# **ORGANOMETALLICS**

# Synthesis, Structure, and Reactivity of Trigonal Bipyramidal Ruthenium(IV) Trialkyl Complexes

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Supporting Information

**ABSTRACT:** The alkylation of  $[Ru(NPPh_3)(PPh_3)_2Cl_3]$  with  $Me_3SiCH_2MgCl$  afforded the  $Ru^{IV}$  trialkyl complex  $[Ru-(CH_2SiMe_3)_3(PPh_3)Cl]$  (1), which exhibits a trigonal bipyramidal geometry with the three alkyl groups occupying the equatorial plane. DFT calculations reveal that 1 possesses a



 $(d_{xz}d_{yz})^4$  singlet ground state, consistent with the observed diamagnetism of the complex. The electronic spectrum of 1 displayed two absorptions at 455 and 505 nm, which, on the basis of TDDFT calculations, are attributed to metal-centered d–d transitions with a significant contribution from the alkyl ligands. Chloride abstraction of 1 with Ag(OTf) (OTf<sup>-</sup> = triflate) provided the triflate complex [Ru(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(PPh<sub>3</sub>)(OTf)] (2) that proved to be a useful starting material for Ru<sup>IV</sup> trialkyl complexes. Substitution of 2 with NaX afforded [Ru(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(PPh<sub>3</sub>)(X)] (X = N<sub>3</sub><sup>-</sup> (3) or SCN<sup>-</sup> (4)). Treatment of 2 with excess sodium 2,3,5,6-tetrafluorophenoxide (NaOR<sub>f</sub>) in tetrahydrofuran resulted in desilylation of two alkyl groups, and formation of the dimethyl complex [Ru(CH<sub>2</sub>SiMe<sub>3</sub>)Me<sub>2</sub>(PPh<sub>3</sub>)(OR<sub>f</sub>)] (5). 2 underwent reductive elimination of the C–C bond with 1,10-phenanthroline (phen) in CH<sub>2</sub>Cl<sub>2</sub> to give *cis*-[Ru(phen)<sub>2</sub>(PPh<sub>3</sub>)Cl](OTf) (6). The crystal structures of 1, 2, 4, and 5 have been determined.

# INTRODUCTION

High-valent late transition metal alkyl complexes are of interest due to their involvement in metal-catalyzed C-H activation and functionalization.<sup>1</sup> Compared with the earlier transition metal counterparts, the chemistry of polyalkyl complexes of late transition metals, particularly Ru,<sup>2-8</sup> is not well developed. Wilkinson and co-workers pioneered the synthesis of homoleptic alkyls of Ru.<sup>2-4</sup> Tetrahedral  $[Ru^{IV}(c-C_6H_{11})_4]^2$ and ethane-like  $[Ru_{2}^{III}(CH_{2}EMe_{3})_{6}]$  (E = C, Si)<sup>3</sup> containing Ru≡Ru triple bonds have been obtained by alkylation of  $[Ru_2(OAc)_4Cl]$  (OAc<sup>-</sup> = acetate) with Grignard reagents. Anionic permethyl complexes such as  $[Li(tmed)]_3[Ru^{III}Me_6]$ and  $[\text{Li}(\text{tmed})]_2[(\text{nbd})\text{Ru}^{II}\text{Me}_4]$  (tmed = N,N,N',N'-tetramethylethylenediamine; nbd = norbornadiene) have also been synthesized.<sup>4,8</sup> These Ru homoleptic alkyls are very air sensitive, and their reaction chemistry has not been studied in detail. It is well-known that multiply bonded ligands can stabilize high-valent organometallic complexes. Thus, stable Ru<sup>VI</sup> nitrido (e.g.,  $[Ru(N)R_4]^-$  where R = Me or CH<sub>2</sub>SiMe<sub>3</sub><sup>9</sup>) and oxo (e.g.,  $[Ru(O)(CH_2SiMe_3)_4]^{-})^{10}$  alkyl complexes have been synthesized.

In the above-mentioned Ru polyalkyl complexes, the metal centers are in either pseudo tetrahedral or octahedral/square pyramidal coordination environments. To our knowledge, Ru alkyl complexes in trigonal bipyramidal geometry have not been isolated to date, although related  $Ru^{IV}$  tetrakis(thiolate) complexes such as  $[Ru(SR)_4(MeCN)]$  (R = 2,3,4,6-tetrame-

thylphenyl)<sup>11</sup> are well documented. In this paper, we describe the synthesis and structures of the Ru<sup>IV</sup> trialkyl complexes [Ru<sup>IV</sup>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(PPh<sub>3</sub>)X] that exhibit trigonal bipyramidal g e o m e t r y. The triflate (OTf<sup>-</sup>) c o m plex [Ru<sup>IV</sup>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(PPh<sub>3</sub>)(OTf)] (2) was found to display interesting reactivity. The desilylation of 2 with sodium 2,3,5,6-tetrafluorophenoxide and ligand-induced reductive elimination of 2 will be reported.

### EXPERIMENTAL SECTION

**General Considerations.** All manipulations were carried out under nitrogen by standard Schlenk techniques. Solvents were purified by standard procedures and distilled prior to use. NMR spectra were recorded on a Bruker AV 400 MHz NMR spectrometer operating at 400, 376.5, and 162.0 MHz for <sup>1</sup>H, <sup>19</sup>F and <sup>31</sup>P, respectively. Chemical shifts ( $\delta$ , ppm) were reported with reference to SiMe<sub>4</sub> (<sup>1</sup>H and <sup>13</sup>C), CF<sub>3</sub>C<sub>6</sub>H<sub>5</sub> (<sup>19</sup>F), and H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P). Infrared spectra (KBr) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer and ESI mass spectra on an Applied Biosystem QSTAR mass spectrometer and quadrupole-time-of-flight tandem mass spectrometer (QTOF Premier, Waters Micromass, Manchester, UK). GC–MS was carried out with an Aglient 5957C gas chromatograph–mass spectrometer. UV–visible spectra were recorded on a Perkin-Elmer LAMBAD 900 UV/vis/NIR spectrophotometer. Elemental analyses were performed by Medac Ltd., Surrey, U.K.

Received: March 5, 2013 Published: August 14, 2013 The compound  $[Ru(NPPh_3)(PPh_3)_2Cl_3]^{12}$  was prepared according to a literature method. Sodium 2,3,5,6-tetrafluorophenoxide  $(NaOR_f)$  was prepared by reaction of 2,3,5,6-tetrafluorophenol with 1 equiv of sodium hydride (60% in mineral oil) in tetrahydrofuran (THF) at room temperature.

**Syntheses.** [*Ru*(*CH*<sub>2</sub>*SiMe*<sub>3</sub>)<sub>3</sub>(*PPh*<sub>3</sub>)*Cl*] (1). To a brown suspension of [Ru(NPPh<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub>] (100 mg, 0.094 mmol) in THF (5 mL) was added Me<sub>3</sub>SiCH<sub>2</sub>MgCl (0.67 mL of a 0.7 M solution in THF, 0.469 mmol) at -78 °C. The resulting deep red mixture was stirred overnight at room temperature, and the volatiles were removed in vacuo. The residue was extracted with hexane. Concentration and cooling at -4 °C afforded air stable red crystals which were suitable for X-ray analysis. Yield: 44.7 mg (72%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.30 (s, 27H, SiMe<sub>3</sub>), 3.20 (d, *J* = 3.2 Hz, 6H, CH<sub>2</sub>SiMe<sub>3</sub>), 6.95 (m, 6H, PPh<sub>3</sub>), 7.02 (m, 3H, PPh<sub>3</sub>), 7.26–7.35 (m, 6H, PPh<sub>3</sub>). <sup>31</sup>P {<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>): δ 54.83 (s). MS (ESI): *m/z* 625.3 (M<sup>+</sup> – Cl). UV/vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub>/nm (ε<sub>max</sub>/M<sup>-1</sup> cm<sup>-1</sup>): 455 (730), 505 (692). Anal. Calcd for C<sub>30</sub>H<sub>48</sub>PRuSi<sub>3</sub>Cl-0.5Et<sub>2</sub>O: C, 52.43; H, 7.29. Found: C, 52.44; H, 7.02.

 $[Ru(CH_2SiMe_3)_3(PPh_3)OTf]$  (2) (OTf<sup>-</sup> = Triflate). To a solution of 1 (50.0 mg, 0.072 mmol) in THF (5 mL) was added AgOTf (18.5 mg, 0.072 mmol) at room temperature. The resulting red mixture was stirred at room temperature overnight and filtered. The volatiles were removed in vacuo, and the residue was washed with hexane and then extracted with Et<sub>2</sub>O. Concentration and cooling at -4 °C afforded red crystals which were suitable for X-ray analysis. Yield: 48.5 mg (87%). <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ ):  $\delta$  0.19 (s, 27H, SiMe<sub>3</sub>), 3.59 (d, J = 4.0Hz, 6H, CH<sub>2</sub>SiMe<sub>3</sub>), 6.87-6.92 (m, 6H, PPh<sub>3</sub>), 6.95-7.02 (m, 6H, PPh<sub>3</sub>), 7.19–7.23 (m, 3H, PPh<sub>3</sub>). <sup>31</sup>P {<sup>1</sup>H} NMR (162 MHz,  $C_6D_6$ ):  $\delta$ 58.03 (s). <sup>19</sup>F NMR (376 MHz,  $C_6D_6$ ):  $\delta$  -75.41 (s). <sup>1</sup>H NMR (400 MHz, THF- $d_8$ ):  $\delta$  -0.06 (s, 9 H, SiMe<sub>3</sub>), 3.37 (d, J = 3.6 Hz, 2H, CH<sub>2</sub>SiMe<sub>3</sub>), 7.22–7.27 (m, 6H, PPh<sub>3</sub>), 7.43–7.47 (m, 6H, PPh<sub>3</sub>), 7.52–7.56 (m, 3H, PPh<sub>3</sub>). <sup>31</sup>P {<sup>1</sup>H} NMR (162 MHz, THF- $d_3$ ):  $\delta$ 56.32 (s). <sup>19</sup>F NMR (376 MHz, THF- $d_8$ ):  $\delta$  -75.68 (s). MS (ESI): m/z 624.3 (M<sup>+</sup> – OTf). UV/vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}/nm$  ( $\varepsilon_{max}/M^{-1}$  cm<sup>-1</sup>): 455 (1034), 505 (980). Anal. Calcd for C<sub>31</sub>H<sub>48</sub>F<sub>3</sub>O<sub>3</sub>PRuSSi<sub>3</sub>: C, 48.10; H, 6.25. Found: C, 48.20; H, 6.30.

[*Ru*(*CH*<sub>2</sub>*SiMe*<sub>3</sub>)<sub>3</sub>(*PPh*<sub>3</sub>)(*N*<sub>3</sub>)] (3). To a solution of 2 (50.0 mg, 0.065 mmol) in THF (5 mL) was added NaN<sub>3</sub> (4.2 mg, 0.065 mmol) at room temperature. The resulting deep purple mixture was stirred at room temperature overnight and filtered. The volatiles were removed in vacuo, and the residue was extracted with hexane. Concentration and cooling at -4 °C gave purple crystals. Yield: 37.3 mg (86%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.24 (s, 27H, SiMe<sub>3</sub>), 3.07 (d, *J* = 7.2 Hz, 6H, CH<sub>2</sub>SiMe<sub>3</sub>), 6.92–6.96 (m, 6H, PPh<sub>3</sub>), 6.99 (m, 3H, PPh<sub>3</sub>), 7.25 (m, 6H, PPh<sub>3</sub>). <sup>31</sup>P {<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  52.37 (s). IR (KBr, cm<sup>-1</sup>): 2020 [ $\nu$ (N<sub>3</sub>)]. Anal. Calcd for C<sub>30</sub>H<sub>48</sub>N<sub>3</sub>PRuSi<sub>3</sub>: C, 54.02; H, 7.25; N, 6.30. Found: C, 53.65; H, 7.21; N, 6.36.

[*Ru*(*CH*<sub>2</sub>*SiMe*<sub>3</sub>)<sub>3</sub>(*PPh*<sub>3</sub>)(*SCN*)] (4). This compound was prepared similarly as for 3 using NaSCN (6.3 mg, 0.065 mmol) in place of NaN<sub>3</sub>. Yield: 40.0 mg (90%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.25 (s, 27H, SiMe<sub>3</sub>), 3.06 (d, *J* = 7.6 Hz, 6H, *CH*<sub>2</sub>SiMe<sub>3</sub>), 6.91 (m, 6H, PPh<sub>3</sub>), 6.98 (m, 3H, PPh<sub>3</sub>), 7.17 (m, 6H, PPh<sub>3</sub>). <sup>31</sup>P {<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  54.20 (s). Anal. Calcd for C<sub>31</sub>H<sub>48</sub>NPRuSSi<sub>3</sub>: C, 54.51; H, 7.08; N, 2.05. Found: C, 54.35; H, 6.74; N, 2.08.

[*Ru*(*CH*<sub>2</sub>*SiMe*<sub>3</sub>)(*Me*)<sub>2</sub>(*PPh*<sub>3</sub>)(*OR*<sub>*p*</sub>] (*R*<sub>f</sub> = *C*<sub>6</sub>*F*<sub>4</sub>*H*) (*5*). To a solution of **2** (50.0 mg, 0.065 mmol) in THF (5 mL) was added NaOR<sub>f</sub> (153 mg, 0.81 mmol) at room temperature. The resulting deep red solution was stirred at room temperature overnight. The volatiles were removed in vacuo, and the residue was extracted with hexane. The red extracts were concentrated and cooled at  $-4 \,^{\circ}$ C to give a red solid, which was further recrystallized from hexane at  $-4 \,^{\circ}$ C four times to give red single crystals. Yield: 18.9 mg (45%). <sup>1</sup>H NMR (400 MHz, *C*<sub>6</sub>*D*<sub>6</sub>):  $\delta$  0.06 (s, 9H, Si*Me*<sub>3</sub>), 2.41 (d, *J* = 4.4 Hz, 6H, *Me*), 3.43 (d, *J* = 6.8 Hz, 2H, *CH*<sub>2</sub>SiMe<sub>3</sub>), 6.11 – 6.17 (m, 1H, OC<sub>6</sub>F<sub>4</sub>H), 6.92 (m, 6H, PPh<sub>3</sub>), 6.98 (m, 3H, PPh<sub>3</sub>), 7.07–7.12 (m, 6H, PPh<sub>3</sub>). <sup>31</sup>P {<sup>1</sup>H} NMR (162 MHz, *C*<sub>6</sub>*D*<sub>6</sub>):  $\delta$  59.15 (s). <sup>19</sup>F NMR (376 MHz, *C*<sub>6</sub>*D*<sub>6</sub>):  $\delta$  –160.94 (m), –144.12 (m). <sup>1</sup>H NMR (400 MHz, THF-*d*<sub>8</sub>):  $\delta$  –0.083 (s, 9H, Si*Me*<sub>3</sub>), 2.32 (d, *J* = 4.8 Hz, 6H, *Me*), 3.33 (d, *J* = 6.4 Hz, 2 H, *CH*<sub>2</sub>SiMe<sub>3</sub>), 6.25–6.34 (m, 1H, OC<sub>6</sub>F<sub>4</sub>H), 7.20–7.24 (m, 6H, PPh<sub>3</sub>),

7.39–7.43 (m, 6H, PPh<sub>3</sub>), 7.44–7.45 (m, 3H, PPh<sub>3</sub>). <sup>31</sup>P {<sup>1</sup>H} NMR (162 MHz, THF- $d_8$ ):  $\delta$  58.73 (s). <sup>19</sup>F NMR (376 MHz, THF- $d_8$ ):  $\delta$  –162.22 (m), –146.10 (m). Anal. Calcd for C<sub>30</sub>H<sub>33</sub>F<sub>4</sub>OPRuSi: C, 55.80; H, 5.15. Found: C, 55.50; H, 5.06.

*cis-[Ru(phen)<sub>2</sub>(PPh<sub>3</sub>)Cl][OTf]* (6). To a solution of 2 (50.0 mg, 0.065 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added 1,10-phenanthroline (23.4 mg, 0.13 mmol) at room temperature. The resulting orange mixture was stirred at room temperature overnight. The volatiles were removed in vacuo, and the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane gave orange crystals which were suitable for X-ray analysis. Yield: 26.5 mg (45%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.02 (m, 9H, PPh<sub>3</sub>), 7.31 (m, 6H, PPh<sub>3</sub>), 7.46 (s, 1H, phen), 7.56 (s, 1H, phen), 7.79 (s, 1H, phen), 7.86 (d, *J* = 4.2 Hz, 1H, phen), 8.09 (d, *J* = 4.6 Hz, 1H, phen), 8.15 (d, *J* = 4.4 Hz, 1H, phen), 8.23 (d, *J* = 4.2 Hz, 1H, phen), 8.54 (d, *J* = 3.8 Hz, 1H, phen). <sup>31</sup>P {<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  42.31 (s). <sup>19</sup>F NMR (376 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -78.24 (s). MS (ES1): *m*/*z* 758 (M<sup>+</sup> - OTf). Anal. Calcd for C<sub>43</sub>H<sub>31</sub>ClF<sub>3</sub>N<sub>4</sub>O<sub>3</sub>PRuS: C, 56.86; H, 3.44 ; N, 6.17. Found: C, 56.88; H, 3.50; N, 6.27.

Computational Details. All calculations were performed with the Gaussian 09 program package.<sup>13</sup> The 6-31+G\* basis set<sup>14</sup> was employed for all atoms except Ru, which was described by the Stuttgart small-core relativistic effective-core potential with its accompanying basis set.<sup>15</sup> The M06L<sup>16</sup> functional developed by Truhlar and Zhao was employed for all DFT calculations. A full geometry optimization using B3LYP<sup>17</sup> functional has also been performed on 1 for comparison in which M06L showed a better agreement, especially on the Ru-carbon bond length, with experimental data of 1 (Table S2, Supporting Information). Therefore, only the M06L-calculated results would be discussed here. Full geometry optimizations without symmetry constraints were carried out in the gas phase for both the singlet and triplet ground states of 1 followed by frequency calculations to ensure that the optimized structures were true energy minima. In addition, full geometry optimizations and time-dependent density functional theory (TD-DFT) calculations have been performed on 1 with  $C_3$  symmetry imposed. The use of  $C_3$  symmetry can provide a simple model to interpret the nature of molecular orbitals, and it is justified because 1 possesses pseudo  $C_3$  symmetry in solution on the NMR time scale. The integral equation formalism model (IEFPCM)<sup>18</sup> has also been applied to account for solvent effects upon the electronic transition (solvent = dichloromethane).

**X-ray Crystallography.** Intensity data were collected on a Bruker APEX 1000 CCD diffractometer using graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å). The collected frames were processed with the software SAINT. Structures were solved by the direct methods and refined by full-matrix least-squares on  $F^2$  using the SHELXTL software package.<sup>19,20</sup> Atomic positions of non-hydrogen atoms were refined with anisotropic parameters and with suitable restraints. However, disordered atoms were refined isotropically. Hydrogen atoms were generated geometrically and allowed to ride on their respective parent carbon atoms before the final cycle of least-squares refinement.

## RESULTS AND DISCUSSION

[Ru<sup>IV</sup>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(PPh<sub>3</sub>)Cl] (1). Treatment of the Ru<sup>IV</sup> phosphoraminato complex [Ru<sup>IV</sup>(NPPh<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub>] with excess Me<sub>3</sub>SiCH<sub>2</sub>MgCl in tetrahydrofuran, followed by recrystallization from hexane, afforded red crystals characterized as the trialkyl complex [Ru<sup>IV</sup>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(PPh<sub>3</sub>)Cl] (1). Complex **1** is remarkably stable and can be purified by column chromatography in air without decomposition. It may be noted that dimeric Ru<sup>III</sup> trimethylsilylmethyl complex [Ru<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>6</sub>] containing a Ru–Ru triple bond has been obtained from the alkylation of [Ru<sub>2</sub>(OAc)<sub>4</sub>Cl] with Me<sub>3</sub>SiCH<sub>2</sub>MgCl.<sup>3</sup> Attempts to prepare analogous trialkyl complexes by treatment of [Ru<sup>IV</sup>(NPPh<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub>] with other alkylating agents, including PhMgCl, PhCH<sub>2</sub>MgCl,

Me<sub>3</sub>CCH<sub>2</sub>Li, and MeLi, failed; these reactions only yielded hexane-insoluble dark materials that did not crystallize. The <sup>1</sup>H NMR spectrum of 1 in  $C_6D_6$  showed sharp peaks, indicative of the diamagnetic nature of the complex. A single set of resonances  $[\delta 0.30 (s), 3.20 (d)]$  was found for the alkyl groups in 1, consistent with its solid-state structure (vide infra). The methylene resonance of 1 occurred at a more upfield position than those for reported Ru trimethylsilylmethyl complexes, such as  $[Ru_2(CH_2SiMe_3)_6]$  ( $\delta$  1.51 ppm)<sup>3</sup> and mer-[Ru- $(dtbpy)(NO)(CH_2SiMe_3)_3]$  ( $\delta$  1.24, 1.59 ppm; dtbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridyl).<sup>7</sup> The <sup>31</sup>P {<sup>1</sup>H} NMR spectrum of 1 showed a singlet at  $\delta$  54.83 ppm. The UV-visible spectrum of 1 in  $CH_2Cl_2$  displayed d-d absorption bands (vide infra) with maxima at ca. 455 ( $\varepsilon = 730 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 505 nm ( $\varepsilon = 692$  $M^{-1}$  cm<sup>-1</sup>). The cyclic voltammogram of complex 1 in CH<sub>2</sub>Cl<sub>2</sub> exhibited an irreversible wave at ca. 0.79 V versus ferroceniumferrocene, which is tentatively assigned as the  $Ru^{IV}-Ru^{V}$ oxidation.

The solid-state structure of complex 1 is shown in Figure 1. The geometry around Ru is pseudo trigonal bipyramidal with



Figure 1. Molecular structure of complex 1. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å): Ru1–C1 2.026(4), Ru1–C2 2.037(4), Ru1–C3 2.026(4), Ru1–Cl1 2.4109(13), Ru1–P1 2.2692(14).

the three alkyl groups occupying the equatorial positions. Although organometallic  $\operatorname{Ru}^{\text{IV}}$  complexes are well-known, to our knowledge, complex 1 is the first example of a trigonal bipyramidal  $\operatorname{Ru}^{\text{IV}}$  alkyl complex. It should be noted that similar trigonal bipyramidal structures have been found for isoelectronic  $[\operatorname{Ru}^{\text{IV}}(\text{SR})_4(\text{MeCN})]$  (R = 2,4,5,6-tetramethylphenyl or 2,4,6-triisopropylphenyl)<sup>11</sup> and  $[\operatorname{Re}^{\text{III}}\text{Ph}_3(\text{PEt}_2\text{Ph})_2]$ .<sup>21</sup> In  $[\operatorname{Ru}^{\text{IV}}(\text{SR})_4(\text{MeCN})]$ , the R substituents of the three equatorial thiolate ligands adopt a "two-up one-down" arrangement, as a consequence of  $d\pi(\text{Ru}) - p\pi(\text{S})$  interactions.<sup>11</sup> Metal-ligand  $\pi$  interactions have also been proposed for  $[\operatorname{Re}^{\text{III}}\text{Ph}_3(\text{PEt}_2\text{Ph})_2]$ , in which the three equatorial phenyl ligands are approximately coplanar.<sup>21</sup> By contrast, trigonal bipyramidal 1 contains pure  $\sigma$  ligands at the equatorial positions. The three trimethylsilyl groups in 1 point toward the chloride apparently because of

steric effects. The Ru–C distances [2.026(4)-2.037(4) Å] are similar to those in  $[\text{Ru}_2(\text{CH}_2\text{SiMe}_3)_6]$  [av 2.031(5) Å].<sup>3</sup> The Ru–Cl bond is rather long (2.4109(13) Å cf. 2.3643(8) Å in  $[\text{Ru}(\text{SR})_3(\text{MeCN})\text{Cl}]$  where R = 2,6-dimethylphenyl<sup>22</sup>) presumably due to steric effects and/or trans influence of PPh<sub>3</sub>.

**DFT and TD-DFT Calculations.** DFT calculations were performed in order to gain insight into the ground state electronic structure of 1. Figure 2 shows the frontier orbitals of



**Figure 2.** Frontier orbitals of **1** imposed with  $C_3$  symmetry (isovalue of 0.05).

1. DFT calculations reveal that the ground state of complex 1 is a singlet,  $(d_{yz}, d_{xz})$ ,<sup>4</sup> consistent with the observed diamagnetism of the complex. The optimized triplet ground state is 26.8 kcal mol<sup>-1</sup> higher than the singlet state. The HOMO of 1 is a nonbonding Ru  $d_{xz}$  orbital whereas the LUMO is an antibonding orbital formed from the Ru  $d_{x^2-y^2}$  and alkyl ligands. Time-dependent DFT (TD-DFT) calculations were also performed to elucidate the nature of electronic absorption bands associated with 1 at 455 and 505 nm (Figure 3 insert). Calculated excitation energies, oscillator strengths, and absorption spectrum constructed by convolution of these calculated transitions with Gaussian functions are depicted in Figure 3. Details of the composition of the molecular orbitals



**Figure 3.** Calculated absorption spectrum for **1** from TD-DFT (M06L functional)/PCM calculations. Excitation energies and oscillator strengths are shown by the blue vertical lines; spectrum (in black) is convoluted with Gaussian function having full width half-maximum of 0.2 eV. Inset: UV/vis spectrum of **1** in CH<sub>2</sub>Cl<sub>2</sub> at 25 °C.

involved in the lowest-energy electronic transition of 1 are summarized in Table S3 of the Supporting Information. The profiles of the convoluted absorption spectrum resemble those observed in the experimental data. The lowest energy absorption bands at around 500 nm for 1 originate from three vertical transitions, which explain the splitting of lowest-energy absorption bands for 1. These transitions are attributed to the mixing of HOMO-1  $\rightarrow$  LUMO (Ru(d<sub>yz</sub>)  $\rightarrow$  Ru(d<sub>x<sup>2</sup>-y<sup>2</sup></sub>)-C<sub>alkyl</sub>( $\sigma$ \*)), HOMO-1  $\rightarrow$  LUMO+1 (Ru(d<sub>yz</sub>)  $\rightarrow$  Ru(d<sub>x<sup>2</sup>-y<sup>2</sup></sub>)-C<sub>alkyl</sub>( $\sigma$ \*)), and HOMO  $\rightarrow$  LUMO+1 (Ru(d<sub>xz</sub>)  $\rightarrow$  Ru(d<sub>x<sup>2</sup>-y<sup>2</sup></sub>)-C<sub>alkyl</sub>( $\sigma$ \*)) transitions. Therefore, the lowest-transition absorption bands for 1 are best described as metal-centered transitions with a significant contribution from the alkyl ligands.

**Chloride Substitution of 1.** Treatment of 1 with [Ag(OTf)] ( $OTf^{-} = triflate$ ) afforded  $[Ru^{IV}(CH_2SiMe_3)_3(PPh_3)(OTf)]$  (2), which can serve as a good starting material for  $Ru^{IV}$  trialkyl complexes. The triflate ligand in 2 is labile and can be easily replaced with other anionic ligands. The reactivity of 2 is summarized in Scheme 1.





"Reagents and conditions: (i) AgOTf, THF; (ii) NaX, THF; (iii) 10 equiv of NaOR<sub>f</sub>, THF; (iv) 2 equiv of phen,  $CH_2Cl_2$ .

Reaction of 2 with NaX yielded  $[Ru^{IV}(CH_2SiMe_3)_3(PPh_3)-(X)]$   $[X^- = N_3^- (3), NCS^- (4)]$ . The <sup>1</sup>H NMR spectra of complexes 2–4 are similar to that of 1, each showing a singlet and a doublet due to the methyl and methylene protons, respectively. Complexes 2 and 4 have been characterized by X-ray diffraction, and their structures are shown in Figures 4 and 5, respectively. Like 1, both 2 and 4 exhibit trigonal bipyramidal geometry with the alkyl groups at the equatorial positions. The Ru–C and Ru–P distances in 2 [av 2.034 and 2.2402(10) Å] and 4 [av 2.017 and 2.2763(13) Å] are similar to those in 1. The thiocyanate ligand in 4 is N-bound and essentially linear [Ru–N–C and N–C–S bond angles are 175.3° and 179.1(6)°, respectively].

**Desilylation of** [**Ru**(**CH**<sub>2</sub>**SiMe**<sub>3</sub>)<sub>3</sub>(**PPh**<sub>3</sub>)(**OTf**)]. Reactions of 2 with alkoxides and aryloxides such as KO-*t*-Bu and NaOPh yielded dark orange materials that did not crystallize. On the other hand, treatment of 2 with excess (~10-fold) sodium 2,3,5,6-tetrafluorophenoxide (NaOR<sub>f</sub>) in THF gave a red oily material, which, after recrystallization from hexane, yielded a dark red crystalline solid characterized as the dimethyl complex  $[Ru^{IV}(CH_2SiMe_3)Me_2(PPh_3)(OR_f)]$  (5). 5 is stable in the solid state but is somewhat air sensitive in solution. The crude product of 5 was found to contain an impurity that exhibited a



Figure 4. Molecular structure of complex 2. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å): Ru1–C1 2.046(5), Ru1–C2 2.021(5), Ru1–C3 2.034(5), Ru1–O1 2.207(4), Ru1–P1 2.2402(10).



**Figure 5.** Molecular structure of complex 4. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angles (deg): Ru1–C1 2.001(6), Ru1–C2 2.022(5), Ru1–C3 2.029(5), Ru1–N1 2.082(4), Ru1–P1 2.2763(13); Ru1–N1–C13 175.3, N1–C13–S1 179.1(6).

<sup>31</sup>P resonance at  $\delta$  60.42 ppm in THF and a doublet at  $\delta$  2.43 ppm assignable to methyl protons (vide infra) in the <sup>1</sup>H NMR spectrum. This impurity, possibly a trimethyl complex (vide infra), could be removed by repeated (at least four times) recrystallization of the crude product from hexane. The <sup>31</sup>P {<sup>1</sup>H} NMR spectrum of a purified sample of **5** showed a singlet

at  $\delta$  58.73 ppm only. In the <sup>1</sup>H NMR spectrum of **5**, the methyl protons appeared as a doublet at  $\delta$  2.32 ppm, which is more upfield than that for the methylene protons of the trimethylsilylmethyl ligand ( $\delta$  3.43 ppm). Attempts to is olate the mono- or trimethyl complex [Ru<sup>IV</sup>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3-x</sub>Me<sub>x</sub>(PPh<sub>3</sub>)(OR<sub>f</sub>)] (x = 1 or 3) by reacting **2** with 1 equiv or a large excess of NaOR<sub>f</sub> failed, although NMR spectroscopy and ESI MS indicated that these complexes should be present in the reaction mixture (vide infra).

Figure 6 shows the molecular structure of 5. The trigonal bipyramidal geometry is retained after the desilylation of the



**Figure 6.** Molecular structure of complex **5**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angle (deg): Ru1–C41 2.021(2), Ru1–C42 2.022(2), Ru1–C7 2.0128(19), Ru1–P1 2.2511(5), Ru1–O1 2.0954(14); Ru1–O1–C1 127.26(13).

alkyl ligands in 2. The Ru–C distances [2.021(2) and 2.022(2) Å] for the two methyls are similar to that for the trimethylsilylmethyl ligand [2.0128(19) Å], which compares well with those in 1. The rather big Ru–O–C angle [127.26(13)°] in 5 is suggestive of  $d\pi(Ru)-p\pi(O)$  interaction for the phenoxide ligand.

The reaction of **2** with NaOR<sub>f</sub> has been monitored by NMR spectroscopy and ESI mass spectrometry (see Supporting Information). Upon addition of excess (10-fold) NaOR<sub>f</sub> to **2** in THF, two singlets at  $\delta$  52.33 and 57.04 ppm along with the signal of **5** at  $\delta$  58.73 ppm were observed in the <sup>31</sup>P {<sup>1</sup>H} NMR spectrum. As the reaction proceeded, the intensity of the signal at  $\delta$  52.33 decreased, whereas that for  $\delta$  57.04 ppm and **5** increased. Later on, the peak at  $\delta$  57.04 ppm also dropped as **5** became the predominant species in the mixture. After 17 h, only the signal of **5** along with a small peak at  $\delta$  60.42 ppm was found in the <sup>31</sup>P NMR spectrum. Therefore, it seems reasonable to assume that the complex with  $\delta$  = 52.33 ppm was converted to **5** via an intermediate with  $\delta$  = 57.04 ppm. At the beginning of the reaction, the high-resolution ESI mass

spectrum of the mixture displayed three major peaks at m/z625.1417, 553.1468, and 481.1049, which can be assigned to  $[Ru(CH_2SiMe_3)_3(PPh_3)]^+$  (calcd m/z 625.1876), [Ru- $(CH_2SiMe_3)_2Me(PPh_3)^{\dagger}$  (calcd m/z 553.1457), and [Ru- $(CH_2SiMe_2)Me_2(PPh_2)^{\dagger}$  (calcd m/z 481.1061), respectively. As the reaction progressed, the intensity of the first two peaks dropped, while that for the third one increased. After 17 h, the peak at m/z 481.1061 was predominant. In addition, a minor peak at m/z 409.0641 assignable to  $[RuMe_3(PPh_3)]^+$  was detected. On the basis of the above results, we tentatively assign the resonances at  $\delta$  52.33 and 57.04 ppm in <sup>31</sup>P NMR spectrum as [Ru(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(PPh<sub>3</sub>)X] and [Ru(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>Me(PPh<sub>3</sub>)-X], respectively, where  $X^-$  is possibly  $R_fO^-$ . The minor product with  $\delta = 60.42$  ppm is attributed to the trimethyl species,  $[RuMe_3(PPh_3)X]$ . Therefore, it is reasonable to assume that the desilylation of 2 into 5 involves a monomethyl intermediate, presumably  $[Ru(CH_2SiMe_3)_2Me(PPh_3)(OR_f)]$ .

Although the hydrolysis of trimethylsilylmethyl acyl complexes to acetyl complexes is well precedented, 23,24 to our knowledge, the desilylation of the  $\sigma$ -bonded trimethylsilylmethyl ligand under mild conditions has not been reported. Previously, Hoffman and co-workers reported that the reaction of  $[Re(O){C(O)CH_2SiMe_3}(CH_2SiMe_3)_2(PMe_3)]$  with bases such as sodium acetate and excess water gave the acetyl complex  $[Re(O){C(O)Me}(CH_2SiMe_3)_2(PMe_3)]$  via hydrolysis of the C-Si bond of the acyl group. It was proposed that the C-Si bond activation results from the attack of the Si atom by the base or water hydrogen-bonded to the base, followed by protonation of a resonance-stabilized enolate ion, [Re(O){C- $(O)CH_2$   $(CH_2SiMe_3)_2$   $(PMe_3)^{-23}$  In this work, the silvlether  $Me_3SiOR_f$  has been detected by GLC in the reaction of 2 with NaOR<sub>ft</sub> indicating that the desilylation involves the nucleophilic attack of the Si atom by the phenoxide.

A plausible mechanism for the formation of complex 5 is shown in Scheme 2. Substitution of 2 with NaOR<sub>f</sub> gives  $[Ru(CH_2SiMe_3)_3(PPh_3)(OR_f)]$ . Nucleophilic attack (possibly Ru-assisted) of the Si atom of an alkyl group by R<sub>f</sub>O<sup>-</sup>, followed by elimination of R<sub>f</sub>OSiMe<sub>3</sub>, affords a methylene intermediate, A. This transient methylene species is apparently very reactive and has not been observed by NMR spectroscopy. Protonation of A by moisture in the solvent or the phenol<sup>25</sup> provides a

#### Scheme 2. Plausible Mechanism for Formation of 5



#### Organometallics

monomethyl complex, **B**. Similarly, the desilylation of the second alkyl group in **B**, followed by protonation, yields the dimethyl complex **5**. It is not clear why the desilylation of the third alkyl in **2** to give the trimethyl complex is more difficult than that of the first two alkyls.

Reductive Elimination of [Ru(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(PPh<sub>3</sub>)(OTf)]. No reaction was found when 2 was reacted with dihydrogen or ethylene in CDCl<sub>3</sub>. Treatment of 2 with nitric oxide resulted in a dark intractable material whereas that with carbon monoxide yielded a yellow solid, possibly a Ru carbonyl complex/cluster, which showed C-O bands at 1994 and 2054 cm<sup>-1</sup> in the IR spectrum. We have not been able to crystallize this carbonyl complex/cluster for structure determination. Treatment of 2 with pyridine gave a green material that did not crystallize. On the other hand, reaction of 2 with 1,10-phenanthroline (phen) in CH<sub>2</sub>Cl<sub>2</sub> afforded the Ru<sup>II</sup> complex *cis*-[Ru<sup>II</sup>(phen)<sub>2</sub>(PPh<sub>3</sub>)-Cl][OTf] (6).<sup>26</sup> Me<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>SiMe<sub>3</sub> was detected by GC-MS in the reaction mixture, indicating that 6 was formed by ligand-induced reductive coupling of the alkyl groups in 2. It seems likely that the reductive elimination of the C-C bond from 2 affords a monoalkyl intermediate, possibly [Ru- $(phen)_2(PPh_3)(CH_2SiMe_3)]^+$ , which reacts with  $CH_2Cl_2$  to yield chloride product 6. Under the same conditions, no reaction was found between 1 and phen, suggesting that dissociation of the labile triflate ligand in 2 to provide a vacant coordination site is essential for the reductive elimination of the Ru<sup>IV</sup> trialkyl complex. 6 also underwent reductive elimination with phen in THF. Unfortunately, we have not been able to crystallize the product for characterization.

# CONCLUSIONS

In summary, we have synthesized and structurally characterized the Ru<sup>IV</sup> trialkyl complexes [Ru(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(PPh<sub>3</sub>)X] (X<sup>-</sup> = monoanionic ligand) that exhibit unique trigonal bipyramidal geometry. [Ru(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(PPh<sub>3</sub>)(OTf)] (**2**) containing a labile triflate ligand was found to display interesting organometallic chemistry. For example, treatment of **2** with NaOR<sub>f</sub> led to desilylation of the alkyl groups and formation of a dimethyl complex, whereas that with phen resulted in reductive elimination of the C–C bond. The investigation of the reaction chemistry and catalytic activity of 5-coordinated, 14-electron Ru<sup>IV</sup> trialkyl complexes is underway.

# ASSOCIATED CONTENT

#### **Supporting Information**

Crystallographic data and cif files for complexes 1, 2, 4, and 5, computational details for 1, and ESI mass and <sup>31</sup>P  $\{^{1}H\}$  NMR spectra for the reaction of 2 with NaOR<sub>f</sub>. This material is available free of charge via the Internet at http://pubs.acs.org.

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# Notes

The authors declare no competing financial interest.

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(25) As suggested by one reviewer, an alternative proton source is  $Na[H(OR_f)_2]$  ( $R_f = C_6F_4H$ ) where one phenol hydrogen bonds to the phenoxide oxygen, which is an intermediate product from the deprotonation of  $R_fOH$ .

(26) The identity of 6 has been established by an X-ray diffraction study. However, the crystal structure of 6 has not refined satisfactorily due to poor quality of the crystal.