Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Expanded Ring N-Heterocyclic Carbenes: A Comparative Study of Ring Size in Palladium (0) Catalysed Mizoroki-Heck Coupling†

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Experimental

General remarks

All manipulations were performed using standard Schlenk techniques under an argon atmosphere, except where otherwise noted. All complexes after their formation were treated under aerobic conditions. Solvents of analytical grade were freshly distilled using an MBraun SPS-800 solvent purification system. Deuterated solvents for NMR measurements were distilled from the appropriate drying agents under N_2 immediately prior to use, following standard literature methods.[1] All other reagents were used as received. NMR spectra were obtained on a Bruker Avance AMX 400 or 500. The chemical shifts are given as dimensionless δ values and are frequency referenced relative to the peak for TMS for ^{1}H and ^{13}C. Coupling constants *J* are given in hertz as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as "s", "d", "t" or "m" for singlet, doublet, triplet or multiplet, respectively. Mass spectra were obtained in electrospray (ES) mode unless otherwise reported on a Waters Q-Tof micromass spectrometer. GC-MS data was obtained via internal standard method of quantification on an Agilent Technologies 6890N GC system with an Aligent Technologies 5973 inert MS detector with MSD. Column: Agilent 190915-433 capillary, 0.25 mm x 30 m x 0.25μm.

General protocol for the synthesis of halide salts

A mixture of 1 mmol of amidine, 0.5 mmol of K_2CO_3 and 1.2 mmol of dihalide in 25 ml of acetonitrile is heated under reflux. At the end of the reaction, the volatiles are removed in *vacuo*, the residue dissolved in dichloromethane and diethyl ether is slowly added until the product began to crystallise.

General protocol for the synthesis of palladium (0) dvtms complexes

The expanded ring NHC halide salt (3.16 mmol) was loaded into a flame driend Schlenk and dried under vacuum for 30 min prior to being suspended in dry toluene (20 ml) with ^{t}BuOK (4.24 mmol) added quickly in one portion. The reaction mixture was stirred at room temperature for 2 h generating the free carbene which was transferred to a flame dried Schlenk via a cannula. The Pd(dvtms) solution (3.16 mmol (8.2 % Pd)) was added to the free carbene solution resulting in a yellow to dark brown colour change. The solution was stirred overnight at room temperature yielding a light brown suspension, which was washed in n-pentane furnishing the desired complex.

1,3-Bis-(2,6-dimethylphenyl)-3,4,5,6-tetrahydro-pyrimidin-1-ium-Palladium (divinyltetramethyldisiloxane) 9. Yield: 41.58% (0.63 g). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.01 (2H, t, $^{3}J_{HH}$ = 6.4, p-CH), 6.98 (4H, d, $^{3}J_{HH}$ = 7.9, m-CH), 3.45 (4H, t, $^{3}J_{HH}$ = 5.6, NCH_2), 2.72 (2H, t, $^{3}J_{HH}$ = 5.3, NCH_2CH_2), 2.42 (6H, s, o-CH_3), 2.36 (6H, s, o-CH_3), 2.24 (4H, d, $^{3}J_{HH}$ = 13.6, HC=CH_2), 1.84 (2H, t, $^{3}J_{HH}$ = 14.07, HC=CH_2), 0.06 (6H, s, $SiCH_{3eq}$), -0.77 (6H, s, $SiCH_{3ax}$). ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ 226.67 (1C, s, NCN), 133.60 (2C, s, p-CH), 127.16 (1C, s, m-CH), 126.62 (1C, s, m-CH), 125.53 (1C, s, m-CH), 124.16 (1C, s, m-CH), 57.46 (4C, s, HC=CH_2), 55.27 (2C, s, NCH_2), 44.55 (2C, s, HC=CH_2), 20.19 (4C, s, o-CH_3), 16.77 (1C, s, NCH_2CH_2), 0.00 (2C, s, $SiCH_{3eq}$), -3.29 (2C, s, $SiCH_{3ax}$). MS (ES): *m/z* 520.13 (M + 3MeCN – dvtms) – $C_{26}H_{33}N_5Pd$ requires 520.18). Anal. Calcd for $C_{28}H_{42}N_2OSi_2Pd$: C, 57.46; H, 7.23; N, 4.78. Found: C, 57.34; H, 6.76; N, 4.45.

1,3-Bis-(2-methylphenyl)-3,4,5,6-tetrahydro-pyrimidin-1-ium-Palladium (divinyltetramethyldisiloxane) 10. Yield: 51.19% (0.73 g). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 7.05 (8H, m, Ar-H), 3.51 (4H, t $^{3}J_{HH}$ = 4.9, NCH_2), 2.37 (2H, t, $^{3}J_{HH}$ = 5.8, NCH_2CH_2), 2.31 (6H, s, o-CH_3), 1.99 (4H, d, $^{3}J_{HH}$ = 12.7, $HC{=}CH_2$), 1.53 (2H, t, $^{3}J_{HH}$ = 13.6, $HC{=}CH_2$), 0.09 (6H, s, $SiCH_{3eq}$), -8.21 (6H, s, $SiCH_{3ax}$). ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ 227.08 (1C, s, NCN), 133.32-128.01 (8C, ms, Ar-CH), 59.53 (4C, s, $HC{=}CH_2$), 56.11 (2C, s, NCH_2), 48.97 (2C, s, $HC{=}CH_2$), 24.17 (2C, s, o-CH_3), 20.19 (1C, s, NCH_2CH_2), 3.76 (2C, s, $SiCH_{3eq}$), 0.32 (2C, s, $SiCH_{3ax}$). MS (ES): *m/z* 452.11 (M + 2MeCN – dvtms).

1-(2-methoxyphenyl)-3-(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydro-pyrimidin-1-ium-Palladium (divinyltetramethyldisiloxane) 11. Yield: 53.64% (0.84 g). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 6.94 (2H, s, m-CH (Mes)), 6.65 (1H, t, $^{3}J_{HH}$ = 8.4, Ar-OCH_3), 6.63 (1H, d, $^{3}J_{HH}$ = 7.4, Ar-OCH_3), 6.59 (1H, d, $^{3}J_{HH}$ = 7.6, Ar-OCH_3), 6.48 (1H, t, $^{3}J_{HH}$ = 8.1, Ar-OCH_3), 3.75 (3H, s, OCH_3), 3.22 (4H, t, $^{3}J_{HH}$ = 5.7, NCH_2), 2.33 (2H, t, $^{3}J_{HH}$ = 5.2, NCH_2CH_2), 2.25 (3H, s, p-CH_3 (Mes)), 2.16 (6H, s, o-CH_3) (Mes)), 2.05 (4H, d, $^{3}J_{HH}$ = 14.2, $HC{=}CH_2$), 1.92 (2H, t, $^{3}J_{HH}$ = 12.4, $HC{=}CH_2$), -0.08 (6H, s, $SiCH_{3eq}$), -0.80 (6H, s, $SiCH_{3ax}$). ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ 226.52 (1C, s, NCN), 135.50 (1C, s, Ar-H), 135.21 (1C, s, Ar-H), 133.50 (1C, s, Ar-H), 128.36 (1C, s, Ar-H), 127.68 (1C, s, Ar-H), 126.15 (1C, s, Ar-H), 56.97 (4H, s, $HC{=}CH_2$), 53.97 2C, s, NCH_2), 44.52 (2C, s, $HC{=}CH_2$), 20.20 (2C, s, NCH_2CH_2), 19.24 (1C, s, CH_3), 16.66 (2C, s, o-CH_3), 16.24 (1C, s, p-CH_3), 0.00 (2C, s, $SiCH_{3eq}$), -3.41 (2C, s, $SiCH_{3ax}$). MS (ES): *m/z* 601.19 (M^+ - H).

1,3-Bis(2,6-dimethylphenyl)-4,5,6,7-tetrahydro-3H-[1,3]-diazipin-1-ium-Palladium (divinyltetramethyldisiloxane) 13. Yield: 37.51% (0.64 g). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 6.99 (6H, m, Ar-H), 4.00 (2H, t, $^{3}J_{HH}$ = 5.7, NCH_2), 3.92 (2H, t, $^{3}J_{HH}$ = 5.6, NCH_2), 2.67 (4H, t, $^{3}J_{HH}$ = 5.6, NCH_2CH_2), 2.53 (6H, s, o-CH_3), 2.39 (6H, s, o-CH_3), 2.22 (4H, d, $^{3}J_{HH}$ = 13.2, $HC{=}CH_2$), 1.79 (2H, t, $^{3}J_{HH}$ = 12.9, $HC{=}CH_2$), 0.09 (6H, s, $SiCH_{3eq}$), -0.75 (6H, s, $SiCH_{3ax}$). ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ 246.89 (1C, s, NCN), 130.46 (2C, s, m-CH), 129.94 (2C, s, m-CH), 128.61 (1C, s, p-CH), 128.61 (1C, s, p-CH), 61.92 (4H, s, $HC{=}CH_2$), 58.18 (2C, s, NCH_2), 56.72 (2C, s, $HC{=}CH_2$), 27.63 (1C, s, NCH_2CH_2), 27.41 (1C, s, NCH_2CH_2), 20.72

(2C, s, o-CH_3), 20.48 (2C, s, o-CH_3), 3.23 (2C, s, $SiCH_{3eq}$), 0.00 (2C, s, $SiCH_{3ax}$). MS (ES): *m/z* 597.15 (M^+ - H) – $C_{29}H_{44}N_2OSi_2Pd$ requires 598.20).

1,3-Bis(2-methylphenyl)-4,5,6,7-tetrahydro-3H-[1,3]-diazipin-1-ium-Palladium (divinyltetramethyldisiloxane) 14. Yield: 50.12% (0.81 g). ^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ 6.99 (8H, m, Ar-H), 3.96 (4H, t, $^3J_{HH}$ = 5.8, NCH_2), 3.02 (4H, t, $^3J_{HH}$ = 5.4, NCH_2CH_2), 2.36 (6H, s, p-CH_3), 2.19 (4H, d, $^3J_{HH}$ = 12.8, HC=CH_2), 2.03 (2H, t, $^3J_{HH}$ = 13.1, HC=CH_2), 0.07 (6H, s, $SiCH_{3eq}$), -0.75 (6H, s, $SiCH_{3ax}$). ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K): δ 128.69-124.41 (8C, ms, Ar-H), 62.36 (4C, s, HC=CH_2), 53.63 (2C, s, NCH_2), 52.49 (2C, s, HC=CH_2), 24.29 (2C, s, NCH_2CH_2), 16.89 (2C, s, o-CH_3), 0.00 (2C, s, $SiCH_{3eq}$), -3.33 (2C, s, $SiCH_{3ax}$). MS (ES): *m/z* 425.16 (M + MeCN – dvtms) – $C_{21}H_{25}N_3Pd$ requires 425.11).

General Heck Coupling Procedure

A 2-neck round bottom flask was charged with 4-bromoacetophenone (0.996g, 5 mmol) and sodium acetate (0.406g, 5.6 mmol) then degassed by successive vacuum-nitrogen cycles. N-N'-dimethylacetamide (10 ml) was injected followed by n-butyl acrylate (0.705g, 6 mmol) and decane (0.711g, 5 mmol) (internal standard). The reaction mixture was equilibrated to 120 ºC for 1 hour followed by the addition of 0.1 mol % of the appropriate palladium (0) complex. 0.5 ml samples were periodically taken every 30 minutes and prepared for GCMS analysis by washing with 5% HCl (5 ml) and extraction with HPLC DCM (2.5 ml).

Identification of the Heck Coupling Product (n-butyl-(E)-4-formylcinnamate)

The Heck coupling product was isolated by vacuum distillation. The stereochemistry of the product was determined by ^1H NMR based upon characteristic olefinic coupling constants. The two protons in the β-(E) isomer are mutually trans with typical $^3J_{HH}$ coupling constants of between 18 and 20 Hz whereas the two protons in the β-(Z) isomer are mutually cis with typical $^3J_{HH}$ coupling constants of between 12 and 16 Hz. The molecular weights of coupled products were determined by the molecular ion peaks present in the GC-MS analysis.

Figure 1 Comparative study of the influence of R group in 6-membered derivatives.

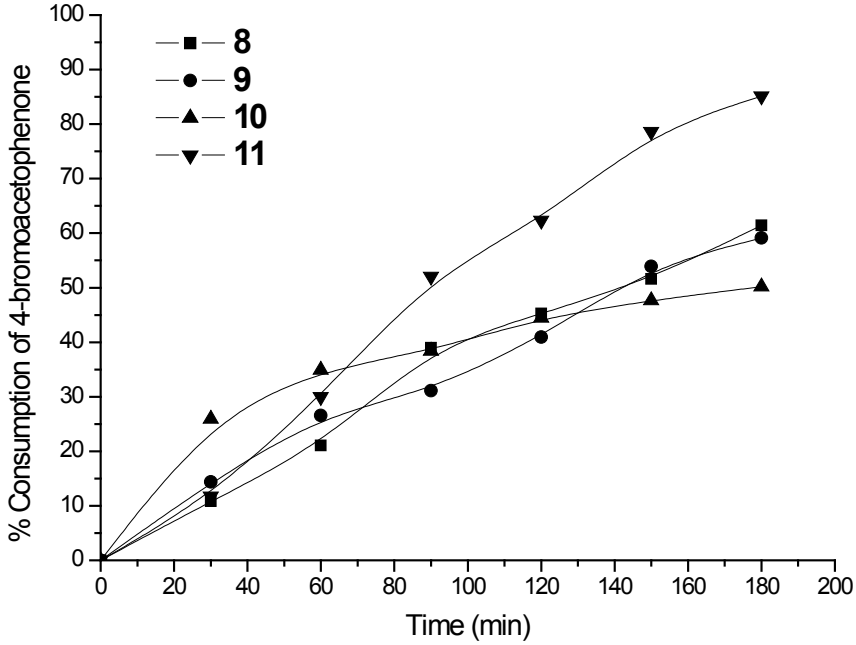
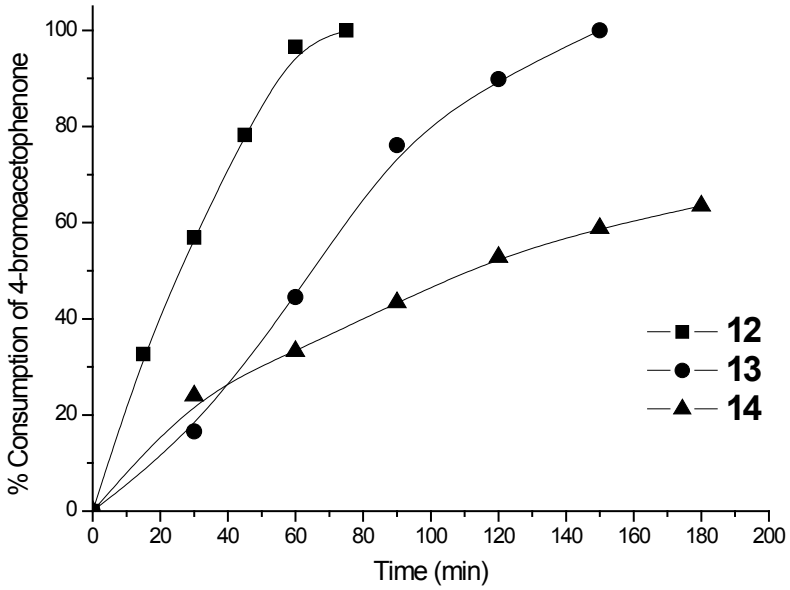


Figure 2 Comparative study of the influence of R group in 7-membered derivatives.



References

[1] D.D. Perrin, W.F.A. Armarego, Purification of Laboratory Chemicals, Pergamon, Oxford 1988.