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FULL PAPER

Co-ordination chemistry and metal catalysed carbonylation reactions using 8-(diphenylphosphino)methylaminoquinoline: a ligand that displays monodentate, bidentate and tridentate co-ordination modes

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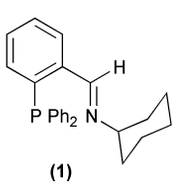
Reaction of (diphenylphosphino)methanol with 8-aminoquinoline gives a novel potentially tridentate ligand, 8-(diphenylphosphino)methylaminoquinoline. The co-ordination chemistry of this ligand has been studied. Reaction with $[Cp^*RhCl_2]_2$ gave a *P*-monodentate complex that was characterised by X-ray crystallography. On addition of one equivalent of silver salts, a 50 : 50 mixture of a tridentate dicationic complex and the starting material is formed. We describe this somewhat unusual co-ordination behaviour as 2/3 labile. If two equivalents of silver salts are used, the tridentate complex can be isolated and fully characterised. Iridium, ruthenium, palladium and platinum complexes are also described in which the ligand acts as mono- bi-, and tri-dentate. The ligand was also tested as a stabilising ligand in palladium and rhodium catalysed carbonylation reactions.

Hemilabile ligands containing P,N donor sets continue to provide novel applications in catalysis and organometallic chemistry.[1] Important examples are the large range of chiral P,N ligands that have been shown to provide excellent enantioselectivity in several asymmetric processes,[2] the use of phosphine-imine ligands (**1**) in palladium catalysed C–C bond forming reactions,[3] pyridylphosphine (**2**)–palladium complexes that catalyse the carbonylation of alkynes,[4] and nickel promoted C–C bond forming reactions.[5] We have recently become interested in synthesising new amine containing phosphine ligands and applying them in catalysis. We have prepared a variety of novel PN ligands and observed a varying propensity towards the formation of η^2-*P,N*-chelate complexes.[6] The co-ordination chemistry observed for these ligands obviously has a profound effect on their catalytic properties, and we have recently found that PN ligands such as (**3**), that do not readily form stable chelate complexes have considerable potential in palladium catalysed C–C bond forming reactions.[7]



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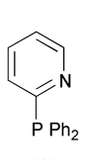

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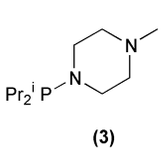

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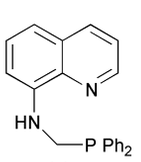

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We envisaged that a phosphine ligand that contains two additional N donor atoms might show interesting co-ordination behaviour. Furthermore, these types of ligand have not been studied in transition metal catalysed reactions that are particularly suited to the use of PN ligands. In this paper we report on the synthesis of a new phosphine ligand (8-(diphenylphosphino)methylaminoquinoline) (**4**) that contains two auxiliary amine substituents, its co-ordination chemistry and application in rhodium and palladium catalysed carbonylation reactions.

Experimental

General

All manipulations were carried out under an atmosphere of nitrogen, unless stated otherwise. All solvents were either freshly distilled from an appropriate drying agent (THF, Et_2O, CH_2Cl_2) or obtained as anhydrous grade. ^1H, and ^{31}P NMR spectra were recorded using a "Varian 2000" 300 MHz spectrometer. IR spectra were recorded as KBr discs (prepared in air) on a Perkin Elmer PE1720 FTIR/RAMAN spectrometer. Silver salts, diphenylphosphine, formaldehyde, 8-aminoquinoline (Accros Organics Ltd.), were purchased and used as received. $[Cp^*MCl_2]_2$ (M = Ir, Rh), $[(COD)PtCl_2]$, $[(PhMe_2P)PtCl_2]_2$, and $[(Cym)RuCl_2]_2$ (Cym = *para*-cymene) were prepared by literature methods.[8–11] All IR bands above 1000 cm^{-1} have been quoted to serve as a fingerprint.

X-Ray crystallography

Crystal structures were obtained using a Bruker SMART diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293 K. Intensity data were collected using 0.3 or 0.15° width ω steps accumulating area detector frames spanning a hemisphere of reciprocal space for all structures. All data were corrected for Lorentz, polarisation and long term intensity fluctuations. Absorption effects were corrected on the basis of multiple equivalent reflections. Structures were solved by direct methods and refined by full-matrix least squares against F^2 (SHELXTL)[12] for all data with $I > 3\sigma(I)$. See Table 1 for details.

CCDC reference numbers 177445 and 177446.

See http://www.rsc.org/suppdata/dt/b2/b200401a/ for crystallographic data in CIF or other electronic format.

 DOI: 10.1039/b200401a

Table 1 Crystal data for compounds (**4**) and (**5**)

	(**4**)	(**5**)
Empirical formula	$C_{22}H_{19}N_2P$	$C_{32}H_{34}Cl_2N_2PRh$
M	342.36	651.39
Crystal system	Orthorhombic	Orthorhombic
Space group	$Pna2_1$	$Pna2_1$
a/Å	8.6824(6)	21.779(2)
b/Å	25.822(2)	8.4708(8)
c/Å	8.2049(5)	16.304(2)
U/Å^3	1839.5(2)	3007.9(5)
Z	4	4
μ/mm^{-1}	0.155	0.822
Reflections measured	7576	12242
Independent reflections	2566	4269
Final *R*1, *wR*2[$I > 2\sigma(I)$]	0.0388, 0.0743	0.0390, 0.0749

8-(Diphenylphosphino)methylaminoquinoline (4)

A solution of (diphenylphosphino)methanol (2.585 g, 11.955 mmol) in degassed acetonitrile (30 ml) was added slowly (*ca.* 2–5 h) to a boiling solution of 8-aminoquinoline in acetonitrile (1.72 g, 11.955 mmol in 30 ml solvent). The reaction mixture was held at reflux overnight prior to cooling and the addition of magnesium sulfate. Filtration (using a filter stick) followed by removing all volatile material gave the crude product (of varying purity) in high yield. Size exclusion chromatography (Biobeads SX80) under anaerobic conditions using degassed dichloromethane as eluent (product is second fraction) and removal of solvents *in vacuo* yielded the analytically pure material as an orange oil that solidified on standing (1.95 g, 5.70 mmol, 48%). Found: C, 76.95; H, 5.53; N, 7.70. $C_{22}H_{19}N_2P$ requires: C, 77.18; H, 5.59; N, 8.18%. IR (ν_{max}/cm^{-1}) 3412, 3070, 1610, 1574, 1524, 1479, 1432, 1385, 1342, 1249, 1228, 1124. ^{31}P NMR (121.4 MHz; $CDCl_3$): δ −20.4. ^{1}H NMR (300 MHz; $CDCl_3$): δ 4.2 (2H, dd, J = 5 Hz, other coupling not fully resolved H^1 and H^2), 6.6 (1H, s, br, H^3), 6.9 (1H, d, J = 7.6 Hz, H^7), 7.15 (1H, dd, J = 0.9, 8.2 Hz, H^6), 7.25–7.7 (12H, m, P-aryl, H^5 and H^8), 8.1 (1H, dd, J = 1.7, 8.3 Hz, H^9), 8.7 (1H, dd, J = 1.7, 4.2 Hz, H^4). ^{13}C NMR (75. 5 MHz, $CDCl_3$) δ 43.7 (d, J = 11 Hz), 105.2, 114.1, 121.1, 127.4, 128.4, 128.5, 128.7 132.7 (d, J = 18.2 Hz), 135.6, 136.6 (d, J = 13.4 Hz), 138.0, 144,7, 147.2.

[Cp*RhCl$_2$(*P*-8-dppmaq)] (5)

This compound was obtained by the addition of a CH_2Cl_2 solution of 8-dppmaq (**4**) to a CH_2Cl_2 solution of $[Cp^*RhCl_2]_2$. After stirring for 30 min, solvent was reduced to near dryness and Et_2O added to give a red precipitate (essentially quantitative yield of pure material) that was dried *in vacuo*. Recrystallisation by slow diffusion (CH_2Cl_2/Et_2O) gave a few high quality crystals suitable for an X-ray crystal structure determination. Found: C, 58.29; H, 4.93; N, 4.07. $C_{32}H_{34}N_2PRhCl_2$ requires: C, 59.00; H, 5.26; N, 4.30%. IR (ν_{max}/cm^{-1}) 3359, 3043, 1611, 1574, 1522, 1479, 1440, 1422, 1379, 1340, 1192, 1123, 1026. ^{31}P NMR (121.4 MHz; $CDCl_3$): δ 31.5 (J_{P-Rh} = 141 Hz). ^{1}H NMR (300 MHz; $CDCl_3$): δ 1.4 (15H, d, J_{H-P} = 3.3 Hz), 5.0 (2H, d, J_{H-P} = 7.4 Hz, H^1 and H^2), 6.4 (1H, d, br, J_{H-H} = 8 Hz, H^3), 6.8 (1H, d, J = 8.0 Hz, H^7), 6.95 (1H, t, J = 8.0 Hz, H^6), 7.2–7.6 (8H, m, P-aryl/quinolineH), 7.9 (1H, d, J = 8.0 Hz, H^9), 8.0 (4H, t, J = 8.7 Hz, PArH), 8.5 (1H, d, J = 2.8 Hz, H^4). ^{13}C NMR (75. 5 MHz, $CDCl_3$) δ 5.4, 40.8 (d, J = 25 Hz), 95, 102.4, 110.4, 117.7, 124.4, 124.9 (d, J = 8.7 Hz), 127.8, 131.7 (d, J = 8.7 Hz), 132.6, 140.2, 143.3. FAB MS: *m*/*z* 651 (MH)$^+$, 615 (M − Cl)$^+$, 580 (M − 2Cl)$^+$. HRMS (ES+): Found: 615.1201, M − Cl requires 615.1203.

[Cp*Rh(8-dppmaq)]2BF$_4$ (6)

Addition of two equivalents of silver tetrafluoroborate to a solution of (**5**) gave, after filtration through Celite™ complex (**6**) as a green/yellow solid in high purity in essentially quantitative yield. Found: C, 51.37; H, 4.33; N, 3.68; $C_{32}H_{34}N_2PRhB_2F_8$ requires: C, 50.97; H, 4.54; N, 3.71%. IR (ν_{max}/cm^{-1}) 3423, 3058, 1640, 1618, 1588, 1574, 1513, 1437, 1378, 1315, 1261, 1034. ^{31}P NMR (121.4 MHz; $CDCl_3$): δ −20.1 (J_{P-Rh} = 118 Hz). ^{1}H NMR (300 MHz; $CDCl_3$): δ 1.6 (15H, d, J_{H-Rh} = 4.1 Hz), 4.8 (2H, dd app. (app. = apparent), J = 4.8, 15.8 Hz, H^1 and H^2), 6.7 (1H, m, H^3), 7.3–8.2 (14H, m, PArH and quinolineH), 8.5 (1H, d, J = 8.3 Hz, H^9), 9.55 (1H, d, J = 4.9 Hz, H^4). ^{13}C NMR (75. 5 MHz, $CDCl_3$) δ 8.9, 53.4, 101.8, 122 (dd app. J_{C-P} = 50Hz), 126.7 (d, J_{C-P} = 39 Hz), 129 (d, J_{C-P} = 9 Hz), 129.8, 130.2, 130.3, 130.4, 130.5 132.3 (d, J_{C-P} = 11 Hz), 133.0, 133.3, 133.4, 140.0, 144.3 (d, J_{C-P} = 27 Hz), 157.4. HRMS (ES+): Found: 667.1546, (M − 2BF$_4$) requires 667.1544.

[Cp*IrCl$_2$(*P*-8-dppmaq)] (7)

This compound was obtained in a similar fashion to the analogous rhodium complex, and precipitated from CH_2Cl_2 solution with diethyl ether to give a burgundy coloured solid. Yield: 50 mg, 6.75 × 10^{-5} mol, 41%. Found: C, 51.96; H, 4.30; N, 3.83. $C_{32}H_{34}N_2PCl_2Ir$ requires: C, 51.89; H, 4.63; N, 3.78%. IR (ν_{max}/cm^{-1}) 3357, 3045, 1612, 1574, 1522, 1479, 1440, 1422, 1379, 1340, 1191, 1122, 1102. ^{31}P NMR (121.4 MHz; $CDCl_3$): δ −1.64. ^{1}H NMR (300 MHz; $CDCl_3$): δ 1.4 (15H, d, J_{H-P} = 1.92 Hz) 5.0 (2H, d, J = 7.2 Hz, H^1 and H^2), 6.4 (1H, d, J = 8 Hz, H^3), 6.8 (1H, d, J = 8.0 Hz, H^7), 6.95 (1H, t, J = 7.8 Hz, H^6), 7.2–7.6 (8H, m, PArH and quinolineH), 7.9 (5H, m, PArH and quinolineH), 8.5 (1H, dd, J = 1.7, 4.0 Hz, H^4). ^{13}C NMR (75. 5 MHz, $CDCl_3$) δ 8.2, 42.4 (d, J_{C-P} = 32 Hz), 92.1, 105.6, 113.6, 121.0, 127.6, 128.0 (d, J_{C-P} = 9.7 Hz), 131.0, 134.7 (d, J_{C-P} = 8.7 Hz), 135.8, 146.5. HRMS (ES+): Found: 669.2012, M − 2Cl − H requires 669.2014.

[Cp*Ir(8-dppmaq)]2BF$_4$ (8)

Compound (**8**) was prepared similarly to the analogous rhodium complex, using 50 mg, 6.75 × 10^{-5} mol of (**7**), and 26 mg, 1.35 × 10^{-4} mol of silver tetrafluoroborate, giving after centrifugation, (**8**) (57 mg, quantitative yield). Found: C, 45.77; H, 3.98; N, 3.25. $C_{32}H_{34}N_2PIrB_2F_8$ requires: C, 45.57; H, 4.00; N, 3.32%. IR (ν_{max}/cm^{-1}) 3438, 2919, 1630, 1589, 1574, 1514, 1438, 1382, 1316, 1261, 1083. ^{31}P NMR (121.4 MHz; $CDCl_3$): δ −38.7. ^{1}H NMR (300 MHz; $CDCl_3$): δ 1.65 (15H, d, J_{H-P} = 2.9 Hz), 5.56 (2H, dd app., J = 16, 2.5 Hz, H$_1$ and H$_2$), 7.3–8.2 (14H, m, PArH and quinolineH), 8.4 (1H, d, J = 8.1 Hz, ArH), 8.8 (1H, t, J = 8.6 Hz, H^6) 9.65 (1H, d, J = 5.3 Hz, H^4). ^{13}C NMR (75. 5 MHz, $CDCl_3$) δ 7.3, 95.7, 126.8, 127.8, 129.3, 130.2, 130.4 (d, 8 Hz), 130.8, 132.6 (d, J_{C-P} = 11.5 Hz), 133.3 (d, J_{C-P} = 11.5 Hz), 133.7, 140.1, 146.4, 157.6. ESMS 757, M − BF$_4$, 669, M − BF$_4$ − HBF$_4$.

[(Cym)RuCl$_2$(*P*-8-dppmaq)] (9)

This compound was obtained in similar fashion to the monodentate Rh and Ir compounds using 8-dppmaq (81 mg, 2.4 × 10^{-4} mol) and $[(Cym)RuCl_2]_2$ (72 mg, 1.18 × 10^{-4} mol), and precipitated from a concentrated CH_2Cl_2 solution with diethyl ether. Yield: 114 mg, 0.176 mmol, 74%. Found: C, 58.81; H, 4.76; N, 4.20. $C_{32}H_{33}N_2PCl_2Ru$ requires: C, 59.26; H, 5.13; N, 4.32%. IR (ν_{max}/cm^{-1}) 3373, 3041, 1612, 1574, 1522, 1481, 1433, 1380, 1339, 1275, 1220, 1194, 1125, 1099. ^{31}P NMR (121.4 MHz; $CDCl_3$): δ 26.4. ^{1}H NMR (300 MHz; $CDCl_3$): δ 0.85 (6H, d, J = 6.9 Hz, Cym CH(CH_3)$_2$), 1.8 (3H, s, Cym CH_3), 2.4 (1H, m, CymCH) 4.7 (2H, d, J = 7.0 Hz, H^1 and H^2), 5.2 (2H, d, J = 6.1 Hz), 6.1 (2H, m), 6.8 (1H, d, J = 8 Hz, H^7), 7.0 (1H, t, J = 8.2 Hz, H^6), 7.1–7.5, (8H, m, ArH), 7.8–8.0 (6H, m, ArH), 8.5 (1H, dd, J = 4.1, 1.7 Hz). ^{13}C NMR (75. 5 MHz, $CDCl_3$) δ 17.2, 21.5, 30.1, 39.0 (d, J = 26 Hz), 86.0, 90.0, 104, 108, 114, 121, 127.4, 128.2 (J = 9.4 Hz), 130.8, 131.4, 134.1 (d, J = 8 Hz), 146.6. HRMS (ES+): Found: 649.0888, MH$^+$ requires 649.0874.

cis- and *trans*-[(*P*-8-dppmaq)$_2$PdCl$_2$] (10) and (11)

To a stirred solution of 8-dppmaq (125 mg, 0.365 mmol) in dichloromethane (8 ml) was added [(COD)PdCl$_2$] (52 mg, 0.183 mmol) in one portion. This reaction was stirred for one hour prior to reducing the solvent volume by half, and precipitating the compound with diethyl ether. The precipitate was washed with Et$_2$O and dried *in vacuo* to give an orange solid. Yield: 115 mg, 0.133 mmol, 73%. Found: C, 60.85; H, 4.57; N, 6.04. $C_{44}H_{38}N_4PCl_2Pd$ requires: C, 61.30; H, 4.44; N, 6.50%. IR (ν_{max}/cm^{-1}) 3374, 3049, 1612, 1574, 1517, 1479, 1435, 1380, 1339, 1255, 1226, 1101, 819, 742. ^{31}P NMR (121.4 MHz; $CDCl_3$): δ 25.7 (s, assumed to be *cis*), 14.2 (s, assumed to be *trans*). ^{1}H NMR (300 MHz; $CDCl_3$): δ 4.63 (2H, d, J = 6.9 Hz) and 4.81 (2H, d, J = 6.9 Hz) (signal for *cis* and *trans* isomers), 6.44 (1H, s, br) and 6.50 (1H, s, br) (signals for *cis* and *trans* isomers), 6.9–8.2 (15H, m, ArH for both *cis* and *trans*), 8.6 (1H, d, J = 4.3 Hz). HRMS (ES+): Found: 825.1306, $C_{44}H_{38}N_4P_2$-PdCl [M − Cl]$^+$ requires 825.1295.

cis-[(8-dppmaq)$_2$PtCl$_2$] (12)

To a stirred solution of 8-dppmaq (133mg, 0.403 mmol) in dichloromethane (8 ml) was added [(COD)PtCl$_2$] (75 mg, 0.202 mmol) in one portion. This reaction was stirred for one hour prior to reducing the solvent volume by half, and precipitating the compound with diethyl ether. The precipitate was washed with Et$_2$O and dried *in vacuo* to give a purple coloured solid. Yield: 0.115 mg, 0.121 mmol, 60%. Found: C, 56.24; H, 3.57; N, 5.76. $C_{44}H_{38}N_4PCl_2Pt$ requires: C, 55.59; H, 4.03; N, 5.89%. IR (ν_{max}/cm^{-1}) 3365, 3057, 1612, 1574, 1516, 1446, 1436, 1380, 1338, 1258, 1227, 1199, 1102. ^{31}P NMR (121.4 MHz; $CDCl_3$): δ 6.10 (s = Pt satellites, J_{P-Pt} = 3653 Hz). ^{1}H NMR (300 MHz; $CDCl_3$): δ 4.72 (2H, d, J = 5.8 Hz, H^1 and H^2), 6.54 (1H, d, J = 7.7 Hz, H^3), 6.57 (1H, t, J = 6.7 Hz, H^7), 6.98 (6H, t, J = 7.1 Hz, ArH), 7.15 (1H, t, J = 8.0 Hz, ArH), 7.27 (1H, t, J = 7.3 Hz, ArH), 7.32 (1H, dd, J = 4.1, 8.2 Hz, ArH), 7.56 (4H, t, J = 8.6 Hz, PArH and quinolineH), 8.0 (1H, dd, J = 7.4, 1.8 Hz, H^9), 8.59 (1H, dd, J = 4.1, 1.7 Hz, H^4). ^{13}C NMR (75.4 MHz; $CDCl_3$): δ 41.7 (d, J = 49 Hz), 102.9, 111.7, 118.4, 124.3, 125.1 (t, J = 5.4 Hz), 128.1, 130.9 (t, J = 4.3 Hz), 132.6, 135.0, 140.2, 144.1. HRMS (ES+): Found: 914.1926, $C_{44}H_{38}N_4P_2PtCl$ [M − Cl]$^+$ requires 914.1908.

Reaction of (12) with silver salts

To a stirred solution of [(8-dppmaq)$_2$PtCl$_2$] in dichloromethane was added silver perchlorate or silver tetrafluoroborate (one or two equivalents) in one portion. This reaction was stirred for overnight prior to filtration through Celite (or centrifugation), and dried *in vacuo*. The crude products were analysed spectroscopically. Attempts to obtain analytically pure material by recyrstallisation/size exclusion chromatography were unsuccessful. IR (ν_{max}/cm^{-1}) 3337, 3055, 1620 (sh), 1613, 1576, 1518, 1473, 1437, 1381, 1100. ^{31}P NMR (121.4 MHz; $CDCl_3$): major product: δ 4.65 (d, $^2J_{P-P}$ = 14.2 Hz, $^1J_{P-Pt}$ = 3686 Hz), 2.60 (d, $^2J_{P-P}$ = 14.2 Hz, $^1J_{P-Pt}$ = 3734 Hz). ^{1}H NMR (300 MHz; $CDCl_3$): the proton NMR was obtained from the crude mixture, thus making it difficult to obtain detailed information and meaningful integrals. δ 3.6 (2H, d, J = 15.8 Hz), 4.5 (m), 4.8 (1H, m), 6.6–8.0 (m, ArH), 8.17 (d, J = 7.14 Hz), 8.26 (d, J = 7.14Hz), 8.87 (dd, J = 1.4, 4.1 Hz), 9.74 (d, J = 3 Hz). MS (ES+): Found: 878.2148, M − Cl − ClO_4 requires 878.2142. Also M − ClO_4 present as highest mass ion.

cis-[(PhMe$_2$P)(8-dppmaq)PtCl$_2$] (13)

A solution of 8-dppmaq (98 mg, 0.286 mmol) in CH_2Cl_2 (5 ml) was added to a solution of the platinum dimer [(PhMe$_2$P)PtCl$_2$]$_2$ (116 mg, 0.143 mmol). After stirring for one hour, solvent was reduced to half the volume and Et$_2$O added to give a purple precipitate. Yield: 110 mg, 0.147 mmol, 52%. Found: C, 46.83; H, 3.63; N, 3.68. $C_{30}H_{30}N_2P_2Cl_2Pt\cdot0.5CH_2Cl_2$ requires: C, 46.43; H, 3.96; N, 3.55%. IR (ν_{max}/cm^{-1}), 3385, 3051, 1611, 1573, 1516, 1479, 4 1435, 1380, 1337, 1124, 1103. ^{31}P NMR (121.4 MHz; $CDCl_3$): δ −15.20 (d + Pt satellites, $^2J_{P-P}$ = 15.6 Hz, $^1J_{P-Pt}$ = 3519 Hz), 5.70 (d + Pt satellites, ^2J = 15.6 Hz, ^1J = 3685 Hz). ^{1}H NMR (300 MHz; $CDCl_3$): δ 1.62 (6H, d, J_{H-P} = 11.3 Hz), 4.71 (2H, d, J = 6.0 Hz, H^1 and H^2), 5.27 (0.6H, s, CH_2Cl_2), 6.38 (1H, d, J = 7.7 Hz, H^7), 6.50 (1H, s, br, H^3), 6.9–7.7 (18H, m, ArH), 8.0 (1H, d, 8.0 Hz, H^6), 8.6 (1H, dd, J = 1.7, 4.1 Hz, H^4). HRMS (ES+) Found: 710.1210; $C_{30}H_{30}N_2PtP_2Cl$ (M − Cl)$^+$ requires 710.1221.

Carbonylation and hydroformylation reactions

These were conducted in a stainless steel autoclave held at constant pressure and connected to a ballast vessel from which CO (or syngas) was fed. Reaction rates were determined by measuring gas uptake over time, and further confirmed by GCMS analysis of the reaction products. The identities of the reaction products were established by comparison of retention times and mass spectra with authentic samples.

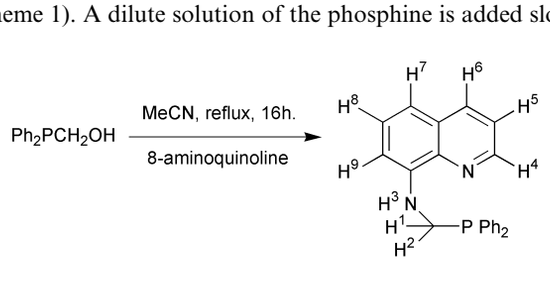
Carbonylation of phenylacetylene. A golden solution of Pd(OAc)$_2$ (1.83×10^{-5} mol), 2-PyPPh$_2$ (**2**) (3.64×10^{-4} mol), and *p*-$MeC_6H_4SO_3H\cdot H_2O$ (7.29×10^{-4} mol) in MeOH (5 ml) was added to the autoclave. The solution was flushed with several cycles of CO (*ca*. 20 bar) while stirring. The autoclave was then pressurised (55 bar) and brought to 60 °C. Phenyl acetylene (1.82×10^{-2} mol) was then injected and the pressure brought up to 60 bar. The gas uptake was followed over time.

Hydroformylation of 1-hexene. Rh(acac)CO$_2$ (0.01 mol dm^{-3}) and 8-dppmaq (0.23 mol dm^{-3}) in toluene (4 ml) were added to the autoclave which was then flushed with syngas. The autoclave was then pressurised (14 bar) and stirred at 100 °C for one hour to allow the catalyst to form. Hex-1-ene (1 ml) was injected and the pressure adjusted to 20 bar. The gas uptake was followed over time.

Results

(a) Ligand synthesis

A simple way to prepare a PNN type phosphine, would be the condensation of a diamine with Ph_2PCH_2OH. This type of reaction is a useful method of phosphine synthesis as products of high purity can often be obtained under mild conditions. Ligand (**4**), which we have given the acronym 8-dppmaq, is obtained by the condensation reaction of diphenylphosphinomethanol with 8-aminoquinoline in refluxing acetonitrile (Scheme 1). A dilute solution of the phosphine is added slowly



(4)

Scheme 1

to the aminoquinoline to prevent di-substitution, although some side products are observed in the crude product. The ligand is obtained in analytically pure form after size exclusion chromatography under anaerobic conditions. On one occasion, this synthesis gave essentially pure ligand directly with no need for any purification. Although we anticipated (**8**) to act as a P,N bidentate ligand, the possibility of tridentate co-ordination is also present.

(b) X-Ray crystal structure of (4)

Orange crystals of 8-dppmaq could be obtained by layering a CH_2Cl_2 solution with hexane. The crystal structure of (**4**), shown in Fig. 1, shows that 8-dppmaq forms a monomeric

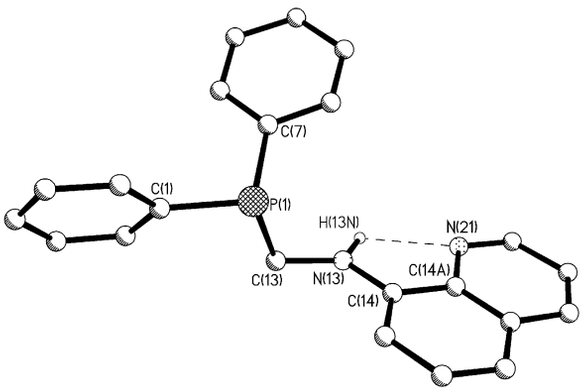
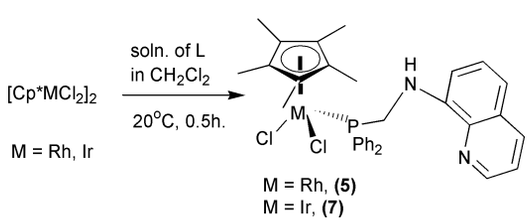


Fig. 1 X-Ray crystal structure of 8-dppmaq (**4**). Selected bond lengths (Å) and angles (°): P(1)–C(1) = 1.832(3), P(1)–C(7) = 1.835(4), P(1)–C(13) = 1.870(3), C(13)–N(13) = 1.429(4), C(14)–N(13) = 1.373(4), C(14A)–N(21) = 1.374(8); N(13)–C(13)–P(1) = 112.3(2), C(14)–N(13)–C(13) = 125.9(3).

structure in the solid state in which the aromatic NH forms an intramolecular hydrogen bond with the quinoline nitrogen (hydrogen bond acceptor) H(13N) ··· N(21) = 2.14(3) Å; N(13) ··· N(21) = 2.676(4) Å; N(13)–H(13N) ··· N(21) = 113(3)°. Selected bond lengths and angles are shown in the figure legend.

(c) Rhodium, iridium and ruthenium complexes derived from 8-dppmaq

A brief study of the co-ordination chemistry shown by this ligand was carried out prior to any catalytic testing. As a starting point, the reaction of this ligand with $[Cp^*RhCl_2]_2$ (and subsequent removal of chloride ions) seemed ideal as we had recently studied the reactions of this metal fragment with several other PN ligands.[6] Reaction of (**4**) and $[Cp^*RhCl_2]_2$ gives the monodentate complex (**5**) (see Scheme 2). It is assigned



Scheme 2

monodentate co-ordination by comparison of its IR and ^{1}H NMR data with that of the free ligand (no major changes). The large downfield shift in the ^{31}P NMR signal from (**5**) (with respect to the free ligand) is fairly typical of a monodentate Rh^{III} complex, as is the magnitude of $^1J_{P–Rh}$. The fact that a monodentate complex is formed suggests that (**4**) does not form extremely strong chelates. We have reported an example of a cationic complex of type [(η^2-L-*P,N*)Rh(Cp*)Cl]Cl with one PN ligand.[6]

The crystal structure of (**5**) (Fig. 2) shows this complex to be a monomeric compound of octahedral geometry. The Cp* ligand occupies three co-ordination sites of this octahedron. There is an asymmetry regarding the Rh–C bond lengths within the η^5-Cp* ligand (Rh–C between 2.144(8) and 2.221(7) Å) which reflects whether the carbon is *trans* to the strongly bound phosphine ligand or the chloride ligands, that exert a much lesser

Table 2 Selected bond lengths (Å) and angles (°) for (**5**)

Rh(1)–Cl(1)	2.413(3)	Rh(1)–P(1)	2.322(2)
Rh(1)–Cl(2)	2.414(3)	P(1)–C(1)	1.806(8)
Rh(1)–C(31)	2.171(8)	P(1)–C(7)	1.820(7)
Rh(1)–C(32)	2.168(5)	P(1)–C(13)	1.869(6)
Rh(1)–C(33)	2.144(8)	N(13)–C(14)	1.372(9)
Rh(1)–C(34)	2.221(7)	C(13)–N(13)	1.444 (8)
Rh(1)–C(35)	2.219(7)	C(14A)–N(21)	1.349(11)
P(1)–Rh(1)–Cl(1)	87.91(6)	Cl(1)–Rh(1)–Cl(2)	91.84(6)
C(14)–N(13)–C(13)	124.6(7)	P(1)–Rh(1)–Cl(2)	87.26(6)

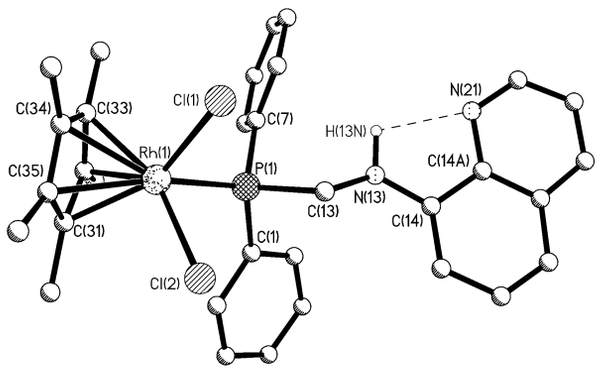
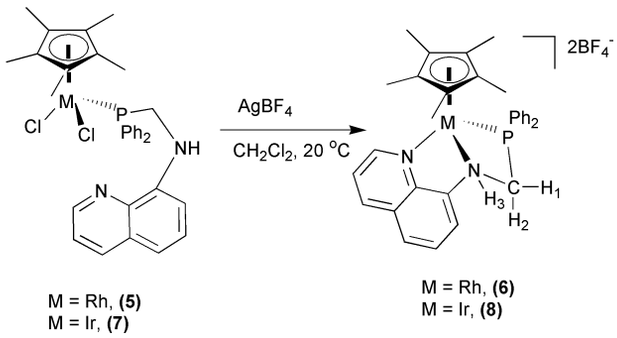


Fig. 2 X-Ray crystal structure of [Cp^*RhCl_2(8-dppmaq)] (**5**).

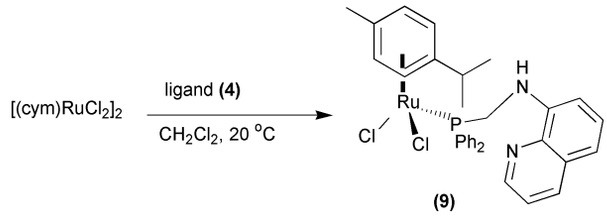
trans influence. The angles between chloride and phosphine ligands are close to the idealised 90°. Rh–C, Rh–P, and Ph–Cl bond lengths are fairly typical for this type of complex.[6] A notable feature of this structure is the intramolecular hydrogen bond between the quinoline nitrogen and the NH functionality (N(13) ··· N(21) = 2.661(9) Å), which is very similar to that found in the free ligand. It is possible that the presence of this hydrogen bond makes the nitrogen atoms less susceptible to co-ordination to transition metals. The ligand geometry and bond lengths within the free ligand and the monodentate complex are very similar. Selected bond lengths and angles are shown in Table 2.

Addition of one equivalent of silver tetrafluoroborate to the monodentate complex (**5**) generates a 1 : 1 mixture of a new complex and the starting material. The new complex has its NMR signal significantly upfield from that of the monodentate compound (δ −20.1 *vs*. 31.5 ppm). This is strong evidence that a four membered chelate ring is present, as this effect has been observed in all other four membered phosphorus containing rings.[13] The ^{1}H NMR spectrum of this mixture shows the proton *ortho* to the quinoline N atom to be significantly shifted downfield (δ 9.6 *vs*. 8.5 ppm), which is a characteristic of aromatic amine co-ordination in other systems. Addition of two equivalents of $AgBF_4$ to (**5**) gives only one product, (**6**). The spectroscopic data for (**6**) corresponds to the compound formed in 50% conversion when one equivalent of silver salt was added.

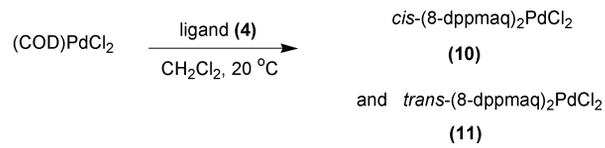
The elucidation of structure (**6**) was achieved from the following data: ^{31}P NMR indicates the formation of a four membered ring system (NH co-ordination), as does the ^{1}H NMR spectrum, which shows a complex group of signals which we have assigned as H_1, H_2 and H_3 (see Scheme 1 and 3). The signal due to the NH group (H_3) appears as five lines. This complicated signal can be rationalised if N co-ordination prevents inversion at the (chiral) nitrogen atom, allowing coupling to nearby protons to be observed. In addition, it is likely that this proton is now coupling to the NMR active rhodium centre. The two CH_2[N–C(H_1H_2)–P] protons appear as two broadened doublets. This multiplicity can be explained by coupling to the NH proton being observed in the N co-ordinated species. Alternatively, the diastereotopic nature of the two protons (due



Scheme 3



Scheme 4



Scheme 5

to the chiral nitrogen atom) results in a separate signal for each proton. The signals in this case could be expected to be complicated by coupling to the P atom, the NH proton, and to each other. Decoupling experiments did not shed any more light on the exact nature of these signals, but in any case the spectrum observed is fully consistent with NH co-ordination. Several of the aromatic protons in the ^{1}H NMR spectrum of (**6**) have been shifted downfield with respect to the free ligand or complex (**5**). Most notably, the signal assigned *ortho* to the aromatic N atom has shifted downfield by *ca.* 1.1 ppm. This is fully consistent with aromatic N co-ordination. We have not assigned every aromatic carbon atom in the (complicated) ^{13}C spectra of 8-dppmaq (**4**) or its complexes (**5**) and (**6**). However, this spectrum also provides support for our proposed structure. In the spectra of (**4**) and (**5**) the furthest downfield peak is the CH carbon *ortho* to the aromatic N atom, and is found at 147 and 143 ppm respectively. In complex (**6**) this signal has shifted downfield to 157 ppm, which must be considered additional evidence for co-ordination from the aromatic amine moiety. Several other aromatic carbons are also shifted downfield from either the free ligand or the monodentate complex.

The IR spectrum of (**6**) shows peaks at 1640, 1618, and 1588 cm^{-1} which are significantly different from either the free ligand (1610, 1574 cm^{-1}) or monodentate complex (1611, 1574 cm^{-1}). The structure is finally confirmed by acceptable elemental analysis and HRMS, which shows peaks corresponding to M − $2BF_4$+. We have coined this co-ordination behaviour 2/3 labile. The ligand has a preference for η^1 co-ordination that can be altered to η^3 co-ordination under the appropriate conditions. It does not appear possible to prepare a bidentate complex with this type of metal fragment, ligand combination.

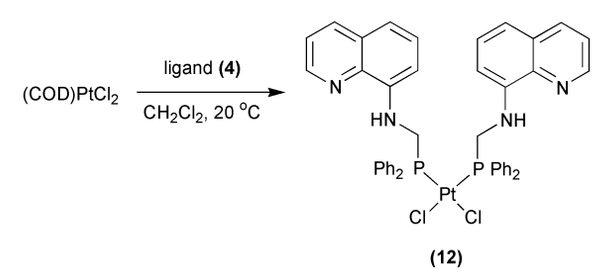
This ligand shows essentially the same behaviour with $[Cp^*IrCl_2]_2$. 8-dppmaq reacts with the iridium dimer to produce a burgundy coloured solid. The ^{31}P NMR spectrum shows a singlet at −1.6 ppm which represents a co-ordination chemical shift of +19 ppm (*cf.* Rh complex $\Delta\delta$ = +51.9 ppm). Reaction with silver tetrafluoroborate gave a cream coloured solid which was assigned the tridentate structure by spectroscopy and chemical analysis. The position of the singlet in the ^{31}P NMR spectra shows a large shift upfield when the two chloride ligands are removed by silver salts (η^1 complex, δ −1.6; η^3 complex, δ −38.7 ppm). The ^{1}H NMR spectrum shows similar features to those discussed for the Rh complex, although the NH signal appears somewhat different, as there is no possibility for M–H coupling.

The reaction of 8-dppmaq with $[(Cym)RuCl_2]_2$ gave the expected monodentate complex (**9**) (see Scheme 4). However, on treatment with either $AgBF_4$ or $AgClO_4$ extensive decomposition took place with formation of an insoluble precipitate.

(d) Palladium and platinum complexes derived from 8-dppmaq

The reaction of two equivalents of 8-dppmaq with $[(COD)PdCl_2]$ gave an orange solid identified as $[(8\text{-dppmaq})_2PdCl_2]$ by HRMS and microanalyses. The ^{31}P NMR spectrum of this compound contains two singlets that we assign, with literature precedent[14] to be the *cis* and *trans* isomers (Scheme 5). No attempt was made to separate these, as we felt that they could well be an equilibrium mixture of the two isomers. The ^{1}H NMR spectrum, which is not especially informative shows the CH_2 protons (a doublet) appearing as two signals which have approximately the same peak integration as that seen in the ^{31}P NMR spectrum. We tentatively assign the *cis* complex as that which is furthest upfield by analogy with the equilibriating isomers of *cis* and *trans* $[(PMe_2Py)_2PtCl_2]$.

If two equivalents of 8-dppmaq are added to $[(COD)PtCl_2]$, a *P*-monodentate bis-complex L_2PtCl_2 (**12**) of *cis* geometry (as judged by the magnitude of J_{P-Pt}) is obtained exclusively. Attempts to obtain a PN chelate complex of formula $LPtCl_2$ by slow addition of one equivalent of ligand to $[(COD)PtCl_2]$ gave a 1 : 1 mixture of the L_2PtCl_2 complex and unreacted $[(COD)PtCl_2]$. From this we can conclude that 8-dppmaq shows a marked preference for monodentate co-ordination with platinum, as a large variety of hemi-labile ligands will form a P,N chelate complex with platinum under these conditions.[15] The ^{31}P NMR spectrum of (**12**) shows the expected singlet with Pt satellites (J_{P-Pt} = 3653 Hz). The IR spectrum resembles the free ligand and shows no evidence of a PN chelate. The proton NMR spectrum of (**12**) does not show any downfield shift in the protons adjacent to the quinoline nitrogen donor, or platinum satellites in the signal attributed to NH. The spectroscopic evidence unambiguously assigns the complex as that depicted in Scheme 6.

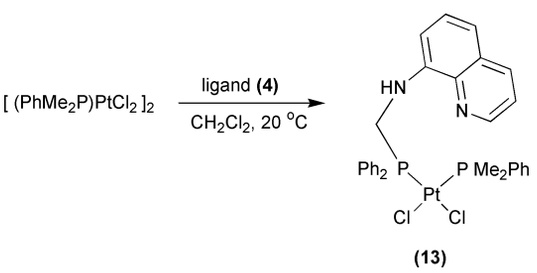


Scheme 6

We now wished to investigate which, if any of the nitrogen donors might chelate to platinum if the chloride ligands were removed. To this end (**12**) was reacted with one equivalent of silver perchlorate (CAUTION: although no problems were encountered during this work, perchlorate salts can be explosive). The ^{31}P NMR spectrum of the compound produced shows a small amount of starting material (*ca.* 15–20%), a very small amount of an unknown impurity, and as the major product, a complex that displays two coupled doublets as its ^{31}P NMR spectrum (δ 4.65, d, $^2J_{P-P}$ = 14.2 Hz, $^1J_{P-Pt}$ = 3686 Hz; 2.60, d, $^2J_{P-P}$ = 14.2 Hz, $^1J_{P-Pt}$ = 3734 Hz). The mass spectrum suggests

that this species is monomeric, by showing peaks due to M − ClO_4 and M − Cl − ClO_4 as the two highest mass ions. These two pieces of data suggest that this is a monomeric complex in which one phosphine is *trans* to chloride, and one phosphine is *trans* to either co-ordinated quinoline nitrogen, perchlorate or solvent. The fact that the ^{31}P resonances appear at chemical shifts very similar to the starting complex (**12**) rules out the presence of a four membered P–C–N–Pt ring system in which the NH is co-ordinated. Inspection of the ^{1}H NMR data immediately suggests that it is the aromatic quinoline nitrogen that is bound to the platinum. The signal assigned to the proton *ortho* to the quinoline nitrogen has shifted upfield to 9.8 ppm. Other protons in the aromatic region are also shifted somewhat upfield. The IR spectrum of this compound shows a weak shoulder on the peak at 1620 cm^{-1}. These two peaks are probably due to co-ordinated and unco-ordinated C=N stretching vibrations. It proved difficult to separate the by-products from this major complex and confirm the molecular formula by chemical analysis. Addition of two equivalents of silver perchlorate to (**12**) gave the same mixture of compounds, the only difference being that the proportion of unknown compound increased at the expense of unreacted starting material. We have also attempted these reactions using silver tetrafluoroborate as halide abstractor. A very similar picture emerges, with one and two equivalents of silver salts giving a mixture of the unknown compound (≈ 15%, δ 6.8, $^{1}J_{P-Pt}$ = 3752 Hz), starting material (≈ 15%, δ 6.1, J_{P-Pt} = 3653 Hz), and what we have assigned as the mono-chelate species as the major product (≈70%).

When 8-dppmaq was added to the Pt dimer [$(PhMe_2P)PtCl_2]_2$, cleavage of the chloride bridges occured giving a product in which the 8-dppmaq and dimethylphenylphosphine are *cis* to each other. This can be readily concluded by inspection of the ^{31}P NMR data (δ 5.70, d, $^{2}J_{P-P}$ = 15.6 Hz, $^{1}J_{P-Pt}$ = 3685 Hz; −15.20, d, $^{2}J_{P-P}$ = 15.6 Hz, $^{1}J_{P-Pt}$ = 3519 Hz). The ^{1}J coupling constants are typical of an alkylarylphosphine *trans* to a chloride ligand. Spectroscopic data are consistent with structure (**13**) (see Scheme 7).



(13)

Scheme 7

When silver perchlorate was added to this monodentate complex, we observed a new complex that has a fairly similar ^{31}P NMR spectrum (δ 3.61, d, $^{2}J_{P-P}$ = 16.2 Hz, $^{1}J_{P-Pt}$ = 3703 Hz; −18.97, d, $^{2}J_{P-P}$ = 16.2 Hz, $^{1}J_{P-Pt}$ = 3500 Hz) to the starting material which was also present as an impurity (even when two equivalents of silver salts were added). Unfortunately, this major species could not be readily purified to give completely pure material. We believe that the chemistry seen when halide ligands are removed from the two platinum complexes we have prepared indicates that the 8-dppmaq ligand can bind to a transition metal as a P,N bidentate chelate (see Fig. 3). The results also suggest that this co-ordination mode is not especially favoured for this ligand.

Having at least a partial understanding of how this new ligand binds to a variety of metal centres, we hoped that the presence of two additional donor atoms within this phosphine may increase stability or alter reactivity/selectivity in transition metal catalysed reactions. We have therefore carried out a preliminary study in which (**4**) was used as ligand in two industrially important carbonylation reactions.

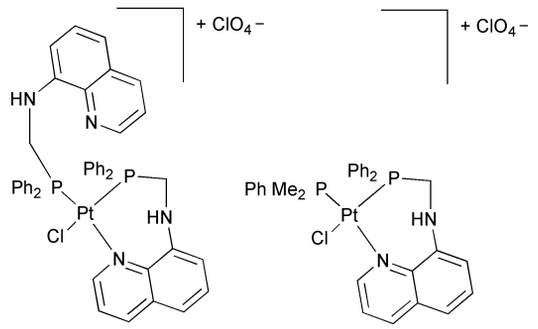
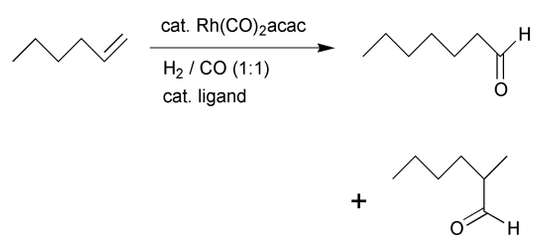


Fig. 3 PN chelate complexes formed on addition of silver salts to complexes (**12**) and (**13**).

(e) Rhodium catalysed hydroformylation of hex-1-ene

As we felt that the 8-dppmaq ligand could act as either a mono-, bi-, or tri-dentate ligand, we were intrigued to know if it was effective at controlling regioselectivity in rhodium catalysed hydroformylation of hex-1-ene. We also wished to find out what effect (if any) the presence of the two additional donor atoms may have on catalyst activity/stability. Reports on the use of PN_x type ligands in hydroformylation are rare. This reaction is of great interest both academically and industrially. The reaction generally gives a mixture of branched and linear isomers (Scheme 8), with complete regioselectivity towards the linear



Scheme 8

isomer being the ideal goal. Recent pioneering research has shown that "wide bite angle" ligands are particularly useful in this respect.[16]

The 8-dppmaq ligand, in combination with $Rh(CO)_2acac$ catalysed the reaction highly effectively, giving essentially complete conversion in less than an hour (turnover frequency (TOF) = 1870 h^{-1}) at 100 °C and 20 bar pressure. Although selectivity to aldehydes is good (96%), the regioselectivity towards the terminal aldehyde was very poor (n : i = 1.8).

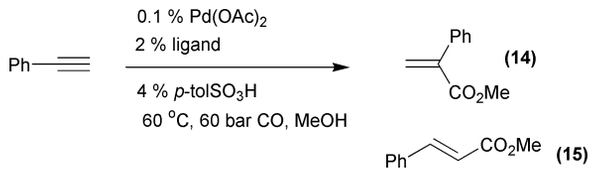
Triphenylphosphine catalyses the reaction at a faster rate and gives an n : i ratio of 2.7 under similar conditions.

(f) Palladium catalysed methoxy carbonylation of phenylacetylene

Quite probably the most well known use of a hemilabile ligand in homogeneous catalysis is the application of palladium diphenyl(2-pyridyl)phosphine complexes as catalyst for carbonylation of alkynes. A combination of palladium acetate, triflic acid and triphenylphosphine catalyses the formation of commercially important methyl methacrylate from propyne with 90% selectivity. However, the reaction proceeds at a very low rate (*ca.* 10 turnovers per hour at 115 °C). Replacing triphenylphosphine with diphenyl(2-pyridyl)phosphine (**2**) gives a remarkable increase in activity with 40,000 turnovers per hour at 45–60 °C. Selectivity is also increased to >99%. It has been reported that this reaction also works well with other alkynes as substrates.[4]

When phenylacetylene was injected into an autoclave containing palladium acetate (0.1%), 2-$PyPPh_2$, p-$MeC_6H_4SO_3H\cdot H_2O$ and pressurised to 55 bar (T = 60 °C) a very exothermic

reaction took place with the autoclave temperature rising to 95 °C, and complete conversion of phenylacetylene occurring within a couple of minutes (Scheme 9). The product, CH_2=



Scheme 9

C(Ph)CO_2Me was formed in quantitative yield and good selectivity towards the terminal alkene (97%). This reaction was too fast for an accurate turnover frequency to be measured. However, 1000 turnovers within minutes is clearly of the same order of magnitude as that reported by Drent and co-workers[4a] for methoxy carbonylation of propyne.

It was of some interest to determine if the 8-dppmaq ligand would show a similar dramatic effect on this reaction in comparison with simple monodentate phosphines. The methoxy carbonylation of phenylacetylene was carried out under similar conditions using 8-dppmaq as ligand. However, there appeared to be very little gas uptake in the first 15 minutes. Consequently the autoclave was sealed and heated to 100 °C for 3.5 hours. GCMS analysis of the reaction mixture after 4 hours reaction time showed that approximately 700 reaction turnovers had occurred within this time. Selectivity was also fairly modest (86%). 2-Pyridylphosphines remain the ligand of choice for this reaction. While 8-dppmaq clearly shows some promotional effect for this reaction (relative to PPh_3), the co-ordination, proton transfer or stabilising qualities of 8-dppmaq are not sufficiently similar to 2-$PyPPh_2$ to give a highly reactive catalytic system.

Conclusions

In this work, we have prepared a new phosphine ligand from 8-aminoquinoline. The ligand prefers to bind to the transition metals studied in a monodentate fashion. However, rhodium and iridium complexes have been prepared in which the ligand adopts a tridentate co-ordination mode. There is good evidence that bidentate ($PN_{aromatic}$) platinum complexes can be prepared from this ligand. The ability of this ligand to activate rhodium and palladium complexes towards carbonylation reactions has also been evaluated. The novel catalysts do promote both hydroformylation and methoxy carbonylation reactions, but they do not match the current state-of-the-art catalysts. Further studies will concentrate on the synthesis of new multifunctionalised phosphines and their catalytic and co-ordination chemistry.

Acknowledgements

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