Novel application of borate esters as alternative acid promoters in the palladium catalyzed methoxycarbonylation of ethylene

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General:

The chemicals Pd(OAc)$_2$, PPh$_3$, MeOH, MePr, B(OH)$_3$, salicylic acid and its derivatives, trifluoroacetic, $p$-toluenesulfonic and MSA were purchased from Aldrich and used as received. The BSA can either be pre-formed or synthesised in-situ in the reaction mixture. Pre-formed BSA was synthesised by refluxing a solution of one mole of B(OH)$_3$ with two moles of salicylic acid in toluene and removing three moles of water with a Dean Stark apparatus. Separate addition of B(OH)$_3$ and salicylic acid to the reaction mixture gives rise to the in-situ prepared BSA. PPh$_3$ was purified prior to use, by recrystallisation from ethanol. C$_2$H$_4$ and high purity grade CO was supplied by Afrox.

General Procedure for the Methoxycarbonylation:

General autoclave run: a 300 ml magnetic-driven Parr autoclave constructed from Hastelloy was charged under a constant flow of argon by addition of the following reagents in the order that they are mentioned: Pd(OAc)$_2$ (0.24 mmol, 0.0539 g), PPh$_3$ (12.0 mmol, 3.148 g), B(OH)$_3$ (18.0 mmol, 1.113 g), salicylic acid (36.0 mmol, 4.972 g) in 120 ml of MeOH. The autoclave was closed and heated under vacuum to 110 °C with constant stirring (ca. 1000 rpm). After the desired temperature was reached, the autoclave was pressurized with a 1:1 mixture of CO and C$_2$H$_4$ to a total pressure of 10 bar. Gas feed was then switched to a prefilled, 1000 ml ballast vessel (same gas mixture) and the reaction progress was followed via pressure drop in the ballast vessel. After the reaction, a sample was taken and analyzed by GC / FID. The activity of the catalyst system is defined as follows: S.T.Y. = mole MePr/ litre reactor contents/ h, TOF = mole MePr/ mole Pd/ h, TON = total mole MePr/ mole Pd, Conversion = mole MePr/ mole MeOH. The formation rate (mM/h) was obtained from the amount
of product per reaction time, in hours. The GC analysis was done on a Shimadzu (GC 17A) using a CP-Select 624 column [dimensions 30mx0.32mmx1.8µm]; Temperature program: Initial oven temperature: 40 °C; Initial hold time: 5 min at 40 °C; First ramp: 15 °C/min to 220 °C; Final hold time: 5 min at 220 °C.

Quantification of phosphonium salts:

Methyl- and ethyltriphenylphosphonium bromide were purchased from Aldrich and utilised as standards for the methyl and ethyl salts. The triphenylphosphonium salts were quantified using $^{31}$P NMR spectroscopy. $^{31}$P NMR spectra were recorded on a 500 MHz Bruker Avance NMR spectrometer operating at 202.466 MHz; calibrated relative to an external sample of H$_3$PO$_4$ at 0 ppm. The high pressure experiments were performed in a 10 mm high pressure Roe$^{[1]}$ cell and spectra were recorded without spinning. The triphenylphosphonium salts were quantified either by tributylphosphine oxide as internal standard, or by oxidizing the free PPh$_3$ in the reaction mixture with H$_2$O$_2$ and integrating the relevant signals relative to OPPh$_3$.

The internal standard method was typically used where the amount of phosphonium salts formed were monitored in an NMR tube. A mixture of PPh$_3$ ligand, the appropriate acid promoter, as well as tri-(tert-buty1)-phosphine oxide as an internal standard in MeOH/MeOH-d$_4$ (1:1) was transferred under argon to a HP NMR cell. The HP NMR cell was pressurized with 20 bar of nitrogen. A $^{31}$P NMR spectrum of the mixture was recorded at 30 °C. The mixture was then heated to 110 °C and the formation of the salt was followed by recording $^{31}$P NMR spectra at 110 °C over a fixed period of time. The H$_2$O$_2$ method was used to determine the amounts of salts formed during catalytic runs and is summarised as follows: H$_2$O$_2$ was added to a sample of the reaction mixture (ca. 10 ml) and the solution was concentrated by using a Büchi-rotovap. CD$_3$OD was added and a $^{31}$P NMR spectrum recorded. With this method all the free and coordinated phosphine is oxidized to the corresponding oxide, while the phosphonium salts are not affected.

Table S1. Formation of methyltriphenylphosphonium salt with time for the reaction of acid with PPh$_3$ in MeOH. Conditions: [PPh$_3$] = 100 mM, [MSA] and [BSA] = 200 mM (for BSA; [B(OH)$_3$] = 200 mM and [salicylic acid] = 400 mM), * [PPh$_3$][MSA] = 23:25 mM, T = 110 °C, P$_{final}$ = 10 bar (CO:C$_2$H$_4$ = 1:1).

<table>
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<th>Time (min.)</th>
<th>Amount of PPh$_3$ converted to MePPh$_3$+ (%)</th>
<th>MSA</th>
<th>MSA*</th>
<th>BSA [in-situ]</th>
<th>BSA [pre-formed]</th>
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References: