SUPPORTING INFORMATION

Application of Palladium(monophosphine)(allyl)chloride complexes as catalysts for the alkoxy carbonylation of styrene; the use of 1,3,5,7-tetramethyl-6-phenyl-2,4,8-trioxo-6-phospha-adamantane as ligand enables successful Pd catalysed tert-butoxycarbonylation of styrene.

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Contents
1. General Methods
2. General procedure for hydroxycarbonylation
3. General procedure for alkoxy carbonylation
4. NMR data for catalysis products
5. Preparation of allyl palladium complexes
6. References
7. NMR spectra of allyl palladium complexes
8. NMR spectra of catalysis products

1. General Methods
Dry ether and THF were obtained from an Innovative Technologies Puresolve 400 solvent still. Other solvents were bought and used as received without further purification. Allylpalladium chloride dimer was purchased from Strem. MeCgPPh, [PdCl₂(MeCgPPh)₂], MeCgPO(Mesityl) and MeCgPO(o-Tolyl) were prepared according to the literature.¹ All manipulations were carried out under an atmosphere of nitrogen unless otherwise stated. CO was obtained from BOC. Solvents were removed by rotary evaporation on a Heidolph labrota 4000. Flash column chromatography was performed on Davisil silica gel Fluorochem 60 Å, particle size 35-70 μm. NMR spectra were recorded on Bruker Avance 300 and 400 instruments. Proton chemical shifts are referenced to internal residual solvent protons. Proton signal multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad) or a combination of the above. When appropriate, coupling constants (J) are quoted in Hz and are reported to the nearest 0.1 Hz. All
spectra were recorded at room temperature and the solvent for a particular spectrum is given in parentheses. Carbon chemical shifts are referenced to the carbon signal of the deuterated solvents. Infrared spectra were recorded on a Perkin Elmer Paragon 1000 Spectrum GX FT-IR system. Chemical ionisation mass spectroscopy and electron ionisation mass spectroscopy were performed on a Micromass GCT spectrometer. Electrospray mass spectroscopy was performed on a Micromass LCT spectrometer. All were operated by Mrs Caroline Horsburgh at St Andrews University, or at the EPSRC National Mass Spectrometry Service Centre, Swansea University, using Waters ZQ4000, Thermofisher LTQ Orbitrap XL and Finnigan MAT 900 XLT Instruments. Only major peaks are reported, and intensities are quoted as percentages of the base peaks.

2. General procedure for hydroxycarbonylation

A Biotage 5 ml microwave vial containing a stirring bar was charged with the appropriate amounts of LiCl, para-toluenesulfonic acid, catalyst and substrate (1 mmol) if the latter was a solid. The vial was sealed with a crimp cap, purged with three vacuum/argon cycles and left under argon atmosphere. The substrate (if a liquid), degassed water (45 μl, 2.5 mmol) and degassed butanone (1.5 ml) were added using a syringe. Two needles were pierced into the vial and this was introduced into the autoclave, which had been previously purged with three vacuum/argon cycles. The autoclave was then purged three times with CO, pressurised to 30 bar and immersed into an oil bath preheated to the desired temperature. After the desired reaction time, the autoclave was cooled down to room temperature, the pressure slowly released and opened. A small sample was taken and analysed by $^1$H NMR to calculate the conversion. The contents of the vial were then diluted with toluene and extracted three times with saturated aqueous NaHCO$_3$ solution. The combined aqueous layers were acidified with concentrated HCl until decidedly acidic pH according to litmus paper. This solution was then extracted with dichloromethane and the combined organic phases dried with MgSO$_4$, filtered and the final solution concentrated to dryness under vacuum. The residue consisted in the pure acid.

3. General procedure for alkoxy carbonylation

A Biotage 5 ml microwave vial containing a stirring bar was charged with the appropriate amounts of LiCl, para-toluenesulfonic acid, catalyst and substrate (1 mmol). The vial was sealed with a crimp cap, purged with three vacuum/argon cycles and left under argon atmosphere. Styrene, tetraethylsilane (20 μl, internal standard) and the appropriate degassed alcohol (1.5 ml) were added with syringe. Two needles were pierced into the vial and this was introduced into the
autoclave, which had been previously purged with three vacuum/argon cycles. The autoclave was then purged three times with CO, pressurised to 30 bar and immersed into an oil bath preheated to the desired temperature. After the desired reaction time, the autoclave was cooled down to room temperature, the pressure slowly released and opened. A small sample was taken and analysed by $^1$H NMR to calculate the conversion. The contents of the vials were vacuumed down to dryness and the crude was purified by column chromatography on SiO$_2$.

4. NMR data for catalysis products

2-phenylpropanoic acid\(^2\)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.27-7.15 (m, 5H), 3.65 (q, 1H, $J = 7.2$ Hz), 1.43 (d, 3H, $J = 7.2$ Hz). $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) δ 180.8 (C=O), 139.8 (ArC), 128.7 (ArCH), 127.7 (ArCH), 127.4 (ArCH), 45.4 (CH), 18.1 (CH$_3$). MS (ES$^+$): 173 (MNa$^+$); (ES$^-$): 149 (M–H).

Ethyl 2-phenylpropanoate\(^3\)

The crude was purified by filtering through a plug of SiO$_2$ using Hexane/EtOAc 7:1 as eluent to give the branched ester as a colorless oil (295 mg, 83%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.27-7.15 (m, 5H), 4.11-3.98 (m, 2H), 3.63 (q, 1H, $J = 7.2$ Hz), 1.42 (d, 3H, $J = 7.2$ Hz), 1.13 (t, 3H, $J = 7.1$ Hz). $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) δ 174.6 (C=O), 140.7 (ArC), 128.6 (ArCH), 127.5 (ArCH), 127.1 (ArCH), 60.7 (CH$_2$), 45.6 (CH), 18.6 (CH$_3$), 14.1 (CH$_3$). MS (ES$^+$): 201 (MNa$^+$); HRMS (ES) calculated for C$_{11}$H$_{14}$NaO$_2$, 201.0891; found 201.0887

Isopropyl 2-phenylpropanoate\(^4\)

The crude was purified by filtering through a plug of SiO$_2$ using Hexane/EtOAc 7:1 as eluent to give the branched ester as a colorless oil (185 mg, 96%). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.35-7.21 (m, 5H), 5.05-4.93 (m, 1H), 3.67 (q, 1H, $J = 7.2$ Hz), 1.48 (q, 3H, $J = 7.2$ Hz), 1.22 (d, 3H,
$J = 6.3 \text{ Hz}$), $1.13$ (d, $3\text{H}, J = 6.3 \text{ Hz}$). $^{13}$C{$^1$H} NMR (75 MHz, CDCl$_3$) $\delta$ 174.9 (C=O), 141.5 (ArC), 128.9 (ArCH), 127.9 (ArCH), 127.4 (ArCH), 68.4 (CH), 46.2 (CH), 22.2 (CH$_3$), 22.0 (CH$_3$), 19.0 (CH$_3$). MS (ES$^+$): 215 (MNa$^+$).

**Benzyl 2-phenylpropanoate$^3$**

Purified by chromatography on SiO$_2$ using Hexane/EtOAc 10:1 as eluent to give the branched ester as a colorless oil (214 mg, 89%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.45-7.29 (m, $5\text{H}$), 5.20 (d, $1\text{H}, J = 12.5 \text{ Hz}$), 5.14 (d, $1\text{H}, J = 12.5 \text{ Hz}$), 3.84 (q, $1\text{H}, J = 7.2 \text{ Hz}$), 1.59 (d, $3\text{H}, J = 7.2 \text{ Hz}$). $^{13}$C{$^1$H} NMR (75 MHz, CDCl$_3$) $\delta$ 174.4 (C=O), 140.5 (C), 136.1 (C), 128.7 (CH), 128.5 (CH), 128.4 (CH), 127.9 (CH), 127.8 (CH), 127.6 (CH), 66.4 (CH$_2$), 45.6 (CH), 18.5 (CH$_3$), 10.2 (CH$_3$). MS (ES$^+$): 263 (MNa$^+$); HRMS (ES) calculated for C$_{16}$H$_{16}$NaO$_2$, 263.1048; found 263.1045.

**tert-Butyl 2-phenylpropanoate$^5$**

The crude was purified by filtering through a plug of SiO$_2$ using Hexane/EtOAc 8:1 as eluent to give the branched ester (containing a small amount of linear and i-Pr ester, c.a. 1% and 2.9% respectively) as a colorless oil (147 mg, 71%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.237-7.25 (m, $5\text{H}$), 3.64 (q, $1\text{H}, J = 7.2 \text{ Hz}$), 1.48 (d, $3\text{H}, J = 7.2 \text{ Hz}$), 1.43 (s, $9\text{H}, t$-Bu). $^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$) $\delta$ 173.9 (C=O), 141.2 (ArC), 128.5 (2xArCH), 127.4 (2xArCH), 126.8 (ArCH), 80.4 (C), 46.5 (CH), 27.9 (3xCH$_3$), 18.5 (CH$_3$). MS (ES$^+$): 229 (MNa$^+$).

5. Preparation of allyl palladium complexes

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\text{PPh}_3 \overset{\text{Pd}}{\rightarrow} [(\eta^3-C_3H_5)\text{PdCl}(\text{PPh}_3)], \ 5^6
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PPh$_3$ (72 mg, 0.273 mmol) and [(\eta$^3$-C$_3$H$_5$)PdCl]$_2$ (50 mg, 0.137 mmol) were placed in a schlenk tube and and left under N$_2$ atmosphere. THF (4ml) and Et$_2$O (4 ml) were then added with a syringe and the reaction mixture stirred for 1 h. Most of the solvent was removed and then a solid crashed from the solution upon addition of dry ether. The white solid formed was filtered
and washed with dry ether. Yield: 92% (110 mg). IR (KBr, cm⁻¹) 3056, 3042, 2999, 2920, 1584, 1478, 1434, 1179, 1095, 1023, 997, 897, 749, 695, 529 and 499 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.61-7.56 (m, 6H), 7.46-7.37 (m, 9H), 5.65-5.55 (m, 1H), 4.77-4.73 (m, 1H), 3.76 (dd, 1H, J = 13.7 Hz, 9.8 Hz), 3.11 (d, 1H, J = 6.5), 2.83 (d, 1H, J = 12.1).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ 133.9 (d, 2JCP = 12.8, ArCH), 132.8 (d, 1JCP = 41.8, ArC), 130.4 (d, 4JCP = 2.0, ArCH), 128.5 (d, 3JCP = 10.3, ArCH), 118.1 (d, JCP = 4.9, CH), 79.9 (d, JCP = 30.9, CH₂), 61.1 (s, CH₂).

³¹P{¹H} NMR (162 MHz, CDCl₃) δ +22.6. HRMS (EI) calculated for C₂₁H₂₀ClP₁₀₄Pd, 442.0026; found 442.0030 ([M⁺]).

MeCgPPh (146 mg, 0.5 mmol) and [(η³-C₃H₅)PdCl]₂ (92 mg, 0.25 mmol) were placed in a schlenck tube and and left under N₂ atmosphere. Et₂O (6 ml) was then added with a syringe and the reaction mixture stirred for 1 h. The white solid formed was filtered and washed with dry ether. Yield: 55% (130 mg). The complex was obtained as a mixture of isomers in the ratio 1:1.15 (determined by ³¹P NMR). IR (KBr, cm⁻¹) 3073, 2987, 2910, 1631, 1480, 1435, 1381, 1344, 1264, 1209, 1136, 1087, 977, 894, 852, 829, 795, 749, 697, 574 and 587 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.04-7.92 (m, 4H), 7.49-7.37 (m, 6H), 5.56-5.41 (m, 2H), 4.81-4.71 (m, 2H), 4.27-4.17 (m, 2H), 3.75-3.69 (m, 2H), 2.92 (d, 1H, J = 11.9), 2.63 (d, 1H, J = 12.0), 2.44 (dd, 1H, J = 13.4 Hz, 5.4 Hz), 2.24 (dd, 1H, J = 13.4 Hz, 5.4 Hz), 2.00-1.24 (m, 30H). ³¹P{¹H} NMR (162 MHz, CDCl₃) δ +19.6 (s), +19.1 (s). HRMS (EI) calculated for C₁₉H₂₆O₃ClP₁₀₂Pd, 470.0359; found 470.0359 ([M⁺]). Calcd. for C₁₉H₂₇ClO₃Pd: C 48.02, H 5.51. Found: C 47.88, H 5.65. This compound was also characterized by X-ray crystallography.

MeCgPO(Mesityl) (96 mg, 0.273 mmol) and [(η³-C₃H₅)PdCl]₂ (50 mg, 0.137 mmol) were placed in a schlenck tube and and left under N₂ atmosphere. THF (2ml) and Et₂O (4 ml) were then added with a syringe and the reaction mixture stirred for 1 h. Most of the solvent was removed and then a solid crashed from the solution upon addition of dry ether. The white solid formed was filtered and washed with dry ether. Yield: 80% (117 mg). The complex was obtained as a
mixture of isomers in the ratio 1:1.05 (determined by $^{31}$P NMR). IR (KBr, cm$^{-1}$) 3075, 2973, 2994, 2909, 1483, 1444, 1389, 1339, 1309, 1200, 1124, 1087, 983, 958, 907, 858, 731, 678, 667, 589, 578 and 731 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.78 (s, 4H), 5.26-5.16 (m, 1H), 5.03-4.93 (m, 1H), 4.75-4.68 (m, 2H), 3.69-3.59 (m, 2H), 3.40 (d, 1H, $J = 6.4$), 3.13 (dd, 1H, $J = 14.0$ Hz, 6.0 Hz), 2.93-2.88 (m, 2H), 2.68-2.59 (m, 2H), 2.45 (s, 6H), 2.40 (s, 6H), 2.23 (s, 3H), 2.22 (s, 3H), 1.96-1.48 (m, 24H), 1.41 (s, 3H), 1.38 (s, 3H). $^{31}$P{$^1$H} NMR (162 MHz, CDCl$_3$) $\delta$ +118.8 (s), +118.2 (s). HRMS (EI) calculated for C$_{22}$H$_{31}$O$_4$P$_{104}$Pd, 494.0994; found 494.0995 ([M-H-Cl]$^+$). Calcd. for C$_{22}$H$_{32}$ClO$_4$PPd: C 49.54, H 6.05. Found: C 49.63, H 6.11. This compound was also characterised by X-ray crystallography.

References

7. NMR spectra of allyl palladium complexes

Ph₃P⁻Pd⁻Cl

ppm (f1)

ppm (f1)
8. NMR spectra of catalysis products