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Rhodium-catalysed aryloxycarbonylation of iodo-aromatics by 4-substituted phenols with carbon monoxide or paraformaldehyde

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ABSTRACT

Rhodium-catalysed phenoxycarbonylation of aryl iodides were carried out under carbon-monoxide atmosphere and in the absence of CO, using paraformaldehyde as an alternative surrogate for carbonylation reactions. Both strategies proved to be efficient for the synthesis of the corresponding phenyl esters. High pressure reactions provided the ester products with good selectivity, however lower activity was achieved compared to palladium containing systems. Using paraformaldehyde as carbon-monoxide source special reaction conditions are required, thus dramatic changes observed during optimisation reactions. Using *in situ* generated Rh-diphosphine catalyst systems, remarkable influence of ligand structure and solvent composition was observed on the activity and chemoselectivity. The substrate scope and the substituent effect were also investigated.

1. Introduction

Since the discovery of the 'Roelen reaction' ('oxo-synthesis') [1] and Reppe carbonylation [2] in the middle of the past century transition metal catalysed carbonylation reactions have become the most developing field of homogeneous catalysis. 25 years later, Heck et al. reported the carbonylation reaction of aryl iodides and nucleophiles (alcohols or amines) [3], which process has been developed as a valuable new method for carbon-carbon bond formation. These reactions utilize carbon monoxide (CO) as C1 building block and can be efficiently catalysed by transition metals such as Rh, Ru or Pd, from which the homogeneous Pd-based catalyst systems have been reported as most outstanding ones for C—C couplings [4–7] so far. In spite of the excellent activity of rhodium-containing systems in the hydroformylation reactions and other non-carbonylative transformations [8–10] their feasibility in the area of other carbonylations such as amino- and alkoxycarbonylations, carbonylative coupling reactions have been less investigated.

The intrinsic properties of widely used carbon monoxide such as toxicity, flammability, as well as the required special equipment for handling justify several efforts of seeking non-gaseous CO sources. Their introduction into these reactions could lead to the realization of environmentally friendly alternatives. Among numerous CO sources [11,12] and precursors [13], formaldehyde as well as solid paraformaldehyde could be considered as most promising alternatives in solution phase. This cheap surrogate is easy to handle, atom economic and proved to be applicable in various homogeneous carbonylation reactions [14]. The use of formaldehyde in Rh-catalyzed hydroformylation reactions as CO surrogate is known for many years [15], however the application of this alternative CO source in homogeneous catalytic carbonylation reactions have become wide-spread only in the last decade.

Beside the thoroughly studied transfer hydroformylation of alkenes in the presence of paraformaldehyde [16,17] hydroalkoxycarbonylation of alkenes were also achieved. Ruthenium and palladium catalysts proved to be able to transform internal and terminal alkenes to methyl esters with moderate or good yields [18,19]. Notably, much more results can be found in the literature on the transition metal catalysed carbonylation of aryl halides with aldehydes. Kakiuchi and co-workers reported the efficient cyclisation of aryl bromides in the presence of various aldehydes [20]. Cinnamaldehyde and pentafluorobenzaldehyde give better results than paraformaldehyde, but the latter is still the prosperous choice in term of atom-economy (by-product is only hydrogen). Numerous other carbocyclic or heterocyclic systems were synthesized using similar strategy, i.e. indenones [21], benzoxazinones [22] or arylbenzofurans [23] catalysed by palladium phosphine systems. Additionally, paraformaldehyde was also effective in palladium catalysed alkoxycarbonylation of aryl bromides to form esters in the presence of alcohols [24]. Recently, *para*-chlorobenzaldehyde-supported alkoxycarbonylation of aryl iodides was also published using

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octanol and phenols as O-nucleophiles [25].

We recently reported the palladium-catalysed hydroaryloxycarbonylation of a set of styrenes under carbon monoxide atmosphere towards the corresponding arylpropanoic acid aryl esters [26]. The substituent effect on the regio- and enantioselectivity was also investigated regarding both the substrate (2- and 4-substituted styrenes) and the O-nucleophile (4-susbstituted phenols) with Pd-DIOP system. We decided to extend our studies on the phenoxycarbonylation reaction of aryl iodides using rhodium catalysts focusing on aromatic O-nucleophiles. The reactions were carried out both under carbon monoxide atmosphere and in the presence of paraformaldehyde as an alternative source of CO.

2. Experimental

2.1. General

The $[Rh(nbd)Cl)]_2$ precursor was synthesized from rhodium trichloride according to the standard procedure [27]. The $[Rh(acac)(CO)_2]$ was also synthesized by published method [28]. Ligands (TPP, DPPP, Xantphos, DPPB, DPPF) phenols, iodoarenes and dry toluene were purchased from Sigma-Aldrich and used without further purification. All reactions were carried out under argon atmosphere using standard Schlenk-techniques. The ^{1}H- and ^{13}C NMR spectra were recorded on a Bruker Avance-III 500 spectrometer. Chemical shifts are reported in ppm relative to TMS (downfield) for ^{1}H- and ^{13}C NMR spectroscopy. Conversions and selectivities were determined using GC and GC–MS. The esters were purified by column chromatography (Silica gel, 0.063 mm; $CHCl_3$) and isolated as pure solids.

2.2. Aryloxycarbonylation of iodoarenes under carbon monoxide atmosphere

In a typical experiment, catalyst precursor $[Rh(acac)(CO)_2]$ (2.68 mg; 0.01 mmol) and Xantphos (11.57 mg; 0.02 mmol) in toluene (10 mL) containing 1.0 mmol substrate, 2.0 mmol nucleophile and 1.2 mmol Et_3N were transferred under argon atmosphere into a 100 ml stainless steel autoclave followed by its pressurization with CO up to total 90 bar and placed in a pre-heated oil bath at 120 °C. The mixture was then stirred with a magnetic stirrer for 48 h. The pressure was monitored throughout the reaction. After cooling and venting of the autoclave at given reaction time, the solution was removed and immediately analyzed by GC and GC–MS.

2.3. Aryloxycarbonylation of iodoarenes using paraformaldehyde as CO surrogate

In a typical experiment, complex precursor $[Rh(nbd)Cl)]_2$ (4.80 mg; 0.01 mmol) and DPPP (20.62 mg; 0.05 mmol) in 10 ml of solvent mixture consists of toluene:ethyl acetate (4:6) containing 0.5 mmol substrate, 3 mmol of nucleophile, 16 mmol paraformaldehyde, 1.5 mmol Na_2CO_3, 1.25 mmol $MgSO_4$, and 1.0 mmol CuCl were transferred under argon atmosphere into three-necked round bottom flask and placed in a pre-heated oil bath. The mixture was then refluxed at 100 °C at atmospheric pressure using a balloon and stirred with a magnetic stirrer for 24 h. After cooling of the flask, the solution was removed and immediately analyzed by GC and GC–MS.

2.4. Characterisation of the products

Phenyl benzoate (**3aa**): δ_H (500 MHz, $CDCl_3$) 8.23–8.24 (2 H, m, *Ph*), 7.65–7.68 (1 H, m, *Ph*), 7.54 (2 H, t, 7.5 Hz, *Ph*), 7.46 (2 H, t, 7.5 Hz, *Ph*), 7.31 (1 H, d, 7.5 Hz, *Ph*), 7.24–7.26 (2 H, m, *Ph*). δ_C (125.7 MHz, $CDCl_3$) 165.2, 151.1, 133.7, 130.3, 129.7, 129.6, 128.7, 126.0, 121.8. IR (KBr (cm^{-1})): 3070, 3050, 1742, 1590, 1495, 1450, 1260, 1200, 1170, 1060, 830, 700. MS m/z (rel int.): 198 (11, M+), 141 (1), 105 (100), 93 (1), 77 (52), 65 (7), 51 (17).

Phenyl 4-fluorobenzoate (**3ba**): δ_H (500 MHz, $CDCl_3$) 8.263 (2 H, dd, 9.0 Hz, 5.5 Hz, *Ph*), 7.469 (2 H, t, 8.0 Hz, *Ph*), 7.314 (1 H, t, 7.5 Hz, *Ph*), 7.203–7.252 (4 H, m, *Ph*). δ_C (125.7 MHz, $CDCl_3$) 166.2 (d, 255.2 Hz), 164.2, 150.9, 132.8 (d, 8.8 Hz), 129.5, 126.0, 125.8, 121.7, 115.8 (d, 22.6 Hz). IR (KBr (cm^{-1})): 3075, 3064, 1734, 1597, 1506, 1273, 1193, 1166, 1078, 854, 759, 687. MS m/z (rel int.): 216 (8, M^+), 123 (100), 95 (40), 75 (15), 65 (5), 51 (4).

Phenyl 4-chlorobenzoate (**3ca**): δ_H (500 MHz, $CDCl_3$) 8.179 (2 H, d, 8.5 Hz, *Ph*), 7.527 (2 H, d, 8.5 Hz, *Ph*), 7.472 (2 H, t, 7.5 Hz, *Ph*), 7.320 (1 H, t, 7.5 Hz, *Ph*), 7.246 (2 H, dd, 8.0 Hz, 1 Hz, *Ph*). δ_C (125.7 MHz, $CDCl_3$) 164.4, 150.8, 140.2, 131.6, 129.6, 129.0, 128.1, 126.1, 121.6. IR (KBr (cm^{-1})): 3092, 3056, 1732, 1612, 1495, 1280, 1076, 853, 756, 723. MS m/z (rel int.): 232, 234 (7, 2, M^+), 139, 141 (100, 33), 111, 113 (33, 11), 93 (2), 75 (20), 65 (7), 50 (9).

Phenyl 4-bromobenzoate (**3 da**): δ_H (500 MHz, $CDCl_3$) 8.101 (2 H, d, 8.5 Hz, *Ph*), 7.694 (2 H, d, 8.5 Hz, *Ph*), 7.457–7.488 (2 H, m, *Ph*), 7.320 (1 H, t, 7.5 Hz, *Ph*), 7.235–7.251 (2 H, m, *Ph*). δ_C (125.7 MHz, $CDCl_3$) 164.5, 150.8, 132.0, 131.7, 129.6, 128.8, 128.5, 126.0, 121.6. IR (KBr (cm^{-1})): 3091, 3053, 1731, 1563, 1492, 1287, 1162, 1083, 850, 753, 668. MS m/z (rel int.): 276, 278 (6, 6, M^+), 183, 185 (100, 100), 155, 157 (29, 29), 104 (6), 76 (24), 65 (13), 51 (6).

Phenyl 4-methylbenzoate (**3ea**): δ_H (500 MHz, $CDCl_3$) 8.131 (2 H, d, 8.0 Hz, *Ph*), 7.461 (2 H, t, 7.5 Hz, *Ph*), 7.345 (2 H, d, 8.0 Hz, *Ph*), 7.301 (1 H, t, 7.5 Hz, *Ph*), 7.246 (2 H, d, 8.0 Hz, *Ph*), 2.488 (3 H, s, *CH*$_3$). δ_C (125.7 MHz, $CDCl_3$) 165.3, 151.1, 144.4, 130.2, 129.5, 129.3, 126.9, 125.8, 121.8, 21.8. IR (KBr (cm^{-1})): 3088, 3039, 2954, 2923, 2856, 1725, 1610, 1477, 1271, 1193, 1080, 751, 688. MS m/z (rel int.): 212 (5, M^+), 119 (100), 91 (43), 65 (23), 51 (3).

Phenyl 4-*tert*-butylbenzoate (**3fa**): δ_H (500 MHz, $CDCl_3$) 8.166 (2 H, d, 8.0 Hz, *Ph*), 7.559 (2 H, d, 8.5 Hz, *Ph*), 7.456 (2 H, t, 7.5 Hz, *Ph*), 7.282–7.349 (1 H, m, *Ph*), 7.235 (2 H, d, 8.0 Hz, *Ph*), 1.402 (9 H, s, *tert-butyl*). δ_C (125.7 MHz, $CDCl_3$) 165.2, 157.4, 151.1, 130.1, 129.5, 126.8, 125.8, 125.6, 121.8, 35.2, 31.1. IR (KBr (cm^{-1})): 3057, 2963, 2932, 2901, 2870, 1735, 1606, 1495, 1269, 1184, 1072, 765, 702. MS m/z (rel int.): 254 (1, M^+), 239 (4), 161 (100), 146 (11), 118 (14), 91 (10), 77 (6), 65 (7), 50 (3).

Phenyl 4-acetylbenzoate (**3ga**): δ_H (500 MHz, $CDCl_3$) 8.322 (2 H, d, 8.0 Hz, *Ph*), 8.106 (2 H, d, 8.5 Hz, *Ph*), 7.476 (2 H, t, 7.5 Hz, *Ph*), 7.325 (1 H, t, 7.5 Hz, *Ph*), 7.260 (2 H, d, 8 Hz, *Ph*), 2.704 (3 H, s, CO*CH*$_3$). δ_C (125.7 MHz, $CDCl_3$) 197.4, 164.3, 150.8, 140.8, 133.4, 130.4, 129.6, 128.4, 126.2, 121.6, 26.9. IR (KBr (cm^{-1})): 3057, 2963, 2834, 1732, 1678, 1489, 1405, 1317, 1271, 1215, 1162, 1091, 859, 762, 691. MS m/z (rel int.): 240 (6, M^+), 147 (100), 119 (15), 104 (11), 91 (17), 76 (14), 65 (11), 51 (4).

Phenyl 4-phenylbenzoate (**3 ha**): δ_H (500 MHz, $CDCl_3$) 8.312 (2 H, d, 8.5 Hz, *Ph*), 7.774 (2 H, d, 8.5 Hz, *Ph*), 7.691–7.709 (2 H, m, *Ph*), 7.529 (2 H, t, 7.5 Hz, *Ph*), 7.442–7.498 (3 H, m, *Ph*), 7.321 (1 H, t, 7.5 Hz, *Ph*), 7.277 (2 H, dd, 8.0 Hz, 1 Hz, *Ph*). δ_C (125.7 MHz, $CDCl_3$) 165.1, 151.0, 146.4, 140.0, 130.7, 129.5, 129.0, 128.3, 127.4, 127.3, 125.9, 121.8. IR (KBr (cm^{-1})): 3039, 1730, 1608, 1494, 1404, 1266, 1190, 1083, 825, 742. MS m/z (rel int.): 274 (3, M^+), 181 (100), 152 (42), 127 (3), 102 (1), 76(2), 65 (7), 51 (3).

4-Fluorophenyl benzoate (**3ab**): δ_H (500 MHz, $CDCl_3$) 8.233 (2 H, dd, 8 Hz, 1 Hz, *Ph*), 7.668–7.698 (1 H, m, *Ph*), 7.555 (2 H, t, 7.5 Hz, *Ph*), 7.200–7.241 (2 H, m, *Ph*), 7.125–7.177 (2 H, m, *Ph*). δ_C (125.7 MHz, $CDCl_3$) 165.2, 160.3 (d, 243.9 Hz), 146.8, 133.7, 130.2, 129.3, 128.6, 123.1(d, 7.5 Hz), 116.2 (d, 22.6 Hz). IR (KBr (cm^{-1})): 3113, 3065, 1731, 1504, 1294, 1188, 1087, 1064, 808, 706. MS m/z (rel int.): 216 (5, M^+), 105 (100), 83 (8), 77 (63), 58 (8), 51 (23).

4-Chlorophenyl benzoate (**3ac**): δ_H (500 MHz, $CDCl_3$) 8.230 (2 H, dd, 8 Hz, 1 Hz, *Ph*), 7.671–7.701 (1 H, m, *Ph*), 7.556 (2 H, t, 7.5 Hz, *Ph*), 7.417–7.448 (2 H, m, *Ph*), 7.193–7.223 (2 H, m, *Ph*). δ_C (125.7 MHz, $CDCl_3$) 165.0, 149.4, 133.8, 131.3, 130.2, 129.6, 129.2, 128.7, 123.1. IR (KBr (cm^{-1})): 3083, 3056, 1734, 1489, 1283, 1219, 1082, 1061, 808, 706. MS m/z (rel int.): 232, 234 (8, 3, M^+), 105 (100), 98 (5), 77 (63),