Second Generation N-Heterocyclic Carbene-Pt(0) Complexes as Efficient Catalysts for the Hydrosilylation of Alkenes.

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General Information. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Thin-layer chromatography (TLC) was performed on Merck 0.25 mm silica gel 60-F_{254} plates. Visualization of the developed chromatogram was performed by fluorescence quenching or $KMnO_4$ stain.

^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 (200 MHz and 50 MHz respectively) as noted, and are internally referenced to residual protio solvent signals. Data for ^{1}H are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported in terms of chemical shift. IR spectra were recorded on a BIO-RAD FTS 135 spectrometer and are reported in terms of frequency of absorption (ν cm^{-1}). Mass spectra were obtained using Varian MAT-44 and Finnigan MATTSQ 70 spectrometers with electron impact (70 eV) and chemical ionisation (100 eV, ionisation gas, isobutane). Gas liquid chromatography (GLC) was performed on a Thermo-Finnigan Trace GC chromatograph equipped with an FID detector using a Chrompack fused silica capillary column (CP Sil 8CB, 30 m*0.25 mm, DF = 0.25 μm).

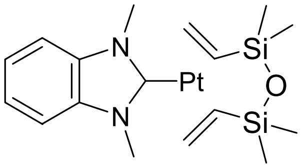
Hydrosilylation reactions were followed using dodecane as an internal standard. The response coefficients were measured for reactants and products against dodecane.

The benzimidazolium salts where synthesized by double alkylation of the corresponding benzimidazole with the desired alkyl and alkenyl bromides.

General procedure for the synthesis of benzimidazolylidene platinum(0) complexes

To a solution of the benzimidazolium salt (1 eq.) and Karstedt's catalyst (16.2 % of Pt in dvtms, 1 eq.), in THF (0.1 M) under argon was added ^{t}BuOK(1.4 eq) at 0 ^{o}C. The reaction mixture was stirred overnight at room temperature. The mixture was filtered and the solids were washed with DCM. The combined filtrates were washed with water, dried over MgSO$_4$ and the solvents were removed *in vacuo*. The crude compound can be further purifed by crystallization from ^{i}PrOH.

3a



C$_{17}$H$_{28}$N$_2$OPtSi$_2$
Mol. Wt.: 527,67

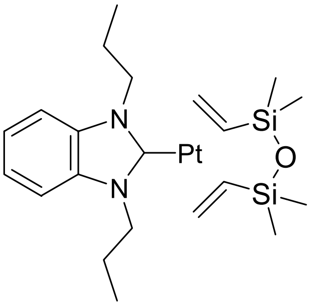
Yield: 66%

^{1}H NMR (200 MHz, CDCl$_3$): δ = 7.42-7.29 (m, 4H, Ph), 3.74 (s, 6H, ^4JPt-H = 5.1 Hz, N-CH$_3$), 2.30 (dd, 2H, ^3J = 9.3 Hz, ^3J = 1.8 Hz, ^2JPt-H.= 40.0 Hz, Si-CH=), 2.22-1.81 (m, 4H, =CH$_2$), 0.35 (s, 6H, SiCH$_{3\ eq.}$), -0.23 (s, 6H, SiCH$_{3\ ax.}$); NMR ^{13}C (50 MHz, CDCl$_3$): δ = 199.5 (^1JPt-C = 1377.9 Hz, Pt-C$_{car}$), 135.7 (^3JPt-C = 39.0 Hz, C=C-N), 122.1 (C$_{arom.}$), 108.9 (^4JPt-C = 9.6 Hz, C$_{arom.}$), 40.7 (^1JPt-C = 155.7 Hz, C-Si), 35.6 (^1JPt-C = 113.7 Hz, $\underline{\mathrm{C}}$=CHSi), 33.4 (^3JPt-C = 47.2 Hz, NCH$_3$), 33.3 (^3JPt-C = 47.1Hz, NCH$_3$), 1.5 (SiCH$_{3\ eq..}$), -1.9 (SiCH$_{3\ ax.}$)

IR(KBr, cm^{-1}) : 1614, 1579, 1489, 1463, 1431, 1382, 1241, 1175, 1089, 1008, 989, 901, 859, 830, 776, 737, 702

MS(E.I.) m/z = 528-527-526 ([M]$^{+°}$); 513-512-511([M-CH3]$^{+°}$); 501-500-499([M-HC=CH$_2$]$^{+°}$); 341-340-339 ([M-dvtms]$^{+°}$); 147 ([BenzNHC]$^{+°}$).

3b



$C_{21}H_{36}N_2OPtSi_2$
Mol. Wt.: 583,77

Yield = 59 %

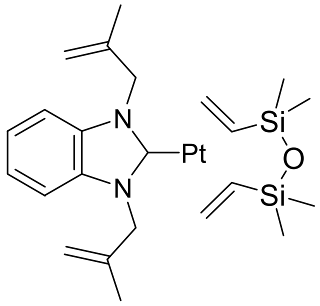
^{1}H NMR (200 MHz, CDCl$_3$): δ = 7.36-7.20 (m, 4H, Ph), 4.15-4.07 (m, 4H, CH$_2$N), 2.28 (dd, 2H, ^3J = 10.2 Hz, ^3J = 1.7 Hz, ^2JPt-H.= 48.1 Hz, Si-CH=), 2.07-1.65 (m, 8H, =CH$_2$+CH$_2$Me), 0.90 (t, 3H, ^3J = 7.4Hz, $_3$), 0.87 (t, 3H, ^3J = 7.4Hz, CH$_3$), 0.33 (s, 6H, SiCH$_{3\ \mathrm{eq.}}$), -0.25 (s, 6H, SiCH$_{3\ \mathrm{ax.}}$); ^{13}C NMR (50 MHz, CDCl$_3$): δ = 198.3 (^1JPt-C = 1373.3 Hz, Pt-C$_{\mathrm{car}}$), 135.1 (^3JPt-C = 41.6 Hz, C=C-N), 121.8 (C$_{\mathrm{arom.}}$), 109.4 (^4JPt-C = 8.3 Hz, C$_{\mathrm{arom.}}$),), 49.0 (^3JPt-C = 40.0 Hz, NCH$_3$), 48.9 (^3JPt-C = 40.4 Hz, NCH$_3$), 43.3 (^1JPt-C = 158.2 Hz, C-Si), 35.1 (^1JPt-C = 113.6 Hz, $\underline{\mathrm{C}}$=C-Si), 22.6 (CH$_2$Me), 22.4 (CH$_2$Me), 11.3 (CH$_3$), 11.2 (CH$_3$), 1.4 (SiCH$_{3\ \mathrm{eq..}}$), -1.9 (SiCH$_{3\ \mathrm{ax.}}$).

IR(KBr, cm^{-1}) : 1610, 1579, 1428, 1402, 1298, 1245, 1175, 990, 860, 836, 785, 741, 573

MS(E.I.) m/z = 584-583-582 (M$^{+\circ}$); 569-568-567([M-CH$_3$]$^{+\circ}$); 556-555-554([M-HC=CH$_2$]$^{+\circ}$); 394-393-392 ([M-dvtms-2H$_2$]$^{+\circ}$); 203 ([BenzNHC]$^{+\circ}$).

Mp = 184 -186 °C

3c



$C_{23}H_{36}N_2OPtSi_2$
Mol. Wt.: 607,79

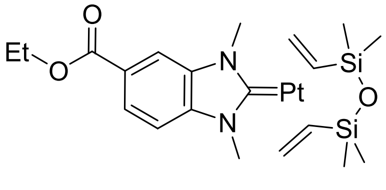
Yield = 70 %

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.33-7.22 (m, 4H, Ph), 4.95 (s, 2H, $C{=}CH_2$), 4,85 (s, 4H, CH_2N), 4.73 (s, 1H, $C{=}CH_2$), 4.55 (s, 1H, $C{=}CH_2$), 2.32 (dd, 2H, ^{3}J = 10.6 Hz, ^{3}J = 1.3 Hz, ^{2}JPt-H.= 54.3 Hz, Si-CH=), 2.1-1.1.8 (m, 8H, $SiC{=}CH_2$), 1.70 (s, 3H, CH_3), 1.68 (s, 3H, CH_3), 0.35 (s, 6H, $SiCH_{3\ eq.}$), -0.26 (s, 6H, $SiCH_{3\ ax.}$); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 198.3 (^{1}JPt-C = 1398.3 Hz, Pt-C_{car}), 139.8 (MeC=), 139.3 (MeC=), 135.3 (^{3}JPt-C = 41.6 Hz, C=C-N), 122.1 ($C_{arom.}$), 112.7 ($=CH_2$), 111.8 ($=CH_2$), 110.1 ($C_{arom.}$), 53.1 (^{3}JPt-C = 42.6 Hz, NCH_2), 52.9 (^{3}JPt-C = 42.8 Hz, NCH_2), 42.1 (^{1}JPt-C = 155.4 Hz, C-Si), 35.9 (^{1}JPt-C = 113.6 Hz, $\underline{C}$=CHSi), 20.0 (CH_3), 1.4 ($SiCH_{3\ eq..}$), -1.9 ($SiCH_{3\ ax.}$).

IR(KBr, cm^{-1}) : 1663, 1480, 1427, 1401, 1299, 1240, 1225, 1174, 981, 905, 884, 838, 780, 739

MS(E.I.) m/z = 607-606-605 ($M^{+\circ}$); 421-420-419 ($[M\text{-dvtms}]^{+\circ}$).

3d

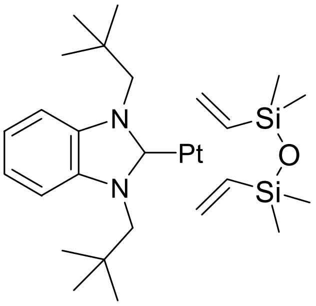


White solid yield = 77%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.06-8.03 (m, 2H, Ph), 7.36 (d, ^{3}J = 8.1 Hz, 1H, Ph), 3.99 (s, 3H, OCH_3), 3.78 (s, 6H, ^{4}JPt-H = 3.9 Hz, N-CH_3), 2.33 (d, 2H, ^{3}J = 10.2 Hz, ^{2}JPt-H.= 55.6 Hz, Si-CH=), 2.05-1.95 (m, 4H, $=CH_2$), 0.36 (s, 6H, $SiCH_{3\ eq.}$), -0.22 (s, 6H, $SiCH_{3\ ax.}$); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 204.3 (^{1}JPt-C = 1385 Hz, Pt-C_{car}), 166.9 (C=O), 138.4 (^{3}JPt-C = 40.0 Hz, C=C-N), 135.5 (^{3}JPt-C = 39.0 Hz, C=C-N), 124.2 ($C_{arom.}$), 110.5 (^{4}JPt-C = 10.0 Hz, $C_{arom.}$), 108.4 (^{4}JPt-C

= 9.5 Hz, C$_{arom.}$), 52.3 (OCH$_3$), 41.1 (^1JPt-C = 155.1 Hz, C-Si), 36.3 (^1JPt-C = 113.2 Hz, $\underline{C}$=CHSi), 33.5 (^3JPt-C = 46 Hz, NCH$_2$), 1.4 (SiCH$_{3\ eq..}$), -1.8 (SiCH$_{3\ ax.}$)

3e



$C_{25}H_{44}N_2OPtSi_2$
Mol. Wt.: 639,88

The corresponding thiourea (1 eq) was reduced over Na/K amalgam in degassed *o*-Xylene for 20 days at room temperature. The reaction mixture was filtered over celite under Ar. To this mixture was added a commercial solution of Karstedt's catalyst (1 eq., 16.7% of Pt in Xylenes). The reaction mixture was stirred overnight. It was then diluted with DCM, washed with water and filtered on deactivated alumina using DCM as the eluent. Evaporation yielded white crystals.
Yield = 50%.
^{1}H NMR (200 MHz, CDCl$_3$): δ = 7.51-7.43 (m, 2H, Ph), 7.30-7.21 (m, 2H, Ph), 4.25 (s, 2H, ^4JPt-H = 5.8 Hz, N-CH$_2$), 4.17 (s, 2H, ^4JPt-H = 5.8 Hz, N-CH$_2$), 2.42 (t, 2H, ^3J = 6.0 Hz, ^2JPt-H.= 55.0 Hz, Si-CH=), 2.41 (d, 4H, ^3J = 6.0 Hz, ^2JPt-H.= 51.0 Hz, =CH$_2$), 1.02 (s, 9H, C(CH$_3$)$_3$), 0.95 (s, 9H, C(CH$_3$)$_3$), 0.39 (s, 6H, SiCH$_{3\ eq.}$), -0.16 (s, 6H, SiCH$_{3\ ax.}$); ^{13}C NMR (50 MHz, CDCl$_3$): δ = 201.9 (^1JPt-C = 1337.0 Hz, Pt-C$_{car}$), 135.9 (^3JPt-C = 40.7 Hz, C=C-N), 121.3 (C$_{arom.}$), 111.2 (^4JPt-C = 9.0 Hz, C$_{arom.}$), 111.1 (^4JPt-C = 9.0 Hz, C$_{arom.}$), 58.7 (^3JPt-C = 55.4 Hz, NCH$_2$), 58.5 (^3JPt-C = 57.2 Hz, NCH$_2$), 43.8 (^1JPt-C = 173.3 Hz, C-Si), 35.1 (^1JPt-C = 114.0 Hz, $\underline{C}$=CHSi), 34.0 ($\underline{C}$(CH$_3$)$_3$), 33.8 ($\underline{C}$(CH$_3$)$_3$), 29.5 (C($\underline{C}$H$_3$)$_3$), 29.3 (C($\underline{C}$H$_3$)$_3$), 1.6 (SiCH$_{3\ eq..}$), -1.9 (SiCH$_{3\ ax.}$)
IR(KBr, cm^{-1}) : 1611, 1478, 1398, 1376, 1339, 1239, 1177, 1159, 1009, 996, 862, 836, 778, 737
MS(E.I.) m/z =640-639-638 (M$^{+°}$); 625-624-623 ([M-CH$_3$]$^{+°}$); 259 ([BenzNHC]$^{+°}$).
Mp = 142-144 °C

General procedure for the hydrosilylation reaction

A 0.5% weight per volume stock solution of each benzimidazolylidene platinum(0) complexes in toluene is prepared and used for the precise addition of the catalyst.

A three-necked 100 ml round-bottomed flask was loaded with 1-octene (5g, 45 mmol), MD'M (9g, 45 mmol), dodecane (5g, GC internal standard) and 56g of *o*-xylene (63 ml). The reaction vessel was heated at 72°C and was thermally equilibrated for 1-2h. The catalyst was injected (0.005 *mol%*) and the progress of the reaction was monitored from that instant. Samples (2 to 3 drops) were taken regularly (every 5 to 15 min.) and eluted with dichloromethane (2 ml) on a small column of activated charcoal, before being analyzed by GC. The reaction was typically over (>90% conversion of octene) within 6 hrs.

The data collected for these kinetic runs is supplied as an Excel spreadsheet with the electronic supporting information.