Supplementary Information

Interplay of bite angle and cone angle effects. A comparison between *o*-$C_6H_4(CH_2PR_2)(PR'_2)$ and *o*-$C_6H_4(CH_2PR_2)(CH_2PR'_2)$ as ligands for Pd-catalysed ethene hydromethoxycarbonylation.

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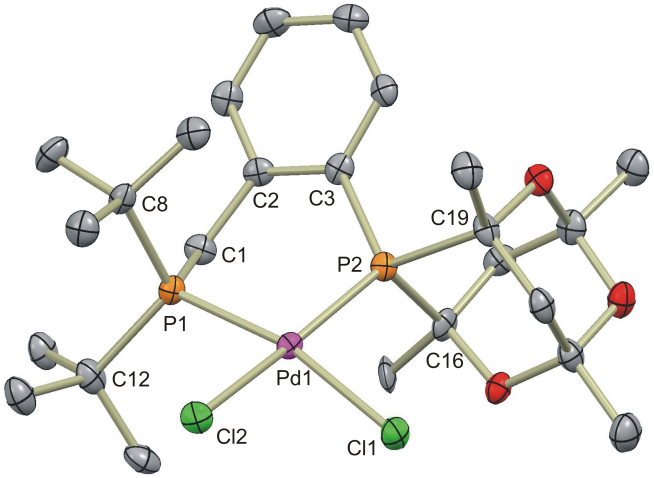
Crystal structure of [$PdCl_2(L_{3b})$]



Selected bond lengths (Å) and angles (°): Pd(1)-P(1) 2.2775(7); Pd(1)-P(2) 2.3004(7); Pd(1)-Cl(2) 2.3282(7); Pd(1)-Cl(1) 2.3837(7); P(1)-C(1) 1.837(2); P(1)-C(8) 1.881(3); P(1)-C(12) 1.901(3); P(2)-C(3) 1.839(3); P(2)-C(16) 1.894(3); P(2)-C(19) 1.903(3); P(1)-Pd(1)-P(2) 94.20(2); P(1)-Pd(1)-Cl(2) 88.65(3); P(2)-Pd(1)-Cl(1) 98.85(2); Cl(2)-Pd(1)-Cl(1) 85.80(3).

X-ray diffraction experiments were carried out using Mo-K_a radiation (λ = 0.71073 Å). Diffraction data for [$PdCl_2$(**L_{3b}**)] were collected on a Bruker SMART diffractometer at 173K. Data collections were performed using a CCD area detector from a single crystal mounted on a glass fibre. Intensities were integrated[1] from several series of exposures measuring 0.5° in ω or ϕ. Absorption corrections were based on equivalent reflections using SADABS.[2] The structures were solved using SHELXS and refined against all F_o^2 data with hydrogen atoms riding in calculated positions using SHELXL.[3] Crystal structure and refinement data are given in Table S1.

Table S1 Crystallographic data for **[$PdCl_2(L_{3b})$]**

Colour, habit	yellow block
Size/mm	0.20×0.20×0.05
Empirical Formula	$C_{25}H_{40}Cl_2O_3P_2Pd$
M	627.81
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.7707(11)
b/Å	15.2847(14)
c/Å	15.9116(15)
a/°	90.00
b/°	103.716(2)
g/°	90.00
V/Å^3	2781.0(4)
Z	4
m/mm^{-1}	0.999
T/K	173
$q_{min,max}$	2.22,27.48
Completeness	0.996 to q = 27.48°
Reflections: total/independent	18043/6349
R_{int}	0.0398
Final *R*1 and *wR*2	0.0297, 0.0679
Largest peak, hole/eÅ^{-3}	0.494, -0.461
r_{calc}/g cm^{-3}	1.499

1 Bruker-AXS SAINT V7.65 or 7.68A, Madison, Wisconsin.

2 G. M. Sheldrick, SADABS V2008/1 or TWINABS V2008/4, University of Göttingen, Germany.

3 G. M. Sheldrick, *Acta Cryst.* **A64**, 2008, 112-122