dissolved in 15 mL of ether and 15 mL of hexane, and a solution of [NBu$_4$][RuN(OSiMe$_3$)$_4$] (100 mg, 0.14 mmol) in 10 mL of ether/hexane was added dropwise with stirring. After being stirred for 2–3 min, the solution was concentrated and cooled to −30 °C. Yellow crystals of [NBu$_4$][RuN(CH$_2$SiMe$_3$)$_4$] were obtained (74 mg, yield 75%). IR (KBr pellet): Ru–N, 1078 cm^{-1} (s). ^{1}H NMR (C$_6$D$_6$, 500 MHz, 295 K): δ 2.23, m, 2 H, NCH_2; δ 1.03, m, 2 H, NCH$_2$CH_2CH$_2$CH$_2$CH$_3$; δ 0.88, m, 2 H, NCH$_2$CH$_2$CH_2CH$_3$; δ 0.77, t, 3 H, NCH$_2$CH$_2$CH$_2$CH_3; δ 1.27, s, 2 H, RuCH_2Si(CH$_3$)$_3$; δ 0.54, s, 9 H, RuCH$_2$Si(CH_3)$_3$. Anal. Calcd: C, 54.41; H, 11.41; N, 3.97. Found: C, 54.04; H, 11.22; N, 3.92. MS: *m/e* 464, RuN(CH$_2$SiMe$_3$)$_4$.

Preparation of [PPh$_4$][RuN(CH$_2$SiMe$_3$)$_4$]. In a 100-mL flask, 380 mg (1.39 mmol) of Mg(CH$_2$SiMe$_3$)$_2$·Et$_2$O was dissolved in 10 mL of ether and 15 mL of hexane, and a solution of [PPh$_4$][RuN(OSiMe$_3$)$_4$] (280 mg, 0.346 mmol) in 10 mL of ether was added dropwise with stirring. After being stirred for 10 min, the solution was concentrated, hexane was added, and it was cooled to −30 °C. A yellow crystalline material was obtained. After recrystallization from methylene chloride/hexane, yellow crystals of [PPh$_4$][RuN(CH$_2$SiMe$_3$)$_4$] were obtained (180 mg, yield 65%). IR (KBr pellet): Ru–N, 1075 cm^{-1} (s). ^{1}H NMR (C$_6$D$_6$, 300 MHz, 295 K): δ 7.5–6.7, m, 5 H, PPh; δ 1.28, s, 2 H, RuCH_2Si(CH$_3$)$_3$; δ 0.50, s 9 H, RuCH$_2$Si(CH_3)$_3$. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 50.3 MHz, 293 K): δ 12.77, RuCH$_2$Si(CH$_3$)$_3$; δ 4.16, RuCH$_2$Si(CH$_3$)$_3$. Anal. Calcd: C, 59.42; H, 8.20; N, 1.62. Found: C, 59.85; H, 8.23; N, 1.75.

Preparation of [NBu$_4$][RuNMe$_4$]. A solution of TMEDA (3 mL) and AlMe$_3$ (0.84 mmol) in 40 mL of toluene was added dropwise to a toluene solution of [NBu$_4$][RuN(OSiMe$_3$)$_4$] (150 mg, 0.21 mmol). The reaction was stirred at room temperature

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for 1 h as the color of the solution changed from purple to yellow. Hexane (60 mL) was added, and the solution was cooled to −30 °C. Yellow-brown crystals formed. The product [NBu$_4$][RuNMe$_4$] was recrystallized from a small amount of CH$_2$Cl$_2$. Yellow crystals were obtained (68 mg, yield 78%). IR (KBr pellet): Ru–N, 1073 cm^{-1} (s). ^{1}H NMR (C$_6$D$_6$, 200 MHz, 295 K): δ 2.70, m, 2 H, NCH_2; δ 1.18, m, 4 H, NCH$_2$CH_2CH_2CH$_2$CH$_3$; δ 0.91, t, 3 H, NCH$_2$CH$_2$CH$_2$CH_3; δ 1.43, s, 3 H, RuMe. Anal. Calcd: C, 57.56; H, 11.25; N, 6.36. Found: C, 57.51; H, 11.58; N, 6.71.

Preparation of [PPh$_4$][RuNMe$_4$]. A toluene solution of [PPh$_4$][RuN(OSiMe$_3$)$_4$] (340 mg, 0.42 mmol) was added dropwise to a solution of TMEDA (5 mL, 33 mmol) and AlMe$_3$ (0.9 mmol) in 40 mL of toluene. After 5 min, the solution became very cloudy due to the formation of [PPh$_4$][RuNMe$_4$] which is insoluble in toluene. Hexane (30 mL) was added, and the solution was cooled to −30 °C. The precipitate was collected by filtration and washed with 10 mL of toluene. The product [PPh$_4$][RuNMe$_4$] was recrystallized from CH$_2$Cl$_2$/toluene. Yellow crystals were obtained (200 mg, yield 93%). IR (KBr pellet): Ru–N, 1077 cm^{-1} (s). ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, 295 K): δ 8.0–7.5, m, 5 H, PPh; δ 0.52, s, 3 H, RuMe. Anal. Calcd: C, 65.09; H, 6.49; N, 2.68. Found: C, 65.37; H, 6.23; N, 2.73.

Reaction of [NBu$_4$][RuN(CH$_2$SiMe$_3$)$_4$] with HCl(g). (A) Reaction with Excess HCl. To a 100-mL flask equipped with a side arm was added [NBu$_4$][RuN(CH$_2$SiMe$_3$)$_4$] (30 mg, 0.043 mmol), 20 mL of ether, and a magnetic stir bar. The flask was sealed with a septum under N$_2$ and cooled to −78 °C. Excess HCl(g) (8 mL, 0.35 mmol) was injected through the septum. The reaction mixture was warmed to room temperature and stirred for 40–60 min. Solvent was removed under vacuum, and the residue was washed with hexane. Orange crystals of *cis*-[NBu$_4$][RuN(CH$_2$SiMe$_3$)$_2$Cl$_2$] (18 mg, yield 71%) were obtained from toluene/hexane solution at −30 °C. In a separate experiment, HCl(g) was bubbled through the toluene solution of [NBu$_4$][RuN(CH$_2$SiMe$_3$)$_4$] at room temperature for 1 h. The reaction mixture was worked up as above, and orange crystals of *cis*-[NBu$_4$][RuN(CH$_2$SiMe$_3$)$_2$Cl$_2$] were obtained (21 mg, 79% yield). IR (KBr pellet): Ru–N, 1091 cm^{-1} (s). ^{1}H NMR (C$_6$D$_6$, 200 MHz, 295 K): δ 2.87, m, 2 H, HCH_2; δ 2.79, d (J = 9 Hz), 1 H, RuCH^aH^b; δ 2.62, d (J = 9 Hz), 1 H, RuCH^aH^b; δ 1.3, m, 4 H, NCH$_2$CH_2CH_2CH$_2$CH$_3$; δ 0.9, t, 3 H, NCH$_2$CH$_2$CH$_2$CH_3; δ 0.49, s, 9 H, RuCH$_2$Si(CH_3)$_3$. Anal. Calcd: C, 47.88; H, 9.58; N, 4.59. Found: C, 47.81; H, 9.63; N, 4.65.

(B) Reaction with 2 Equiv of HCl. To a 100-mL flask equipped with a side arm was added [NBu$_4$][RuN(CH$_2$SiMe$_3$)$_4$] (30 mg, 0.043 mmol), 20 mL of ether, and a magnetic stir bar. The flask was sealed with a septum under N$_2$ and cooled to −78 °C. HCl(g) (2 mL, 0.085 mmol) was injected through the septum while the solution was vigorously stirred. After 20 min at −78 °C, the reaction mixture was slowly warmed to room temperature and was stirred for 1 h. Solvent was removed under vacuum, and the residue was dissolved in toluene/hexane solution and cooled to −30 °C. Orange crystals of [NBu$_4$][RuN(CH$_2$SiMe$_3$)$_3$Cl] were obtained. ^{1}H NMR (C$_6$D$_6$, 200 MHz, 293 K): δ 2.75, m, 8 H, NCH_2; δ 1.98, s, 2 H, RuCH_2; δ 1.86, d (J = 8 Hz), 2 H, RuCH^aH^b; δ 1.78, d (J = 8 Hz), 2 H, RuCH^aH^b; δ 1.12, m, 16 H, NCH$_2$CH_2CH_2CH$_2$CH$_3$; δ 0.9, t, 12 H, NCH$_2$CH$_2$CH$_2$CH_3; δ 0.57, s, 18 H, RuSi(CH_3)$_3$; δ 0.46, s, 9 H, RuSi(CH_3)$_3$.

Reaction of [PPh$_4$][RuNMe$_4$] with HCl(g). (A) Preparation of [PPh$_4$][RuNMe$_2$Cl$_2$]. A 50-mL flask containing [PPh$_4$][RuNMe$_4$] (100 mg, 0.195 mmol), 35 mL of THF, and a stir bar was sealed with a septum. With vigorous stirring HCl(g) was bubbled through the solution for 5 min. An immediate color change from yellow to orange was observed. Excess HCl was removed under vacuum. The solution was filtered, 20 mL of toluene was added, and the mixture was cooled to −30 °C. Orange solid [PPh$_4$][RuNMe$_2$Cl$_2$] was collected by filtration (80 mg, 74% yield). IR (KBr pellet): Ru–N, 1099 cm^{-1} (s). ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, 295 K): δ 8.0–7.5, m, 10 H, PPh; δ 1.86, s, 3 H, RuMe. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 50.3 MHz, 293 K): δ 16.45, Ru(CH$_3$). Anal. Calcd: C, 56.56; H, 4.81; N, 2.32. Found: C, 56.22; H, 4.68; N, 2.52.

(B) Preparation of [PPh$_4$][RuNMeCl$_3$]. A 50-mL flask containing [PPh$_4$][RuNMe$_4$] (100 mg, 0.195 mmol), 20 mL of THF, 20 mL of CH$_2$Cl$_2$, and a stir bar was sealed with a septum. With vigorous stirring HCl(g) was bubbled through the solution for 1 h. An immediate color change from yellow to orange was observed. Excess HCl was removed under vacuum. The solution was filtered, 20 mL of toluene was added, and the mixture was cooled to −30 °C. Orange solid [PPh$_4$][RuNMeCl$_3$] was collected by filtration (73 mg, 65% yield). IR (KBr pellet): Ru–N, 1100 cm^{-1} (s). ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, 295 K): δ 8.0–7.5, m, 20 H, PPh; δ 2.71, s, 3 H, RuMe. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 50.3 MHz, 293 K): δ 19.9, Ru(CH$_3$). Anal. Calcd: C, 51.22; H, 4.00; N, 2.32; Cl, 18.11. Found: C, 52.13; H, 4.00; N, 2.43; Cl, 18.50.

(C) Preparation of [PPh$_4$][RuNMe$_3$Cl]. A 100-mL flask containing [PPh$_4$][RuNMe$_4$] (50 mg, 0.0972 mmol) in 40 mL of THF and a stir bar was cooled to −78 °C. To this was added HCl(g) (2.4 mL, 0.099 mmol) by syringe. The reaction mixture was stirred at −78 °C for 30 min. Excess HCl was removed under vacuum, and the flask was warmed to room temperature. The solution was concentrated to 20 mL and filtered, 20 mL of toluene was added, and the solution was cooled to −30 °C. Orange crystals of [PPh$_4$][RuNMe$_3$Cl] were collected and dried under vacuum (38 mg, 73% yield). IR (KBr pellet): Ru–N, 1080 cm^{-1} (s). ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, 295 K): δ 8.0–7.5, m, 20 H, PPh; δ 1.21, s, 3 H, RuMe^a; δ 0.97, s, 6 H, RuMe^b. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 50.3 MHz, 293 K): δ 6.67, RuMe^a; δ 10.98, RuMe^b. Anal. Calcd: C, 60.61; H, 5.55; N, 2.59. Found: C, 60.62; H, 5.43; N, 2.62.

Reaction of [PPh$_4$][RuNMe$_4$] with TMEDA·2HCl. To a solution of [PPh$_4$][RuNMe$_4$] (100 mg, 0.194 mmol) in 40 mL of THF was added TMEDA·2HCl (50 mg, mmol). After being stirred for 4 min at room temperature, the mixture was filtered. Solvent was removed under vacuum, and the residue was crystallized from a 1:1 mixture of THF/toluene at −30 °C. Orange crystals of [PPh$_4$][RuNMe$_3$Cl] were collected and dried under vacuum (80 mg, 77% yield).

Reaction of [PPh$_4$][RuNMe$_4$] with ClCH$_2$CO$_2$H. (A) Reaction with 1 Equiv. To a solution of [PPh$_4$][RuNMe$_4$] (33 mg, 0.064 mmol) in 5 mL of CH$_2$Cl$_2$ was added a solution of ClCH$_2$CO$_2$H (6 mg, 0.0635 mmol) in 30 mL of THF. After being stirred for 2 h at room temperature, the mixture was filtered. Solvent was removed under vacuum, and the residue was crystallized from a 1:1 mixture of THF/toluene at −30 °C. Orange crystals of [PPh$_4$][RuNMe$_3$Cl] were collected and dried under vacuum (25 mg, 73% yield).

(B) Reaction with 2 Equiv. To a solution of [PPh$_4$][RuNMe$_4$] (30 mg, 0.058 mmol) in 5 mL of CH$_2$Cl$_2$ was added a solution of ClCH$_2$CO$_2$H (11 mg, 0.117 mmol) in 30 mL of THF. After being stirred for 2 h at room temperature, the mixture was filtered. Solvent was removed under vacuum, and the residue was crystallized from a 1:1 mixture of THF/toluene at −30 °C. Orange crystals of [PPh$_4$][RuNMe$_2$Cl$_2$] were collected and dried under vacuum (23 mg, 71% yield).

Reaction of [PPh$_4$][RuNMe$_4$] with BrCH$_2$CO$_2$H. (A) Reaction with 1 Equiv. To a solution of [PPh$_4$][RuNMe$_4$] (40 mg, 0.078 mmol) in 5 mL of CH$_2$Cl$_2$ was added a solution of BrCH$_2$CO$_2$H (10 mg, 0.072 mmol) in 30 mL of THF. After being stirred for 5 min at room temperature, the mixture was filtered. Solvent was removed under vacuum, and the residue was crystallized from a mixture of THF/toluene at −30 °C. Orange-brown crystals of [PPh$_4$][RuNMe$_3$Br] were collected and dried under vacuum (34 mg, 75% yield). IR (KBr pellet): Ru–N, 1080 cm^{-1} (s). ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, 295 K): δ 8.0–7.5, m, 20 H, PPh; δ 1.26, s, 3 H, RuMe^a; δ 1.08, s, 6 H, RuMe^b. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 50.3 MHz, 293 K): δ 8.88, RuMe^a; δ 9.85, RuMe^b. Anal. Calcd: C, 56.18; H, 5.00; N, 2.32. Found: C, 55.97; H, 5.01; N, 2.41.

(B) Reaction with 2 Equiv. To a solution of [PPh$_4$][RuNMe$_4$] (40 mg, 0.078 mmol) in 5 mL of CH$_2$Cl$_2$ was added a solution of BrCH$_2$CO$_2$H (22 mg, 0.288 mmol) in 30 mL of THF. After being stirred for 30 min at room temperature, the mixture was filtered. Solvent was removed under vacuum, and the residue was crystallized from a mixture of THF/toluene at −30 °C. Orange-brown crystals of [PPh$_4$][RuNMe$_2$Br$_2$] were collected and dried under vacuum (32 mg, 64% yield). IR (KBr pellet): Ru–N, 1097 cm^{-1} (s). ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, 295 K): δ 8.0–7.5, m, 10 H, PPh; δ 2.0, s, 3 H, RuMe. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 50.3 MHz, 293 K): δ 12.97, Ru(CH$_3$). Anal. Calcd: C, 48.82; H, 4.04; N, 1.88. Found: C, 48.45; H, 4.03; N, 2.17.

Reaction of [PPh$_4$][RuNMe$_4$] with Au(PPh$_3$)Cl. A solution of [PPh$_4$][RuNMe$_4$] (30 mg, 0.058 mmol) and Au(PPh$_3$)Cl (30 mg, 0.061 mmol) in 30 mL of THF was stirred for 2 h. The solvent

Table III. Crystal and Data Statistics

chemical formula	$RuN_2C_{20}H_{48}$
space group	$P2_1/n$
a, Å	9.359 (3)
b, Å	18.368 (4)
c, Å	15.193 (5)
β, deg	105.31 (2)
V, Å^3	2519 (1)
Z	4
d(calcd), g/cm^3	1.101
temp, °C	27
radiatn	Mo/Kα (graphite/monochromator)p Kα, 0.709 30, Kα_2, 0.713 59, Kα, 710 73 Å
abs coeff (μ), cm^{-1}	6.129
transmissn factors, range	0.850–0.816 (numerical correction)
scan rate, deg/min	variable from 6 to 20
$2\theta{:}\theta$ scan range, deg 2θ	Mo Kα_1 − 0.8 to Kα_2 + 0.9
bkgd ratio	0.25
2θ limit, deg (octants)	46 ($\pm h$, $+ k$, $+ l$)
reflctns (unique, consistency)	3934 (3515, $R_i = 0.013$)
reflctns with $l > 2.58\sigma(l)$	1480

was removed under vacuum, and the resulting solid was washed with 10 mL of toluene. Hexane was added to the toluene solution, and it was cooled. White crystals of $Au(PPh_3)Me$ (20 mg, 72%) were obtained. The orange solid (toluene insoluble) was crystallized from THF/toluene at −30 °C giving $[PPh_4][RuNMe_3Cl]$ (26 mg, 83%). ^1H NMR (C_6D_6, 300 MHz, 295 K) for $Au(PPh_3)Me$: δ 7.5–6.8, m, 15 H, PPh; δ 1.48, d (J_{P-H} = 7.8 Hz), 3 H, AuMe. Anal. Calcd: C, 47.83; H, 3.69. Found: C, 48.08; H, 3.79.

Preparation of $Ru(NSiMe_3)(CH_2SiMe_3)_4$. A solution of $[NBu_4][RuN(CH_2SiMe_3)_4]$ (30 mg, 0.0425 mmol) in 20 mL of diethyl ether was cooled to −30 °C, and $CF_3SO_3SiMe_3$ (8.3 μL, 0.0425 mmol) was added. Soon after the addition of $CF_3SO_3SiMe_3$, the solution became cloudy due to the precipitation of $CF_3SO_3NBu_4$ and the color of the solution changed from yellow to orange. The solution was filtered through Celite, and the solvent was removed under vacuum. The residue was dissolved in hexane, filtered, and concentrated. Oily orange crystals of $Ru(NSiMe_3)(CH_2SiMe_3)_4$ were obtained after the concentrated solution was cooled (21 mg, 92% yield). Elemental analysis could not be obtained due to the extreme instability of the compound to air and water. IR (KBr pellet): 1578 (br), 1252 (s), 1057 (m), 843 (s), 756 cm^{-1} (w). ^1H NMR (C_6D_6, 200 MHz, 293 K): δ 2.65, s, 8 H, $RuCH_2Si(CH_3)_3$; δ 0.282, s, 36 H, $RuCH_2Si(CH_3)_3$; δ 0.095, 9 H, $RuNSi(CH_3)_3$. $^{13}C\{^1H\}$ NMR (C_6D_6, 50.3 MHz, 295 K): δ 39.99, $RuCH_2Si(CH_3)_3$; δ 1.93, $RuNSi(CH_3)_3$; δ 2.95, $RuCH_2Si(CH_3)_3$.

Structure Determination of [N-*n*-Bu_4][Ru(N)Me_4]. A transparent, yellow crystal, grown from methylene chloride/toluene solution, of dimensions 0.3 × 0.3 × 0.4mm was used. The diffractometer, a Syntex $P2_1$ automated four-circle diffractometer, was sealed to omit room light while data were collected. The crystal was monoclinic, space group $P2_1/n$, and there were four molecules per unit cell.[46] The structure was solved by Patterson methods, SHELX-86, unweighted difference Fourier synthesis, and full-matrix least squares.[47,48] The correct ruthenium atom position was automatically selected from a vector map, and subsequent partial structure expansion gave positions for the nitrogen atoms, the anion carbon atoms, and 12 of the cation carbon atoms. Contributions from hydrogen atoms were not included in calculated structure factors. Least-squares difference Fourier calculations revealed two sets of disordered positions for the four *n*-butyl groups of the cation. In the final cycle of least squares, anisotropic thermal coefficients were refined for the ruthenium, nitrogen, and anion carbon atoms, and independent isotropic thermal coefficients were refined for the cation carbon atoms. To circumvent high correlation between disordered cation carbon atom positions, a damping factor was applied to the least-squares calculated shifts. The highest peaks in the final difference Fourier map were in the vicinity of the ruthenium atom. A final analysis of variance between observed and calculated structure factors showed a slight dependence of sin θ. Disorder of the *n*-butyl groups of the cation and excessive thermal motion led to the high estimated standard deviations. The final agreement factors were $R = 0.063$ and $R_w = 0.075$.

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Registry No. $[NBu_4][RuN(OSiMe_3)_4]$, 102649-19-4; $[PPh_4][RuN(OSiMe_3)_4]$, 112817-61-5; $[NBu_4][RuN(CH_2SiMe_3)_4]$, 102649-21-8; $[PPh_4][RuN(CH_2SiMe_3)_4]$, 112817-62-6; $[NBu_4][RuNMe_4]$, 102649-23-0; $[PPh_4][RuNMe_4]$, 112817-63-7; *cis*-$[NBu_4][RuN(CH_2SiMe_3)_2Cl_2]$, 112817-65-9; $[NBu_4][RuN(CH_2SiMe_3)_3Cl]$, 112817-67-1; *cis*-$[PPh_4][RuNMe_2Cl_2]$, 112817-69-3; $[PPh_4][RuNMeCl_3]$, 112817-71-7; $[PPh_4][RuNMe_3Cl]$, 112817-73-9; $[PPh_4][RuNMe_3Br]$, 112817-75-1; *cis*-$[PPh_4][RuNMe_2Br_2]$, 112817-77-3; $Ru[NSiMe_3)(CH_2SiMe_3)_4$, 112817-78-4; $[NBu_4][RuNCl_4]$, 42862-74-8; $[PPh_4][RuNCl_4]$, 112817-79-5; $Mg(CH_2SiMe_3)_2{\cdot}Et_2O$, 63817-04-9; $AlMe_3$, 75-24-1; $Au(PPh_3)Cl$, 14243-64-2; $NaOSiMe_3$, 18027-10-6; $ClCH_2CO_2H$, 79-11-8; $BrCH_2CO_2H$, 79-08-3; $CF_3SO_3SiMe_3$, 27607-77-8.

Supplementary Material Available: Tables of thermal parameters, distances and angles, and least-squares and planes, cation figures (15 pages); a listing of observed and calculated structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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(46) Final cell dimensions were obtained by a least-squares fit to the automatically centered settings for 15 reflections.

(47) Sheldrick, G. M., Kruger, C., Goddard, R., Eds. In *Crystallographic Computing 3*; Oxford University Press: Oxford, 1985; pp 175–189.

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