Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Titanium and Zirconium Complexes of *N*,*N*'-Bis(2,6-diisopropylphenyl)-1,4-diaza-butadiene Ligand: Syntheses, Structures and Their use in Catalytic Hydrosilylation Reactions

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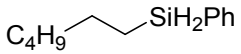
Table TS1

^{1}H NMR of the silanes obtained after catalytic hydrosilylation reactions

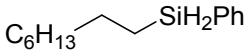
Table TS1. Crystallographic data and structure refinement parameters for complexes **1-7.**

Crystal	**2**	**3.THF**	**5**	**6**	**7**	**8**
CCDC No.	1011649	1011650	1011651	1011652	1011653	1011654
Empirical formula	$C_{31}H_{41}ClN_2Ti$	$C_{40}H_{56}N_2OZr$	$C_{60}H_{92}Cl_5LiN_4O_2Zr_2$	$C_{52}H_{72}N_4Ti$	$C_{35}H_{52}N_2SiTi$	$C_{34}H_{58}N_2Si_2Zr$
Formula weight	524.98	672.09	1268.01	801.01	576.75	642.22
T (K)	150.0	150	150	150	150	150
λ (Å)	1.54184 A	1.54184	1.54184	1.54184	1.54184	1.54184
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P 21/c*	P -1	P 21/c	*P 21/c*	P 21/c	P 21/c
a (Å)	12.9556(6)	9.6518(6)	14.4496(2)	22.7866(5)	13.2634(3)	12.4742(3)
b (Å)	19.4949(15)	11.7505(9)	31.1845(4)	10.1450(2)	18.8633(4)	17.2640(6)
c (Å)	11.6445(11)	17.6246(16)	17.2519(3)	21.9021(6)	13.4564(3)	19.0503(5)
α (°)	90	95.550(7)	90	90	90	90
β (°)	104.004(7)	104.747(7)	109.929(2)	113.251(3)	93.844(2)	114.746(2)
γ (°)	90	107.587(6)	90	90	90	90
V (Å^3)	2853.6(4)	1809.7(2)	7308.24(19)	4651.90(19)	3359.10(13)	3725.84(19)
Z	4	2	4	4	4	4
D_{calc} g cm^{-3}	1.222	1.233	1.152	1.144	1.140	1.145
μ (mm^{-1})	3.546	2.717	4.300	1.833	2.667	3.186
F (000)	1120	716	2656	1736	1248	1376
Theta range for data collection	4.18 to 70.70 deg.	5.04 to 70.77 deg.	3.55 to 70.80 deg	4.05 to 70.81 deg.	3.34 to 70.79 deg.	3.62 to 70.72 deg.
Limiting indices	-15<=h<=15 -17<=k<=23 -8<=l<=14	-11<=h<=11 -14<=k<=10 -21<=l<=18	-17<=h<=17 -37<=k<=34 -20<=l<=17	-27<=h<=23 -12<=k<=12 -15<=l<=26	-15<=h<=13, -22<=k<=14 -16<=l<=15	-15<=h<=13 -15<=k<=20 -23<=l<=23
Reflections collected / unique	11950 / 5373 [R(int) = 0.0434]	12719 / 6778 [R(int) = 0.0349]	32666 / 13792 [R(int) = 0.0326]	19762 / 8784 [R(int) = 0.0332]	13920 / 6309 [R(int) = 0.0443]	15450 / 7017 [R(int) = 0.0388]
Completeness to theta = 71.25	97.9 %	97.2 %	98.1 %	97.9 %	97.6 %	98.0 %
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Max. and min. transmission	1.00000 and 0.43828	1.00000 and 0.47778	1.00000 and 0.61871	1.00000 and 0.78810	1.00000 and 0.52597	1.00000 and 0.63878
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5373 / 0 / 328	6778 / 0 / 407	13792 / 0 / 687	8784 / 0 / 546	6309 / 0 / 363	7017 / 0 / 366
Goodness-of-fit on F^2	1.119	1.043	1.089	1.047	1.021	0.703
Final R indices [I>2sigma(I)]	R1 = 0.0480, wR2 = 0.1280	R1 = 0.0288, wR2 = 0.0768	R1 = 0.0558, wR2 = 0.1789	R1 = 0.0425, wR2 = 0.1120	R1 = 0.0558, wR2 = 0.1498	R1 = 0.0369, wR2 = 0.0960
R indices (all data)	R1 = 0.0599, wR2 = 0.1389	R1 = 0.0292, wR2 = 0.0772	R1 = 0.0591, wR2 = 0.1826	R1 = 0.0499, wR2 = 0.1192	R1 = 0.0720, wR2 = 0.1700	R1 = 0.0498, wR2 = 0.1127
Absolute structure parameter	0.594 and -0.605 e.A^{-3}	0.633 and -0.812 e.A^{-3}	2.356 and -1.110 e.A^{-3}	0.197 and -0.536 e.A^{-3}	0.561 and -0.685 e.A^{-3}	0.405 and -0.943 e.A^{-3}
Largest diff. peak and hole						

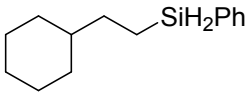
Typical Hydrosilylation Procedure: In a glove box a precatalyst **8** (0.018 mmol), appropriate alkene (0.370 mmol), phenylsilane (0.407 mmol) and then C6D6 (3 mL) were introduced into NMR tube and tube was sealed with Teflon. The reaction was monitored by ^{1}H NMR spectroscopy. The ratio of *n* and *iso* products was calculated by integration of the appropriate signals in the ^{1}H NMR spectra.



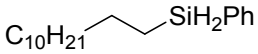
1. (1-Hexyl)(Phenyl) silane: ^{1}H NMR (400 MHz, C_6D_6): δ 7.48-7.46 (m, 2H), 7.14-7.11 (m, 3H), 4.46 (t, 2H, *J* = 3.7 Hz), 1.40-1.10(m, 8H), 0.84-0.80 (m, 5H).



2. (1-Octyl)(Phenyl)silane: ^{1}H NMR (400 MHz, C_6D_6): δ 7.47-7.46 (m, 2H), 7.14-7.11 (m, 3H), 4.48(t, 2H, *J* = 3.6 Hz), 1.28-1.18(m, 12H), 0.88-0.85 (m, 5H).

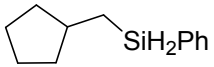


3. 2-Cyclohexyl (1-ethyl)(Phenyl)silane: : ^{1}H NMR (400 MHz, C_6D_6): δ 7.49-7.47(m, 2H), 7.14-7.12 (m, 3H), 4.46 (t, 2H, *J* = 3.6 Hz), 1.65-1.63 (m, 5H), 1.32-1.26 (m, 2H), 1.21-1.02 (m, 4H), 0.84-0.69 c (m, 4H). ^{13}C NMR (100 MHz, C6D6): δ 135.5 (Ar-*C*), 129.8 (Ar-*C*), 128.3 (Ar-*C*), 40.5(*C*H), 33.1 (*C*H_2), 32.9 (*C*H_2), 27.1 (*C*H_2), 26.7 (*C*H_2), 7.5 (CH_2).

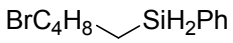


4. (1-Dodecyl)(Phenyl)silane: : ^{1}H NMR (400 MHz, C_6D_6): δ 7.39-7.37 (m, 2H), 7.13-7.11 (m, 3H), 4.46 (t, 2H, *J* = 3.6 Hz), 1.45-1.19(m, 22H), 0.90 (t, 3H).

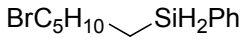
5. PhHC(SiH_2Ph)CH_3(*n*): ^{1}H NMR (C_6D_6,400 MHz): δ 7.21-6.94 (m, 10H), 4.85 (m, 2H), 2.70 (m, 1H), 1.03 (d, J = 7.6 Hz, 3H). **PhCHzCHZSiH_2Ph (*iso*):** ^{1}H NMR (C_6D_6, 400 MHz): δ 7.21-6.94 (m, 10H), 4.40 (t, J = 3.8 Hz, 2H), 2.40 (m, 2H), 1.05 (m, 2H).



6. (Cyclopentylmethyl)(phenyl)silane: : ^{1}H NMR (400 MHz, C_6D_6): δ 7.50-7.47 (m, 2H), 7.14-7.10 (m, 3H), 4.47(t, 2H, *J* = 3.8Hz), 1.86-1.78 (m, 1H), 1.75-1.68 (m, 2H), 1.57-1.46 (m, 2H), 1.41-1.36(m, 2H), 1.07-0.98 (m, 2H), 0.91-87 (m, 2H).



7. (5-Bromopentyl)(Phenyl)silane: ^{1}H NMR (400 MHz, C_6D_6): δ 7.45-7.43 (m, 2H), 7.15-7.13 (m, 3H), 4.36 (t, 2H, *J* = 3.8Hz), 2.90-2.83 (m, 2H), 1.85-1.79 (m, 2H), 1.50-1.43 (m, 2H), 1.15-1.06 (m, 2H), 0.64-58 (m, 2H).



8. (6-Bromohexyl)(phenyl)silane: : ^{1}H NMR (400 MHz, C_6D_6): δ 7.47-7.45 (m, 2H), 7.15-7.14 (m, 3H), 4.42 (t, 2H, *J* = 3.8Hz), 2.95-2.87 (m, 2H), 1.45-1.38 (m, 2H), 1.26-1.19 (m, 2H), 1.09-1.00 (m, 4H), 0.74-0.68 (m, 2H).