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SUPPORTING INFORMATION FOR

Phenylsilane as a safe, versatile alternative to hydrogen for the synthesis of actinide hydrides

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Experimental

General Considerations

Unless otherwise noted, all reactions and manipulations were performed at ambient temperature in a recirculating Vacuum Atmospheres NEXUS model inert atmosphere (N_2) drybox equipped with a 40CFM Dual Purifier NI-Train. Glassware was dried overnight at 150 °C before use. All NMR spectra were obtained using a Bruker Avance 400 MHz spectrometer. Chemical shifts for ^{1}H NMR spectra are reported in parts per million (ppm) were referenced to proteo solvent impurities ($\delta = 7.16$ for benzene-d_6, 3.58 for tetrahydrofuran-d_8).

Materials

Unless otherwise noted, reagents were purchased from commercial suppliers and were used without further purification. Benzene-d_6 and tetrahydrofuran-d_8 (Cambridge Isotope Laboratories) were purified by storage over activated 3 Å molecular sieves for at least 48 h prior to use. Celite and 3 Å molecular sieves (Aldrich) were dried under dynamic vacuum at 250 °C for 48 h before use. All solvents (Aldrich) were purchased anhydrous and were dried over KH for at least 24 h, passed through a column of activated alumina, and were stored over activated 3 Å molecular sieves prior to use.

Caution: Depleted uranium (primary isotope ^{238}U) is a weak α-emitter (4.197 MeV) with a half life of 4.47 x 10^9 years and natural thorium (primary isotope ^{232}Th) is a weak α-emitter (4.012 MeV) with a half life of 1.41 x 10^{10} years; manipulations should be carried out in a monitored fume hood or in an inert atmosphere drybox in a radiation laboratory equipped with α- and β-counting equipment.

Synthesis of $(C_5Me_5)_2ThMe_2$ (3): A 50-mL round-bottom flask equipped with a stir bar was charged with $(C_5Me_5)_2ThCl_2$ (1.03 g, 1.79 mmol) and Et_2O (15 mL). To this stirring solution, MeMgBr (3.0 M in Et_2O, 1.79 mL, 5.38 mmol, 3 equiv.) was added by syringe. After 5 minutes, 1,4-dioxane (0.790 g, 8.96 mmol, 5 equiv.) was added drop-wise to the solution over the course of another 5 minutes, resulting in an exothermic reaction and the precipitation of a white solid. After stirring at room temperature for 18 h, the volatiles were removed from the reaction mixture under reduced pressure; first at room temperature, then at 50 °C to ensure the removal of all excess 1,4-dioxane. The residual white solid was extracted with hexane (75 mL), and the hexane extract was filtered through a Celite-padded coarse-porosity frit. The filtrate was collected, and the volatiles removed under reduced pressure to give $(C_5Me_5)_2ThMe_2$ (**3**) as a white powder (0.844 g, 1.58 mmol, 88%). The ^1H NMR spectrum collected in benzene-d_6 was consistent with the data previously reported for complex **3**.[1] ^1H NMR (benzene-d_6): δ 1.91 (s, 30H, C_5Me_5), –0.18 (s, 6H, Th–*Me*).

Synthesis of $(C_5Me_5)_2UMe_2$ (4): A 100-mL round-bottom flask equipped with a stir bar was charged with $(C_5Me_5)_2UCl_2$ (2.59g, 4.47 mmol) and Et_2O (25 mL). To this stirring solution, MeMgBr (3.0 M in Et_2O, 4.47 mL, 13.4 mmol, 3 equiv.) was added by syringe. After 5 minutes, 1,4-dioxane (1.97 g, 22.3 mmol, 5 equiv.) was added drop-wise to the solution over the course of another 5 minutes, resulting in an exothermic reaction and the precipitation of a white solid. After stirring at room temperature for 18 h, the volatiles were removed from the reaction mixture under reduced pressure; first at room temperature, then at 50 °C to ensure the removal of all excess 1,4-dioxane. The residual red-orange solid was extracted with hexane (150 mL), and the hexane extract was filtered through a Celite-padded coarse-porosity frit. The filtrate was collected, and the volatiles removed under reduced pressure to give $(C_5Me_5)_2UMe_2$ (**4**) as a orange powder (1.89 g, 3.52 mmol, 79%). The ^{1}H NMR spectrum collected in benzene-d_6 was consistent with the data previously reported for complex **4**.[1] ^{1}H NMR (benzene-d_6): δ 5.20 (s, 30H, C_5Me_5), –134.1 (s, 6H, U–*Me*).

Synthesis of $(C_5Me_5)_2Th(SPh)_2$ (6): A 20-mL scintillation vial equipped with a stir bar was charged with $(C_5Me_5)_2ThMe_2$ (**3**) (0.0997 g, 0.187 mmol) and toluene (2 mL). The reaction mixture was heated to 50 °C and $PhSiH_3$ (0.0987 g, 0.912 mmol) added, which resulted in an immediate color change from pale yellow to red along with the evolution of gas. The reaction was stirred at 50 °C in an open scintillation vial until gas evolution had ceased (5 minutes). PhSSPh (0.0411 mg, 0.188 mmol) was added to the reaction mixture, which resulted in an immediate color change from red to yellow and vigorous gas evolution. After stirring for 5 h at 50 °C, the volatiles were removed from the reaction mixture under reduced pressure to give $(C_5Me_5)_2Th(SPh)_2$ (**6**) as an off-white, semi-crystalline powder (0.126 g, 0.187 mmol, 100%). The ^{1}H NMR spectrum collected in benzene-d_6 was consistent with the data previously reported for complex **6**.[2] ^{1}H NMR (benzene-d_6, 298 K): δ 7.84 (d, J = 7.8 Hz, 4H, *o*-Ar-*H*), 7.04 (t, J = 7.8 Hz, 4H, *m*-Ar-*H*), 6.90 (t, J = 7.0 Hz, 2H, *p*-Ar-*H*), 2.02 (s, 30H, C_5Me_5).

Synthesis of $(C_5Me_5)_2U(SPh)_2$ (7): A 20-mL scintillation vial equipped with a stir bar was charged with $(C_5Me_5)_2UMe_2$ (**4**) (0.0260 g, 0.0483 mmol) and toluene (1 mL). The reaction was heated to 50 °C and $PhSiH_3$ (0.0261 g, 0.241 mmol) added, which resulted in a color change from red-orange to dark brown along with the evolution of gas. The reaction was stirred at 50 °C in an open scintillation vial until gas evolution had ceased (10 minutes). PhSSPh (0.0105 g, 0.0483 mmol) was added to the reaction mixture, resulting in a color change to dark red and the evolution of gas. After stirring for 1 h at 50 °C, the volatiles were removed from the reaction mixture under reduced pressure to give $(C_5Me_5)_2U(SPh)_2$ (**7**) as a red solid (0.0421 g, 0.0646 mmol, 69%). The ^{1}H NMR spectrum collected in benzene-d_6 was consistent with the data previously reported for complex **7**.[3] ^{1}H NMR (benzene-d_6, 298 K): δ 13.13 (s, 30H, C_5Me_5), 1.24 (t, J = 7.0 Hz, 2H, p-Ar-H), 0.34 (s, 4H, m-Ar-H), –33.43 (s, 4H, o-Ar-H).

Synthesis of $(C_5Me_5)_2U(SePh)_2$ (8): A 20-mL scintillation vial equipped with a stir bar was charged with $(C_5Me_5)_2UMe_2$ (**4**) (0.0325 g, 0.0603 mmol) and toluene (2 mL). The reaction was heated to 50 °C and $PhSiH_3$ (0.0327 g, 0.302 mmol) added, which resulted in an immediate color change from red-orange to dark brown along with the evolution of gas. The reaction was stirred at 50 °C in an open scintillation vial until gas evolution had ceased (5 minutes). PhSeSePh (0.0188 g, 0.0603 mmol) was added to the reaction mixture at 50 °C, which resulted in an immediate color change to dark red and the evolution of gas. After stirring for 1 h at 50 °C, the volatiles were removed from the reaction mixture under reduced pressure to give $(C_5Me_5)_2U(SePh)_2$ (**8**) as a red solid (0.0399 g, 0.0486 mmol, 81%). The ^{1}H NMR spectrum collected in benzene-d_6 was consistent with the data previously reported for complex **8**.[2] ^{1}H NMR (benzene-d_6, 298 K): δ 14.08 (s, 30H, C_5Me_5), 2.58 (t, J = 6.9 Hz, 2H, p-Ar-H), 0.92 (d, 4H, J = 5.2 Hz, o-Ar-H), –31.67 (s, 4H, m-Ar-H).

Synthesis of $(C_5Me_5)_2U(TePh)_2$ (9): A 20-mL scintillation vial equipped with a stir bar was charged with $(C_5Me_5)_2UMe_2$ (**4**) (0.0300 g, 0.0557 mmol) and toluene (3 mL). The reaction mixture was heated to 50 °C and $PhSiH_3$ (0.0301 g, 0.279 mmol) added, which resulted in an immediate color change from orange-red to dark brown along with the evolution of gas. The reaction was stirred at 50 °C in an open scintillation vial until gas evolution had ceased (10 minutes). PhTeTePh (0.0228 g, 0.0557 mmol) was added to the reaction mixture at 50 °C, which resulted in a color change to red and vigorous evolution of gas. After stirring for 3 h at 50 °C, the volatiles were removed from the reaction mixture under reduced pressure to give

$(C_5Me_5)_2U(TePh)_2$ (**9**) as a red solid (0.0485 g, 0.0528 mmol, 95%). The ^1H NMR spectrum collected in benzene-d_6 was consistent with the data previously reported for complex **9**.[4] ^1H NMR (benzene-d_6): δ 15.28 (s, 30H, C_5Me_5), 3.88 (t, J = 7.1 Hz, 2H, *p*-Ar-*H*), 1.73 (d, J = 7.2 Hz, 4H, *m*-Ar-*H*), –27.22 (s, 4H, *o*-Ar-*H*).

Synthesis of $(C_5Me_5)_2U(SMe)_2$ (10): A 20-mL scintillation vial equipped with a stir bar was charged with $(C_5Me_5)_2UMe_2$ (**4**) (0.0355 g, 0.0659 mmol) and toluene (2 mL). The reaction was heated to 50 °C and $PhSiH_3$ (0.0357 g, 0.330 mmol) added, which resulted in an immediate color change from red-orange to dark brown along with the evolution of gas. The reaction was stirred at 50 °C in an open scintillation vial until gas evolution had ceased (5 minutes). MeSSMe (0.0062 g, 0.0659 mmol) was added to the reaction mixture at 50 °C, which resulted in an immediate color change to dark red and the evolution of gas. After stirring for 1 h at 50 °C, the volatiles were removed from the reaction mixture under reduced pressure to give $(C_5Me_5)_2U(SMe)_2$ (**10**) as a red solid (0.0307 g, 0.0510 mmol, 77%). The ^1H NMR spectrum collected in benzene-d_6 was consistent with the data previously reported for complex **10**.[3] ^1H NMR (benzene-d_6, 298 K): δ 10.86 (s, 30H, C_5Me_5), –20.88 (s, 6H, S–*Me*).

Synthesis of $(C_5Me_5)_2Th(C_4Ph_4)$ (11): A 20-mL scintillation vial equipped with a stir bar was charged with $(C_5Me_5)_2ThMe_2$ (**3**) (0.0635 g, 0.119 mmol) and toluene (3 mL). The reaction mixture was heated to 50 °C and $PhSiH_3$ (0.0645 g, 0.597 mmol) added, which resulted in a color change from beige to dark orange-red along with the vigorous evolution of gas. The reaction was stirred at 50 °C in an open scintillation vial until gas evolution had ceased (10 minutes). Diphenylacetylene (0.0425 g, 0.239 mmol) was added to the reaction, which resulted in more vigorous gas evolution. The reaction was allowed to stir while open an additional 5 minutes, after which it was closed and allowed to react at 50 °C for 3 hours. The volatiles were removed from the reaction mixture under reduced pressure to afford a brown oil. The oil was layered with hexane (5 mL), which resulted in the immediate precipitation of a yellow solid. The solid was collected by filtration (medium porosity fritted funnel), washed with hexane (3 mL), and dried under reduced pressure to give $(C_5Me_5)_2Th(C_4Ph_4)$ (**11**) as a bright yellow crystalline solid (0.0695 g, 0.0812 mmol, 68%). The ^1H NMR spectrum collected in tetrahydrofuran-d_8 was consistent with the data previously reported for complex **11**.[5] ^1H NMR (tetrahydrofuran-d_8, 298 K): δ 7.50 (d, J = 5.1 Hz, 2H, *p*-Ar-*H*), 7.32 (m, 2H, *p*-Ar-*H*), 7.01 (t, J = 7.0 Hz, 4H, *m*-Ar-*H*), 6.81 (t, J = 7.0 Hz, 4H, *m*-Ar-*H*), 6.70 (d, J = 7.0 Hz, 4H, *o*-Ar-*H*), 6.43 (d, J = 7.0 Hz, 4H, *o*-Ar-*H*), 1.99 (s, 30H, C_5Me_5).

Synthesis of $(C_5Me_5)U(C_4Ph_4)$ (12): A 20-mL scintillation vial equipped with a stir bar was charged with $(C_5Me_5)_2UMe_2$ (**4**) (0.0460 g, 0.0854 mmol) and toluene (3 mL). The reaction mixture was heated to 50 °C and $PhSiH_3$ (0.0462 g, 0.427) added, which resulted in a color change from dark orange to dark brown along with the vigorous evolution of gas. The reaction was stirred at 50 °C in an open scintillation vial until gas evolution had ceased (10 minutes). Diphenylacetylene (0.0304 g, 0.171 mmol) was added to the reaction, which resulted in more vigorous gas evolution. The reaction was allowed to stir while open an additional 5 minutes, after which it was closed and allowed to react at 50 °C for 3 hours. The volatiles were removed from the reaction mixture under reduced pressure to give a brown oily residue, which was redissolved in minimal hexane (1 mL), and cooled to –30 °C to give $(C_5Me_5)_2U(C_4Ph_4)$ (**12**) as a brown crystalline solid (0.0451 g, 0.0524 mmol, 61%). The ^1H NMR spectrum collected in benzene-d_6 was consistent with the data previously reported for complex **12**.[1] ^1H NMR (benzene-d_6, 298 K): δ 6.15 (s, 30H, C_5Me_5), 5.68 (m, 4H, *m*-Ar-*H*), 4.47 (m, 4H, *o*-Ar-*H*), –0.66 (t, J = 6.8 Hz, 2H, *p*-Ar-*H*), –1.42 (t, J = 6.8 Hz, *m*-Ar-*H*), –37.32 (t, J = 6.9 Hz, *o*-Ar-*H*). One *p*-Ar-*H* resonance is located under the C_5Me_5 resonance.

Synthesis of $(C_5Me_5)_2ThS_5$ (13): A 20-mL scintillation vial equipped with a stir bar was charged with $(C_5Me_5)ThMe_2$ (**3**) (0.0260 g, 0.0488 mmol) and toluene (1 mL). The reaction mixture was heated to 50 °C and $PhSiH_3$ (0.0264 g, 0.244 mmol) added, which resulted in a color change from beige to dark orange-red along with the evolution of gas. The reaction was stirred at 50 °C in an open scintillation vial until gas evolution had ceased (10 minutes). The reaction was cooled to ambient temperature and S_8 (0.0078 g, 0.0305 mmol) was added, which immediately resulted in more vigorous gas evolution and a color change to bright yellow. The volatiles were removed from the reaction mixture under reduced pressure to give $(C_5Me_5)_2ThS_5$ (**13**) as a yellow powder (0.0259 g, 0.0388 mmol, 80%). The ^1H NMR spectrum collected in benzene-d_6 was consistent with the data previously reported for complex **13**.[6] ^1H NMR (benzene-d_6, 298 K): δ 2.04 (s, 30H, C_5Me_5).

Synthesis of $(C_5Me_5)_2U(bipy)$ (14): A 20-mL scintillation vial equipped with a stir bar was charged with $(C_5Me_5)_2UMe_2$ (**4**) (0.0785 g, 0.146 mmol) and toluene (3 mL). The reaction mixture was heated to 50 °C and $PhSiH_3$ (0.0789 g, 0.729 mmol) added, which resulted in the vigorous evolution of gas and a color change from dark orange to dark brown. The reaction was stirred at 50 °C in an open scintillation vial until gas evolution had ceased (10 minutes). 2,2′-Bipyridine (0.0225 g, 0.146 mmol) was added to the reaction mixture, which resulted in more (slow) gas evolution. The scintillation vial was sealed and the reaction was heated at 50 °C for 15 h. The volatiles were removed from the reaction mixture under reduced pressure, yielding an oily brown residue. This residue was taken up in hexane (7 mL) and filtered (medium porosity fritted funnel). The filtrate was collected and placed under reduced pressure until the volume of the solution reached ~ 1 mL. The solution was cooled to –30 °C overnight, which resulted in the precipitation of a green solid. The solid was collected on a medium-porosity frit, washed with hexane (1 mL), and dried under reduced pressure to give $(C_5Me_5)_2U(bipy)$ (**14**) as a green solid (0.0668 g, 0.101

mmol, 69%). The ^{1}H NMR spectrum collected in toluene-d_8 was consistent with the data previously reported for complex **14**.[7] ^{1}H NMR (toluene-d_8, 298 K): δ 0.13 (s, 30H, C_5Me_5), –19.93 (d, *J* = 6.0Hz, 2H, bipy), –41.38 (t, *J* = 6.0 Hz, 2H, bipy), –81.30 (t, *J* = 6.0 Hz, 2H, bipy), –93.77 (t, *J* = 6.1 Hz, 2H, bipy).

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