A highly selective water-soluble dicationic palladium catalyst for the biphasic hydroxycarbonylation of alkenes

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The application of a water-soluble diphosphine with a xanthene-type backbone in the biphasic palladium-catalysed hydroxycarbonylation reaction of alkenes leads to the selective formation of carboxylic acids.

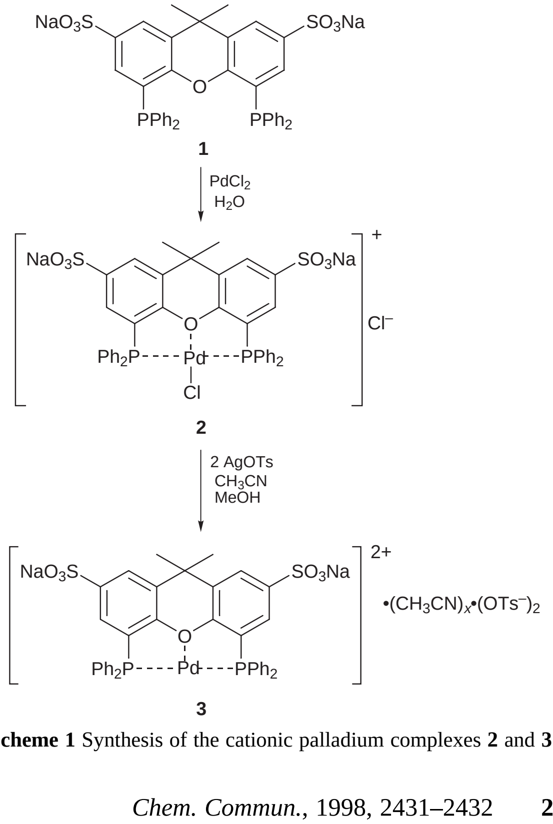
Water-soluble organometallic compounds have attracted considerable interest as catalysts.[1] Application of these compounds in two-phase catalysis results in easy separation and recycling of the catalyst.[2]

Various alkenes can be hydroxycarbonylated with carbon monoxide and water using transition metal compounds to yield the corresponding carboxylic acids.[3] Recently, the use of palladium catalysts for the biphasic hydroxycarbonylation of alkenes was reported.[4] The hydroxycarbonylation of alkenes in a two-phase system with the water-soluble palladium catalyst [Pd(TPPTS)$_3$] in the presence of a Brønsted acid as promoter yields carboxylic acids.[4,5] The catalyst predominantly affords carboxylic acids, but in most cases it suffers from low activities and selectivities. Water-soluble bidentate phosphines have been used to form active catalysts for palladium-catalysed alternating copolymerisation, *e.g.* a catalyst formed with the bidentate water-soluble phosphine C_3H_6-1,3-[P(C_6H_4-*m*-$SO_3Na)_2]_2$ (dppp-s) produces polyketone from ethylene and carbon monoxide.[6]

Recently, we developed the water-soluble bidentate diphosphine 2,7-bis(SO_3Na)-Xantphos (**1**) which was successfully applied in the two-phase rhodium-catalysed hydroformylation reaction of alkenes.[7] Here, the highly selective palladium-catalysed formation of carboxylic acids from alkenes and carbon monoxide in the presence of **1** and a Brønsted acid as a cocatalyst will be described.

Complex **2** was prepared by reaction of **1** with $PdCl_2$. Addition of two equivalents of AgOTs (OTs = *p*-$CH_3C_6H_4SO_3^-$) to a solution of **2** resulted in the dicationic palladium complex **3** which was isolated as an orange powder. The $^{31}P\{^1H\}$ NMR spectrum in CD_3OD shows only a singlet at 25.6 ppm which indicates that a *trans* complex is formed exclusively at room temperature.† This is probably due to the large natural bite angle of the xanthene backbone and the coordination of the oxygen atom to the dicationic palladium center.‡ The preferential formation of the *trans* complex, excluding copolymerisation activity which requires a *cis* coordination,[8] prompted us to investigate the applicability of **3** (and **2**) toward the selective formation of carboxylic acids. Indeed, hydroxycarbonylation of ethylene was 100% selective towards the formation of propionic acid without formation of oligomers or copolymers as indicated by ^1H NMR spectroscopy.§ The reaction proceeded at relatively low concentrations of palladium (1.6 mmol l^{-1}). As expected, the activity increased with increasing temperature. The addition of TsOH as a promoter was necessary to stabilise the catalyst as otherwise palladium black is formed during the reaction. The use of propionic acid as the proton donor instead of TsOH gave rise to formation of metallic palladium as well. More strongly coordinating anions stabilise the cationic center which results in a slower reaction and eventually in decomposition of the catalyst at elevated temperatures.[5,6] Run 1 was performed at 95 °C using 50 equivalents of TsOH and a total initial pressure of 30 bar (CO–ethylene = 1 : 1; Table 1). After the reaction very small amounts of palladium metal were formed. The activity (TOF¶ = 133 h^{-1}) increased to 180 h^{-1} when the reaction was carried out at 120 °C (run 2). When an additional equivalent of **1** was added to the catalyst solution an even higher activity was observed (TOF = 304 h^{-1}; run 3). Furthermore, no formation of palladium metal was observed during this run suggesting that the stability of the catalyst system had increased. Lower activities were found when **2** was used as the catalyst (TOF = 218 h^{-1} and 272 h^{-1}; runs 4 and 5) suggesting the higher activity for **3**. Catalysts prepared *in situ* (runs 6 and 7) gave rise to lower rates compared to **3** as well. In this case, the formation of the active catalyst is slower.

In order to investigate the regioselectivity of the catalytic system towards the formation of linear (l) and branched (b) carboxylic acids styrene and propene were also studied as substrates. The hydroxycarbonylation of styrene catalysed by **3** led to a mixture of 2- and 3-phenylpropionic acid (Scheme 2). The l/b ratio of the carboxylic acids was *ca.* 65/35 and a TOF of 40 h^{-1} was observed (run 9). A l/b ratio of *ca.* 70/30 was found when Pd(TPPTS)$_3$ was used as the catalyst (60% selectivity towards the formation of acids). This suggests that **3** does not induce higher selectivity compared to monodentate phosphines.‖ At 70 °C, 30 bar CO pressure and in the presence of 4-*tert*-butylcatechol as a polymerisation inhibitor less thermal polymerisation was observed without any change in activity and l/b ratio.

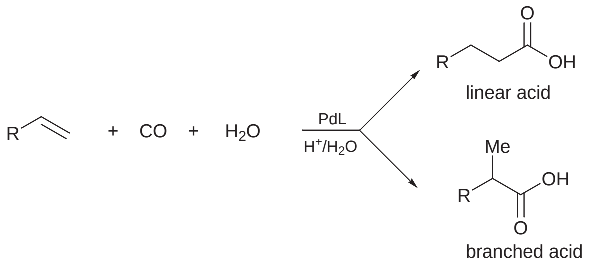


Scheme 1 Synthesis of the cationic palladium complexes **2** and **3**.

Table 1 Palladium-catalysed hydroxycarbonylation of ethylene (**4**), styrene (**5**) and propene (**6**)[a]

Run	Olefin	p-$CH_3C_6H_4SO_3H$/ mmol	T/°C	t/min	l/b	TOF/h^{-1}
1	**4**	0.9	95	180	—	133
2	**4**	0.9	120	180	—	180
3[b]	**4**	0.9	120	180	—	304
4[c]	**4**	0.9	120	180	—	218
5[b,c]	**4**	0.9	120	180	—	272
6[d]	**4**	0.9	120	180	—	266
7[e]	**4**	0.9	120	180	—	259
8	**4**	2.7	120	180	—	260
9[f]	**5**	2.7	95	180	65/35	40
10[g]	**5**	2.7	70	180	65/35	40
11	**6**	0.9	100	180	60/40	55
12	**6**	2.7	120	80	63/37	300
13[h]	**6**	2.7	120	45	65/35	140
14[i]	**6**	2.7	120	60	66/34	76
15	**6**	2.7	120	30	65/35	373
16	**6**	2.7	120	180	63/37	262
17[j]	**6**	2.7	120	180	65/35	163
18[k]	**6**	2.7	120	180	64/36	129

[a] Reaction conditions: 15.8×10^{-3} mmol Pd complex **3**, Brønsted acid, amount of olefin (15 bar of **4** or 9 bar of **6**) without the addition of organic solvent; initial total pressure at RT: 30 bar unless otherwise stated, 10 mL of H_2O. [b] 1 equiv. Xantphos-s added to **3**. [c] Palladium complex **2** was used as precursor. [d] Catalyst prepared *in situ* from $PdCl_2$ and 1 equiv. Xantphos-s. [e] Catalyst prepared *in situ* from $Pd(OAc)_2$ and 1 equiv. Xantphos-s. [f] 35% of polystyrene formed. [g] 4-*tert*-Butylcatechol (5 mmol) was added; 19% of polystyrene formed. [h] pressure **6** = 9 bar; pressure CO = 2 bar at RT. [i] pressure **6** = 9 bar; pressure CO = 1 bar at RT. [j] L/Pd ratio = 2; no formation of palladium black observed. [k] pressure **6** = 4.5 bar.



Scheme 2 Palladium-catalysed hydroxycarbonylation of ethylene (**4**; R = H), styrene (**5**; R = Ph) and propene (**6**; R = CH_3) (L = **1**).

Propene was hydroxycarbonylated at higher temperatures (100 °C) than styrene since it is not susceptible to polymerisation (runs 11–17). Under the given reaction conditions (9 bar of propene pressure) no polymer formation was detected, but activities were low (TOF = 55 h^{-1}). At 120 °C the TOF increased significantly [373 h^{-1} after 30 min reaction (run 15) and 262 h^{-1} after 3 h reaction (run 16)]. For the $Pd(TPPTS)_3$ catalyst high rates [TOF = 2507 h^{-1} (15 min); 1307 h^{-1}(30 min)] were observed, but in contrast with our system fast catalyst deactivation was reported.[5] At lower CO pressures the rate decreased and selectivity increased towards the linear acid (runs 13 and 14). At low pressures, the observed rates suggest that the reaction has an approximate first-order dependence on CO and alkene concentrations. Higher ligand to palladium ratios did not improve the selectivity, while a somewhat lower rate was observed (run 17). With a ligand to palladium ratio of 3 (or more) no catalytic activity at all was observed which suggests that a catalytically inactive coordinatively saturated bis-ligand Pd(II) species is formed.

In conclusion, we have shown that the dicationic Pd/Xantphos-s/TsOH system is very effective and 100% selective in the hydroxycarbonylation reaction of alkenes (no traces of oligomeric or polymeric species were observed) towards carboxylic acids. Furthermore, under optimised reaction conditions, no formation of metallic palladium was observed and initial turnover frequencies dropped only slightly within hours indicating that the system is highly stable under the reaction conditions employed. The scope of this useful system is currently under investigation.

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Notes and references

† *Selected data* for **2**: ^1H NMR (CD_3OD): δ 8.32 (s, 2H, ArH), 8.01 (d, J = 7.6 Hz, 2H, ArH), 7.32 (t, J = 5.1 Hz, 8H, ArH), 7.26 (t, J = 5.1 Hz, 8H, ArH), 7.12 (t, J = 5.1 Hz, 4H, ArH), 1.92 (s, 6H, ArH). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 23.8. (Found: C, 42.2; H, 4.1. Calc. for $C_{39}H_{30}O_7S_2P_2PdCl_2$: C, 42.4; H, 4.2%).For **3**: ^1H NMR (CD_3OD; only the dication): δ 8.38 (s, 2H, ArH), 7.42–7.34 (b, 20H, ArH), 6.99 (b, 2H, ArH), 2.03 (s, 6H, CH_3). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 25.6. (Found: C, 54.5; H, 4.2. Calc. for $C_{53}H_{44}O_{13}S_4P_2Pd{\cdot}2(CH_3CN)$: C, 54.0; H, 4.0%).

‡ These type of *trans* complexes were also found in the solid state.

§ *Catalysis:* the appropriate amount of catalyst (15.8 μmol), prepared from **2**, **3** or *in situ* from $PdCl_2$ or $Pd(OAc)_2$ and **1**, was mixed with 0.9 or 2.7 mmol of TsOH. The mixture was charged into a 200 mL stainless steel reaction vessel (ethylene) or a 50 mL Hastelloy C autoclave (styrene and propene) under an atmosphere of argon. Degassed water (10 mL) was added and after five pressurizing–depressurizing cycles with CO, to remove traces of argon/air, the autoclave was pressurized with the appropriate substrates (ethylene and propene) and CO or charged with styrene and pressurized with CO. The contents were heated to the desired temperature and magnetically stirred (840 rpm). After the reaction the autoclave was cooled to room temperature in a ice bath and slowly depressurized. The hydroxycarbonylation products were analysed by ^1H NMR (300 MHz, $CDCl_3$).

¶ All TOFs mentioned are average TOFs calculated over the given reaction time.

‖ Since styrene is susceptible to polymerisation, reactions were carried out at lower temperatures (70–95 °C). At 95 °C the selectivity towards carboxylic acids is 65% (35% polystyrene). When no catalyst is present the same amount of polystyrene is formed thermally. The preference for the formation of the linear acid is in contrast with that reported for the $Pd(TPPTS)_3$ catalyst (l/b ratio *ca*. 27/73; TOF = 49 h^{-1}).[5]

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