Hydrosilylation of a Dinuclear Tantalum Dinitrogen Complex: Cleavage of N_2 and Functionalization of Both Nitrogen Atoms

Michael D. Fryzuk,* Bruce A. MacKay, and Brian O. Patrick

Department of Chemistry, University of British Columbia,
2036 Main Mall, Vancouver, BC Canada V6T 1Z1
fryzuk@chem.ubc.ca

Experimental Section

Crystallographic Section:

Structure of 2: A crystal of **2** suitable for X-ray diffraction analysis was obtained from slow evaporation of a 15 °C solution of **2** in benzene and hexamethyldisiloxane (1:1) in a glove box. Red triclinic crystal, dimensions 0.50 x 0.40 x 0.20 mm, space group $P\bar{1}$ (#2), a = 11.843(1) Å, b = 11.853(1) Å, c = 23.382(2) Å, α = 86.68(1)°, β = 76.24(1)°, γ = 79.36(1)°, V= 3132.8(5) Å^3, ρ_{calc} = 1.52 g cm^{-3} $2\theta_{max}$ = 59.6°. Measurements were made using an ADSC CCD area detector coupled with a Rigaku AFC7 diffractometer with graphite monochromated MoKα radiation (λ = 71069 Å) at –75±1°C in 0.50° oscillations with 20.0 second exposures using ω oscillations from 0.0 to 190.0° at χ = -90°. A second sweep was performed using ω oscillations between –17.0 and 23.0° at χ = -90º. 44484 reflections were collected; 20277 were unique (R_{int} = 0.127); equivalent reflections were merged. The data could not be indexed using the d*TREK program, and the Twinsolve function in CrystalClear[1] determined the crystal was a two-component twin (components

related by a rotation of 44° normal to (-0.1, -1.0, -1.2) with the cited unit cell parameters. Structure solved by direct methods using the program SIR97,[2] refined (17597 reflections, 676 variables) as full-matrix least-squares against $|F^2|$ using SHELX97[3] with residuals: R1, 0.097 ($I>2.00\sigma(I)$), wR2 0.211. Crystal structure data are available as .cif files via www.pubs.acs.org/jacsat/index.htm as supplementary information.

Structure of 3: Crystals of **3** suitable for X-ray diffraction analysis were obtained from a -60 °C solution of **3** in pentane in a glove box freezer. Orange orthorhombic crystal, dimensions 0.25 x 0.10 x 0.05 mm, space group Pna21 (#33), a = 27.600(6) Å, b = 17.262(4) Å, c = 14.701(3) Å, V= 7004(3) $Å^3$, ρ_{calc} = 1.286 g cm^{-3} $2\theta_{max}$ = 50.2°. Measurements were made using an ADSC CCD area detector coupled with a Rigaku AFC7 diffractometer with graphic monochromated MoKα radiation (λ = 71069 Å) at –75±1°C in 0.50° oscillations with 17.0 second exposures using ω oscillations from 0.0 to 190.0° at χ = -90°. 61129 reflections were collected; 8511 were unique (R_{int} = 0.101); equivalent reflections were merged. Data were collected and processed using d*TREK Area Detector Software.[4] Structure solved by direct methods and expanded using Fourier techniques, refined (14507 reflections, 604 variables) as full-matrix least-squares against $|F^2|$ using SHELX97.[3] Residuals: R1, 0.0566 ($I>2.00\sigma(I)$), wR2 0.1353. Crystal structure data are available as .cif files via www.pubs.acs.org/jacsat/index.htm as supplementary information.

Synthesis of Complexes:

General Considerations - Unless otherwise stated, all manipulations were performed under an atmosphere of dry oxygen-free dinitrogen by means of standard Schlenk or glovebox techniques (Vacuum Atmospheres HE-553-2 glovebox equipped with a MO-

40-2H purification system and a -60°C freezer). Butylsilane was purchased from Fluka and distilled under dinitrogen prior to use. Hexanes and toluene were purchased anhydrous from Aldrich, sparged with dinitrogen, and passed through columns containing activated alumina and Ridox catalyst before use following the method of Grubbs. Pentane, benzene, and hexamethyldisiloxane were each distilled from sodium benzophenone ketyl solublized by tetraglyme under dry dinitrogen prior to distillation. Dry pentane was stored over a potassium mirror. Nitrogen gas was dried and deoxygenated by passage through a column containing activated molecular sieves and MnO. Deuterated benzene was dried by refluxing with sodium/potassium alloy in a sealed vessel under partial pressure, then trap-to-trap distilled, and freeze-pump-thaw-degassed three times. Deuterated tetrahydrofuran and toluene were dried by refluxing with molten potassium metal in a sealed vessel under partial pressure, then trap-to-trap-distilled, and freeze-pump-thaw-degassed three times. ^{1}H, $^{31}P\{^{1}H\}$, $^{1}H\{^{31}P\}$, $^{13}C\{^{1}H\}$, $^{15}N\{^{1}H\}$, $^{29}Si\{^{1}H\}$ and two-dimensional NMR spectra were recorded on a Bruker AVANCE 400 instrument operating at 400.1 MHz for ^{1}H. ^{1}H NMR spectra were referenced to residual proton in deuterated solvent as follows: C_4D_7HO (δ 3.58 ppm), C_6D_5H (δ 7.15 ppm), and C_7D_7H (δ 2.09 ppm). $^{31}P\{^{1}H\}$ NMR spectra were referenced to external $P(OMe)_3$ (δ 141.0 ppm with respect to 85% H_3PO_4 at δ 0.0 ppm), ^{13}C NMR spectra to $^{13}CC_5D_6$ (δ 128.4 ppm), $^{13}CD_3C_6D_5$ (δ 20.4 ppm), and $^{13}CC_3D_8O$ (δ 67.4 ppm), ^{15}N spectra to external nitromethane at 0.0 ppm, and ^{29}Si to external TMS 50% in $CDCl_3$ (δ 0.0 ppm). Elemental analyses were performed by Mr. P. Borda or Mr. M. Lakha, and mass spectrometry (EI/MS) was performed by Mr. M. Lapawa, all of the University of British Columbia Department of Chemistry.

Syntheses of 1 and its isotopomers are published elsewhere.[5]

Synthesis of 2. To a stirred solution of 488 mg (0.387 mmol) **1** in 10 mL toluene was added 75.4 mg (0.855 mmol, 2.2 equiv) of butylsilane in *ca*. 2 mL toluene in a glove box. The dark brown solution turned dark red over the course of 36 h and solvent was removed under vacuum, leaving a red/purple residue that was triturated under hexanes. The resulting precipitate was recovered on a glass frit and dissolved in ca. 10 mL 1:1 benzene/hexamethyldisiloxane, and 323 mg (0.245 mmol, 63% yield) of pure crystalline **2** was recovered after slow evaporation. $^{1}H\{^{31}P\}$ NMR (C_6D_6, 30°C, 400 MHz): □ -0.01, 0.40, (s, 12H each, SiCH_3), 1.60 and 1.71 ppm (d, 4H each, $^{2}J_{HH}$ = 14.1 Hz, SiCH_2P), -0.31 (br, 2H, SiCH_2CH$_2$-), 0.66 (br m, 2H, -CH$_2$CH_2CH$_2$-), 1.10 (br, 2H, -CH$_2$CH_2CH$_3$), 0.856 (d, 3H, CH$_2$CH_3), 4.91 (s, 2H, SiH_2) 6.941 (d, 4H, *p*-*H*PhN), 7.11 (dd, 8H, *m*-*H*PhN), 6.52 (d, 8H, *m*-*H*PhN), 7.12 (d, 2H, *p*-*H*PhP), 7.20 (dd, 4H, *m*-*H*PhP) and 7.65 (d, 2H, *o*-*H*PhP). $^{31}P\{^{1}H\}$ NMR (C_6D_6, 30°C, 161.97 MHz): □ 0.08 ppm (s). $^{29}Si\{^{1}H\}$ NMR (C_6D_6, 30 °C, 79.5 MHz) □ 8.70, (d, $^{2}J_{PSi}$ = 7.0 Hz), -1.74 (dd, $^{2}J_{PSi}$ = 4.1 Hz, dd, $^{2}J_{PSi}$ = 3.9 Hz) Anal. Calc'd for $C_{56}H_{84}N_6P_2Si_6Ta_2$: C 46.91; H 5.91; N 5.86. Found: C 47.10; H 5.95; N 6.06. Mass Spec (EI/MS) M/z 1383.26 (100%).

Synthesis of $^{15}N_2$-2. 2 equivalents of $BuSiH_3$ was allowed to react with 1 equivalent of $^{15}N_2$-**1** in a manner similar to that outlined above for synthesis of **2**. ^{15}N NMR (C_6D_6, 30°C, 40 MHz) □ –23.4 (dd, J_{PN} = 5.1 Hz, 11.4 Hz). Additional couplings of 5.1 and 11.4 Hz were observed in the $^{31}P\{^{1}H\}$ spectrum. The □ -1.74 ppm resonance of the $^{29}Si\{^{1}H\}$ spectrum was broadened by an unresolvable coupling to ^{15}N.

Synthesis of 3. To a stirred solution of 758 mg (0.601 mmol) **1** in 30 mL toluene was added 53.2 mg (0.603 mmol, ~1 equiv) of butylsilane in *ca*. 3 mL toluene in a glove box. The flask was stored for 24 h in a freezer, after which the dark brown solution turned red-orange. Solvent was removed under vacuum, leaving a pinkish residue which was triturated under hexanes. The resulting precipitate was recovered on a glass frit, yielding 729 g (0.593 mmol, 98.6% yield) **3**. ^{1}H NMR (C_7D_8, -60°C, 400 MHz): □ -0.17, -0.09, 0.01, 0.02, 0.04, 0.40 (s, 3H each) 0.03 (s, 6H, total 24 SiCH_3), 0.72, 1.05, 0.46, 1.23, 0.78, 1.29, 1.20, and 1.81 (AMX, 1H each, SiCH_2P), 5.05 and 3.97 (d, $^{2}J_{HH}$ 11.7 Hz, 1H each, NSiH_2Bu), -0.25 (br, 2H, SiCH_2CH_2-), 0.74 (br m, 2H, -$CH_2CH_2CH_2$-), 1.05 (br, 2H, -$CH_2CH_2CH_3$), 0.81 (d, 3H, CH_2CH_3), 7.13, 7.01, 7.79, 7.20, 7.33, 7.42, 7.07, 7.13, 7.225, 6.93, 7.32, 7.50, 7.24, 7.34, 7.19, and 7.24 (overlapping m, PPh-*H* and NPh-*H*) 8.342 and 7.77 (m, 2H each, PPh-*o*-*H*), 11.21 and 11.23 (ddd, 1H each, J_{HbHb} = 3.8 Hz, $^{2}J_{HbHt}$ = 5.52 Hz, $^{2}J_{HP}$ = 11.7 Hz, Ta*H*Ta) 14.27 (dd, $^{2}J_{HP}$ = 17.99 Hz, J_{HH} = 5.52 Hz, 1H, Ta-H_t). ^{13}C NMR (C_7D_8, -60 °C, 100.61 MHz): 0.29, 0.41, 0.49, 1.11, 2.21, 2.38, 3.27, 3.93 (s or d, SiCH_3), 14.98, 23.61, 26.20, 32.61 (br s, SiCH_2P), 1.81 (s, SiCH_2CH_2-), 34.81 (s, -$CH_2CH_2CH_2$-), 18.54 (s, -$CH_2CH_2CH_3$), 14.09 (s, CH_2CH_3), 127.47, 121.82, 128.52, 122.19, 129.46, 134.03, 121.33, and 134.93 (P(C_6H_5) and N(C_6H_5). ^{31}P{^{1}H} NMR (C_7D_8, -60°C, 161.97 MHz): □ 23.32 (d, J_{PP} = 17.83 Hz), 8.91 (d, J_{PP} = 17.83 Hz). ^{29}Si{^{1}H} NMR (C_7D_8, -60 °C, 79.5 MHz) □ -14.96 (s, N*Si*H_2Bu) 11.17 (d, $^{2}J_{PSi}$ = 11.3 Hz), 8.98 (d, $^{2}J_{PSi}$ = 9.6 Hz) 8.79 (d, $^{2}J_{PSi}$ = 8.7 Hz), 8.49 (d, $^{2}J_{PSi}$ = 14.3 Hz). Anal. Calc'd for $C_{52}H_{76}N_6P_2Si_5Ta_2$: C 46.28; H 5.68; N 6.23. Found: C 45.98; H 5.45; N 6.48.

Synthesis of $^{15}N_2$-3. 1 equivalent of $BuSiH_3$ was allowed to react with 1 equivalent of $^{15}N_2$-**1** in a manner similar to that outlined above for the synthesis of **3**. ^{15}N NMR (C_7D_8, -

60°C, 40 MHz) δ –163.5 (d, $^{1}J_{NN}$ = 16.6 Hz) –52.5 (dd, $^{2}J_{PN}$ = 26.4 Hz, $^{1}J_{NN}$ = 16.6 Hz). Additional coupling of 26.4 Hz was observed in the δ 23.32 ppm resonance in the $^{31}P\{^{1}H\}$ spectrum, as was an additional coupling of 5.2 Hz in the δ -14.96 ppm resonance of the $^{29}Si\{^{1}H\}$ spectrum.

Synthesis of 4. A red/orange toluene solution of **3** (231 mg, 0.188 mmol) was left at 15°C in a glove box for 36 h, after which the solvent was removed under vacuum, leaving a yellow-brown residue which was triturated under hexanes. Fine yellow-white needles of **4** were recovered on a glass frit (212 mg, 0.173 mmol, 92 % yield). ^{1}H NMR (C_6D_6, 30°C, 400 MHz): δ -0.12, 0.06, 0.17 and 0.38 (s, 6H each, 24H total, SiCH_3), 1.00, 1.26, 1.22, and 1.43 (d, 2H each, SiCH_2P), 4.38 (b, 2H, NSiH_2Bu), -0.18 (br, 2H, SiCH_2CH$_2$-), 0.78 (br m, 2H, -CH$_2$CH_2CH$_2$-), 1.11 (br, 2H, -CH$_2$CH_2CH$_3$), 0.86 (d, 3H, CH$_2$CH_3), 7.05, 7.19, 7.38, 7.47, 6.94, 6.98, 7.12, 7.26, 7.36, and 7.53 (overlapping m, PPh-*H* and NPh-*H*) 7.85 and 7.30 (m, 2H each, PPh-*o*-*H*), 17.27 (d, $^{2}J_{HP}$ = 41.14 Hz, 1H, Ta-H$_t$). ^{13}C NMR (C_6D_6, 30°C, 100.61 MHz): 0.37, 0.98, 1.29, 1.41, (s, Si*C*H$_3$), 22.12 and 31.45 (br s, Si*C*H$_2$P), 2.88 (s, Si*C*H$_2$CH$_2$-), 25.47 (s, -CH$_2$*C*H$_2$CH$_2$-), 14.39 (s, -CH$_2$CH$_2$*C*H$_3$), 22.44 (s, CH$_2$*C*H$_3$), 116.66, 121.58, 122.41, 127.33, 127.90, 1288.36, 129.57, 133.12 (broad overlapping resonances, P(*C*$_6$H$_5$) and N(*C*$_6$H$_5$)). $^{31}P\{^{1}H\}$ NMR (C_6D_6, 30°C, 161.97 MHz): δ -5.73 (b), -12.26 (b). $^{29}Si\{^{1}H\}$ NMR (C_6D_6, 30°C, 79.5 MHz) δ -31.47 (s, N*Si*H$_2$Bu) 11.29 (d, $^{2}J_{PSi}$ = 11.3 Hz), 11.47 (d, $^{2}J_{PSi}$ = 12.0 Hz). Anal. Calc'd for $C_{52}H_{74}N_6P_2Si_5Ta_2$: C 46.35; H 5.54; N 6.24. Found: C 46.04; H 5.24; N 5.94.

Synthesis of $^{15}N_2$-4. A solution of $^{15}N_2$-**3** in C_6D_6 was allowed to decompose overnight at room temperature. ^{15}N NMR (C_6D_6, 30°C, 40 MHz) δ 284.4 (b) –44.8 (d, $^{2}J_{PN}$ = 18.7

Hz,). Additional coupling of 18.7 Hz was observed in the δ -12.26 ppm resonance in the $^{31}P\{^{1}H\}$ spectrum, as was an additional coupling of 4.4 Hz in the δ -31.47 ppm resonance of the $^{29}Si\{^{1}H\}$ spectrum.

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[1] CrystalClear: Version 1.3.5b20. Molecular Structure Corporation (2002).

[2] SIR97: Altomare, A. Burla, M.C., Cammalli, G., Cascarano, M., Giacovazzo, C., Guagliardi, A., Moliterni, A.G.G., Polidori, G., Spagna, A. SIR97: a new tool for crystal structure determination and refinement. J. Appl. Cryst., 32, 115-119 (1999).

[3] SHELXL-97: Sheldrick, G.M. University of Göttingen, Germany (1997).

[4] D*TREK: Version 4.13, Molecular Structure Corporation (1996-1998).

[5] M.D. Fryzuk, S.A. Johnson, B.O. Patrick, A. Albinati, S.A. Mason, T.F. Koetzle, *J. Am. Chem. Soc.* **2001**, *123*, 3960-3973.