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NMR data for η^3-allyl palladium complexes (4-13)

The ^{1}H and ^{13}C NMR data for the allyl moiety are given in Table E S 1 and Table E S 2 respectively. The remaining NMR data are listed below under each complex.

Endo- (**4a**) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 – 6.93 (m, aryl protons); 6.28 (br.s, CH-$N_2C_3HMe_2$-3,5); 3.79 (m, CH-$CHMe_2$); 2.65 (s, 5-CH_3-$N_2C_3HMe_2$-3,5); 2.05 (s, 3-CH_3-$N_2C_3HMe_2$-3,5); 1.25 (d, ^{3}J(H,H) = 6.4 Hz, CH_3-$CHMe_2$); 1.15 (d, ^{3}J(H,H) = 6.4 Hz, CH_3-$CHMe_2$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 158.5 – 129.7 (aryl carbons); 110.4 (s, *CH*-$N_2C_3HMe_2$-3,5); 53.2 (dd, ^{2}J(C,P) = 27.6 and 5.9 Hz, CH-$CHMe_2$); 26.1 (d, ^{3}J(C,P) = 9.2 Hz, CH_3-$CHMe_2$); 24.9 (d, ^{3}J(C,P) = 18.2 Hz, CH_3-$CHMe_2$); 16.2 (s, CH_3-$N_2C_3HMe_2$-3,5); 13.8 (s, CH_3-$N_2C_3HMe_2$-3,5).

Exo- (**4b**) ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.34 (br.s, CH-$N_2C_3HMe_2$-3,5); 3.79 (merged with CH-$CHMe_2$ signal arising from isomer **4a**, CH-$CHMe_2$); 2.61 (s, 5-CH_3-$N_2C_3HMe_2$-3,5); 2.30 (s, 3-CH_3-$N_2C_3HMe_2$-3,5); 1.37 (d, ^{3}J(H,H) = 6.4 Hz, CH_3-$CHMe_2$); 0.97 (d, ^{3}J(H,H) = 6.4 Hz, CH_3-$CHMe_2$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 110.4 (merged with CH-$N_2C_3HMe_2$-3,5 signal arising from isomer **4a**, CH-$N_2C_3HMe_2$-3,5); 53.2 (merged with CH-$CHMe_2$ signal arising from isomer **4a**, CH-$CHMe_2$); 26.0 (d, ^{3}J(C,P) = 9.3 Hz, CH_3-$CHMe_2$); 24.6 (d, ^{3}J(C,P) = 16.2 Hz, CH_3-$CHMe_2$); 16.1 (s, *CH_3*-$N_2C_3HMe_2$-3,5); 13.9 (d, ^{3}J(C,P) = 6.5, CH_3-$N_2C_3HMe_2$-3,5).

Endo- (**5a**) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 – 6.65 (m, aryl protons); 6.24 (d, ^{4}J(H,P) = 2.2 Hz, CH-$N_2C_3HMe_2$-3,5); 4.66 (m, CH-*CHMePh); 2.77 (s, 5-CH_3-$N_2C_3HMe_2$-3,5); 1.84 (d,

^{3}J(H,H) = 6.3 Hz, CH_3-*CHMePh); 1.78 (s, 3-CH_3-$N_2C_3HMe_2$-3,5). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 158.4 – 127.2 (m, aryl carbons); 110.5 (s, *CH*-$N_2C_3HMe_2$-3,5); 61.1 (dd, ^{2}J(C,P) = 24.0 and 6.8 Hz, CH-*CHMePh); 25.1 (d, ^{3}J(C,P) = 21.6 Hz, CH_3-*CHMePh); 15.8 (s, *CH_3*-$N_2C_3HMe_2$-3,5); 14.0 (d, ^{3}J(C,P) = 18.1 Hz, *CH_3*-$N_2C_3HMe_2$-3,5).

Exo- (**5b**) ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.31 (d, ^{4}J(H,P) = 2.5 Hz, CH-$N_2C_3HMe_2$-3,5); 4.66 (merged with CH-*CHMePh signal arising from isomer **5a**, CH-*CHMePh); 2.73 (s, 5-CH_3-$N_2C_3HMe_2$-3,5); 2.03 (s, 3-CH_3-$N_2C_3HMe_2$-3,5); 1.69 (d, ^{3}J(H,H) = 6.1 Hz, CH_3-*CHMePh). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 110.6 (s, CH-$N_2C_3HMe_2$-3,5); 60.7 (dd, ^{2}J(C,P) = 23.4 and 6.8 Hz, CH-*CHMePh); 25.0 (d, ^{3}J(C,P) = 20.9 Hz, CH_3-*CHMePh); 15.8 (merged with CH_3-$N_2C_3HMe_2$-3,5 signal arising from isomer **5a**, CH_3-$N_2C_3HMe_2$-3,5); 14.0 (merged with CH_3-$N_2C_3HMe_2$-3,5 signal arising from isomer **5a**, CH_3-$N_2C_3HMe_2$-3,5).

Endo, syn/syn- (**6a**) ^{1}H NMR (400 MHz, CD_3COCD_3): δ 7.90 – 7.01 (m, aryl protons); 6.52 (br.d, CH-$N_2C_3HMe_2$-3,5); 3.89 (m, CH-$CHMe_2$); 2.90 (s, 5-CH_3-$N_2C_3HMe_2$-3,5); 1.89 (s, 3-CH_3-$N_2C_3HMe_2$-3,5); 1.58 (d, ^{3}J(H,H) = 6.6 Hz, CH_3-$CHMe_2$); 0.96 (d, ^{3}J(H,H) = 6.4 Hz, CH_3-$CHMe_2$). ^{13}C NMR (100.6 MHz, 1:1 mixture of $CDCl_3$ and CH_2Cl_2): δ 158.5 – 129.7 (m, aryl carbons); 110.4 (s, CH-$N_2C_3HMe_2$-3,5); 64.9 (br.s, CH-$CHMe_2$); 25.6 – 13.1 (methyl carbon resonances).

Exo, *syn/syn*- (**6b**) ^{1}H NMR (400 MHz, CD_3COCD_3): δ 6.38 (br.d, CH-$N_2C_3HMe_2$-3,5); 3.89 (merged with CH-$CHMe_2$ signal arising from isomer **6a**, CH-$CHMe_2$); 2.71 (s, 5-CH_3-

$N_2C_3HMe_2$-3,5); 2.61 (s, 3-CH_3-$N_2C_3HMe_2$-3,5); 1.69 (d, $^3J(H,H)$ = 6.4 Hz, CH_3-$CHMe_2$); 0.82 (d, $^3J(H,H)$ = 6.4 Hz, CH_3-$CHMe_2$).

Exo, *anti/syn*- (**6c**) ^{1}H NMR (400 MHz, CD_3COCD_3): δ 6.53 (br.s, CH- $N_2C_3HMe_2$-3,5); 3.89 (merged with CH-$CHMe_2$ signal arising from isomer **6a**, CH-$CHMe_2$); 2.92 (s, 5-CH_3-$N_2C_3HMe_2$-3,5); 2.61 (s, 3-CH_3- $N_2C_3HMe_2$-3,5); 1.80 (d, $^3J(H,H)$ = 6.4 Hz, CH_3-$CHMe_2$); 0.63 (d, $^3J(H,H)$ = 6.4 Hz, CH_3-$CHMe_2$).

Endo, anti/syn- (**6d**) ^{1}H NMR (400 MHz, CD_3COCD_3): δ 6.43 (br.s, CH-$N_2C_3HMe_2$-3,5); 3.89 (merged with CH-$CHMe_2$ signal arising from isomer **6a**, CH-$CHMe_2$); 2.68 (s, 5-CH_3-$N_2C_3HMe_2$-3,5); 2.53 (s, 3-CH_3-$N_2C_3HMe_2$-3,5); 1.42 (d, $^3J(H,H)$ = 6.4 Hz, CH_3-$CHMe_2$); 1.05 (d, $^3J(H,H)$ = 6.3 Hz, CH_3-$CHMe_2$).

Endo, *syn/syn*- (**7a**) ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 – 6.60 (m, aryl protons); 6.20 (br.s, CH-$N_2C_3HMe_2$-3,5); 4.65 (m, CH-*CHMePh); 2.80 (s, 5-CH_3-$N_2C_3HMe_2$-3,5); 1.94 (d, $^3J(H,H)$ = 6.8 Hz, CH_3-*CHMePh); 1.69 (s, 3-CH_3-$N_2C_3HMe_2$-3,5). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 160.0 – 125.1 (aryl carbons); 110.4 (s, CH-$N_2C_3HMe_2$-3,5); 60.6 (dd, $^2J(C,P)$ = 24.8 and 6.7 Hz, CH-*CHMePh); 25.4 (d, $^3J(C,P)$ = 22.6 Hz, *CH_3*-*CHMePh); 18.5 (d, $^3J(C,P)$ = 4.0 Hz, CH_3-allyl *trans* to the coordinated phosphorus centre); 17.9 (s, CH_3-allyl *cis* to the coordinated phosphorus centre); 14.7 (s, CH_3-$N_2C_3HMe_2$-3,5); 13.7 (d, $^3J(C,P)$ = 17.6 Hz, CH_3-$N_2C_3HMe_2$-3,5).

Exo, *syn/syn*- (**7b**) ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.31 (br.s, CH-$N_2C_3HMe_2$-3,5); 4.65 (merged with CH-*CHMePh signal arising from isomer **7a**, CH-*CHMePh); 2.67 (s, 5-CH_3-$N_2C_3HMe_2$-

3,5); 2.30 (s, 3-CH_3-$N_2C_3HMe_2$-3,5); 1.45 (merged with CH_3-*CHMePh signal arising from isomer **7a**, CH_3-*CHMePh). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 110.7 (s, CH-$N_2C_3HMe_2$-3,5); 61.3 (dd, CH-*CHMePh); 25.3 (merged with CH_3-*CHMePh signal arising from isomer **7a**, CH_3-*CHMePh); 17.9 (br.s, CH_3-allyl *trans* to the coordinated phosphorus centre); 16.1 (s, CH_3-allyl *cis* to the coordinated phosphorus centre); 15.1 (s, *CH_3*-$N_2C_3HMe_2$-3,5).

Exo, anti/syn- (**7c**) ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.31 (merged with CH-$N_2C_3HMe_2$-3,5 signal arising from isomer **7b**, CH-$N_2C_3HMe_2$-3,5); 4.65 (merged with CH-*CHMePh signal arising from isomer **7a**, CH-*CHMePh); 2.76 (s, 5-CH_3-$N_2C_3HMe_2$-3,5); 2.05 (s, 3-CH_3-$N_2C_3HMe_2$-3,5); 1.80 (d, ^{3}J(H,H) = 6.9 Hz, CH_3-*CHMePh).

Endo, *anti/syn*- (**7d**) ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.42 (br.s, CH-$N_2C_3HMe_2$-3,5); 4.65 (merged with CH-*CHMePh signal arising from isomer **7a**, CH-*CHMePh); 2.67 (merged with 5-CH_3-$N_2C_3HMe_2$-3,5 signal arising from isomer **7b**, 5-CH_3-$N_2C_3HMe_2$-3,5); 2.33 (s, 3-CH_3-$N_2C_3HMe_2$-3,5); 1.80 (merged with CH_3-*CHMePh signal arising from isomer **7c**, CH_3-*CHMePh).

Endo, *syn/syn*- (**8a**) ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 – 6.58 (m, aryl protons); 6.00 (d, ^{4}J(H,P) = 1.7 Hz, CH-$N_2C_3HMe_2$-3,5); 3.55 (m, CH-$CHMe_2$); 2.61 (s, 5-CH_3-$N_2C_3HMe_2$-3,5); 1.28 (d, ^{3}J(H,H) = 6.5 Hz, CH_3-$CHMe_2$); 0.99 (s, 3-CH_3-$N_2C_3HMe_2$-3,5); 0.92 (d, ^{3}J(H,H) = 6.4 Hz, CH_3-$CHMe_2$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 159.0 – 125.6 (aryl carbons); 110.0 (s, CH-$N_2C_3HMe_2$-3,5); 53.6 (dd, ^{2}J(C,P) = 28.6 and 6.1 Hz, CH-$CHMe_2$); 25.9 (d, ^{3}J(C,P) = 7.4 Hz,

CH_3-$CHMe_2$); 25.1 (d, $^3J(C,P)$ = 20.5 Hz, CH_3-$CHMe_2$); 13.9 (s, CH_3-$N_2C_3HMe_2$-3,5); 13.7 (s, CH_3-$N_2C_3HMe_2$-3,5).

Endo, *syn/syn*- (**8b**) ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.89 (br.s, CH-$N_2C_3HMe_2$-3,5); 3.99 (m, CH-$CHMe_2$); 2.32 (s, 5-CH_3-$N_2C_3HMe_2$-3,5); 1.22 (s, 3-CH_3-$N_2C_3HMe_2$-3,5); 1.00 (merged with 3-CH_3-$N_2C_3HMe_2$-3,5 signal arising from isomer **8a**, CH_3-$CHMe_2$); 0.12 (d, $^3J(H,H)$ = 6.8 Hz, CH_3-$CHMe_2$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 110.9 (s, CH-$N_2C_3HMe_2$-3,5); 56.7 (d, $^2J(C,P)$ = 20.9 Hz, CH-$CHMe_2$); 23.3 (br.s, CH_3-$CHMe_2$); 14.5 (d, $^3J(C,P)$ = 13.8 Hz, CH_3-$N_2C_3HMe_2$-3,5); 11.7 (d, $^4J(C,P)$ = 6.9 Hz, CH_3-$N_2C_3HMe_2$-3,5).

Exo, *syn/syn*- (**8c**) ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.10 (br.s, CH-$N_2C_3HMe_2$-3,5); 3.89 (m, CH-$CHMe_2$); 2.43 (s, 5-CH_3-$N_2C_3HMe_2$-3,5); 2.27 (s, 3-CH_3-$N_2C_3HMe_2$-3,5); 0.84 (d, $^3J(H,H)$ = 6.7 Hz, CH_3-$CHMe_2$); 0.32 (d, $^3J(H,H)$ = 6.6 Hz, CH_3-$CHMe_2$).

Endo, *syn/syn*- (**9**) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 – 6.46 (m, aryl protons); 6.01 (br.s, CH-$N_2C_3HMe_2$-3,5); 4.45 (m, CH-*CHMePh); 2.76 (s, 5-CH_3-$N_2C_3HMe_2$-3,5); 1.81 (d, $^3J(H,H)$ = 6.8 Hz, CH_3-*CHMePh); 0.79 (s, 3-CH_3-$N_2C_3HMe_2$-3,5). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 159.1 – 124.3 (aryl carbons); 110.8 (s, CH-$N_2C_3HMe_2$-3,5); 60.9 (dd, $^2J(C,P)$ = 24.6 and 6.7 Hz, CH-*CHMePh); 25.4 (d, $^3J(C,P)$ = 22.4 Hz, CH_3-*CHMePh); 14.1 (d, $^3J(C,P)$ = 18.2 Hz, CH_3-$N_2C_3HMe_2$-3,5); 13.5 (s, CH_3-$N_2C_3HMe_2$-3,5).

Endo, syn/syn- (**10**) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 – 6.94 (m, aryl protons); 5.77 (d, $^4J(H,P)$ = 2.2 Hz, CH-$N_2C_3HMe_2$-3,5); 4.46 (m, CH-*CHMePh); 1.91 (s, 5-CH_3-$N_2C_3HMe_2$-3,5); 1.22 (d, $^3J(H,H)$ = 6.8 Hz, CH_3-*CHMePh); 0.65 (s, 3-CH_3-$N_2C_3HMe_2$-3,5). ^{13}C NMR (100.6

MHz, $CDCl_3$): δ 158.5 – 127.5 (aryl carbons); 109.7 (br.s, CH-$N_2C_3HMe_2$-3,5); 60.4 (dd, $^2J(C,P)$ = 28.2 and 6.0 Hz, CH-*CHMePh); 23.8 (d, $^3J(C,P)$ = 10.0 Hz, CH_3-*CHMePh); 13.1 (s, CH_3-$N_2C_3HMe_2$-3,5); 12.4 (d, $^3J(C,P)$ = 16.1 Hz, CH_3-$N_2C_3HMe_2$-3,5).

Endo (**11a**) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 – 7.24 (m, aryl protons); 6.15 (br.s, CH-$N_2C_3HMe_2$-3,5); 4.70 (m, CH-$CHMe_2$); 2.40 (s, 3-CH_3-$N_2C_3HMe_2$-3,5); 1.87 (s, 5-CH_3-$N_2C_3HMe_2$-3,5); 1.13 (d, $^3J(H,H)$ = 6.7 Hz, CH_3-$CHMe_2$); 0.44 (d, $^3J(H,H)$ = 6.9 Hz, CH_3-$CHMe_2$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 157.7 – 126.9 (aryl carbons); 110.8 (s, CH-$N_2C_3HMe_2$-3,5); 57.6 (s, CH-$CHMe_2$), 23.3 (s, CH_3-$CHMe_2$), 23.1 (s, CH_3-$CHMe_2$); 13.8 (s, CH_3-$N_2C_3HMe_2$-3,5); 13.7 (s, CH_3- $N_2C_3HMe_2$-3,5).

Exo- (**11b**): ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.15 (merged with CH-$N_2C_3HMe_2$-3,5 signal arising from isomer **11a**, CH-$N_2C_3HMe_2$-3,5); 4.70 (merged with CH-$CHMe_2$ signal arising from isomer **11a**, CH-$CHMe_2$); 2.40 (merged with 3-CH_3-$N_2C_3HMe_2$-3,5 signal arising from isomer **11a**, 3-CH_3-$N_2C_3HMe_2$-3,5); 2.19 (br.s, 5-CH_3-$N_2C_3HMe_2$-3,5); 1.07 (br.d, CH_3-$CHMe_2$); 0.44 (merged with CH_3-$CHMe_2$ signal arising from isomer **11a**, CH_3-$CHMe_2$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 110.8 (merged with CH-$N_2C_3HMe_2$-3,5 signal arising from isomer **11a**, CH-$N_2C_3HMe_2$-3,5); 57.6 (merged with CH-$CHMe_2$ signal arising from isomer **11a**, CH-$CHMe_2$); 23.3 (s, CH_3-$CHMe_2$); 23.1 (s, CH_3-$CHMe_2$); 13.8 (merged with CH_3-$N_2C_3HMe_2$-3,5 signal arising from isomer **11a**, CH_3-$N_2C_3HMe_2$-3,5).

Exo, syn/syn- (**12a**) ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 – 7.05 (m, aryl protons), 6.21 (br.s, CH-$N_2C_3HMe_2$-3,5); 5 4.65 (m, CH-$CHMe_2$); 2.40 (s, 3-CH_3-$N_2C_3HMe_2$-3,5); 2.12 (s, 5-CH_3-

$N_2C_3HMe_2$-3,5); 1.12 (d, $^3J(H,H)$ = 6.1 Hz, CH_3-$CHMe_2$); 0.45 (d, $^3J(H,H)$ = 6.9 Hz, CH_3-$CHMe_2$). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 156.1-129.3 (aryl carbons); 110.7 (br.s, CH-$N_2C_3HMe_2$-3,5); 57.8 (dd, $^2J(C,P)$ = 20.1 and 4.0 Hz, CH-$CHMe_2$); 23.6 (s, CH_3-$CHMe_2$), 23.3 (s, CH_3-$CHMe_2$); 18.3 (d, $^3J(C,P)$ = 13.3 Hz, CH_3-allyl *trans* to the coordinated phosphorus centre); 17.5 (s, CH_3-allyl *cis* to the coordinated phosphorus centre); 14.0 (s, CH_3-$N_2C_3HMe_2$-3,5); 13.8 (s, CH_3-$N_2C_3HMe_2$-3,5).

Endo, syn/syn- (**12b**) ^1H NMR (500 MHz, $CDCl_3$): δ 6.19 (br.d, CH-$N_2C_3HMe_2$-3,5); 4.65 (merged with CH-$CHMe_2$ signal arising from isomer **12a**, CH-$CHMe_2$); 2.38 (s, 3-CH_3-$N_2C_3HMe_2$-3,5); 2.16 (s, 5-CH_3- $N_2C_3HMe_2$-3,5); 1.11 (d, $^3J(H,H)$ = 6.1 Hz, CH_3-$CHMe_2$); 0.37 (d, $^3J(H,H)$ = 6.9 Hz, CH_3-$CHMe_2$). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 18.3 (d, $^3J(C,P)$ = 13.8 Hz, CH_3-allyl *trans* to the coordinated phosphorus centre); 17.4 (s, CH_3-allyl *cis* to the coordinated phosphorus centre).

Endo, anti/syn- (**12c**) ^1H NMR (500 MHz, $CDCl_3$): δ 6.19 (merged with CH-$N_2C_3HMe_2$-3,5 signal arising from isomer **12b**, CH-$N_2C_3HMe_2$-3,5); 4.65 (merged with CH-$CHMe_2$ signal arising from isomer **12a**, CH-$CHMe_2$); 2.37 (s, 3-CH_3-$N_2C_3HMe_2$-3,5); 1.89 (s, 5-CH_3-$N_2C_3HMe_2$-3,5); 1.12 (merged with CH_3-$CHMe_2$ signal arising from isomer **12a**, CH_3-$CHMe_2$); 0.51 (d, $^3J(H,H)$ = 7.0 Hz, CH_3-$CHMe_2$).

Exo, syn/syn- (**13a**) ^1H NMR (400 MHz, $CDCl_3$): δ 6.16 (d, $^4J(H,P)$ = 2.6 Hz, CH-$N_2C_3HMe_2$-3,5); 4.41 (m, CH-$CHMe_2$); 2.44 (s, 3-CH_3-$N_2C_3HMe_2$-3,5); 2.31 (s, 5-CH_3-$N_2C_3HMe_2$-3,5); 0.98 (d, $^3J(H,H)$ = 6.8 Hz, CH_3-$CHMe_2$); 0.29 (d, $^3J(H,H)$ = 6.6 Hz, CH_3-$CHMe_2$). ^{13}C NMR

(100.6 MHz, 1:1 mixture of $CDCl_3$ and CH_2Cl_2): δ 110.9 (br.s, CH-$N_2C_3HMe_2$-3,5); 58.3 (br.d, CH-$CHMe_2$, ^2J(C,P) = 20.1 and 4.0 Hz); 22.8 (s, CH_3-$CHMe_2$); 22.6 (s, CH_3-$CHMe_2$); 14.2 (s, CH_3-$N_2C_3HMe_2$-3,5); 13.5 (s, CH_3-$N_2C_3HMe_2$-3,5).

Endo, syn/syn- (**13b**) ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 – 6.70 (m, aryl protons); 5.88 (d, ^4J(H,P) = 2.8 Hz, CH-$N_2C_3HMe_2$-3,5); 4.41(merged with CH-$CHMe_2$ signal arising from isomer **13a**, CH-$CHMe_2$); 2.28 (s, 3-CH_3-$N_2C_3HMe_2$-3,5); 2.11 (s, 5-CH_3-$N_2C_3HMe_2$-3,5); 0.98 (merged with CH_3-$CHMe_2$ signal arising from isomer **13a**, CH_3-$CHMe_2$); 0.29 (merged with CH_3-$CHMe_2$ signal arising from isomer **13a**, CH_3-$CHMe_2$). ^{13}C NMR (100.6 MHz, 1:1 mixture of $CDCl_3$ and CH_2Cl_2): δ 148.3 – 126.2 (aryl carbons); 110.1 (br.s, CH-$N_2C_3HMe_2$-3,5); 57.6 (br.d, CH-$CHMe_2$); 23.0 (s, CH_3-$CHMe_2$); 22.9 (s, CH_3-$CHMe_2$); 14.4 (s, CH_3-$N_2C_3HMe_2$-3,5); 13.6 (s, CH_3-$N_2C_3HMe_2$-3,5).

Table E. S .1 : Selected ^{1}H NMR data[a] for complexes **4 -13**

Complex	H_s	H_a	H_s'	H_a'	H_c	CH_3[b]	CH_3[c]
4a	4.73 br t (7.3)[d] (7.3)[e]	2.16 dd (13.8)[d] (11.0)[e]	3.25 br d (6.5)[d]	1.63[f]	5.58 m	–	–
4b	4.30 br t (7.2)[d] (7.2)[e]	3.55 dd (13.0)[d] (10.5)[e]	2.76 br	2.79 br	4.09 m	–	–
5a	4.60[f]	2.07 dd (13.6)[d] (10.5)[e]	3.26d (6.5)[d]	1.59[f]	5.48 m	–	–
5b	4.15 br t (7.1)[d] (7.1)[e]	3.41dd (13.3)[d] (10.8)[e]	2.99d (6.7)[d]	2.68 d (12.4)[d]	4.06 m	–	–
6a	–	2.95 m	–	2.7 m	5.57 dd (12.7)[d] (10.8)[d]	1.55 dd (11.2)[e] (6.4)[d]	0.94 dd (10.2)[e] (6.5)[d]
6b	–	4.83 m	–	3.45 m	3.89 t (11.1)[d]	1.51 dd (11.1)[e] (6.4)[d]	0.20 dd (8.3)[e] (6.3)[d]
6c	–	5.02 m	3.79 m	–	4.18[f]	1.50[f]	0.86 t (7.3)[d] (7.3)[e]
6d	–	(–)[g]	3.55	–	5.60 m	(–)[g]	-0.34 t (7.3)[d] (7.3)[e]
7a	–	2.65 m	–	2.50 m	5.22 dd (12.7)[d] (10.7)[d]	1.45[f]	0.85 dd (10.3)[e] (6.3)[d]
7b	–	4.43	–	3.25 m	3.86 t (11.5)[d]	1.46 dd (10.5)[e] (6.5)[d]	0.29 dd (8.3)[e] (6.3)[d]

7c	–	4.70 m	3.74 m	–	3.93 dd (13.5)[d] (8.0)[d]	1.45[f]	0.73 t (7.1)[d] (7.1)[e]
7d	–	3.80 m	3.30 m	–	5.33 dd (12.2)[d] (7.8)[d]	1.74 dd (11.0)[e] (6.3)[d]	-0.39 t (7.2)[d] (7.2)[e]
8a	–	4.28 t (13.5)[d] (13.5)[e]	–	3.46 d (10.8)[d]	6.29 dd (13.5)[d] (10.8)[d]	–	–
8b	–	6.11[f]	–	5.57 dt (13.3)[d] (13.3)[e] (5.1)[e]	6.48 t (13.3)[d]	–	–
8c	–	5.28 dt (9.2)[d] (9.2)[e] (5.4)[e]	–	5.38 dt (12.9)[d] (13.0)[e] (5.3)[e]	6.79 dd (12.9)[d] (9.2)[d]	–	–
9	–	4.16 t (12.8)[d] (12.8)[e]	–	3.33 d (9.6)[d]	6.26 dd (13.4)[d] (10.8)[d]	–	–
10	–	4.19 t (12.0)[d] (12.0)[e]	–	3.56 d (10.8)[d]	6.30 dd (12.0)[d] (10.8)[d]	–	–
11a	4.78 t (6.2)[d,e]	3.57 t (12.7)[d,e]	4.23 d (6.6)[d]	2.56 d (12.9)[d]	5.50 m	–	–
11b	4.88 br s	3.57[f]	3.79 br s	3.15 br d	5.50[f]	–	–
12a	–	4.36 m	–	3.84 m	5.29 t (12.0)[d]	1.95 dd (12.1)[e] (6.2)[d]	0.93 dd (9.8)[e] (6.5)[d]
12b	–	4.41 m	–	3.49 m	5.39 t (12.0)[d]	1.90 dd (12.1)[e] (6.2)[d]	1.30 dd (10.2)[e] (6.5)[d]
12c	–	4.75 m	4.75[f]	–	5.22 dd	1.99[f]	0.31 t (7.5)[d,e]

13a	–	5.80 t (12.4)[d,e]	–	4.97 t (11.8)[d,e]	6.62 t (12.4)[d]	–	–
13b	–	5.65 t (12.4)[d,e]	–	5.12 t (12.4)[d,e]	6.45 t (12.4)[d]	–	–

Abbreviations: s, singlet; br, broad; br s, broad singlet; d, doublet; t, triplet; dd, doublet of doublets; dt, doublet of triplets; m, multiplet.

[a] Solvent $CDCl_3$ for all the complexes except for complex **6** for which acetone-d_6 was used as solvent. Coupling constants in Hz are given in parenthesis. [b] Allyl CH_3 *trans* to the coordinated phosphorus centre. [c] CH_3-allyl *cis* to the coordinated phosphorus centre. [d] J(H,H). [e] J(P,H). [f] Overlapped with signals arising from other allyl or ligand protons. [g] The signal could not be assigned unequivocally.

Table E. S .2: The ^{13}C NMR data[a] for the allyl carbon nuclei of η^3-allyl palladium complexes(**4**-**13**)

Complex	$\delta(C_t)$	$\delta(C_t')$	$\delta(C_t) - \delta(C_t')$	δC_c
4a	80.3 d (31.7)[b]	59.1 d (3.2)[c]	21.2	119.9 d (6.3)
4b	76.1 d (30.8)[b]	61.5 d (3.1)[c]	14.6	122.1 d (5.9)
5a	80.0 d (32.3)[b]	58.8 d (3.6)[c]	21.2	119.5 d (6.5)
5b	75.1 d (31.5)[b]	61.4 d (3.6)[c]	13.7	121.7 d (6.1)
6a	103.3 d (26.2)[b]	65.0 d (6.0)[c]	38.3	119.6 d (6.0)
6b	92.8 d (27.1)[b]	68.8 d (4.0)[c]	24.0	122.5 d (6.0)
7a	103.3 d (27.4)[b]	66.0 d (5.3)[c]	37.3	120.0 d (5.9)
7b	92.4 d (26.8)[b]	69.9 d (5.2)[c]	22.5	122.0 d (5.8)
7c	90.5 d (26.2)[b]	69.6 d (5.2)[c]	20.9	116.8 d (5.9)
8a	102.1 d (25.5)[b]	72.2 d (6.2)[c]	29.9	110.1 d (6.1)
8b[d]	85.7 dd (33.3)[b](10.6)[c]	95.0 dd (29.7)[b](11.2)[c]	9.3	112.2 t (11.8)
8c[d]	92.0 dd (31.9)[b](10.4)[c]	89.3 dd (33.7)[b](9.7)[c]	2.7	113.8 t (11.0)
9	101.6 d (25.9)[b]	73.1 d (6.2)[c]	28.5	111.0 d (5.9)
10	101.6 d (24.1)[b]	72.1 d (7.0)[c]	29.5	110.6 d (5.0)
11a	74.3 d (32.9)[b]	70.3 br s	4.0	120.2 d (7.0)
11b	76.6 d (30.8)[b]	70.3[e]	6.3	121.2 br s
12a	92.4 d (30.5)[b]	84.0 d (5.4)[c]	8.4	121.2 d (6.9)
12b	90.4 d (30.7)[b]	86.5 d (6.0)[c]	3.9	120.9 d (8.2)
13a	93.7 d (28.4)[b]	86.9 d (6.9)[c]	6.8	108.1 d (6.9)
13b	91.1 d (27.8)[b]	89.7 d (6.0)[c]	1.4	108.5 d (7.0)

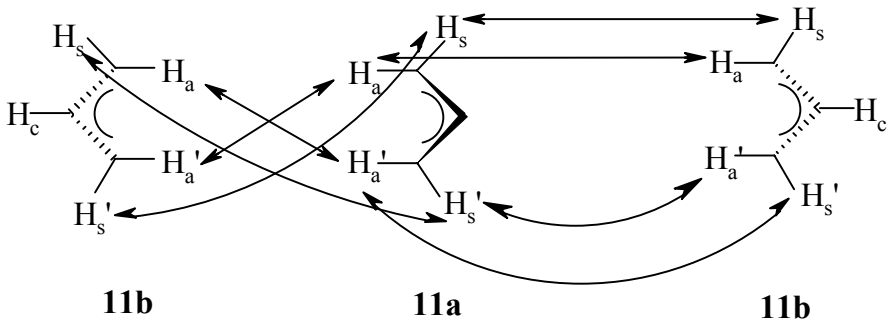
Abbreviations: d, doublet; dd, doublet of doublets; t, triplet; br s, broad singlet.

[a] The ^{13}C NMR spectra were recorded in $CDCl_3$ at 298 K except for **6** and **13** in which cases a 1:1 mixture of $CDCl_3$ and CH_2Cl_2 was used. The $^{13}C–^{31}P$ coupling constants are given in parenthesis. C_t is terminal allyl carbon *trans* to the coordinated phosphorus atom. C_t' is terminal allyl carbon *cis* to the coordinated phosphorus centre. C_c is central allyl carbon. [b] $J(P,C)_{trans}$. [c] $J(P,C)_{cis}$. [d] For the isomers **8b** and **8c**, C_t and C_t' are the terminal allyl carbon *trans* to $–PPh_2$ and *trans* to $–PPh(N_2C_3HMe_2\text{-}3,5)$ groups respectively. [e] Overlapped with signal arising from the terminal allyl carbon resonance of major isomer, **11a**.

Stereodynamic Behaviour of Allyl Complexes 11-13 in Solution

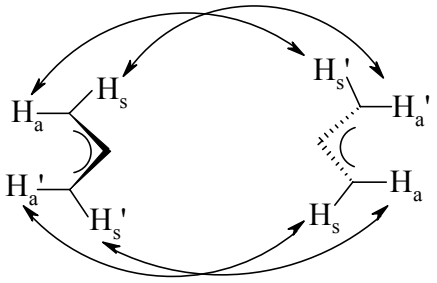
The selective exchanges observed between the two diastereomers of **11** are summarised in Scheme E.S.1.

Scheme E. S. 1



The exchange cross-peaks in the phase sensitive $^{1}H - {}^{1}H$ NOESY spectrum are identified as negative phase cross-peaks (appear as dis-continuous cross-peaks) while the positive phase cross-peaks (appear as continuous cross-peaks) which usually arise because of proximal relationships of the interacting protons. There are various positive phase NOE cross-peaks between the two isomers **11a** and **11b**. This type of unusual positive NOE between the two diastereomers arises as a result of a fast dynamic process. The exchange observations are summarised in Scheme E.S. 2.

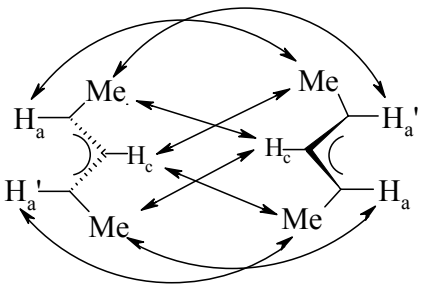
Scheme E.S. 2



11a **11b**

The $^{1}H–^{1}H$ NOESY spectrum of **12** (illustrated in Fig. E.S.1) shows positive NOE cross-peaks between the isomers **12a** and **12b** (see Scheme E.S.3) and the pattern of this interaction is similar to that observed for isomers **11a** and **11b** (shown in Scheme E.S. 2) indicating that similar mechanistic pathways operate in both the cases.

Scheme E.S.3



12a **12b**

Fig. E.S.1 The ^{1}H-^{1}H NOESY spectrum of complex **12** showing positive phase NOE cross-peaks between the isomers **12a** and **12b**.