Synthesis and Reactivity of the Cationic Ruthenium Germylene Complexes, [Cp*(PiPr₃)RuH₂(=GeRR')]⁺

Supporting Information

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General Considerations. All experiments were carried out under a nitrogen atmosphere using standard Schlenk techniques or an inert atmosphere (N_2) glovebox. Olefin impurities were removed from pentane by treatment with concentrated H_2SO_4 , 0.5 N KMnO₄ in 3 M H_2SO_4 , and NaHCO₃. Pentane was then dried over MgSO₄ and stored over activated 4 Å molecular sieves, and dried over alumina. Thiophene impurities were removed from benzene and toluene by treatment with H_2SO_4 and saturated NaHCO₃. Toluene and pentane were dried over Na and distilled under N₂. Benzene-d₆ was dried by vacuum distillation from Na/K alloy. Bromobenzene-d₅ was refluxed over CaH₂ for 20 h and then distilled under nitrogen. Fluorobenzene was dried over P₂O₅, degassed, and distilled under N₂. Cp*(PiPr₃)RuCl,¹ Cp*(PiPr₃)RuOTf,² Mes₂GeH₂,³ and TripGeH₃⁴ were prepared according to literature methods. All other chemicals were purchased from commercial sources and used without further purification.

NMR spectra were recorded using Bruker AVB 400, AV-500 or AV-600 spectrometers equipped with a 5 mm BB probe. Spectra were recorded at room temperature and referenced to the residual protonated solvent for ¹H. ³¹P{¹H} NMR spectra were referenced relative to 85% H₃PO₄ external standard ($\delta = 0$). ¹³C{¹H} NMR spectra were calibrated internally with the resonance for the solvent relative to tetramethylsilane. For ¹³C{¹H} NMR spectra, resonances obscured by the solvent signal are omitted. Elemental analyses were performed by the College of Chemistry Microanalytical Laboratory at the University of California, Berkeley or Atlantic Microlab, Inc.

 $[Cp*(PiPr_3)Ru(H)_2(GeMes_2)][OTf]$ (1). A solution of Mes₂GeH₂ (0.050 g, 0.16 mmol) in 1 mL of C₆H₅F was added to a solution of Cp*(PiPr₃)RuOTf (0.050 g, 0.092 mmol) in 1 mL of

C₆H₅F. The reaction solution was stirred for 1 h. To the resulting C₆H₅F solution was added 10 mL of cold pentane, and the solution was placed in the -30 °C freezer. After 1 h, the yellow oil was isolated by carefully decanting off the solution. The oil was washed with pentane and dried to give a yellow solid (0.037 g, 48% yield). ¹H NMR (C₆D₅Br, 600 MHz): δ 6.89 (2H, s, Ar*H*), 6.82 (2H, s, Ar*H*), 2.45 (6H, s, ArC*H*₃), 2.38 (6H, s, ArC*H*₃), 2.33 (3H, s, ArC*H*₃), 2.28 (3H, s, Ar*CH*₃), 1.79 (15H, s, C₅*Me*₅), 1.74 (3H, septet, *J* = 7.0 Hz, PC*H*(CH₃)₂), 1.02 (18H, dd, *J* = 7.0 Hz, 14.5 Hz, PCH(CH₃)₂), -8.82 (2H, d, ²*J*_{PH} = 26.2 Hz, Ru*H*). ¹³C{¹H} NMR (C₆D₅Br, 150.9 MHz): 139.1 (Ar*C*), 138.9 (Ar*C*), 128.8 (Ar*C*), 115.5 (Ar*C*), 115.4 (Ar*C*), 100.1 (*C*₅Me₅), 29.2 (br, PCH(CH₃)₂), 23.2 (MesCH₃), 22.8 (MesCH₃), 21.4 (MesCH₃), 21.3 (MesCH₃), 19.1 (PCH(CH₃)₂), 19.3 (PCH(CH₃)₂), 11.4 (C₅*Me*₅). ³¹P{¹H} NMR (C₆D₅Br, 163.0 MHz): δ 77.8. ¹⁹F{¹H} NMR (C₆D₆, 376.5 MHz): δ -76.3. Anal. Calcd for C₃₈H₆₀F₃GeO₃PRuS: C, 53.16; H, 7.04. Found: C, 53.41; H, 7.15.

Cp*(PiPr₃)Ru(H)(=GeMes₂) (2). A solution of DMAP (0.004 g, 0.035 mmol) in 1 mL of C₆H₅F was added to a solution of $[Cp*(PiPr_3)Ru(H)_2(GeMes_2)][OTf]$ (0.030 g, 0.035 mmol) in 1 mL of C₆H₅F. The reaction solution was stirred for 1 h to give a magenta solution, and then the solution was stripped to dryness. The dark pink oil was dissolved in pentane, filtered through Celite, and dried to give a pink solid. Recrystallization from pentane at -30 °C gave **2** as dark pink crystals (0.023 g, 92% yield). ¹H NMR (C₆D₆, 600 MHz): δ 6.92 (1H, s, Ar*H*), 6.83 (1H, s, Ar*H*), 6.66 (1H, s, Ar*H*), 6.57 (1H, s, Ar*H*), 3.17 (3H, s, ArCH₃), 2.99 (3H, s, ArCH₃), 2.28 (3H, s, ArCH₃), 2.18 (3H, s, ArCH₃), 2.14 (3H, s, ArCH₃), 2.11 (3H, s, ArCH₃), 1.86 (3H, septet, *J* = 7.2 Hz, PCH(CH₃)₂), 1.79 (15H, s, C₅Me₅), 1.08 (18H, m, PCH(CH₃)₂), -12.47 (1H, d, ²J_{PH} = 36.0 Hz, Ru*H*). ¹³C{¹H} NMR (C₆D₆, 150.9 MHz): 156.5 (ArC), 154.7 (ArC), 141.8 (ArC),

141.5 (Ar*C*), 138.7 (Ar*C*), 138.0 (Ar*C*), 136.7 (Ar*C*), 136.3 (Ar*C*), 128.7 (Ar*C*), 128.4 (Ar*C*), 128.3 (Ar*C*), 128.1 (Ar*C*), 92.0 (C_5 Me₅), 29.3 (br, PCH(CH₃)₂), 23.2 (MesCH₃), 23.1 (MesCH₃), 22.9 (MesCH₃), 22.6 (MesCH₃), 20.8 (MesCH₃), 20.7 (MesCH₃), 20.1 (PCH(CH₃)₂), 19.6 (PCH(CH₃)₂), 11.8 (C_5Me_5). ³¹P{¹H} NMR (C_6D_6 , 163.0 MHz): δ 84.5. Anal. Calcd for $C_{37}H_{59}$ GePRu•1/2(C_6H_5F): C, 63.50; H, 8.19. Found: C, 63.48; H, 8.23.

Cp*(PiPr₃)Ru(H)₂(**GeHTripCl**) (**3**). A solution of TripGeH₃ (0.070 g, 0.25 mmol) in 1 mL of diethyl ether was added to a solution of Cp*(PiPr₃)RuCl (0.10 g, 0.23 mmol) in 2 mL of diethyl ether. The reaction solution was stirred for 20 min before being filtered through a Celite plug. The resulting solution was striped to dryness to give a dark orange solid (0.095 g, 79% yield). ¹H NMR (C₆D₆, 600 MHz): δ 7.20 (2H, s, Ar*H*), 7.17 (1H, s, Ge*H*), 2.67 (2H, septet, *J* = 6.5 Hz, TripC*H*), 2.11 (1H, septet, *J* = 6.9 Hz, TripC*H*), 1.84 (15H, s, C₅*Me*₅), 1.77 (3H, septet, *J* = 7.1 Hz, PC*H*(CH₃)₂), 1.59 (6H, d, *J* = 6.5 Hz, TripC*H*₃), 1.48 (6H, d, *J* = 6.5 Hz, TripC*H*₃), 1.32 (6H, dd, *J* = 2.1 Hz, 6.9 Hz, TripC*H*₃), 1.06 (9H, dd, *J* = 7.1 Hz, *J*_{PH} = 13.4 Hz, PCH(C*H*₃)₂), 0.88 (9H, dd, *J* = 7.1 Hz, *J*_{PH} = 13.3 Hz, PCH(C*H*₃)₂), -9.89 (1H, d, ²*J*_{PH} = 30.0 Hz, Ru*H*), -10.62 (1H, d, ²*J*_{PH} = 28.2 Hz, Ru*H*). ¹³C{¹H} NMR (C₆D₆, 150.9 MHz): 153.4 (ArC), 148.5 (ArC), 141.5 (ArC), 121.0 (ArC), 95.6 (*C*₅Me₅), 34.3 (TripCH₃), 19.1 (PCH(CH₃)₂), 18.7 (PCH(CH₃)₂), 25.1 (TripCH₃), 24.0 (TripCH₃), 22.6 (TripCH₃), 19.1 (PCH(CH₃)₂), 18.7 (PCH(CH₃)₂), 10.6 (C₅Me₅). ³¹P{¹H} NMR (C₆D₆, 163.0 MHz): δ 82.9. Anal. Calcd for C₃₄H₆₂ClPRuGe: C, 57.44; H, 8.79. Found: C, 57.60; H, 8.46.

 $[Cp*(PiPr_3)Ru(H)_2(=GeHTrip)][B(C_6F_5)_4]$ (4). A solution of Li(Et₂O)₂B(C₆F₅)₄ (0.058 g, 0.07 mmol) in 0.5 mL of C₆H₅F was added to a solution of 3 (0.050 g, 0.07 mmol) in 1 mL of C₆H₅F. After stirring for 5 min at room temperature, 15 mL of pentane was added to the bright orange

solution and the reaction vessel was placed in the -30 °C freezer. After 1 h, an orange oil settled to the bottom of the vial. The solution was carefully decanted and the resulting orange oil was dried under vacuum for 1 h to afford **4** as an orange solid in 60% yield (0.057 g). ¹H NMR (C₆D₆, 600 MHz): δ 12.73 (1H, s, Ge*H*), 7.22 (2H, s, Ar*H*), 3.43 (1H, br s, TripC*H*), 3.03 (1H, br s, TripC*H*), 2.47 (1H, br s, TripC*H*), 1.97 (3H, br s, PC*H*(CH₃)₂), 1.78 (15H, s, C₅*Me*₅), 1.62 (6H, br s, TripC*H*₃), 1.59 (6H, d, *J* = 6.5 Hz, TripC*H*₃), 1.48 (6H, d, *J* = 6.5 Hz, TripC*H*₃), 1.07 (18H, dd, *J* = 6.0 Hz, *J*_{PH} = 14.4 Hz, PCH(C*H*₃)₂), -10.09 (2H, d, ²*J*_{PH} = 24.1 Hz, Ru*H*). ¹³C{¹H} NMR (C₆D₆, 150.9 MHz): 150.7 (ArC), 149.7 (ArC), 148.1 (ArC), 140.9 (ArC), 139.5 (ArC), 137.6 (ArC), 135.9 (ArC), 133.3 (ArC), 100.0 (*C*₅Me₅), 35.0 (TripCH), 34.8 (TripCH), 31.9 (TripCH), 27.5 (d, *J*_{PC} = 30.2 Hz, PCH(CH₃)₂), 24.5 (TripCH₃), 24.1 (TripCH₃), 23.0 (TripCH₃), 18.9 (PCH(*C*H₃)₂), 10.9 (C₅*Me*₅). ³¹P{¹H} NMR (C₆D₆, 163.0 MHz): δ 77.9. ¹⁹F{¹H} NMR (C₆D₆, 376.5 MHz): δ -132.3, -162.8, -166.6. Anal. Calcd for C₅₈H₆₂BF₂₀GePRu•1/2(C₆H₅F): C, 52.23; H, 4.64. Found: C, 52.21; H, 4.94.

[Cp*(PiPr₃)Ru(H)₂(=GeHexylTrip)][B(C₆F₅)₄] (5). An excess of 1-hexene (*ca.* 0.1 mL) was added to a solution of **4** (0.020 g, 0.015 mmol) in 1 mL of C₆H₃F to give a bright yellow solution. After 5 min, the reaction mixture was dried under vacuum. The resulting oil was washed with 3 aliquots of hexanes (ca. 10 mL) and then dried under vacuum to give a bright yellow solid in 95% yield (0.020 g). ¹H NMR (C₆D₆, 600 MHz): δ 7.20 (2H, s, Ar*H*), 2.99 (1H, septet, J = 6.6 Hz, TripC*H*), 2.20 (2H, br m, TripC*H*), 1.87 (15H, s, C₅Me₅), 1.69 (3H, m, PC*H*(CH₃)₂), 1.49 – 1.30 (29H, ov m, TripC*H*₃ + Hexyl), 1.00 (18H, m, PCH(CH₃)₂), -9.21 (2H, br d, ²*J*_{PH} = 24.9 Hz, Ru*H*). ¹³C{¹H} NMR (C₆D₆, 150.9 MHz): 153.0 (Ar*C*), 145.8 (Ar*C*), 99.3 (*C*₅Me₅), 46.1 (Hexyl), 36.1 (Hexyl), 35.9 (Trip*C*H), 33.5 (Trip*C*H), 32.0 (Hexyl), 28.6 (Hexyl),

26.1 (Hexyl), 24.3 (Hexyl), 23.8 (br, PCH(CH₃)₂), 22.7 (br, TripCH₃), 17.2 (PCH(CH₃)₂), 9.8 (C₅ Me_5). ³¹P{¹H} NMR (C₆D₆, 163.0 MHz): δ 77.8. ¹⁹F{¹H} NMR (C₆D₆, 376.5 MHz): δ - 132.6, -163.2, -166.9. Anal. Calcd for C₆₄H₇₄BF₂₀GePRu: C, 53.43; H, 5.18. Found: C, 53.24; H, 5.00.

 $[Cp^{*}(PiPr_{3})Ru(H)_{2}(=Ge(CH_{2}CH_{2}Ph)Trip)][B(C_{6}F_{5})_{4}]$ (6). By a procedure analogous to that for 5, complex 6 was obtained as a bright yellow solid in 88% yield (0.019 g). ¹H NMR (C_6D_6 , 600 MHz): δ 7.42 (2H, t, J = 7.3 Hz, ArH), 7.35 (1H, t, J = 7.3 Hz, ArH), 7.24 (2H, s, ArH), 7.22 (2H, s, ArH), 3.02 (1H, septet, J = 6.9 Hz, TripCH), 2.93 (2H, m, CH₂), 2.48 (2H, m, CH₂), 2.23 (2H, septet, J = 6.5 Hz, TripCH), 1.87 (15H, s, C₅Me₅), 1.73 (3H, m, PCH(CH₃)₂), 1.47 (6H, d, J = 6.5 Hz, TripCH₃), 1.42 (6H, d, J = 6.9 Hz, TripCH₃), 1.36 (6H, d, J = 6.5 Hz, TripCH₃), 1.01 (18H, dd, J = 7.1, $J_{PH} = 14.6$ Hz, PCH(CH₃)₂), -9.07 (2H, d, ${}^{2}J_{PH} = 25.3$ Hz, RuH). ${}^{13}C{}^{1}H{}$ NMR (C₆D₆, 150.9 MHz): 153.3 (ArC), 149.8 (ArC), 149.6 (ArC), 147.6 (ArC), 146.1 (ArC), 141.2 (ArC), 139.3 (ArC), 137.5 (ArC), 135.5 (ArC), 99.5 (C₅Me₅), 47.7 (CH₂), 37.6 (TripCH), 34.4 (TripCH), 31.0 (CH₂), 29.1 (PCH(CH₃)₂), 25.4 (TripCH₃), 23.8 (TripCH₃), 22.8 (TripCH₃), 18.6 (PCH(*C*H₃)₂), 11.2 (C₅*Me*₅). ${}^{31}P{}^{1}H{}$ NMR (C₆D₆, 163.0 MHz): δ 77.9. ${}^{19}F{}^{1}H{}$ NMR $(C_6D_6, 376.5 \text{ MHz}): \delta -130.4, -160.9, -164.8$. Anal. Calcd for $C_{66}H_{70}BF_{20}GePRu: C, 54.34; H$, 4.84. Found: C, 52.97; H, 4.51. The low value observed for carbon may be due to incomplete combustion of the complex during analysis; alternatively, it may reflect a small amount of impurity that is not observed by NMR spectroscopy.

 $[Cp^{*}(PiPr_{3})Ru(H)_{2}(=Ge(CH_{2}CH_{2}tBu)Trip)][B(C_{6}F_{5})_{4}]$ (7). By a procedure analogous to that for 5, complex 7 was obtained as a bright yellow solid in 95% yield (0.020 g). ¹H NMR (C₆D₆,

600 MHz): δ 7.23 (2H, s, Ar*H*), 3.69 (1H, septet, J = 6.9 Hz, TripC*H*), 3.00 (2H, m, C*H*₂), 2.25 (2H, m, C*H*₂), 2.23 (2H, septet, J = 6.5 Hz, TripC*H*), 1.87 (15H, s, C₅*Me*₅), 1.76 (3H, m, PC*H*(CH₃)₂), 1.39 (18H, m, TripC*H*₃), 1.03 (18H, dd, J = 6.8, $J_{PH} = 14.0$ Hz, PCH(C*H*₃)₂), 0.95 (9H, s, tBu), -9.27 (2H, d, ${}^{2}J_{PH} = 24.4$ Hz, Ru*H*). ${}^{13}C{}^{1}H$ NMR (C₆D₆, 150.9 MHz): 149.8 (ArC), 149.2 (ArC), 147.6 (ArC), 145.3 (ArC), 139.0 (ArC), 137.3 (ArC), 135.6 (ArC), 99.5 (C₅Me₅), 42.3 (CH₂), 37.6 (TripCH), 34.2 (TripCH), 31.4 (CH₂), 30.6 (PCH(CH₃)₂), 28.3 (tBu), 26.2 (TripCH₃), 24.1 (tBu), 23.7 (TripCH₃), 22.8 (TripCH₃), 18.6 (PCH(CH₃)₂), 11.2 (C₅*Me*₅). ${}^{31}P{}^{1}H$ NMR (C₆D₆, 163.0 MHz): δ 77.4. ${}^{19}F{}^{1}H$ NMR (C₆D₆, 376.5 MHz): δ -132.9, -162.9, -166.9. Anal. Calcd for C₆₄H₇₄BF₂₀GePRu: C, 53.43; H, 5.18. Found: C, 53.16; H, 4.96.

[Cp*(PiPr₃)Ru(H)₂(=Ge(CH₂CH₂CH₂Cl)Trip)][B(C₆F₅)₄] (8). By a procedure analogous to that for **5**, complex **8** was obtained as a golden yellow solid in 81% yield (0.017 g). ¹H NMR (C₆D₆, 600 MHz): δ 7.24 (2H, s, Ar*H*), 4.00 (2H, m, C*H*₂), 3.51 (4H, m, C*H*₂), 3.01 (3H, ov m, TripC*H*), 2.04 (15H, s, C₅*Me*₅), 1.97 (3H, m, PC*H*(CH₃)₂), 1.55 (6H, d, *J* = 6.9 Hz, TripC*H*₃), 1.37 (12H, d, *J* = 6.9 Hz, TripC*H*₃), 1.08 (18H, dd, *J* = 7.2, *J*_{PH} = 14.7 Hz, PCH(C*H*₃)₂), -11.03 (2H, br s, Ru*H*). ¹³C{¹H} NMR (C₆D₆, 150.9 MHz): 149.6 (ArC), 148.0 (ArC), 140.3 (ArC), 139.4 (ArC), 137.8 (ArC), 137.6 (ArC), 136.0 (ArC), 133.9 (ArC), 100.6 (*C*₅Me₅), 65.9 (*C*H₂), 45.2 (*C*H₂), 34.8 (TripCH), 34.1 (TripCH), 29.1 (PCH(CH₃)₂), 24.6 (TripCH₃), 23.8 (TripCH₃), 18.6 (PCH(*C*H₃)₂), 11.7 (C₅*Me*₅). ³¹P{¹H} NMR (C₆D₆, 163.0 MHz): δ 74.5. ¹⁹F{¹H} NMR (C₆D₆, 376.5 MHz): δ -132.4, -162.6, -166.6. Anal. Calcd for C₆₁H6₇BClF₂₀GePRu•1/2(C₆H₅F): C, 52.80; H, 4.87. Found: C, 52.69; H, 4.75.

[Cp*(PiPr₃)Ru(H)₂(=Ge(CH=CHtBu)Trip)][B(C₆F₅)₄] (9). By a procedure analogous to that for **5**, complex **9** was obtained as a bright yellow solid in 95% yield (0.020 g). ¹H NMR (C₆D₆, 600 MHz): δ 7.24 (1H, d, J = 17.9 Hz, Ge-CH), 7.22 (2H, s, ArH), 6.42 (1H, d, J = 17.9 Hz, CH=CH), 3.00 (1H, septet, J = 6.5 Hz, TripCH), 2.33 (2H, septet, J = 6.5 Hz, TripCH), 1.87 (15H, s, C₅*Me*₅), 1.78 (3H, m, PCH(CH₃)₂), 1.46 (6H, d, J = 6.5 Hz, TripCH₃), 1.48 (6H, d, J =6.5 Hz, TripCH₃), 1.29 (6H, dd, J = 6.5 Hz, TripCH₃), 1.05 (9H, s, tBu), 1.03 (18H, dd, J = 7.3, $J_{PH} = 14.4$ Hz, PCH(CH₃)₂), -9.31 (2H, d, ² $J_{PH} = 25.1$ Hz, RuH). ¹³C{¹H} NMR (C₆D₆, 150.9 MHz): 164.6 (CH=CHtBu), 153.3 (ArC), 152.6 (ArC), 150.9 (ArC), 149.5 (ArC), 147.6 (ArC), 142.7 (CH=CHtBu), 142.1 (CMe₃), 140.8 (ArC), 139.7 (ArC), 139.2 (ArC), 137.4 (ArC), 135.5 (ArC), 99.2 (C₃Me₅), 37.0 (TripCH), 35.5 (TripCH), 34.4 (TripCH), 28.0 (tBu), 25.5 (TripCH₃), 23.8 (PCH(CH₃)₂), 22.9 (TripCH₃), 22.7 (TripCH₃), 18.6 (PCH(CH₃)₂), 11.2 (C₅*Me*₅). ³¹P{¹H} NMR (C₆D₆, 163.0 MHz): δ 78.1. ¹⁹F{¹H} NMR (C₆D₆, 376.5 MHz): δ -130.8, -161.3, -165.2. Anal. Calcd for C₆₄H₇₂BF₂₀GePRu: C, 53.50; H, 5.05. Found: C, 53.30; H, 5.24.

[Cp*(PiPr₃)Ru(H)₂(=Ge(CMe=CHMe)Trip)][B(C₆F₅)₄] (10). By a procedure analogous to that for **5**, complex **10** was obtained as a bright yellow solid in 86% yield (0.018 g). ¹H NMR (C₆D₆, 600 MHz): δ 7.23 (2H, s, Ar*H*), 6.32 (1H, m, CMe=C*H*Me), 3.70 (1H, septet, J = 6.9 Hz, TripC*H*), 2.99 (2H, septet, J = 6.9 Hz, TripC*H*), 1.98 (3H, s, C*Me*=CHMe), 1.79 (15H, s, C₅*Me*₅), 1.66 (3H, br m, PC*H*(CH₃)₂), 1.38 (18H, m, TripC*H*₃), 1.26 (3H, d, J = 6.4 Hz, CMe=CH*Me*), 1.01 (18H, dd, J = 6.9, 14.3 Hz, PCH(CH₃)₂), -8.70 (2H, br d, ²*J*_{PH} = 21.4 Hz, Ru*H*). ¹³C{¹H} NMR (C₆D₆, 150.9 MHz): 158.9 (CMe=CHMe), 153.5 (Ar*C*), 150.8 (Ar*C*), 149.6 (Ar*C*), 148.0 (Ar*C*), 147.3 (CMe=CHMe), 145.7 (Ar*C*), 140.4 (Ar*C*), 139.5 (Ar*C*), 137.7 (Ar*C*), 135.9 (Ar*C*), 99.3 (*C*₅Me₅), 37.4 (Trip*C*H), 34.6 (Trip*C*H), 34.6 (Trip*C*H), 30.9

(CMe=CHMe), 25.5 (TripCH₃), 24.4 (PCH(CH₃)₂), 24.0 (TripCH₃), 23.2 (TripCH₃), 18.6 (PCH(CH₃)₂), 11.1 (C₅Me₅). ³¹P{¹H} NMR (C₆D₆, 163.0 MHz): δ 78.7. ¹⁹F{¹H} NMR (C₆D₆, 376.5 MHz): δ -132.5, -162.7, -166.6. Anal. Calcd for C₆₂H₆₈BF₂₀GePRu: C, 52.86; H, 4.87. Found: C, 52.80; H, 4.65.

X-ray Crystallography. The single-crystal X-ray analysis of compounds **1**, **2**, and **3** were carried out at the UC Berkeley CHEXRAY crystallographic facility. Measurements were made on a Bruker APEX CCD area detector with graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å). Data was integrated and analyzed for agreement using Bruker APEX2 v. 2009.1. Empirical absorption correction were made using SADABS. Structures were solved by direct methods using the SHELX program package.

Figure S1. Molecular structure of **3** displaying thermal ellipsoids at the 50% probability level. Selected H-atoms are omitted for clarity. Selected bond lengths (Å): Ru(1)-Ge(1) 2.4376(10), Ru(1)-P(1) 2.3180(8), Ge(1)-Cl(1) 2.2883(17).



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