Hydrosilation of Carbonyl-Containing Substrates Catalyzed by an Electrophilic η^1-Silane Iridium(III) Complex

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Supporting Information

Hydrosilation of Acetone by 1 (Table 1, entry 1). ^{1}H NMR (C_6D_5Cl): δ 4.12 (septet, *J* = 6 Hz, 1H); 1.28 (d, *J* = 6 Hz, 6 H); 1.14 (m, 9H, overlapped with Et_3SiH); 0.75 (m, 6H, overlapped with Et_3SiH). $^{13}C\{^1H\}$ NMR (C_6D_5Cl): δ 64.5, 25.8, 6.7, 5.1.

Hydrosilation of 2,4-Dimethyl-3-pentanone by 1 (Table 1, entry 2). ^{1}H NMR (C_6D_5Cl): δ 3.39 (t, *J* = 6.5 Hz, 1H); 1.96 (dq, 2 H); 1.23 (m, 9 H); 0.90-0.86 (m, 18 H). $^{13}C\{^1H\}$ NMR (C_6D_5Cl): δ 83.0, 31.7, 20.4, 17.9, 7.3, 5.9.

Hydrosilation of 3,3-Dimethyl-2-butanone by 1 (Table 1, entry 3). ^{1}H NMR (C_6D_5Cl): δ 3.62 (q, *J* =8 Hz, 1H); 1.22 (d, *J* =8 Hz, 3 H); 1.05 (s, 9H). $^{13}C\{^1H\}$ NMR (C_6D_5Cl): δ 76.0, 35.4, 25.6, 18.4, 6.9, 5.3.

Hydrosilation of Acetophenone by 1 (Table 1, entry 5). ^{1}H NMR (C_6D_5Cl): δ 7.52-7.31 (m, 5H, overlapped with solvent peaks), 5.05 (q, *J* =8 Hz, 1H); 1.59 (d, *J* =8 Hz, 3 H); 1.15 (m, 9H, overlapped with Et_3SiH); 0.80 (m, 6H, overlapped with Et_3SiH). $^{13}C\{^{1}H\}$ NMR (C_6D_5Cl): δ 147.1, 128.1, 126.8, 125.2, 70.9, 27.4, 6.8, 5.1.

Hydrosilation of Benzaldehyde by 1 (Table 1, entry 7). ^{1}H NMR (C_6D_5Cl): δ 7.56-7.41 (m, 5H, overlapped with solvent peaks), 4.68 (s, 2H); 1.59 (d, *J* =8 Hz, 3 H); 1.15 (m, 9H, overlapped with Et_3SiH); 0.80 (m, 6H, overlapped with Et_3SiH). $^{13}C\{^{1}H\}$ NMR (C_6D_5Cl): δ 138.9, 128.5, 127.7, 127.6, 72.2, 7.1, 6.8.

Hydrosilation of Ethyl Acetate by 1 (Table 1, entry 8). ^{1}H NMR (C_6D_5Cl): δ 3.79 (q, *J* = 7 Hz, 2H, $CH_3CH_2OSiEt_3$); 3.52 (q, *J* = 8 Hz, 4 H, $CH_3CH_2OCH_2CH_3$); 1.30 (m, 3H, $CH_3CH_2OSiEt_3$, overlapped with $-OSiEt_3$); 1.15 (m, 6H, $CH_3CH_2OCH_2CH_3$, overlapped with Et_3SiH and $-OSiEt_3$); 0.70 (m, $-OSiEt_3$, overlapped with Et_3SiH). $^{13}C\{^{1}H\}$ NMR (C_6D_5Cl): δ 65.6 ($CH_3CH_2OCH_2CH_3$), 58.1 ($CH_3CH_2OSiEt_3$) , 18.6($CH_3CH_2OSiEt_3$), 15.1 ($CH_3CH_2OCH_2CH_3$), 6.9, 6.8, 4.7, 4.4 ($-OSiEt_3$).

Hydrosilation of Methyl Isobutanoate by 1 (Table 1, entry 9). ^{1}H NMR (C_6D_5Cl): δ 3.52 (s, 3H, $MeOSiEt_3$), 3.50 (d, 2H, $Me_2CHCH_2OSiEt_3$), 1.86 (m, *J* = 6.8 Hz, 1H, $Me_2CHCH_2OSiEt_3$); 1.05 (d, *J* = 6.8 Hz, 6H, $Me_2CHCH_2OSiEt_3$); 1.15 (m, 18H, $-OSiEt_3$, overlapped with Et_3SiH); 0.70 (m, 12H, $-OSiEt_3$, overlapped with Et_3SiH). $^{13}C\{^{1}H\}$ NMR (C_6D_5Cl): δ 69.4 ($Me_2CHCH_2OSiEt_3$), 50.0 ($MeOSiEt_3$), 31.1 ($Me_2CHCH_2OSiEt_3$), 18.8 ($Me_2CHCH_2OSiEt_3$), 6.6, 6.5, 4.6, 4.3 ($-OSiEt_3$).

Hydrosilation of Ethyl Trifluoroacetate by 1 (Table 1, entry 10). ^{1}H NMR (C_6D_5Cl): δ 5.02 (q, *J* = 3.6 Hz, 1H), 3.84 (m, 1H), 3.73 (m, 1H), 1.15 (m, 12H, overlapped with Et_3SiH), 0.75 (m,

6H, overlapped with Et_3SiH). $^{13}C\{^1H\}$ NMR (C_6D_5Cl): δ 123.6 (q, $J_{C\text{-}F}$ = 1132 Hz), 92.8 (q, $J_{C\text{-}F}$ = 144 Hz), 63.4, 14.7, 6.1, 4.8.

Hydrosilation of *N*,*N*-Diethyl Acetamide by 1 (Table 1, entry 11). ^1H NMR (C_6D_5Cl): δ 2.56 (q, *J* = 7 Hz, 6H), 1.10 (t, 9H, overlapped with Et_3SiH), 1.10 (m, 18H, overlapped with Et_3SiH), 0.75 (m, 12H, overlapped with Et_3SiH). $^{13}C\{^1H\}$ NMR (C_6D_5Cl): δ 46.6, 12.2, 6.6, 6.3.

Table 2, entry 2,4-8

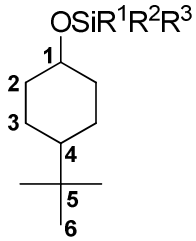
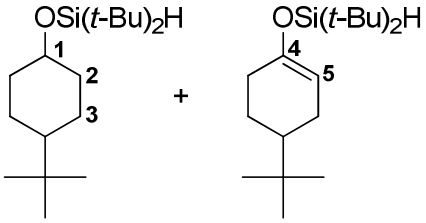


Table 2, entry 9



^1H NMR (C_6D_5Cl, **Table 2**, **entry 2**): δ 0.1-2.1 (m, 29H, β, γ, δ-H, *t*-Bu, and $OSiMe_2Et$, overlapped with $EtMe_2SiH$), 3.63 (m, 0.69H, axial-α-H), and 4.09 (m, 0.31H, equatorial-α-H, overlapped with solvent peaks). $^{13}C\{^1H\}$ NMR (C_6D_5Cl): δ -2.3, -2.0, -0.4, 6.6, 8.8, and 10.1 (s, $OSiMe_2Et$), 21.1, 25.9, 27.5, 32.1, 32.5, 34.4, 36.7, 47.4, 48.3 (C2-6), 66.2, 71.6 (C1). ^1H NMR (C_6D_5Cl, **Table 2**, **entry 4**, characteristic signals): δ 3.65 (m, 0.74H, axial-α-H), and 4.12 (m, 0.26H, equatorial-α-H). $^{13}C\{^1H\}$ NMR (C_6D_5Cl, characteristic signals): δ 21.1, 26.0, 27.5, 27.6, 32.1, 32.5, 34.5, 36.8, 47.5, 48.3 (C2-6), 66.3, 71.8 (C1). ^1H NMR (C_6D_5Cl, **Table 2**, **entry 5**, characteristic signals): δ 3.55 (m, 0.68H, axial-α-H), and 4.02 (m, 0.32H, equatorial-α-H). $^{13}C\{^1H\}$ NMR (C_6D_5Cl, characteristic signals): δ 21.0, 25.8, 27.3, 27.4, 32.0, 32.4, 34.4, 36.7, 47.4, 48.1 (C2-6), 66.0, 71.5 (C1). ^1H NMR (C_6D_5Cl, **Table 2**, **entry 6**, characteristic signals): δ 3.69 (m, 0.76H, axial-α-H), and 4.14 (m, 0.24H, equatorial-α-H). $^{13}C\{^1H\}$ NMR (C_6D_5Cl, characteristic signals): δ 21.1, 26.0, 27.6, 27.8, 32.2, 32.5, 34.4, 36.8, 47.5, 48.2 (C2-6), 66.3,

71.9 (C1). ^{1}H NMR (C_6D_5Cl, **Table 2**, **entry 7**, characteristic signals): δ 3.63 (m, 0.87H, axial-α-H), and 4.11 (m, 0.13H, equatorial-α-H). $^{13}C\{^{1}H\}$ NMR (C_6D_5Cl, characteristic signals): δ 21.0, 25.9, 27.5, 27.7, 32.2, 32.6, 34.3, 36.7, 47.5, 48.0 (C2-6), 66.3, 71.9 (C1). ^{1}H NMR (C_6D_5Cl, **Table 2**, **entry 8**, characteristic signals): δ 3.76 (m, 0.51H, axial-α-H), and 4.24 (m, 0.49H, equatorial-α-H). $^{13}C\{^{1}H\}$ NMR (C_6D_5Cl, characteristic signals): δ 21.0, 26.0, 27.5, 27.7, 32.2, 32.6, 34.5, 37.0, 47.5, 48.1 (C2-6), 66.5, 72.0 (C1). ^{1}H NMR (C_6D_5Cl, **Table 2**, **entry 9**): δ 0.8-2.4 (m, 37H, β, γ, δ-H, *t*-Bu, and OSi(*t*-Bu)$_2$H overlapped with (*t*-Bu)$_2$SiH$_2$), 3.70 (m, 0.57H, axial-α-H, overlapped with (*t*-Bu)$_2$SiH$_2$), 4.22 (m, 0.43H, equatorial-α-H), 4.28 (s, 1H, OSi(*t*-Bu)$_2$*H*), 4.49 (s, 1H, =C-OSi(*t*-Bu)$_2$*H*), and 5.10 (d, 1H, *H*C=C-OSi(*t*-Bu)$_2$H). $^{13}C\{^{1}H\}$ NMR (C_6D_5Cl, characteristic signals): δ 36.1, 33.5, 48.0, 47.5 (C2, C3), 74.9, 69.5 (C1), 151.6 (C4), 102.2 (C5).

Table 4, entry 1

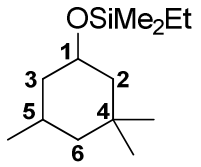


Table 4, entry 2

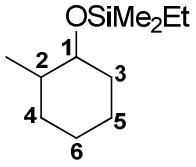


Table 4, entry 3

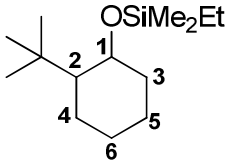
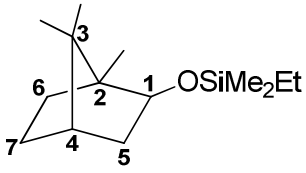


Table 4, entry 4



Hydrosilation of 3,3,5-Trimethyl Cyclohexanone by 1 (Table 4, entry 1). ^{1}H NMR (C_6D_5Cl, characteristic signals): δ 4.23 (m, 0.86H, equatorial-α-H), 4.12 (m, 0.14H, axial-α-H, overlapped with EtMe$_2$SiH), 2.30-1.35 (m, 4H, β-Hs). $^{13}C\{^{1}H\}$ NMR (C_6D_5Cl, characteristic signals): δ 70.2, 68.2 (C1), 48.8, 47.6 (C2), 45.1, 44.9, 42.5, 34.0, 33.0, 32.0, 30.8, 27.8, 27.2, 22.8, 22.4, 22.1 (C3-6, Me).

Hydrosilation of 2-Methyl Cyclohexanone by 1 (Table 4, entry 2). ^{1}H NMR (C_6D_5Cl, characteristic signals): δ 3.88 (m, 0.71H, equatorial-α-H), 3.28 (m, 0.29H, axial-α-H), 2.20-1.10 (m, 9H, H2-6, overlapped with $EtMe_2SiH$), 1.04 (d, 3H, Me). $^{13}C\{^{1}H\}$ NMR (C_6D_5Cl, characteristic signals): δ 77.0, 71.4 (C1), 40.5, 37.0 (C2), 36.3, 35.6 (C3), 33.8, 33.7 (C4), 28.9, 25.9, 25.3, 20.6(C5-6), 19.1, 17.9 (Me).

Hydrosilation of 2-*tert*-Butyl Cyclohexanone by 1 (Table 4, entry 3). ^{1}H NMR (C_6D_5Cl, characteristic signals): δ 4.43 (m, 0.76H, equatorial-α-H), 3.73 (m, 0.24H, axial-α-H), 2.20-1.00 (m, 18H, H2-6 and t-Bu, overlapped with $EtMe_2SiH$). $^{13}C\{^{1}H\}$ NMR (C_6D_5Cl, characteristic signals): δ 74.8, 68.9 (C1), 53.5, 52.1 (C2), 37.8, 35.5 (C3), 32.9, 32.6 (C4), 29.2, 28.4, 27.3, 26.9, 26.5, 25.2, 21.7, 20.4 (C5-6, t-Bu).

Hydrosilation of Camphor by 1 (Table 4, entry 4). ^{1}H NMR (C_6D_5Cl, characteristic signals): δ 4.18 (m, 0.79H, *endo*-H), 3.73 (m, 0.21H, *exo*-H). $^{13}C\{^{1}H\}$ NMR (C_6D_5Cl, characteristic signals): δ 79.8, 77.3 (C1), 49.8, 48.9 (C2), 47.4, 46.6 (C3), 45.6, 45.5 (C4), 42.4, 39.8 (C5), 34.1, 28.5, 27.6, 26.4 (C6-7), 20.6, 20.3, 18.8, 13.6, 12.0, 10.3 (Me).