Supplementary information for:

α-Zirconium phosphonates: versatile supports for N-heterocyclic carbenes

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General

Chemicals were obtained from Aldrich, Alfa Aesar or Fisher, and were used as received unless otherwise noted. Solvents were dried by standard methods prior to use,[S1] and stored under nitrogen over 4 Å molecular sieves. Petroleum ethers refers to the fraction with b.p. 40–60 °C. ε-Caprolactone was dried over CaH_2 and distilled *in vacuo* before use. All air- or moisture-sensitive reactions were carried out under dry nitrogen using either standard Schlenk techniques, or a Saffron Scientific glovebox. Solution NMR spectra were recorded at 25 °C in 5 mm tubes, at 300.1 MHz (^{1}H) or 75.5 MHz (^{13}C) using a Bruker Avance 300 spectrometer. Solid-state magic-angle spinning NMR spectroscopy (SS MAS NMR) was carried out on a Bruker Avance III 300 instrument. Chemical shifts are given in parts per million and quoted relative to the residual solvent peak (7.26 δ for ^{1}H and 77.0 δ for ^{13}C in $CDCl_3$); coupling constants (*J*) are given in Hz. Proton signal multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet) and m (multiplet), br indicates a broad signal. IR data of neat solids were recorded on a Perkin–Elemer Spectrum 1000 FT spectrometer equipped with a SensIR DuraSampl*IR* II diamond ATR attachment. Powder X-ray diffraction data were acquired on an ARL Xtra, equipped with a Cu tube, working in reflection mode at 45 kV and 40 mA. Diisoproyl 4-bromobutylphosphonate,[T2] 1-(2,6-diisopropylphenyl)-1*H*-imidazole,[S2] 1-(2,4,6-trimethylphenyl)-1*H*-imidazole[S2] and (tetrahydrothiophene)gold(I) chloride[S3] were synthesised following the literature procedures. Metal loading of representative supported catalysts were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Phosphonic esters and acids

1. 4-Bromobutylphosphonic acid

Diisopropyl 4-bromobutylphosphonate (**1**) was mixed with aq. HBr (48 %, 100 cm^3) and refluxed for 5 hours. The water was distilled out, and the product dried *in vacu*o at elevated temperature. The title compound was obtained as an off-white solid (29.2 g, 66 %). ^{1}H NMR (D_2O, 25 °C, 300.1 MHz): δ 1.51–1.78 (m, 6H, alkyl chain), 3.32 (t, 2H, J = 6.5 Hz, CH_2Br).

2. Reaction of 4-Bromobutylphosphonic acid with N- 2,6-di-isopropylphenyl imidazole

A mixture of **1** (16 g, 53 mmol), and 1-(2,6-diisopropylphenyl)-1*H*-imidazole (10.9 g, 48 mmol) in 1,4-dioxane (100 cm^3) was heated to 80 °C for 8 hours under nitrogen and with vigorous stirring. The solvent was removed *in vacuo* to give a mixture of **4b** and **1** as a yellow oil (25.5 g). Consumption of the free imidazole was complete by ^{1}H NMR spectroscopy. ν_{max}(solid)/cm^{-1} 2961, 2853, 1562, 1544, 1454, 136, 1253, 1119, 981, 872. ^{1}H NMR ($CDCl_3$, 25 °C, 300.1 MHz): δ 1.15 (s, 12H, 2 × Me), 1.30 (s, 12H, 2 × Me) 1.73 (m, 4H, alkyl chain), 2.01 (m, 2H, alkyl chain), 3.40 (CH_2Br),

4.67 (m, 2H, C*H*(CH_3)$_2$), 4.84 (br s, 2H, NCH_2), 4.65 (m, 2H, C*H*(CH_3)$_2$), 7.25 (s, 1H, imidazolium C^4/C^5), 7.57 (s, 1H, imidazolium C^4/C^5), 8.00 (br s, 3H, aromatic), 10.41 (s, 1H, imidazolium C^2). ^{13}C NMR ($CDCl_3$, 25 °C, 75.5 MHz): δ 19.60 (CH_2Br), 21.57 (CH_2), 24.45 (Me), 24.68 (Me), 28.49 (Me), 29.10 (Me), 33.88 (CH_2Br), 50.42 (NCH_2), 67.21 (*C*H(CH_3)$_2$), 70.50 (O*C*H(CH_3)$_2$), 123.69 (imidazolium C^4/C^5), 124.63 (imidazolium C^4/C^5), 130.56 (aromatic), 131.30, (aromatic), 132.23 (aromatic), 138.59 (imidazolium C^2), 145.72 (aromatic). ^{31}P NMR ($CDCl_3$, 25 °C, 121.5 MHz): δ26.63 (25 %), 32.59 (75 %).

3. Formation of [H_2O_3P-C_4H_8-$C_3H_3N_2$DIPP]Br

The mixture **4b** (25.5 g, 53 mmol of total phophonate esters) and conc. HBr (30 cm^3, 40 %) were refluxed under nitrogen for 4 hours. The aqueous phase was removed by distillation, and the product was dried *in vacuo* to give a yellow oil, which was used directly in the next step. ν_{max}(solid)/cm^{-1} 2965, 2870, 1562, 1544, 1458, 1366, 1245, 1186, 996, 952 ,807, 758. ^{1}H NMR (D_2O, 25 °C, 300.1 MHz): δ 0.93 (m, 6H, Me), 1.10 (m, 6H, Me), 1.56, 1.73 (m, 4H, alkyl), 2.13 (m, 2H, CH_2), 2.28 (m, 2H, CH_2Br), 3.30 (t, 2H, J = 6.48 Hz, NCH_2), 3.99 (m, 2H, C*H*(CH_3)$_2$), 7.25 (s, 2H, imidazolium C^4/C^5), 7.47, 7.48, 7.53 (each 1H, aromatic), 8.83 (s, 1H, imidazolium C^2). ^{13}C NMR (D_2O, 25 °C, 75.5 MHz): δ 19.2 (CH_2), 21.6 (CH_2), 23.5 (Me), 28.5 (CH_2), 28.5 (*C*H(CH_3)$_2$), 34.0 (CH_2Br), 50.4 (NCH_2), 123.69 (imidazolium C^4/C^5), 124.63 (imidazolium C^4/C^5), 125.02 (aromatic), 130.56 (aromatic), 132.23 (aromatic), 138.59 (imidazolium C^2), 145.72 (aromatic). ^{31}P NMR (D_2O, 25 °C, 121.5 MHz): δ 31.33, 35.84.

4. Reaction of 1 with *N*-mesitylimidazole

A mixture of **1** (16 g, 53 mmol), and 1-(2,4,6-trimethylphenyl)-1*H*-imidazole (7.92 g 42.4 mmol,) in toluene (100 cm^3) was heated to 80 °C for 10 hours under nitrogen and with vigorous stirring. The solvent was removed *in vacuo* and the residue washed with toluene to give a mixture of (Pr^iO)$_2$P(O)C_4H_8-$C_3H_3N_2$-$C_6H_2Me_3$-2,4,6 (**4c)** and **1** (24.5 g) as a yellow solid. Consumption of the free imidazole was complete by ^{1}H NMR spectroscopy. ν_{max}(solid)/cm^{-1} 2978, 1609, 1565, 1547, 1487, 1454, 1385, 1374, 1223, 1205, 1178, 1106, 976, 888. ^{1}H NMR ($CDCl_3$, 25 °C, 300.1 MHz): δ 1.28 (d, 12H, J = 6.2 Hz, CH(C*H*$_3$)$_2$), 1.68 (m, 4H, alkyl), 1.96 (m, 2H, CH_2Br), 1.94 (6H, s, Me), 2.16 (m, 2H, CH_2), 2.31 (s, 3H, Me), 3.38 (m, 2H, CH_2Br), 4.64 (m, 2H, C*H*(CH_3)$_2$), 4.74 (t, 2H, J = 7.2 Hz, NCH_2), 6.95 (s, 2H, aromatic), 7.17 (1H, s, imidazolium C^4/C^5), 7.86 (1H, s, imidazolium C^4/C^5), 10.30 (s, 1H, imidazolium C^2). ^{13}C NMR ($CDCl_3$, 25 °C, 75.5 MHz): δ17.70 (CH_2Br), 18.00 (CH_2Br), 19.76 (alkyl), 19.73 (alkyl), 21.48 (Me), 25.44 (Me), 27.36 (Me), 31.35 (alkyl), 33.26 (CH_2Br), 33.66 (CH_2Br), 50.03 (NCH_2), 70.40 (OCH), 123.34 (imidazolium C^4/C^5), 124.45 (imidazolium C^4/C^5), 130.27 (aromatic), 131.05 (aromatic), 134.57 (aromatic), 138.57 (imidazolium C^2), 141.72 (aromatic). ^{31}P NMR ($CDCl_3$, 25 °C, 121.5 MHz): δ32.87 (25 %), 33.00 (75 %).

5. Hydrolysis of 4c

The mixture **5b** (24.5 g, 53 mmol of total phophonate esters) and conc. HBr (30 cm^3, 40 %) were refluxed under nitrogen for 4 hours. The aqueous phase was removed by distillation, and the product was dried *in vacuo* to give a yellow oil, which was used directly in the next step. ν_{max}(solid)/cm^{-1} 3126 (br), 2982, 2928, 1604, 1564, 1547, 1485, 1455, 1378, 1201, 1144, 997, 856. ^{1}H NMR (D_2O, 25 °C, 300.1 MHz): δ1.48 (m, 2H, CH_2), 1.65 (m, 4H, CH_2), 1.88 (s, 6H, Me), 1.96 (m, 2H, CH_2), 2.19 (s, 3H,

Me), 3.36 (m, 2H, CH_2Br), 4.23 (t, 2H, J = 6.0 Hz, NCH_2), 6.92 (s, 2H, aromatic), 7.42 (s, 1H, imidazolium C^4/C^5), 7.63 (s, 1H, imidazolium C^4/C^5), 8.85 (s, 1H, imidazolium C^2). ^{13}C NMR (D_2O, 25 °C, 75.5 MHz): δ 16.69 (alkyl), 19.34 (alkyl), 20.54 (Me), 31.19 (alkyl), 33.66 (CH_2Br), 49.77 (NCH_2), 123.38 (imidazolium C^4/C^5), 124.65 (imidazolium C^4/C^5), 129.57 (aromatic), 131.12 (aromatic), 135.01 (aromatic), 136.61 (imidazolium C^2), 141.72 (aromatic). ^{31}P NMR (D_2O, 25 °C, 121.5 MHz): δ 34.47 (25 %), 35.20 (75 %).

Zirconium phosphonates

6. Zirconium bis(4-bromobutylphosphonate) (2)

4-Bromobutylphosphonic acid **1** (18.3 g, 90 mmol) was dissolved in a mixture of water (25 cm^3) and propan-1-ol (75 cm^3). This solution was then added dropwise to $ZrOCl_2 \cdot 8\ H_2O$ (14.5 g, 45.0 mmol) and aq. HF (40 %, 4.0 cm^3, 89 mmol) in water (50 cm^3), contained in a 250 cm^3 polypropylene conical flask. A white solid precipitated immediately. The flask was connected to a stainless steel reflux condenser and heated to 80 °C for 5 days. After cooling to room temperature, the resulting solid was washed several times with water and acetone. The solid was dried *in vacuo* at 110 °C for 6 hours. Found C 18.37, H 3.13 %; $C_8H_{16}Br_2O_6P_2Zr$ requires C 18.44, H 3.09 %. XRD: d(0 0 1) = 15.8 Å. ν_{max}(solid)/cm^{-1} 2940, 2873, 1443, 1408, 1275, 1238, 1010 (P=O), 806, 725. ^{13}C MAS-NMR (25 °C, 300.1 MHz): δ 20.6 (alkyl), 25.8, 27.8 (alkyl), 34.3 (alkyl), 45.3 (CH_2Br), 62.2, 71.3. ^{31}P MAS-NMR (25 °C, 121.5 MHz): δ 5.7.

7. Methylimidazolium Zirconioum Phosphonate (3a)

To a suspension of **2** (500 mg, 1.0 mmol) in 1,4-dioxane (50 cm^3) was added *N*-methylimidazole (410 mg, 5.0 mmol), and the mixture was stirred at 90 °C for 48 h. The solid was washed with copious toluene and dried *in vacuo*, to give the title compound (870 mg, 96 %). Found C 27.93, H 4.19, N 8.11 %; $C_{16}H_{28}Br_2N_4O_6P_2Zr$ requires C 28.04, H 4.12, N 8.17 %. ν_{max}(solid)/cm^{-1} 2939, 2869, 1573, 1452, 1410, 1171, 1004. ^{13}C MAS-NMR (25 °C, 300.1 MHz): δ 20.6 (alkyl), 27.5 (alkyl), 31.7 (alkyl), 34.9 (alkyl), 37.2 (Me), 49.5 (NCH_2), 61.6, 122.9 (imidazolium C^4/C^5), 124.1 (imidazolium C^4/C^5), 137.7 (imidazolium C^2). ^{31}P MAS-NMR (25 °C, 121.5 MHz): δ 5.7.

8. Formation of $Zr(O_3PC_4H_8Br)_{1.4}(O_3PC_4H_8C_3H_3N_2C_6H_3Pr^i_2Br)_{0.6}$ (5b)

To a solution of $ZrOCl_2 \cdot 8\ H_2O$ (8.7 g, 27 mmol) in water (40 cm^3), containing aqueous HF (40 %, 2.4 cm^3), was added dropwise the product of reaction 3 (53 mmol total phosphonic acid) dissolved in a water (15 cm^3) and propan-1-ol (44 cm^3). A pale yellow solid precipitated immediately. The flask was connected to a stainless steel reflux condenser and heated to 80 °C for 5 days. The powder was washed several times with water and acetone, and finally dried *in vacuo* at 110 °C. The product was obtained as a white solid (7.0 g). ^{13}C MAS-NMR spectroscopy indicated an approximate ratio of imidazolium to butyl bromide of 1:1.5 corresponding to a composition of $Zr(O_3PC_4H_8Br)_{1.2}(O_3PC_{19}H_{26}N_2Br)_{0.8}$. Found C 32.00, H 5.06, N 2.69 %, corresponding to a composition of $Zr(O_3PC_4H_8Br)_{1.4}(O_3PN_2C_{19}H_{28}Br)_{0.6}$ indicating an approximate ratio of imidazolium to butyl bromide of 1:2.33. ν_{max}(solid)/cm^{-1} 2936, 2870, 1545, 1458, 1241, 1187, 1010, 803, 758, 722. ^{13}C MAS-NMR (25 °C, 300.1 MHz): δ 20.71, 24.89, 28.97, 34.22, 45.21 (CH_2Br), 50.16

(CH_2N), 61.64, 70.29, 124.63, 131.14, 138.24, 145.92. ^{31}P MAS-NMR (25 °C, 121.5 MHz): δ 5.9.

9. $Zr(O_3PC_4H_8Br)_{0.9}(O_3PC_4H_8C_3H_3N_2C_6H_3Me_3Br)_{1.1}$ (5c)

The product from reaction 5 (53 mmol total phosphonic acid) dissolved in a water (25 cm^3) and propan-1-ol (74 cm^3) was added dropwise to a solution of $ZrOCl_2 \cdot 8\ H_2O$ (8.7 g, 27 mmol,) in water (40 cm^3), containing aqueous HF (40 %, 2.4 cm^3). A pale yellow solid precipitated immediately. The flask was connected to a stainless steel reflux condenser and heated to 80 °C for 5 days. The powder was washed several times with water and acetone, and finally dried *in vacuo* at 110 °C. The product was obtained as a white solid (7.0 g). ν_{max}(solid)/cm^{-1} 2918, 2861, 1604, 1562, 1545, 1485, 1457, 1409, 1201, 1160, 1018, 855, 800, 725, 668. ^{13}C MAS-NMR (25 °C, 300.1 MHz): δ 20.3, 28.1, 33.3, 46.3 (CH_2Br), 50.5 (CH_2N), 61.9, 71.3, 124.6, 138.0, 140.0. ^{31}P MAS-NMR (25 °C, 121.5 MHz): δ 5.5. Found C 35.65, H 4.87, N 4.69 %, corresponding to a composition of $Zr(O_3PC_4H_8Br)_{0.9}(O_3PN_2C_{16}H_{22}Br)_{1.1}$ indicating an approximate ratio of butyl bromide to imidazolium of 1: 1.22**.** ^{13}C MAS-NMR spectroscopy indicated an approximate ratio of butyl bromide to imidazolium of 1:1.66 corresponding to a composition of $Zr(O_3PC_4H_8Br)_{0.8}(O_3PC_{16}H2_2N_2Br)_{1.2}$**.**

Supported metal complexes

10. Supported [(NHC^R)Ir(COD)Cl], R = Me

The phosphonate **3a** (100 mg, 0.30 mmol imidazolium/g) was suspended in dry THF (5 cm^3) under a nitrogen atmosphere. A solution of $KOBu^t$ (47 mg, 0.38 mmol) in dry THF (5 cm^3) was added slowly at room temperature, to give a cloudy yellow suspension. The reaction mixture was allowed to stir at room temperature for 3 h. To this solution was added $[Ir(COD)Cl]_2$ (97 mg, 0.15 mmol) in dry toluene (5 cm^3). The orange reaction mixture was stirred overnight. The volatiles were removed *in vacuo*, and the residue was washed with pentane to give a yellow-brown solid (150 mg). ν_{max}(solid)/cm^{-1} 2941, 2876, 1573, 1450, 1324, 1172, 1016, 891, 807, 728, 615. ^{13}C MAS-NMR (25 °C, 300.1 MHz): δ 1.5, 20.9, 30.0, 37.2, 49.3 (CH_2N), 62.0 (COD), 68.9 (COD), 88.5 (br, COD), 123.4 (br, imidazole C^4/C^5), 137.6 (br, imidazole C^4/C^5), 180.0 (br, imidazole C^2). ^{31}P MAS-NMR (25 °C, 121.5 MHz): δ 5.7.

11. Supported [(NHC^R)Ir(COD)Cl], R = DiPP

The mixed phosphonate **5b** (290 mg, approx. 0.1 mmol imidazolium/g) was suspended in dry THF (5 cm^3) under a nitrogen atmosphere. A solution of $KOBu^t$ (18 mg, 0.15 mmol) in dry THF (5 cm^3) was added slowly at room temperature, to give a cloudy yellow suspension. The reaction mixture was allowed to stir at room temperature for 3 h. To this solution was added $[Ir(COD)Cl]_2$ (40 mg, 0.06 mmol) in dry toluene (5 cm^3). The orange reaction mixture was stirred overnight. The volatiles were removed *in vacuo*, and the residue was washed with pentane to give a yellow-brown solid. ν_{max}(solid)/cm^{-1} 2961, 2868, 1684, 1559, 1541, 1457, 1260, 1016, 801, 722.

12. Supported [(NHC^R)$Ir(CO)_2$Cl], R = Me (7a)

Carbon monoxide was passed through a suspension of the product of reaction 10 in CH_2Cl_2 for 2 h, before the solvent was removed *in vacuo*. ν_{max}(solid)/cm^{-1} 2962, 2940, 2054 (C≡O), 1973 (C≡O), 1573, 1455, 1170, 1016, 802.

13. Supported [(NHC^R)Ir(CO)$_2$Cl], R = DiPP (7b)
Carbon monoxide was passed through a suspension of the product of reaction 11 in CH_2Cl_2 for 30 min, before the solvent was removed *in vacuo*. ν_{max}(solid)/cm^{-1} 2961, 2870, 2053 (C≡O), 1971 (C≡O), 1566, 1548, 1462, 1366, 1260, 1016, 800, 759, 721.

14. Supported [(NHC^R)Rh(COD)Cl], R = Me
The phosphonate **3a** (100 mg, approx. 0.3 mmol imidazolium/g) was suspended in dry THF (5 cm^3) under a nitrogen atmosphere. A solution of KOBu^t (47 mg, 0.38 mmol) in dry THF (5 cm^3) was added slowly at room temperature, to give a cloudy yellow suspension. The reaction mixture was allowed to stir at room temperature for 3 h. To this solution was added [Rh(COD)Cl]$_2$ (74 mg, 0.15 mmol) in dry toluene (10 cm^3). The orange reaction mixture was stirred overnight. The volatiles were removed under high vacuum, and the residue was washed with pentane to give a yellow-brown solid (120 mg). ICP-AERS: 0.60 mmol Rh/g. ν_{max}(solid)/cm^{-1} 2939, 2869, 2341, 1573, 1456, 1171, 1017, 722. ^{13}C MAS-NMR (25 °C, 300.1 MHz): δ 1.4 (alkyl), 21.2 (alkyl), 31.1 (alkyl), 37.2 (alkyl), 49.3 (CH_2N), 62.0 (COD), 68.9 (COD), 96.8 (COD), 123.4 (br, imidazole C^4/C^5), 137.6 (br, imidazole C^4/C^5), 180.0 (br, imidazole C^2). ^{31}P MAS-NMR (25 °C, 121.5 MHz): δ 5.5.

15. Supported [(NHC^R)Rh(COD)Cl], R = DiPP
The mixed phosphonate **5b** (400 mg, approx. 0.14 mmol imidazolium/g) was suspended in dry THF (5 cm^3) under a nitrogen atmosphere. A solution of KOBu^t (48 mg, 0.44 mmol) in dry THF (5 cm^3) was added slowly at room temperature, to give a cloudy yellow suspension. The reaction mixture was allowed to stir at room temperature for 3 h. To this solution was added [Rh(COD)Cl]$_2$ (99 mg, 0.20 mmol) in dry toluene (5 cm^3). The orange reaction mixture was stirred overnight. The volatiles were removed under high vacuum, and the residue was washed with pentane to give a yellow-brown solid (420 mg). ν_{max}(solid)/cm^{-1} 2962, 2871, 1560, 1542, 1458, 1259, 1014, 800, 759, 727.

16. Supported [(NHC^R)Rh(CO)$_2$Cl], R = Me (8a)
Carbon monoxide was passed through a suspension of the product of reaction **14** in CH_2Cl_2 for 30 min, before the solvent was removed *in vacuo*. ν_{max}(solid)/cm^{-1} 2961, 2871, 2068 (C≡O), 1990 (C≡O), 1765, 1547, 1462, 1366, 1260, 1209, 1182, 1009, 800, 759, 722.

17. Supported [(NHC^R)Rh(CO)$_2$Cl], R = DiPP (8b)
Carbon monoxide was passed through a suspension of the product of reaction 15in CH_2Cl_2 for 2 h, before the solvent was removed *in vacuo*. ν_{max}(solid)/cm^{-1} 2960, 2870, 2073 (C≡O), 1993 (C≡O), 1573, 1455, 1260, 1017, 725. ^{13}C MAS-NMR (25 °C, 300.1 MHz): δ 21.2 (alkyl), 31.1 (alkyl), 37.2 (alkyl), 49.3 (CH_2N), 123.4 (br, imidazole C^4/C^5), 137.6 (br, imidazole C^4/C^5), 168.2 (imidazole C^2), 180.0 (br, C≡O). ^{31}P MAS-NMR (25 °C, 121.5 MHz): δ 5.5.

18. Supported [(NHC^R)Rh(COD)Cl], R = Mes (8c)
The mixed phosphonate **5c** (500 mg, approx. 0.265 mmol imidazolium/g) was suspended in dry THF (5 cm^3) under a nitrogen atmosphere. A solution of KOBu^t (33 mg, 0.3 mmol) in dry THF (5 cm^3) was added slowly at room temperature, to give a cloudy yellow suspension. The reaction mixture was allowed to stir at room temperature for 3 h. To this solution was added [Rh(COD)Cl]$_2$ (65 mg, 0.13 mmol) in

dry toluene (5 cm^3). The orange reaction mixture was stirred overnight. The volatiles were removed under high vacuum, and the residue was washed with pentane to give a yellow-brown solid (420 mg). ν_{max}(solid)/cm^{-1} 2922, 2856, 2826, 1560, 1557 (br) cm^{-1}, 1454 (br), 1200 cm^{-1}, 1026 (br), 853, 805, 720. ^{13}C MAS-NMR (25 °C, 300.1 MHz): δ 21.0 (alkyl), 31.1 (br, Me), 34.2 (Me), 50.5 (alkyl), 62.0 (COD), 74.1 (CH_{COD}), 96.65 (CH_{COD}), 131.86 (aromatic), 135.32 (br, aromatic). ICP-AES: 0.12 mmol Rh /g.

19. Supported [(NHC^R)RuCl$_2$(=CHPh)PCy$_3$], R = DiPP (15b)

The mixed phosphonate **5b** (400 mg, approx. 0.14 mmol imidazolium/g) was suspended in dry THF (5 cm^3) under a nitrogen atmosphere. A solution of KOBu^t (48 mg, 0.44 mmol) in dry THF (5 cm^3) was added slowly at room temperature, to give a cloudy yellow suspension. The reaction mixture was allowed to stir at room temperature for 3 h. To this solution was added $RuCl_2(CHPh)(PCy_3)_2$ (123 mg, 0.15 mmol) in dry toluene (5 cm^3). The purple reaction mixture was stirred overnight. The volatiles were removed *in vacuo*, and the residue was washed with pentane to give a light pink solid (450 mg). ν_{max}(solid)/cm^{-1} 2926, 2850, 1588, 1445, 1260, 1173, 1024, 916, 847, 801, 739, 686. ^{31}P MAS-NMR (25 °C, 121.5 MHz): δ 5.9, 37.3. MAS-NMR: 1 Ru / 8 imidazoles.

20. Supported [(NHC^R)RuCl$_2$(=CHPh)PCy$_3$], R = Mes (15c)

The mixed phosphonate **5c** (300 mg, approx 0.14 mmol imidazolium) was suspended in dry THF (5 cm^3) under a nitrogen atmosphere. A solution of KOBu^t (48 mg, 0.44 mmol) in dry THF (5 cm^3) was added slowly at room temperature, to give a cloudy yellow suspension. The reaction mixture was allowed to stir at room temperature for 4 h. To this solution was added $RuCl_2(CHPh)(PCy_3)_2$ (123 mg, 0.15 mmol) in dry toluene (5 cm^3). The purple reaction mixture was stirred overnight. The volatiles were removed *in vacuo*, and the residue was washed with pentane to give a light pink solid. ν_{max}(solid)/cm^{-1} 2924, 2849, 1547, 1445, 1258, 1248, 1201, 1023, 896, 850, 798, 730. ^{31}P MAS-NMR (25 °C, 121.5 MHz): δ 5.9, 36.0. MAS-NMR: 1 Ru / 12 imidazoles.

21. Supported [(NHC^R)RuCl$_2$(=CHPh)py$_2$], R = Mes (16c)

A suspension of **15b** (60 mg) was suspended in toluene (3 cm^3) and pyridine (0.27 cm^3) was added. The reaction was stirred for 10 min, during which time a change colour from light purple to green was observed. The solid was recovered by filtration, washed with pentane and dried *in vacuo* to afford a green solid. ν_{max}(solid)/cm^{-1} 2942, 2860, 1663, 1609, 1561, 1546, 1455, 1415, 1378, 1245, 1203, 1016, 854, 799, 728.

22. Supported [(NHC^R)AuCl], R = DiPP (17b)

A suspension of **5b** (500 mg, approx 0.17 mmol imidazolium) and Ag_2O (16 mg, 0.07 mmol) was suspended in CH_2Cl_2 (10 cm^3) and stirred for 6 hours. (Tetrahydrothiophene)gold(I) chloride (53 mg, 17 mmol) was added, and the system stirred for 3 h. The solvent was then removed *in vacuo* to afford a grey solid. ν_{max}(solid)/cm^{-1} 2959, 2857, 1604, 1559, 1545, 1480, 1456, 1401, 1259, 1199, 1007, 853, 797, 726. ^{13}C MAS-NMR (25 °C, 300.1 MHz): δ 18.7 (alkyl), 21.2 (alkyl), 27.0 (alkyl), 31.3 (Me), 34.3 (Me), 45.3 (alkyl), 51.4 (alkyl), 123.6 (aromatic), 130.1 (aromatic), 131.5 (aromatic), 135.6 (aromatic), 139.9 (aromatic), 171.0 (imidazole C^2). ICP-AES: 0.4 mmol Au /g.

23. Supported [(NHC^{R})AuCl], R = Mes (17c)
A suspension of **5c** (300 mg, approx 0.14 mmol imidazolium) and Ag_2O (16 mg, 0.07 mmol) was suspended in CH_2Cl_2 (10 cm^3) and stirred for 6 hours. (Tetrahydrothiophene)gold(I) chloride (53 mg, 17 mmol) was added, and the system stirred for 3 h. The solvent was then removed *in vacuo* to afford a grey solid. ν_{max}(solid)/cm^{-1} 2959, 2857, 1604, 1560, 1544, 1483, 1455, 1405, 1259, 1199, 1010, 853, 797, 726. ^{13}C MAS-NMR (25 °C, 300.1 MHz): δ 18.7 (alkyl), 21.2 (alkyl), 27.0 (alkyl), 31.4 (Me), 34.2 (Me), 45.5 (alkyl), 51.4 (alkyl), 123.5 (aromatic), 130.0 (aromatic), 131.5 (aromatic), 135.6 (aromatic), 139.9 (aromatic), 171.0 (imidazole C^2). ICP-AES: 0.12 mmol Au /g. Au/imid = 1:8 from analysis.

Model complexes

24. 1-Butyl-3-methylimidazolium bromide
To a solution of *N*-methylimidazole (6.0 g, 72 mmol) in 1,4-dioxane (50 cm^3) was added 1-bromobutane (9.8 g, 72 mmol) and the mixture was stirred under nitrogen at 90 °C for 6 hours. The solvent was removed *in vacuo*, yielding a yellow oil (15.0 g, 94 %). ν_{max}(solid)/cm^{-1} 3062, 2958, 2936, 2836, 2871, 1567, 1461, 1380, 1337, 1167, 825, 752. ^{1}H NMR ($CDCl_3$, 25 °C, 300.1 MHz): δ 0.85 (t, 3H, J = 9.0 Hz, CH_3), 1.26 (m, 2H, alkyl), 1.80 (m, 2H, alkyl), 4.02 (s, 3H, Me), 4.24 (t, 2H, J = 9.0 Hz, NCH_2), 7.46 (d, 1H, J = 3.0 Hz, imidazolium C^4/C^5), 7.58 (d, 1H, J = 3.0 Hz, imidazolium C^4/C^5), 10.00 (s, 1H, imidazolium C^2).

25. 1-Butyl-3-(2,6-diisopropylphenyl)imidazolium bromide
To a solution of 1-(2,6-diisopropylphenyl)-1*H*-imidazole (4.0 g, 18 mmol) in 1,4-dioxane (50 cm^3) was added 1-bromobutane (2.0 g, 15 mmol) and the mixture was stirred under nitrogen at 90 °C for 8 h. The solvent was removed *in vacuo*, yielding a yellow solid (5.5 g, 91 %). ν_{max}(solid)/cm^{-1} 3036, 2962, 2870, 1561, 1541, 1541, 1540, 1378, 1366, 1281, 1254, 1182, 1117, 1071, 940, 871, 866, 761. ^{1}H NMR ($CDCl_3$, 25 °C, 300.1 MHz): δ 0.94 (q, 3H, J = 6.1 Hz, Me), 1.15 (m, 12H, Me), 1.37 (m, 2H, Bu), 1.95 (m, 2H, m, C*H*$(CH_3)_2$), 2.25 (m, 2H, Bu), 4.77 (t, 2H, J = 7.8 Hz, NCH_2), 7.24 (m, 3H, aromatic plus imidazolium C^4/C^5), 7.50 (m, 1H, aromatic), 8.08 (d, 1H, J = 1.6 Hz, imidazolium C^4/C^5), 10.41 (s, 1H, imidazolium C^2). ^{13}C NMR ($CDCl_3$, 25 °C, 75.5 MHz): δ 13.97 (Bu), 19.64 (Bu), 24.65 (Me), 29.10 (Me), 32.88 (Bu), 50.46 (NCH_2), 123.69, 124.63, 125.02, 130.56, 132.29, 138.59, 145.72 (all aromatic/imidazolium).

26. 1-Butyl-3-(2,4,6-trimethylphenyl)imidazolium bromide
To a solution of 1-(2,4,6-trimethylphenyl)-1*H*-imidazole (1.2 g, 6.6 mmol) in 1,4-dioxane (50 cm^3) was added 1-bromobutane (1.0 g, 7.3 mmol) and the mixture was stirred under nitrogen at 90 °C for 6 hours. The solvent was removed *in vacuo*, yielding a yellow solid (1.8 g, 84 %). ν_{max}(solid)/cm^{-1} 3028, 2959, 2870, 1607, 1563, 1544, 1486, 1457, 1378, 1330, 1260, 1199, 1159, 1095, 1067, 1019, 968, 935, 866, 871, 855, 798, 730, 669. ^{1}H NMR ($CDCl_3$, 25 °C, 300.1 MHz): δ 0.94 (t, 3H, J = 7.4 Hz, Me), 1.38 (m, 2H, Bu), 1.95 (m, 2H, Bu), 2.03 (s, 6H, Me), 2.30 (s, 3H, Me), 4.70 (t, 2H, J = 7.2 Hz, NCH_2), 6.94 (s, 2H, aromatic), 7.16 (s, 1H, imidazolium C^4/C^5), 7.78 (s, 1H, imidazolium C^4/C^5), 10.43 (s, 1H imidazolium C^2). ^{13}C NMR ($CDCl_3$, 25 °C, 75.5 MHz): δ 14.00 (Bu), 18.07 (Me), 19.64 (Bu), 21.51 (Me), 32.88 (Bu), 50.46 (NCH_2), 123.13, 123.54, 129.50, 131.07, 134.58, 138.60, 141.69 (all aromatic/imidazolium).

27. [1-Butyl-3-(2,6-diisopropylphenyl)imidazol-2-ylidene]chloro(η^4-cyclo-octa-1,5-diene)iridium(I)

1-Butyl-3-(2,6-diisopropylphenyl)imidazolium bromide (100 mg, 0.27 mmol) and dry THF (5 cm^3) were mixed under a nitrogen atmosphere. To this suspension was added a solution of $KOBu^t$ (33 mg, 0.30 mmol) in dry THF (5 cm^3) dropwise. The bromide salt dissolved to give a cloudy yellow solution. The reaction mixture was allowed to stir at room temperature for 2 h, before filtration under an inert atmosphere. To this solution was added $[Ir(COD)Cl]_2$ (92 mg, 0.14 mmol) in dry toluene (5 cm^3). The yellow/brown reaction mixture was stirred overnight. The volatiles were removed *in vacuo*, and the residue was washed with pentane to give a yellow solid (115 mg, 65 %). ν_{max}(solid)/cm^{-1} 2960, 2929, 2869, 2831, 1670, 1458, 1409, 1385, 1362, 1259, 1081, 1056, 1017, 801, 761. ^{1}H NMR ($CDCl_3$, 25 °C, 300.1 MHz): δ 0.96 (br s, 3H, Me), 1.17 (m, 12H, Me), 1.37 (m, 2H, Bu), 1.50 (br s, 2H, COD), 1.97 (m, 2H, C*H*$(CH_3)_2$), 2.25 (br s, 2H, Bu), 2.62 (br s, 2H, COD), 2.94 (br s, 4H, COD), 3.40 (br s, 4H, COD), 4.79 (br s, 2H, NCH_2), 5.10 (br s, 2H, COD), 6.82 (d, 1H, J = 2.9 Hz, imidazole C^4/C^5), 7.22 (m, 3H, aromatic), 8.22 (d, 1H, J = 2.9 Hz, imidazole C^4/C^5). ^{13}C NMR ($CDCl_3$, 25 °C, 75.5 MHz): δ 14.40 (Bu), 20.43 (Bu), 24.08 (Me), 30.60 (*C*H$(CH_3)_2$), 30.16 (COD), 32.36 (Bu), 33.51 (COD), 51.8 (NCH_2), 83.09 (COD), 123.32, 124.90, 130.03, 135.85, 137.64, 145.66 (all aromatic/imidazole/COD), 175.45 (imidazole C^2).

28. [1-Butyl-3-(2,6-diisopropylphenyl)imidazol-2-ylidene]dicarbonylchloro-iridium(I) (9)

Carbon monoxide was passed through a solution of [1-butyl-3-(2,6-diisopropyl-phenyl)imidazol-2-ylidene]chloro(η^4-cyclo-octa-1,5-diene)iridium (115 mg, 0.19 mmol) in CH_2Cl_2 (5 cm^3) for 30 min, the solvent was removed *in vacuo* and the solid washed with pentane to give a yellow-brown solid (105 mg, 99 %). ν_{max}(solid)/cm^{-1} 2962, 2929, 2869, 2056 (C≡O), 1972 (C≡O), 1667, 1460, 1384, 1363, 1257, 1057, 1016, 801, 759, 706. ^{13}C NMR ($CDCl_3$, 25 °C, 75.5 MHz): δ 14.12 (Me), 20.15 (Bu), 24.79 (Me), 30.12 (*C*H$(CH_3)_2$), 32.9 (Bu), 51.77 (NCH_2), 123.39, 124.60, 125.5, 130.88, 137.64, 146.53 (all aromatic/imidazole), 168.39 (C≡O), 175.93 (C≡O), 181.17 (imidazole C^2).

29. (1-Butyl-3-methylimidazol-2-ylidene)chloro(η^4-cyclo-octa-1,5-diene)-rhodium(I)

1-Butyl-3-methylimidazolium bromide (0.20 g, 0.91 mmol) and dry THF (5 cm^3) were mixed under a nitrogen atmosphere. To this suspension was added a solution of $KOBu^t$ (112 mg, 1.0 mmol) in dry THF (5 cm^3) dropwise. The bromide salt dissolved to give a cloudy yellow solution. The reaction mixture was allowed to stir at room temperature for 2 h, before filtration under an inert atmosphere. To this solution was added $[Rh(COD)Cl]_2$ (224 mg, 0.45 mmol) in dry toluene (5 cm^3). The yellow reaction mixture was stirred overnight. The volatiles were removed *in vacuo*, and the residue was washed with pentane to give a yellow solid (380 mg, 90 %). ν_{max}(solid)/cm^{-1} 2960, 2925, 2863, 2821, 1454, 1444, 1408, 1400, 1257, 1229, 1078, 1010, 862, 788. ^{1}H NMR ($CDCl_3$, 25 °C, 300.1 MHz): δ 0.92 (br s, 2H, COD), 1.04 (t, 2H, J = 7.3 Hz, Me), 1.32 (m, 2H, COD), 1.48 (m, 2H, Bu), 1.90 (m, 2H, Bu), 2.37 (m, 2H, COD), 3.30 (m, 2H, COD) 3.35 (m, 2H, COD), 3.39 (s, 3H, NMe), 4.47 (t, 2H, J = 9 Hz NCH_2), 5.09 (br s, 2H, COD), 6.83 (d, 2H, J = 1.7 Hz, imidazole C^4/C^5). ^{13}C NMR ($CDCl_3$, 25 °C, 75.5 MHz): δ 14.17 (Me), 14.50 (COD), 19.96 (COD), 20.51 (Bu), 29.81 (COD), 31.89 (COD), 32.76 (Bu), 33.48 (COD) 38.18 (NCH_3),

50.79 (NCH_2) 53.90 (COD), 68.77 (d, J = 15 Hz, COD), 69.47 (d, J = 15.0 Hz, COD), 98.03 (d, J = 5.0 Hz, COD), 120.48 (imidazole C^4/C^5), 122.51 (imidazole C^4/C^5), 182.07 (d, J = 49.5 Hz, imidazole C^2).

30. (1-Butyl-3-methylimidazol-2-ylidene)dicarbonylchlororhodium(I) (10)

Carbon monoxide was passed through a solution of (1-butyl-3-methylimidazol-2-ylidene)chloro(η^4-cyclo-octa-1,5-diene)rhodium(I) (380 mg, 0.99 mmol) in CH_2Cl_2 (5 cm^3) for 30 min, the solvent was removed *in vacuo* and the solid washed with pentane to give a yellow-brown solid (328 mg, 99 %). ν_{max}(solid)/cm^{-1} 2959, 2872, 2361, 2342, 2066 (C≡O), 1989 (C≡O), 1616, 1455, 1259, 1082, 1015, 796. ^{13}C NMR ($CDCl_3$, 25 °C, 75.5 MHz): δ 14.11 (Me), 20.14 (Bu), 33.07 (Bu), 38.94 (MeN), 51.42 (NCH_2), 121.78 (imidazole C^4/C^5), 123.27 (imidazole C^4/C^5), C≡O and carbene carbons not observed.

31. [1-Butyl-3-(2,6-diisopropylphenyl)imidazol-2-ylidene]chloro(η^4-cyclo-octa-1,5-diene)rhodium(I)

1-Butyl-3-(2,6-diisopropylphenyl)imidazolium bromide (148 mg, 0.41 mmol) and dry THF (5 cm^3) were mixed under a nitrogen atmosphere. To this suspension was added a solution of $KOBu^t$ (50 mg, 0.44 mmol) in dry THF (5 cm^3) dropwise. The bromide salt dissolved to give a cloudy yellow solution. The reaction mixture was allowed to stir at room temperature for 2 h, before filtration under an inert atmosphere. To this solution was added $[Rh(COD)Cl]_2$ (100 mg, 0.20 mmol) in dry toluene (5 cm^3). The yellow reaction mixture was stirred overnight. The volatiles were removed *in vacuo*, and the residue was washed with pentane to give a yellow solid (90 mg, 60 %). ν_{max}(solid)/cm^{-1} 3126, 3094, 2963, 2934, 2870, 2829, 1679, 1468, 1455, 1408, 1381, 1222, 957, 855, 703. ^{1}H NMR ($CDCl_3$, 25 °C, 300.1 MHz): δ 0.96 (br s, 3H, Me), 1.15 (m, 12H, Me), 1.57 (m, 2H, COD), 1.39 (m, 2H, Bu), 1.94 (m, 2H, C*H*(CH_3)), 2.25 (m, 2H, Bu), 2.86 (m, 2H, COD), 3.40 (m, 4H, COD), 4.35 (br s, 2H, NCH_2), 4.90 (br s, 2H, COD), 5.25 (br s, 2H, COD), 6.84 (s, 1H, imidazole C^4/C^5), 7.22 (m, 3H, aromatic), 8.22 (1H, s, imidazole C^4/C^5). ^{13}C NMR ($CDCl_3$, 25 °C, 75.5 MHz): δ 14.48 (Me), 20.12 (Bu), 24.27 (Me), 28.61 (COD), 30.02 (*C*H(CH_3)), 31.27 (Bu), 33.47 (COD), 52.66 (NCH_2), 68.01 (COD), 99.00 (COD), 123.38, 124.82, 130.07, 136.11, 136.64, 145.75 (all aromatic/imidazole/COD).

32. [1-Butyl-3-(2,6-diisopropylphenyl)imidazol-2-ylidene]dicarbonylchloro-rhodium(I) (11)

Carbon monoxide was passed through a solution of [1-butyl-3-(2,6-diisopropyl-phenyl)imidazol-2-ylidene]chloro(η^4-cyclo-octa-1,5-diene)rhodium(I) (90 mg, 0.17 mmol) in CH_2Cl_2 (5 cm^3) for 30 min, the solvent was removed *in vacuo* and the solid washed with pentane to give a yellow-brown solid (81 mg, 99 %). ν_{max}(solid)/cm^{-1} 3052, 2987, 2873, 2306, 2079 (C≡O), 2000 (C≡O), 1673, 1629, 1551, 1422, 1265, 1014, 896, 791. ^{1}H NMR ($CDCl_3$, 25 °C, 300.1 MHz): δ 0.96 (br s, 3H, Me), 1.15 (m, 12H, Me), 1.39 (m, 2H, Bu), 1.97 (m, 2H, C*H*(CH_3)$_2$), 2.25 (m, 2H, Bu), 4.35 (br s, 2H, NCH_2), 7.01 (s, 1H, imidazole C^4/C^5), 7.22 (m, 3H, aromatic), 8.22 (s, 1H, imidazole C^4/C^5). ^{13}C NMR ($CDCl_3$, 25 °C, 75.5 MHz): δ 14.01 (Me), 20.16 (Bu), 23.35 (Me), 29.56 (*C*H(CH_3)$_2$), 33.05 (Bu), 51.80 (NCH_2), 123.39, 124.57, 125.57, 130.77, 137.64, 146.65 (all aromatic/imidazole), 182.59 (d, J = 74.0 Hz, C≡O or imidazole C^2), 211.05 (d, J = 42.2 Hz, C≡O or imidazole C^2).

Carbonyl stretching frequencies

Entry	Complex	ν(C≡O)/cm^{-1}
1	**7a**	2053, 1971
2	**7b**	2053, 1971
3	**8a**	2068, 1990
4	**8b**	2073, 1993
5	**9**	2056, 1972
6	**10**	2066, 1989
7	**11**	2079, 2000

33. Benzylidene[1-butyl-3-(2,6-diisopropylphenyl)imidazol-2-ylidene] dichloro-(tricyclohexylphosphino)ruthenium(IV) (12)

1-Butyl-3-(2,6-diisopropylphenyl)imidazolium bromide (100 mg, 0.27 mmol) and dry THF (5 cm^3) were mixed under a nitrogen atmosphere. To this suspension was added a solution of KOBu^t (33 mg, 0.30 mmol) in dry THF (5 cm^3) dropwise. The bromide salt dissolved to give a cloudy yellow solution. The reaction mixture was allowed to stir at room temperature for 2 h, before filtration under an inert atmosphere. To this solution was added Grubbs' I (225 mg, 0.27 mmol) in dry toluene (5 cm^3). The purple reaction mixture was stirred overnight. The volatiles were removed *in vacuo*, and the residue was washed with pentane to give a light pink solid (160 mg, 65 %). ν_{max}(solid)/cm^{-1} 2923, 2850, 1670, 1445, 1409, 1383, 1332, 1261, 1173, 1073, 1004, 915, 895, 848, 801, 760, 728, 687. ^{1}H NMR ($CDCl_3$, 25 °C, 300.1 MHz): δ 1.24 (m, 26H, Cy), 1.40 (m, 10H, Cy), 1.84 (m, 14H, Pr^i and Cy), 2.25 (m, 2H, Bu), 4.78 (t, 2H, J = 6.7 Hz, NCH_2), 6.80 (s, 1H, imidazole C^4/C^5), 6.90 (m, 1H, aromatic), 7.06 (m, 1H, aromatic), 7.11 (m, 1H, aromatic), 7.20 (m, 1H, aromatic), 7.27 (m, 1H, aromatic), 7.34 (m, 1H, aromatic), 7.53 (m, 1H, aromatic), 7.88 (m, 1H, aromatic), 8.45 (s, 1H, imidazole C^4/C^5), 19.58(s, 1H, alkylidene CH). ^{13}C NMR ($CDCl_3$, 25 °C, 75.5 MHz): δ 14.02 (Bu), 19.58 (Bu), 24.03 (Me), 26.74 (Cy), 26.98, 27.22, 27.41, 28.00, 28.13 (all Cy), 29.75 (*C*H(CH$_3$)$_2$), 32.41 (Bu), 51.03 (NCH_2), 123.67, 123.96, 125.00, 130.62, 132.29, 138.59, 145.70 (all alkene/aromatic/imidazole C^4/C^5), alkylidene not observed. ^{31}P NMR ($CDCl_3$, 25 °C, 121.5 MHz): δ 34.54.

34. Benzylidene[1-butyl-3-(2,4,6-trimethylphenylphenyl)imidazol-2-ylidene] dichloro(tricyclohexylphosphino)ruthenium(IV) (13)

1-Butyl-3-(2,4,6-trimethylmethylphenyl)imidazolium bromide (40 mg, 0.12 mmol) and dry THF (5 cm^3) were mixed under a nitrogen atmosphere. To this suspension was added a solution of KOBu^t (13 mg, 0.12 mmol) in dry THF (5 cm^3) dropwise. The bromide salt dissolved to give a cloudy yellow solution. The reaction mixture was allowed to stir at room temperature for 2 h, before filtration under an inert atmosphere. To this solution was added Grubbs' I (102 mg, 0.12 mmol) in dry toluene (5 cm^3). The purple reaction mixture was stirred for 2 h. The volatiles were removed *in vacuo*, and the residue was washed with pentane to give a light pink solid (50 mg, 50 %). ν_{max}(solid)/cm^{-1} 2961, 2919, 2847, 1731, 1485, 1445, 1395, 1259, 1173, 1077, 1015, 896, 844, 796. ^{1}H NMR ($CDCl_3$, 25 °C, 300.1 MHz): δ 1.06 (m, 10H, Cy), 1.27 (m, 10H, Bu and Cy), 1.57 (m, 12H, Bu and Cy), 1.82 (s, 6H, Me), 2.14 (t, 3H, J = 8.0 Hz, Me), 2.30 (m, 4H, CH_2), 4.68 (t, 2H, J = 7.2 Hz, NCH_2), 6.76 (d, 1H, J = 1.8 Hz, imidazole C^4/C^5), 7.08 (t, 2H, J = 8.0 Hz, aromatic), 7.17 (d, 1H, J = 1.8 Hz, imidazole C^4/C^5) 7.39 (m, 1H, aromatic), 19.42 (alkylidene CH). ^{13}C NMR ($CDCl_3$, 25 °C, 75.5 MHz): δ 14.07 (Bu), 18.14 (Me), 20.01 (Bu), 21.49 (Me), 22.70

(Cy), 28.17 (Cy), 30.02 (Cy), 32.28 (Cy), 33.44 (Bu), 59.96 (NCH_2), 123.12, 123.51, 128.30, 128.33, 129.66, 130.62, 131.18, 132.34, 136.55, 138.86 (all aromatic/imidazole C^4/C^5), 172.74 (imidazole C^2), alkylidene not observed. ^{31}P NMR ($CDCl_3$, 25 °C, 121.5 MHz): δ 36.88.

35. Benzylidene[1-butyl-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene]dichloro-dipyridineruthenium(IV) (14)

Complex **13** (50 mg, 0.050 mmol) was dissolved in toluene (3 cm^3), and pyridine (0.27 cm^3, 0.33 mmol) was added. The reaction was stirred for 10 min, during which time a change colour from light purple to green was observed. The reaction mixture poured into cold pentane, and a green solid precipitated. The solution was left overnight at –28 °C to allow crystallisation. The precipitate was filtered, washed with pentane and dried *in vacuo* to afford **35** as a green powder (15 mg, 40 %). ν_{max}(solid)/cm^{-1} 3063, 2960, 2865, 2857, 1602, 1484, 1444, 1404, 1379, 1296, 1259, 1221, 1085, 1068, 1024, 929, 872, 851, 799, 762, 730, 694.

36. [1-Butyl-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene]chlorogold(I)

A mixture of 1-butyl-3-(2,4,6-trimethylphenyl)imidazolium bromide (30 mg, 0.10 mmol) and Ag_2O (11 mg, 0.05 mmol) in DCM (10 cm^3) and stirred for 4 hours. (Tetrahydrothiophene)gold(I) chloride (33 mg, 0.10 mmol) was added, and the resulting mixture stirred for 3 hours. The solution was then filtered through Celite, and the solvent removed *in vacuo* to give a white solid (47 mg, 85 %). ν_{max}(solid)/cm^{-1} 2961, 2904, 1447, 1411, 1257, 1077, 1009, 861, 783, 742, 694. ^1H NMR ($CDCl_3$, 25 °C, 300.1 MHz): δ 0.94 (t, 3H, J = 7.4 Hz, Me), 1.35 (m, 2H, alkyl), 1.86 (2H, m, alkyl), 1.90 (s, 6H, Me), 2.30 (s, 3H, Me), 4.27 (t, 2H, J = 7.2 Hz, NCH_2), 6.85 (d, 1H, J = 1.8 Hz, imidazole C^4/C^5), 6.92 (s, 2H, aromatic), 7.12 (d, 1H, J = 1.8 Hz, imidazole C^4/C^5). ^{13}C NMR ($CDCl_3$, 25 °C, 75.5 MHz): δ 14.12 (alkyl), 18.19 (Me), 20.03 (alkyl), 21.52 (Me), 33.49 (alkyl), 51.65 (NCH_2), 122.49, 123.49, 129.79, 135.18, 140.02 (all aromatic/imidazole C^4/C^5), 172.20 (imidazole C^2).

Catalysis studies

37. Hydroformylation of hex-1-ene

A Büchi 1 litre steel autoclave was charged with **8a** (150 mg), toluene (250 cm^3) and hex-1-ene (6 cm^3); dodecane was added as internal standard. The mixture was pressurised to 10 bar with synthesis gas ($CO–H_2$, 1:1). The autoclave was then heated to 100 °C and kept at this temperature for 6 h with mechanical stirring. The system was cooled to room temperature, and the catalyst allowed to settle out. The supernatant was then decanted, leaving the solid in the vessel. The reaction mixture was evaporated *in vacuo*, and the products examined by ^1H NMR spectroscopy.

38. Ring-closing metathesis of diethyl diallylmalonate

The appropriate NHC–Ru complex was suspended (for the supported systems) or dissolved (for the model compounds) in CH_2Cl_2 (5 cm^3). Diethyl diallylmalonate was added and the mixture was stirred at the appropriate temperature for the given time (Table S1), during which time the catalyst turned from light purple to light brown. For the solid catalysts, the solution was then filtered and the spent catalyst washed with Et_2O. The solvent was removed *in vacuo*, giving the crude product as a brown oil. Detailed conditions are summarised in Table S1.

Table S1. Reaction details for RCM reactions

Entry	Catalyst.	Catalyst		Substrate		Temp. /K	Time /h	Yield /%
		Mass /mg	[Ru] loading /mmol	vol. /cm^3	moles /mmol			
1	**15b**	150	0.053	3.8	15	22	0.5	100
2	**15c**	300	0.016	2.9	12	22	0.5	100
3	**12**	130	0.140	1.5	6.2	22	0.5	100
4	**16c**	300	0.016	2.9	12	40	28	0
5	**14**	150	0.230	0.5	2.3	40	28	83

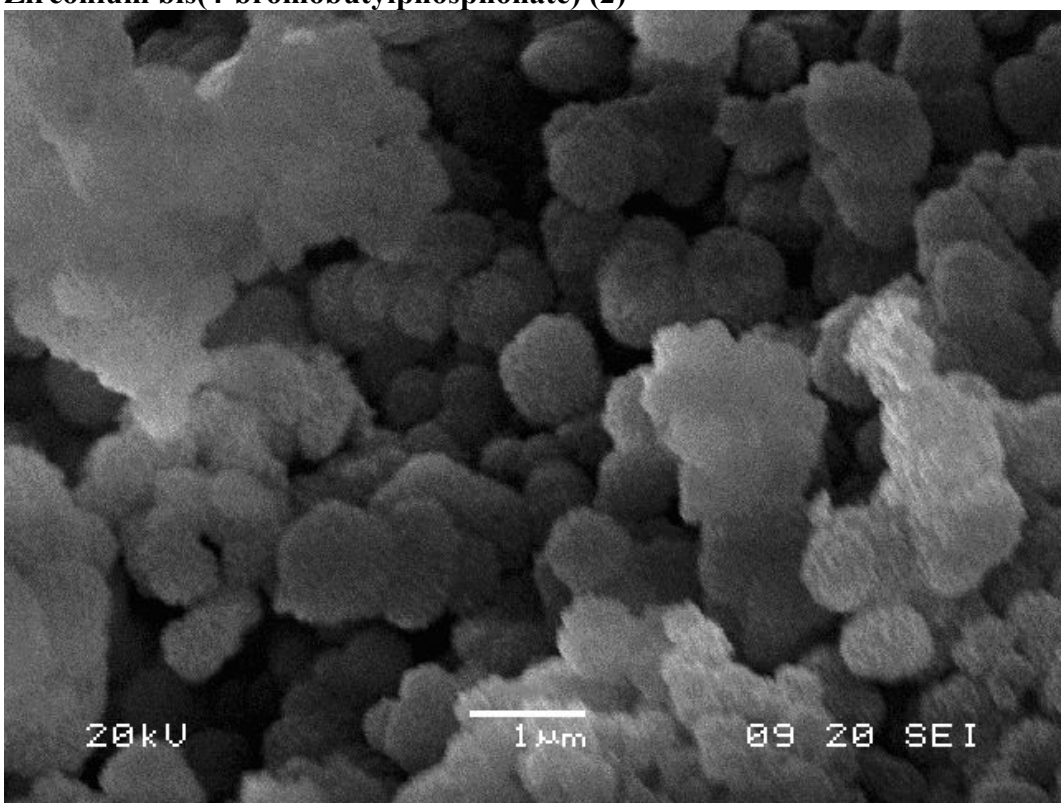
39. Hydroamination of phenylacetylene

The supported gold catalyst **17c** (300 mg), AgOTf (15 mg, 0.06 mmol), phenylacetylene (62 mg, 0.60 mmol) and aniline (61 mg, 0.66 mmol) were suspended in 1,4-dioxane. This mixture was then heated to 70 ºC under nitrogen for 6 h; over this time, the solution became purple. After cooling to room temperature and filtration, evaporation of the solvent *in vacuo* gave the product (47 mg, 40 %). ^{1}H NMR spectroscopy showed only Ph(Me)C=NPh (**18**) was present.

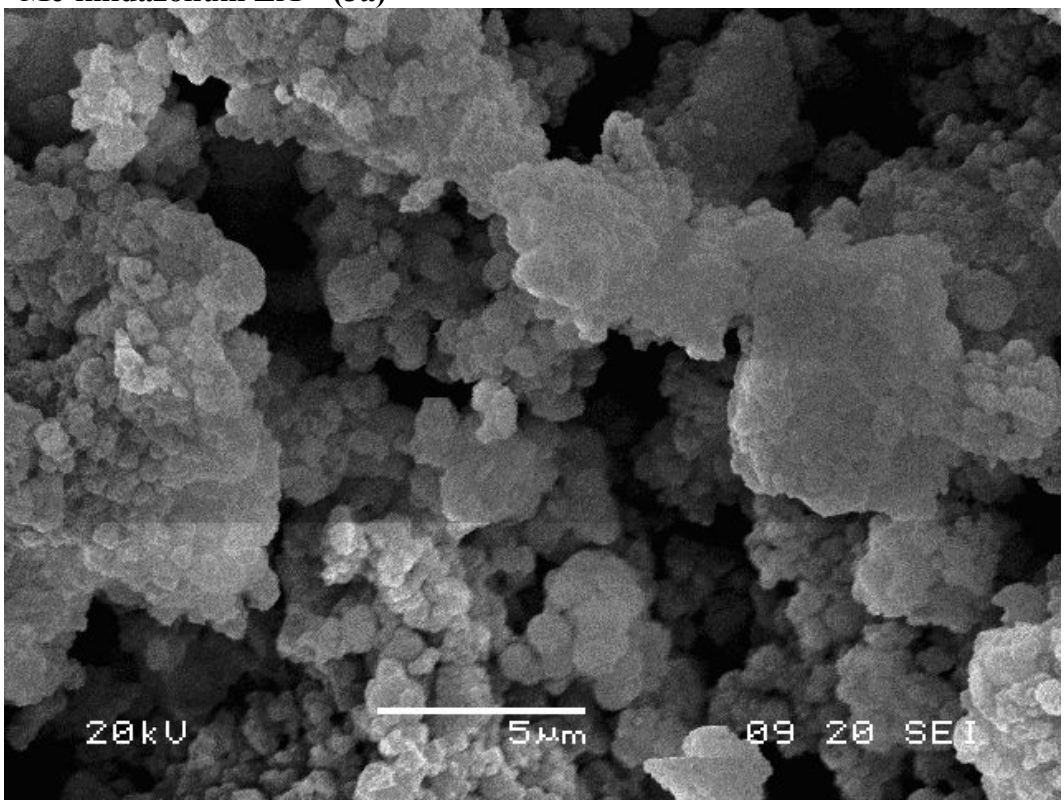
The same reaction could be carried out using unsupported **[1-butyl-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene]gold chloride** (14 mg, 0.06 mmol), the other conditions remaining identical. After 2.5 h, complete conversion of the substrate had occurred,to give Ph(Me)C=NPh and $PhCH_2CH$=NPh in a ratio of 75:25.

SEM images

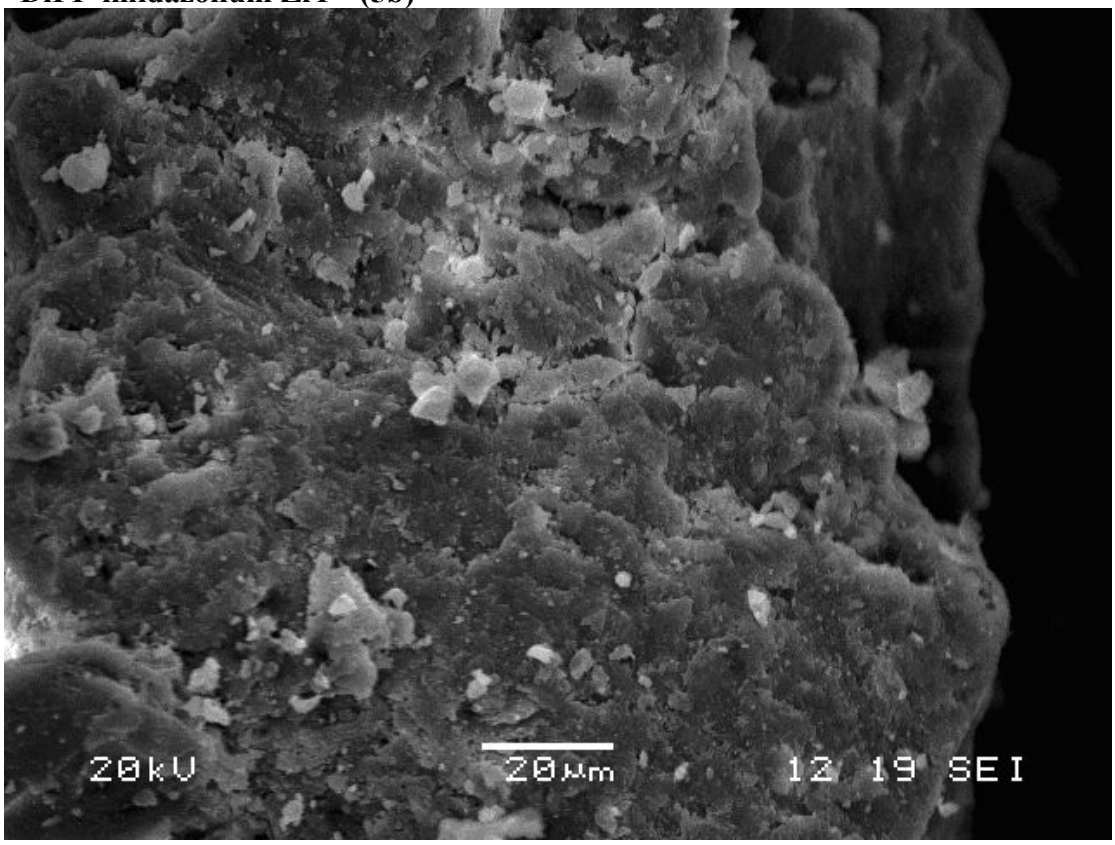
Zirconium bis(4-bromobutylphosphonate) (2)



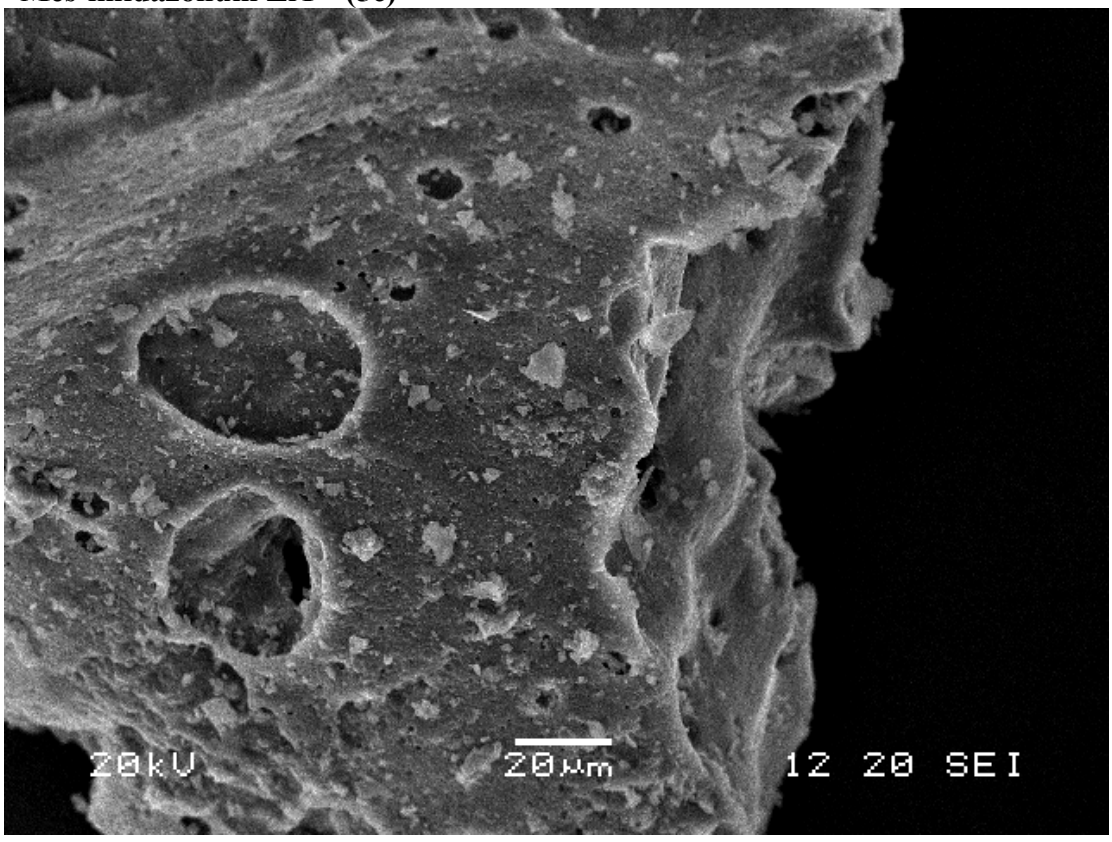
"Me-imidazolium ZrP" (3a)



“DiPP-imidazolium ZrP” (5b)

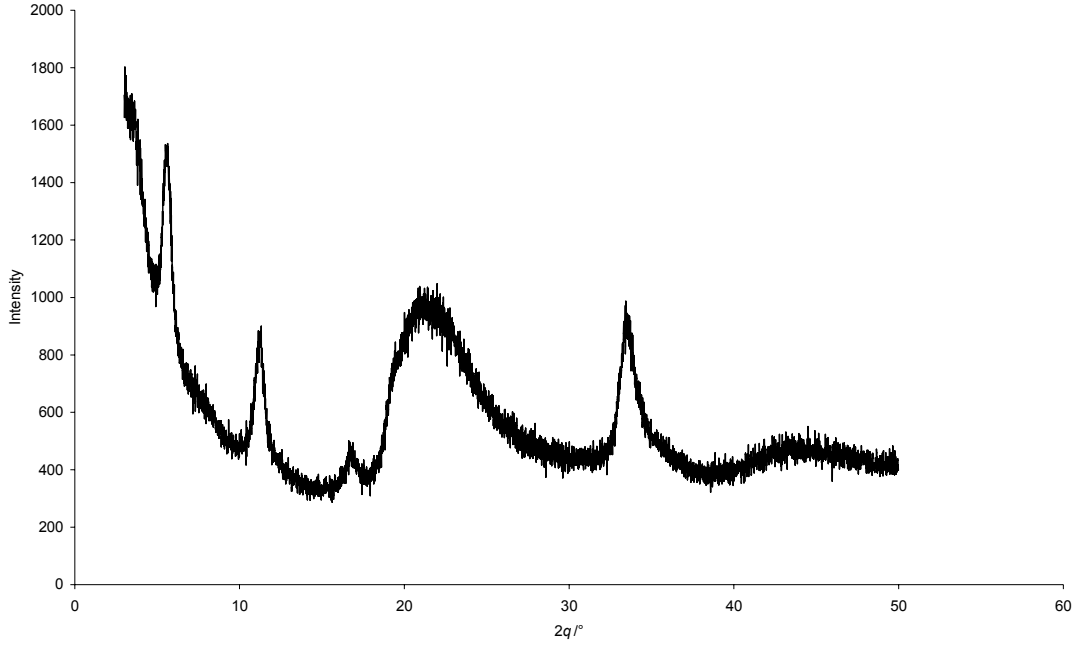


“Mes-imidazolium ZrP” (5c)

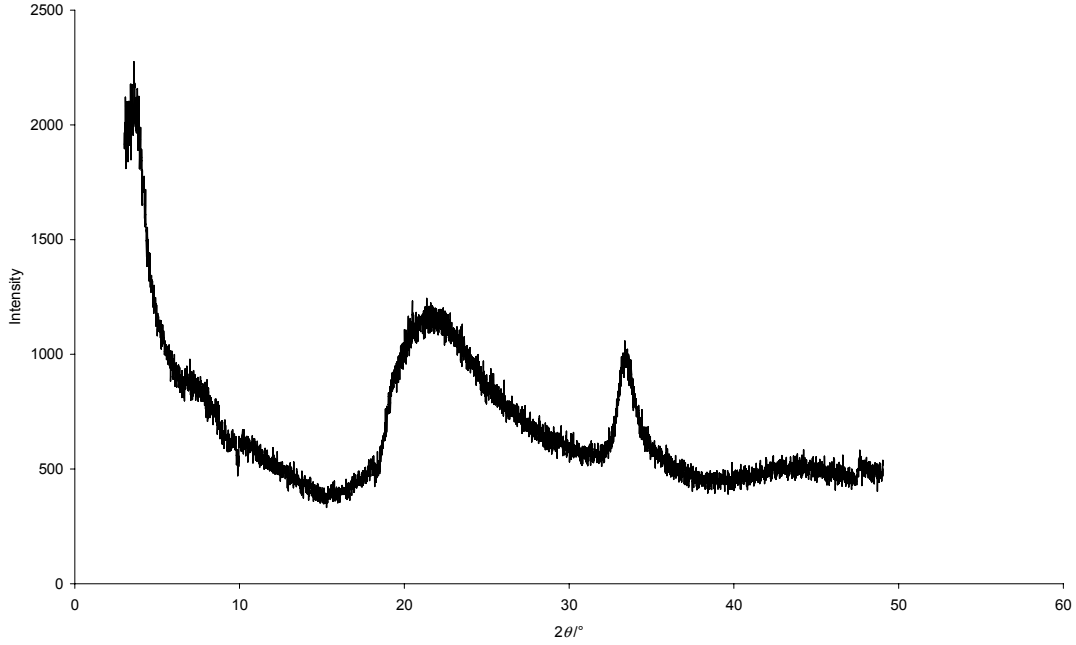


Powder diffraction traces

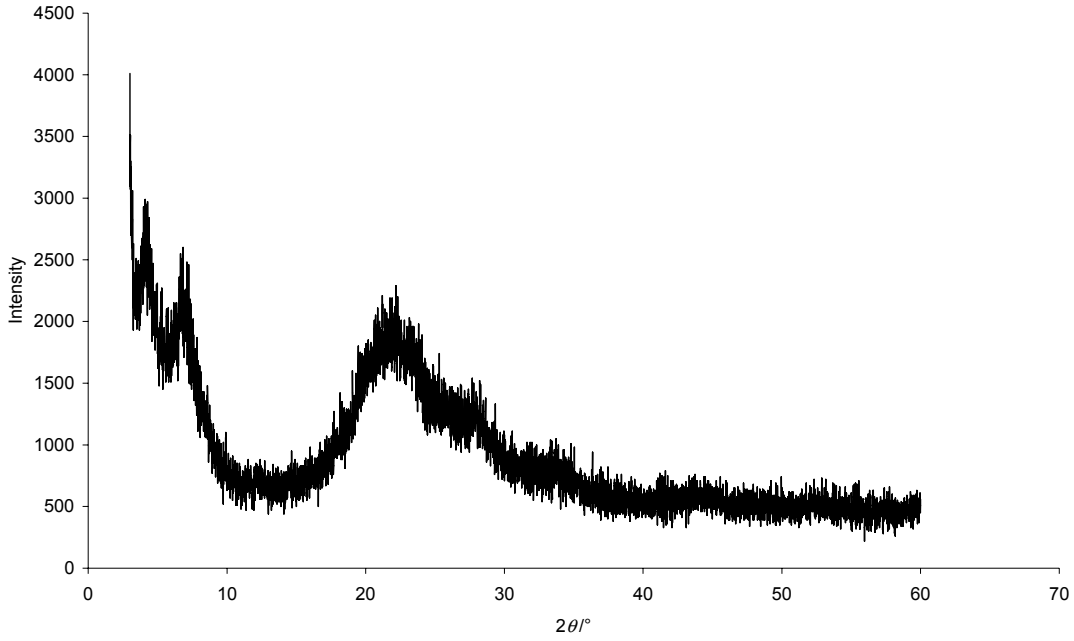
Zirconium bis(4-bromobutylphosphonate) (2)



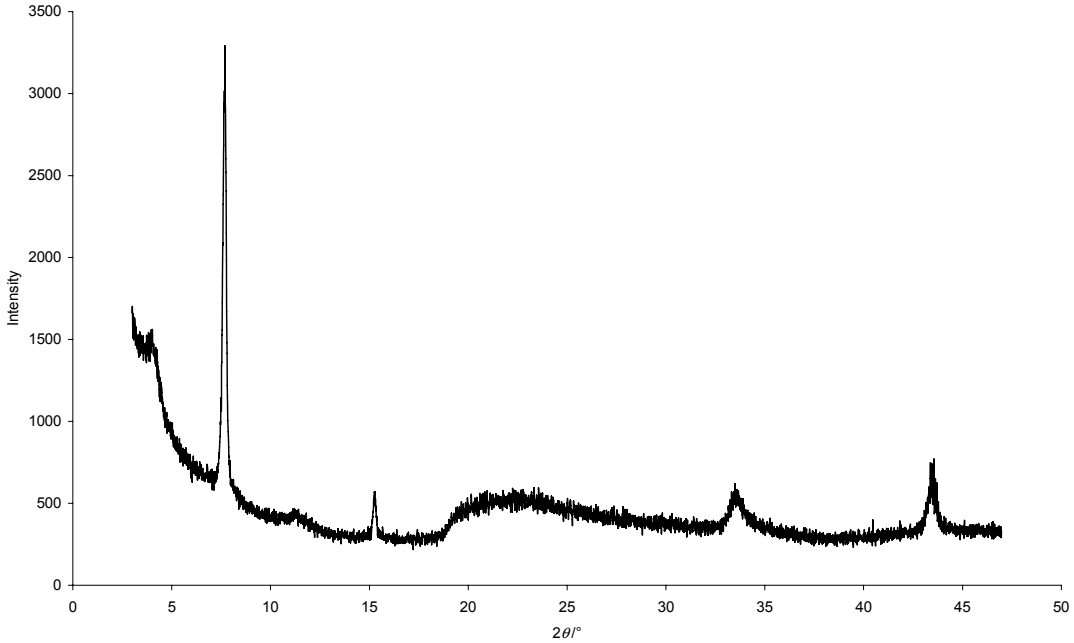
Me-imidazolium butyl-ZrP (3a)



$Zr(O_3PC_4H_8Br)_{1.4}(O_3PC_4H_8C_3H_3N_2C_6H_3Pr^i_2Br)_{0.6}$ (5b)



$Zr(O_3PC_4H_8Br)_{0.9}(O_3PC_4H_8C_3H_3N_2C_6H_3Me_3Br)_{1.1}$ (5c)



References

S1. W. L. F. Armarego and D. D. Perrin, *Purification of Laboratory Chemicals*, 4th edition, Butterworth–Heinemann, Oxford, 1996.
S2. A. L. Johnson, *U.S. Patent*, 1972, 3 637 731.
S3. R. Uson, A. Laguna and M. Laguna, *Inorg. Synth.*, 1989, **26**, 85–91.