Eur. J. Inorg. Chem. **2009** · © WILEY-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2009 · ISSN 1434–1948

SUPPORTING INFORMATION

Title: A Simple Building-Block Route to (Phosphanyl-carbene)palladium Complexes via Intermolecular Addition of Functionalised Phosphanes to Isocyanides

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Ref. No.: I200801067

General procedure for the synthesis of complexes 7 – 22.

A solution of the relevant phosphine ligand (0.25 mmol) in anhydrous CH_2Cl_2 (5mL) was added dropwise to a solution of the palladium complex (0.25 mmol) in 5 mL of anhydrous CH_2Cl_2 under nitrogen. The solution was then stirred for 1 h, during which period the colour changed to intense yellow or orange and in some cases a precipitate may form. Next, a solution of the respective isocyanide (0.25 mmol) in anhydrous CH_2Cl_2 (5 mL) was added dropwise to the reaction mixture. The colour of the solution may change to yellow or become colourless, in several cases the previously formed precipitate will redissolve and a precipitate may form again, or the product will precipitate from the homogeneous solution. In case a precipitate forms, these are only soluble in DMSO or methanol. Generally, after stirring overnight, the solvent is removed under vacuum (in case of a precipitate this may also be filtered off and washed with CH_2Cl_2 and diethyl ether and dried in vacuum). The residue is then suspended in pentane or diethyl ether and washed a few times and dried in vacuum.

Analytical data of new compounds:

7. Orange solid; recrystallised from pentane/CH_2Cl_2. Yield: 38%.

^{1}H NMR (dmso-d6): δ 8.40-7.40 (m, 15H), 5.75 (s, 1H), 1.29 (s, 9H).

$^{31}P\{^1H\}$ NMR (dmso-d6): □ 56.8.

FAB-MS: m/z 503 (M^+ - Cl + H).

Elemental analysis $C_{23}H_{25}PN_2PdCl_2$: C: 43.98 (51.37) H: 4.97 (4.68) N: 3.80 (5.20).

8. Beige solid. Yield: 78%.

^{1}H NMR (dmso-d6): δ 11.03 (s, 1H), 8.00-6.60 (m, 14H), 1.10 (s, 9H).

^{13}C NMR (dmso-d6): δ 175.8, 159.5, 135.1, 134.7, 133.5, 132.2, 129.8, 129.2, 121.9, 120.0, 117.0, 116.1, (overlapping signals in aromatic region) 59.6, 29.3.

$^{31}P\{^1H\}$ NMR (dmso-d6): δ 24.2.

FAB-MS: m/z 526 (M^+ - H).

Elemental analysis $C_{22}H_{24}PNOPdCl_2$: C: 49.89 (50.16) H: 4.46 (4.59) N: 2.60 (2.65).

9. Beige solid. Yield: 72%.

^{1}H NMR (CD_2Cl_2): δ 10.68 (s, 1H), 8.00-6.60 (m, 14H), 4.07 (s, 2H), 3.63 (s, 3H).

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 21.5.

FAB-MS: m/z 540 (M^+ - CH_3), 517 (M^+ - Cl –2H), 482 (M^+ - 2 Cl –2H).

Elemental analysis $C_{22}H_{20}PNO_3PdCl_2$: C: 46.25 (47.63) H: 3.45 (3.63) N: 2.38 (2.52).

10. Greyish solid. Yield: 81%.

^{1}H NMR (dmso-d6): δ 11.16 (very br s, 1H), 8.00-6.80 (m, 14H), 1.90-1.00 (m, 11H).

$^{31}P\{^{1}H\}$ NMR (dmso-d6): δ 24.4.

FAB-MS: m/z 482 (M^+ - 2 Cl –H).

Elemental analysis $C_{25}H_{26}PNOPdCl_2$: C: 50.46 (53.16) H: 4.83 (4.64) N: 2.60 (2.47).

11. Greyish solid. Yield: 75% (ca. 95% pure).

^{1}H NMR (dmso-d6): δ 11.10 (br s, 1H), 8.00-6.80 (m, 18H), 3.77 (s, 3H).

$^{31}P\{^{1}H\}$ NMR (dmso-d6): δ 24.5.

FAB-MS: m/z 516 (M^+ - 2 Cl –2H).

Elemental analysis $C_{26}H_{22}PNO_2PdCl_2$: C: 52.78 (53.04) H: 3.70 (3.76) N: 2.30 (2.37).

12. Yellow solid. Yield: 48%.

^{1}H NMR (CD_2Cl_2): δ 8.20-6.80 (m, 14H), 6.18 (s, 1H), 4.71 (s, 2H), 1.09 (s, 9H).

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 27.0.

FAB-MS: m/z 516 (M^+ - Cl - H), 480 (M^+ - 2 Cl - 2 H) (dimer in MS).

Elemental analysis $C_{24}H_{26}PNOPdCl_2$: C: 56.89 (52.15) H: 6.43 (4.74) N: 3.38 (2.53).

13. Yellow solid. Yield: 58% (ca. 80% pure).

^{1}H NMR (CD_2Cl_2): δ 8.20-6.80 (m, 14H), 6.18 (s, 1H), 4.11 (s, 2H), 3.62 (s, 3H) (signals at 4.11 and 3.62 tentatively assigned).

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 14.9.

FAB-MS: m/z 534 (M^+ - Cl + H), 4496 (M^+ - 2 Cl - 2 H)

Elemental analysis $C_{23}H_{22}PNO_3PdCl_2$: C: 48.49 (48.57) H: 3.96 (3.90) N: 3.38 (3.46).

14. Yellow solid. Yield: 62% (ca. 95% pure).

^{1}H NMR ($CDCl_3$): δ 8.20-6.60 (m, 18H), 6.25 (s, 1H), 5.52 (s, 2H), 3.79 (s, 3H).

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 24.6.

Elemental analysis $C_{27}H_{24}PNO_2PdCl_2$: C: 53.74 (53.80) H: 4.15 (4.01) N: 2.24 (2.32).

15. Colourless solid. Yield: 81%.

^{1}H NMR (CD_2Cl_2): δ 3.99 (br, 1H), 2.60-1.10 (m, 28H).

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 114.2.

FAB-MS: m/z 470 (M^+ - Cl).

Elemental analysis $C_{19}H_{38}PNOPdCl_2$: C: 45.12 (45.21) H: 7.65 (7.58) N: 2.68 (2.77).

16. Yellow solid. Yield: 76%.

^{1}H NMR (CD_2Cl_2): δ 4.96 (s, 1H), 4.05 (broad, 2H, tentatively assigned), 3.76 (s, 3H), 2.60-0.80 (m, 28H).

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 118.0.

Elemental analysis $C_{18}H_{34}PNO_3PdCl_2$: to be submitted.

17. Yellow solid. Yield: 84%.

^{1}H NMR (CD_2Cl_2): δ 7.42 (d, 2H, ^{1}J(HH) = 3.6 *Hz*), 6.98 (d, 2H, ^{1}J(HH) = 3.6 *Hz*), 3.80 (s, 3H), 2.60-1.10 (m, 28H).

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 115.6.

FAB-MS: m/z 518 (M^+ - Cl - H).

Elemental analysis $C_{22}H_{36}PNO_2PdCl_2$: C: 45.77 (47.62) H: 6.35 (6.54) N: 2.32 (2.52).

18. Yellow solid. Yield: n.d.

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 32.4, 31.9 (1:2 ratio; possibly two isomers).

Elemental analysis $C_{17}H_{30}PNO_3PdCl_2$: C: 46.98 (47.12) H: 4.60 (4.67) N: 2.54 (2.49).

19. Pale yellow solid. Yield: 79%.

^{1}H NMR (CD_2Cl_2): δ 4.30 (s, 2H), 2.20-1.10 (m, 31H).

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 51.5.

Elemental analysis $C_{18}H_{34}PNOPdCl_2$: C: 44.30 (44.23) H: 6.95 (7.01) N: 2.76 (2.86).

20. Yellow solid. Yield: 68%.

^{1}H NMR (CD_2Cl_2): δ 10.09 (br s, 1H), 4.61 (s, 2H), 4.11 (d, 2H, ^{2}J(PH) = 2.4 *Hz*), 3.80 (s, 3H), 2.60-0.90 (m, 22H).

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 97.9.

Elemental analysis $C_{17}H_{30}PNO_3PdCl_2$: C: 42.86 (40.45) H: 5.82 (5.99) N: 2.65 (2.77).

21. Yellow solid. Yield: 91%.

$^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 51.9.

22. Yellow solid. Yield: 94%.

$^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 99.2.