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A direct synthesis of carboxylic acids *via* platinum-catalysed
hydroxycarbonylation of olefins

A direct synthesis of carboxylic acids *via* platinum-catalysed hydroxycarbonylation of olefins†

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The platinum-catalysed hydroxycarbonylation of olefins is reported for the first time. Using a combination of PtCl$_2$/2,2′-bis(*tert*-butyl(pyridin-2-yl)phosphanyl)-1,1′-binaphthalene (Neolephos) in the presence of sulfuric acid [0.6 M] in acetic acid selective carbonylation of terminal aliphatic olefins proceeds to good yields and selectivities to the corresponding carboxylic acids. Comparing the reactivity of different butenes (iso- and *n*-butenes), the terminal olefin can be selectively carbonylated.

More than 80 years ago, Roelen and Reppe reported their seminal findings on cobalt- and nickel-catalysed carbonylation reactions.[1] Since then, these methodologies experienced rapid growth and numerous scientists from industry and academia contributed to their development.[2] As a result, homogeneous carbonylation reactions constitute a powerful tool box and allow to produce all kinds of carboxylic acids[3] and their derivatives, *e.g.* esters,[4] or amides[5] (hydroxy-, alkoxy-, or amino-carbonylation) using easily available starting materials, specifically olefins,[6] alcohols,[7] and ethers.[8]

Today, apart from hydroformylations of olefins, the largest carbonylative process in industry is the carbonylation of methanol (Rh-based Monsanto-[9] and Ir-based Cativa[10]-processes). In addition to acetic acid, the higher homologous carboxylic acids are of significant interest in industry, too. The important physical characteristics of this functional group such as acidity, polarity, and surface properties, make carboxylic acids useful for a wide range of applications, *e.g.* surfactants, coatings, preservatives, pharmaceuticals, agrochemicals, cosmetics, and other uses.[11] Moreover, carboxylic acids are versatile building blocks for the manufacture of the corresponding esters, nitriles, carboxylate salts, amides, anhydrides, and so on. Thus, numerous publications addressed catalytic hydroxycarbonylations, either applying new catalysts/ligands or optimizing reaction conditions, for example the advantageous addition of halide additives (CuCl$_2$, HCl, or LiCl).[12] In this respect, notable improvements have been disclosed by the groups of Mecking,[13] Drent,[14] van Leeuwen,[15] Sheldon,[16] or Laurenczy.[17]

An important parameter for any industrial application, especially in the area of bulk chemicals, is the price of the catalyst system. So far, the currently known methodologies for hydroxycarbonylation of olefins are difficult to be applied in industry due to problems of catalyst stability and recyclability. To address the latter issue, Monflier and co-workers[18] and afterwards Ionescu and co-workers[19] explored water-soluble Pd-catalysts, which can be recycled by phase seperation. In addition, Drent *et al.* at Shell proposed a catalyst recycling for the industrially relevant Pd/1,2-bis((di-*tert*-butylphosphanyl)-methyl)benzene (d*t*bpx; **L6**) catalyst system.[20]
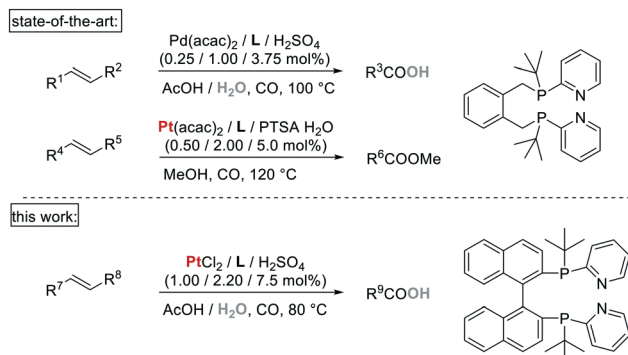
More recently, our group reported a palladium-based alkoxy-carbonylation catalyst with a built-in-base ligand (**L7**),[21] which also allowed for aqueous-phase hydroxycarbonylations to transform all kinds of olefins, including tetra-, tri-, and 1,1-disubstituted substrates, into their acids. Notably, this catalyst showed outstanding stability in more than 25 recycling runs (Scheme 1, top).[22] Despite this improved recycling, there is on-going interest to replace the expensive palladium metal, due to its growing price. Interestingly, in the last two years platinum metal became significantly less expensive than palladium. Thus, we started to investigate the catalytic activity of platinum complexes in carbonylation reactions and succeeded to develop a general Pt-catalysed alkoxycarbonylation (Scheme 1).[23] Unfortunately, testing this Pt-based methoxycarbonylation catalyst (Pt(acac)$_2$/**L7**) in related hydroxycarbonylation reactions was proved not successful and even traces of the desired carboxylic acids were not observed.

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Scheme 1 State-of-the-art palladium-based hydroxycarbonylation and platinum-based methoxycarbonylation (top). This work: first platinum-catalysed hydroxycarbonylation (bottom, racemic ligand is used).

Introducing an alternative platinum catalyst, herein we report the first platinum-catalysed hydroxycarbonylation of olefins. Our investigations started with exploring the reaction conditions for the model reaction of 1-octene to give pelargonic acid. Taking previous experiences into account,[22,23] we explored different mono- and bidentate

phosphine ligands in the presence of platinum(II) acetylacetonate and sulfuric acid as acid co-catalyst. As shown in Table 1, 13 different phosphines were tested and most of the monodentate (**L15–L13**) and bidentate ligands (**L2–L8**) displayed no conversion. However, in the presence of ligands **L1** and **L10** traces (<5%) of nonanoic acids were observed. Surprisingly, our recently introduced Neolephos ligand (**L9**)[24] gave the best result (28% of **2**). Apparently, for catalytic activity, the presence of basic pyridyl substituents on the phosphorus atom seems to be indispensable.
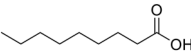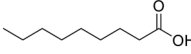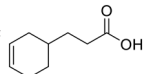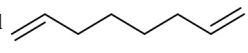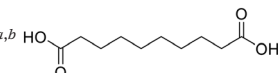
Previously, it was shown that the presence of halide ions had positive effects on palladium-catalysed carbonylations.[25] Therefore, PtCl$_2$ was tested as an alternative precursor. Indeed, enhanced reactivity is observed using ligands **L1**, **L2**, **L4**, **L7**, **L9–L11**, and **L13**. In particular, ligands with the designed built-in-base function resulted in improved yields. Again, the best result was obtained applying **L9** leading to nonanoic acids in 53% yield. Thus, additional o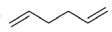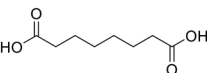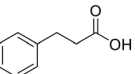ptimizations were performed using PtCl$_2$ and Neolephos (**L9**) as catalyst systems. Those studies included variations of the acid and the acid concentration (ESI-S3† Table S2), solvents (ESI-S3† Table S3), the acid to solvent ratio (ESI-S3† Table S4), and additives such as LiCl, acetonitrile, pyridine (ESI-S3† Table

Table 1 Pt-catalysed hydroxycarbonylation of 1-octene **1a**: the effect of ligands

Ligand		Yield (**2a** + **2a'**), n:iso	
		Pt(acac)$_2$	PtCl$_2$
No ligand	—	0%	0%
	L1: R^1 = ^{t}Bu R^2 = 2-Py	2%	41% (70/30)
	L2: R^1 = R^2 = Ph	0%	13% (57/43)
	L3: R = Ph	0%	0%
	L4: R = Ph	0%	23% (64/36)
	L5: R^1 = ^{t}Bu R^2 = Ph	0%	0%
	L6: R^1 = R^2 = ^{t}Bu	0%	0%
	L7: R^1 = ^{t}Bu R^2 = 2-Py	0%	45%
	L8: R^1 = R^2 = Ph	0%	0%
	L9: R^1 = ^{t}Bu R^2 = 2-Py	28% (80/20)	53% (70/30)
	L10: R^1 = Ph R^2 = 2-Py	3%	32% (65/35)
	L11: R^1 = R^2 = Ph	0%	25% (47/53)
	L12: R^1 = R^2 = C$_6$H$_{11}$	0%	0%
	L13: R^1 = C$_6$H$_{11}$ R^2 = 2-Py	0%	8% (47/53)

Reaction conditions: 1.0 mmol **1a**, 1.0 mol% [Pt], 2.2 mol% **L** (bidentate) or 4.0 mol% **L** (monodentate), 0.5 mL 0.3 M H$_2$SO$_4$, 1.5 ml acetic acid, 40 bar CO, 120 °C, 18 h. Yields (**2a** + **2a'**) and selectivities (n:iso) are obtained by GC analysis. Due to the measurement error range selectivities are not determined for yields ≤5%.

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Table 2 Substrate scope for platinum-catalysed hydroxycarbonylation reactions

Substrate	Product	Yield (*n*:iso)
1a 1-Octene	**2a**	70% (90/10)
		80% (90/10)
1b 2-Octene	**2b**	30% (44/56)
1c	**2c**[a]	91% (98/2)
1d	**2d**[a,b]	50% (90/10)
1e	**2e**	15% (88/12)
1f	**2f**	20% (66/34)

Reaction conditions: 1.0 mmol **1a**, 1.0 mol% $PtCl_2$, 2.2 mol% **L9**, 0.5 mL 0.6 M H_2SO_4, 1.5 ml acetic acid, 40 bar CO, 80 °C, 20 h. Yields and selectivity are obtained by GC analysis.[a] Isolated yields. [b] Scale 10 mmol, reaction time 40 h.
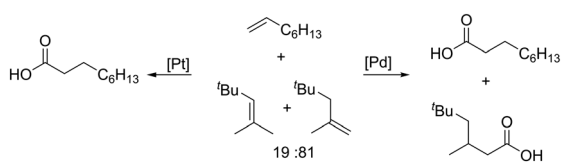
S5). A crucial parameter in this transformation is the reaction temperature. The first experiments were conducted at 120 °C and larger amounts of different side-products including alcohols, acetates, olefin isomers, *etc.* could be observed (ESI-S5†). Gratifyingly, lowering the temperature to 80 °C resulted in good yield of **2** (70%), while at the same time the chemo- and regioselectivity is increased to give preferentially the linear nonanoic acid (*n*:iso = 90/10). Comparing this yield and selectivity with an analogous $PdCl_2$-catalysed reaction (ESI-S4†), revealed that the palladium system is giving better yields of the desired acids. However, the presented platinum catalyst system showed higher selectivity for the desired linear acid. Notably, the platinum system showed at 80 °C an excellent catalyst stability for 48 h reaction time (ESI-S4†).

Having a suitable catalyst in hand, we studied the reactivity of different kinds of olefins to prove the scope and limitations of this platinum system (Table 2).
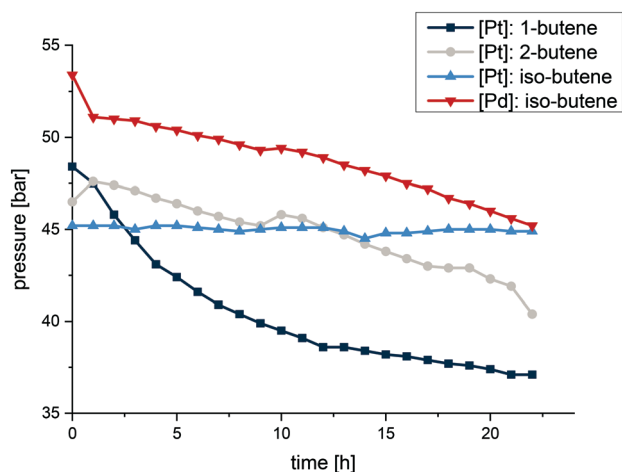
Comparing the reactivity of 1- and 2-octene under similar reaction conditions, the latter gave a significantly lower yield of nonanoic acids (Table 2, entries 1–2). Unfortunately, also at higher reaction temperature (120 °C) only low product yields were observed, while at the same time hydrogenation to alcohols and formation of acetates are observed. The low reactivity of internal olefins is also proven in the reaction of cyclohexene and 2,3-dimethylbut-2-ene, which gave no

desired carboxylic acids. This reactivity difference can be favourably exploited in the selective mono-carbonylation of 1-vinyl-3-cyclohexene yielding **2c** in very good yield and regioselectivity (Table 2, entry 3). In contrast to this, 1,7-octadiene and 1,5-hexadiene led to the corresponding dicarboxylic acids in moderate yields (Table 2, entries 4–5). In general, styrene – as an example for an aromatic olefin – can be also hydroxycarbonylated, albeit with reduced activity.

To demonstrate the different activities and selectivities of palladium- and platinum-based catalysts, olefinic mixtures were carbonylated. In a first try, 1-octene and di-*iso*-butylene (DIB) were mixed in a one to one ratio and applied to both the platinum and the palladium-based systems (1.0 mmol substrate mixture 1 : 1, 1.0 mol% [M]Cl_2, 2.2 mol% **L9**, 0.5 ml

Fig. 1 Pressure lines for hydroxycarbonylation reactions with Pt and 1-butene (dark-blue), 2-butene (grey), and iso-butene (light-blue) as well as Pd and iso-butene (red). Data are displayed by the beginning of a stable reaction temperature. Reaction conditions: 20 mmol substrate, 0.5 mol% [M], 2.2 mol% **L9**, 8.0 ml AcOH, 4.0 ml H_2SO_4 [0.6 M], 80 °C.

Scheme 2 Olefinic mixtures used in analogous platinum and palladium catalysis.

0.6 M H_2SO_4, 1.5 ml acetic acid, 40 bar CO, 80 °C, and 20 h). As shown in Scheme 2, the palladium catalyst formed all expected C-9 acids, while in the presence of the platinum system only 1-octene is carbonylated.

Finally, hydroxycarbonylation reactions of 1-butene, 2-butene, and iso-butene, which resemble the main constituents of the industrially produced and used olefin mixture raffinate 1 were explored. Measuring the pressure consumption during the reactions revealed again that platinum prefers hydroxycarbonylation of the terminal unbranched olefin (1-butene), while no reaction occurred with iso-butene Fig. 1).

Conclusions

In conclusion, we report the first protocol for a platinum-catalysed hydroxycarbonylation of olefins. Specifically the combination of $PtCl_2$/2,2′-bis(*tert*-butyl(pyridin-2-yl) phosphanyl)-1,1′-binaphthalene (Neolephos) allowed for selective carbonylation of aliphatic olefins to the corresponding carboxylic acids. Compared to related palladium complexes, the work here presented a catalyst system which selectively addresses terminal unbranched aliphatic olefins, which can be useful for process intensification applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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