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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),

63 (5), 51 (23).

4-Bromophenyl benzoate (**3ad**): δ_H (500 MHz, $CDCl_3$) 8.216–8.232 (2 H, m, *Ph*), 7.670–7.700 (1 H, m, *Ph*), 7.539–7.597 (4 H, m, *Ph*), 7.138–7.168 (2 H, m, *Ph*). δ_C (125.7 MHz, $CDCl_3$) 164.9, 150.0, 133.8, 132.6, 130.2, 129.2, 128.7, 123.6, 119.0. IR (KBr (cm^{-1})): 3083, 3061, 1733, 1486, 1281, 1217, 1060, 806, 707. MS m/z (rel int.): 276, 278 (5, 5, M^+), 171, 173 (1, 1), 143, 145 (3, 3), 105 (100), 77 (55), 63 (8), 51 (20).

4-Trifluoromethylphenyl benzoate (**3ai**): δ_H (500 MHz, $CDCl_3$) 8.316–8.338 (1 H, m, *Ph*), 8.230–8.269 (1 H, m, *Ph*), 7.696–7.762 (2 H, m, *Ph*), 7.500–7.596 (2 H, m, *Ph*), 7.427–7.456 (1 H, m, *Ph*), 7.384–7.409 (1 H, m, *Ph*), 7.205–7.270 (1 H, m, *Ph*). δ_C (125.7 MHz, $CDCl_3$) 164.7, 153.5, 134.0, 130.3, 129.0, 128.7, 128.2 (quartet, 32.8 Hz), 126.9 (quartet, 3.8 Hz), 123.9 (quartet, 271.6 Hz), 122.3. IR (KBr (cm^{-1})): 3066, 2923, 1734, 1612, 1600, 1517, 1453, 1340, 1272, 1134, 1071, 817, 705. MS m/z (rel int.): 266 (1, M^+), 133 (4), 113 (2), 105 (100), 83 (2), 77 (56), 63 (2), 51 (19).

4-Isopropylphenyl benzoate (**3aj**): δ_H (500 MHz, $CDCl_3$) 8.233–8.252 (2 H, m, *Ph*), 7.651–7.683 (1 H, m, *Ph*), 7.531–7.562 (2 H, m, *Ph*), 7.303–7.331 (2 H, m, *Ph*), 7.155–7.183 (2 H, m, *Ph*), 2.980 (1 H, septet, 7.0 Hz, $(CH_3)_2CH$), 1.308 (6 H, d, 7.0 Hz, $(CH_3)_2CH$). δ_C (125.7 MHz, $CDCl_3$) 165.4, 148.9, 146.4, 133.5, 130.2, 129.8, 128.6, 127.4, 121.4, 33.7, 24. IR (KBr (cm^{-1})):): 3052, 3030, 2972, 2960, 2932, 2892, 1732, 1508, 1450, 1268, 1195, 1081, 1064, 809, 712. MS m/z (rel int.): 240 (13, M^+), 105 (100), 91 (8), 77 (48), 65 (3), 51 (11).

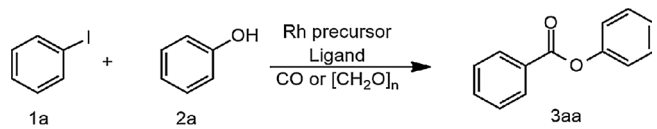
4-Methoxyphenyl benzoate (**3ak**): δ_H (500 MHz, $CDCl_3$) 8.238 (2 H, d, 7 Hz, *Ph*), 7.668 (1 H, t, 7.5 Hz, *Ph*), 7.545 (2 H, t, 7.5 Hz, *Ph*), 7.156–7.189 (2 H, m, *Ph*), 6.964–6.997 (2 H, m, *Ph*), 3.863 (3 H, s, OCH_3). δ_C (125.7 MHz, $CDCl_3$) 165.6, 157.4, 144.5, 133.5, 130.2, 129.7, 128.6, 122.5, 114.6, 55.6. IR (KBr (cm^{-1})): 3113, 3070, 2999, 2959, 2932, 2834, 1730, 1505, 1271, 1195, 1087, 1064, 808, 709. MS *m/z* (rel int.): 228 (19, M^+), 123 (3), 105 (100), 95 (3), 77 (48), 63 (1), 51 (13).

4-Phenoxyphenyl benzoate (**3 al**): δ_H (500 MHz, $CDCl_3$) 8.247 (2 H, dd, 8.0 Hz, 1 Hz, *Ph*), 7.663–7.698 (1 H, m, *Ph*), 7.556 (2 H, t, 7.5 Hz, *Ph*), 7.369–7.411 (2 H, m, *Ph*), 7.207–7.239 (2 H, m, *Ph*), 7.139–7.173 (1 H, m, *Ph*), 7.074–7.117 (4 H, m, *Ph*). δ_C (125.7 MHz, $CDCl_3$) 165.3, 157.3, 154.9, 146.4, 133.7, 130.2, 129.8, 129.5, 128.6, 123.4, 122.9, 119.7, 118.9. IR (KBr (cm^{-1})):): 3055, 1735, 1600, 1586, 1498, 1488,1450, 1269, 1184, 1093, 1066, 810, 710. MS m/z (rel int.): 290 (25, M^+), 185 (3), 157 (1), 129 (4), 105 (100), 77 (56), 63 (3), 51 (17).

4-Biphenyl benzoate (**3am**): δ_H (500 MHz, $CDCl_3$) 8.263–8.280 (2 H, m, *Ph*), 7.671–7.706 (3 H, m, *Ph*), 7.629–7.646 (2 H, m, *Ph*), 7.569 (2 H, t, 7.5 Hz, *Ph*), 7.476–7.506 (2 H, m, Ph), 7.399 (1 H, t, 7.5 Hz, *Ph*), 7.322–7.351 (2 H, m, *Ph*). δ_C (125.7 MHz, $CDCl_3$) 165.3, 150.4, 140.4, 139.1, 133.7, 130.2, 129.6, 128.8, 128.6, 128.3, 127.4, 127.2, 122.0. IR (KBr (cm^{-1})): 3057, 3027, 1732, 1486, 1272, 1220, 1087, 1065, 759, 703. MS m/z (rel int.): 274 (20, M^+), 169 (3), 141 (6), 115 (9), 105 (100), 77 (40), 51 (9).

3. Results and discussions

The transformation of the substrate iodobenzene (**1a**) and O-nucleophile phenol (**2a**) in the presence of rhodium catalysts to afford phenyl benzoate (**3aa**) was selected as a model reaction (Scheme 1). Two methods of carbonylation were conducted considering the source of the carbonyl group. Carbon monoxide was used in a conventional aryloxycarbonylation process and paraformaldehyde as its economical surrogate. Both strategies proved to be efficient in ester syntheses. First, the optimisation of the reaction was performed by the modification of the catalyst system as well as the reaction conditions using iodobenzene (**1a)** and phenol (**2a)**, respectively. Furthermore, *para*-substituted iodoarenes as well as *para*-substituted phenols were tested in the carbonylation reactions.



Scheme 1. Aryloxycarbonylation reactions with carbon monoxide or paraformaldehyde.

3.1. Reactions under carbon monoxide atmosphere

In general, the reaction was carried out in the presence of triethylamine as a base in toluene while the catalyst to substrate ratio was kept at 1/100. Incomplete, but satisfying conversions can be reached after 48 h which cannot be enhanced with longer reaction times. Beside the targeted esters, side products were formed in all cases in small extent, because of the reduction of the iodobenzene (benzene formation) or ester hydrolysis (carboxylic acid formation). The chemoselectivity of the reaction varied between 80–95%, where lower ester yields were achieved at elevated temperatures (120 °C).

All the tested ligands, including the parent monodentate triphenylphosphine (TPP), formed catalytically active complexes (Table 1, entries 1,2,6,11,13) though with DPPB lower activities and selectivities were obtained (entries 11, 12). DPPP, DPPF and Xantphos gave similar conversions, but the latter one provided notably higher ester chemoselectivity (67%, 81% and 95%, respectively). The results with TPP was promising, but 90% chemoselectivity lags behind the tem. Therefore, the Rh-xantphos system was selected for further investigations regarding the scope of the reaction (See below, Table 2). Significant differences were observed for different rhodium precursors, that is, reactions using dinuclear $[Rh(nbd)Cl]_2$ showed lower activity in the phenoxycarbonylation reaction (compare entries 7 and 10; 11 and 12) than chlorine-free $Rh(CO)_2(acac)$. It can be supposed that the formation of the catalytically active $Rh(CO)_n$(diphosphine) (n = 1,2) species took place much easier in the latter case due to two reasons: *i)* no dehalogenation (in case of Rh(I) species) or dehydrohalogenation on the influence of the base (in case of Rh(III) species formed in the catalytic cycle) was necessary, *ii)* no preliminary activation of CO was necessary.

Using Xantphos as ligand no significant difference was detected between catalyst precursors (entry 3 and 5) keeping metal to ligand ratio of 1:2. As expected, the carbon-monoxide pressure has a significant effect on the carbonylation reaction. Lower pressures resulted lower conversions (compare entries 2 and 4, or 8 and 9). The best result was obtained by using Xantphos as ligand under 90 bar of CO at 120 °C, which conditions were selected for subsequent experiments (entry 3).

With the optimum reaction conditions, the effect of the *para*-substituents on the substrate's reactivity was studied by varying both substrate iodoarene and the nucleophile phenol, as well (Table 2). 4-Substituted aryl iodides were found to be more reactive substrates than iodo benzene, regardless of whether electron withdrawing or donating substituents are located in *para* position. The corresponding phenyl 4-substituted benzoates (**3ba–3 ha**) were formed in 72–97%. However, aryl iodide bearing *tert*-butyl group afforded particularly lower conversion and chemoselectivity (entry 5). The highest yield (97%) was provided by the acetyl substituted substrate (**1 g**). Similarly, using *para*-substituted phenols the corresponding aryl benzoates (**3ab-3am**) were obtained in high yields independently on the electronic properties of the substituents (91–98%).

Noteworthy, similar results, *i.e.* increased reactivity of the substrate (4-iodotoluene) were observed in Pd-catalysed aryloxycarbonylation both with electron-withdrawing or electron donating substituents in the *para*-position of the phenol nucleophile [29]. Surprisingly, not only the O-nucleophile but the iodoarene substrates behaved similarly as follow: enhanced reactivity of the 4-substituted iodoarenes was observed possessing substituents either with positive or negative Hammett-*para*-substituent constant values (*vide supra*). Since not the expected electronic effect due to *para*-substituents of the substrate was observed, it can be stated that the rate-determining step of the aryloxycarbonylation

Table 1
Optimization of the phenoxycarbonylation reaction under CO atmosphere.[a].

Entry	Precursor	Ligand (eq.)	Temperature [°C]	p(CO) [bar]	Conv.[b] [%]	Yield (**3aa**)	Chemosel.[c] [%]
1	$Rh(CO)_2(acac)$	TPP (4)	90	90	> 99	90	90
2	$Rh(CO)_2(acac)$	Xantphos (2)	90	90	62	51	82
3	$Rh(CO)_2(acac)$	Xantphos (2)	120	90	80	76	95
4	$Rh(CO)_2(acac)$	Xantphos (2)	90	60	58	52	90
5	$[Rh(nbd)Cl]_2$	Xantphos (4)	120	90	79	76	96
6	$Rh(CO)_2(acac)$	DPPP (2)	90	90	76	72	95
7	$Rh(CO)_2(acac)$	DPPP (2)	120	90	92	62	67
8	$[Rh(nbd)Cl]_2$	DPPP (4)	90	90	27	21	78
9	$[Rh(nbd)Cl]_2$	DPPP (4)	90	60	8	6	75
10	$[Rh(nbd)Cl]_2$	DPPP (4)	120	90	60	53	88
11	$Rh(CO)_2(acac)$	DPPB (2)	90	90	20	19	95
12	$[Rh(nbd)Cl]_2$	DPPB (4)	90	90	7	4	57
13	$Rh(CO)_2(acac)$	DPPF (2)	90	90	64	57	89
14	$Rh(CO)_2(acac)$	DPPF (2)	120	90	82	67	82

[a] Reaction conditions: precursor: 0.01 mmol, substrate 1 mmol, phenol: 2 mmol, Et_3N: 1.2 mmol, toluene: 10 mL, reaction time: 48 h.
[b] Determined by GC.
[c] Chemoselectivity toward ester (**3aa**) product (moles of **3aa** / moles of converted **1a** x 100).

should be after the formation of the palladium(II)-acyl complex, *i.e.*, the rate and selectivity of the reaction are determined followed the oxidative addition step (see proposed catalytic cycle below; Fig. 1).

When the widely accepted mechanism of palladium-catalysed alkoxycarbonylation [30,31] as well as the observation of Miura et al is considered [29], the following catalytic cycle for the rhodium-catalysed reaction can be supposed. The oxidative addition of the iodoarene onto rhodium(I) species resulted in rhodium(III)-aryl complex (**B**). It is followed by CO insertion forming the corresponding rhodium(III)-acyl intermediate (**C**). The nucleophilic attack of the phenol (**D**) is accompanied by HI elimination resulting in the rhodium(III)-acyl-phenoxy complex (**E**). The reductive elimination of the phenyl benzoate product gave the coordinatively unsaturated rhodium(I) species (**F**) which yields the 'starting' complex via CO coordination.

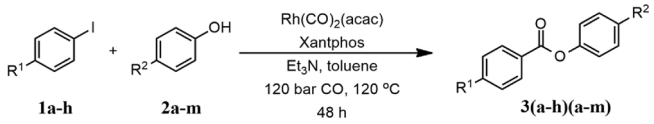
If the formation of **C** (or **D**) was the rate-determining step, it should be influenced by the acidity of the phenol, *i.e.*, a Hammett-plot should be obtained. Based on the reproducible catalytic results, the 'interplay' of the substituents on the aryl and phenol moieties may be supposed. Consequently, the reductive elimination step (or alternatively, the phenolic cleavage of the acyl-complex (**E**) could be considered as a rate-determining one.

3.2. *Reactions in the presence of paraformaldehyde as CO source*

The rhodium-catalysed phenoxycarbonylation reaction was carried out using the above substrates and phenols as well as rhodium-precursors in the absence of carbon monoxide enabling direct comparison between two methodologies. Based on preliminary results, the reaction seemed to be feasible using paraformaldehyde as CO source.

First, the reaction conditions were optimized using the model reaction involving substrate (**1a**) and phenol nucleophile (**2a**) (Table 3). Similarly to the experiments carried out under carbon-monoxide atmosphere, *in situ* generated catalysts were used with substrate to catalyst ratio of 50/1. Disappointingly, the experiments performed in

Table 2
Aryloxycarbonylation reaction with substituted iodoarenes and phenols.[a].



1a-h **2a-m** **3(a-h)(a-m)**

Entry	R^1 (iodoarene)	R^2 (phenol)	Conv.[b] [%]	Yield[c] (ester) [%]
1	F (**1b**)	H (**2a**)	80	72 (**3ba**)
2	Cl (**1c**)	H (**2a**)	95	88 (**3ca**)
3	Br (**1d**)	H (**2a**)	97	87 (**3 da**)
4	Me (**1e**)	H (**2a**)	97	88 (**3ea**)
5	*t*Bu (**1f**)	H (**2a**)	27	12 (**3fa**)
6	Ac (**1 g**)	H (**2a**)	> 99	97 (**3ga**)
7	Ph (**1 h**)	H (**2a**)	96	86 (**3 ha**)
8	H (**1a**)	F (**2b**)	> 99	94 (**3ab**)
9	H (**1a**)	Cl (**2c**)	> 99	98 (**3ac**)
10	H (**1a**)	Br (**2d**)	> 99	95 (**3ad**)
11	H (**1a**)	CF_3 (**2i**)	98	93 (**3ai**)
12	H (**1a**)	*i*Pr (**2 j**)	98	95 (**3aj**)
13	H (**1a**)	OMe (**2k**)	98	91 (**3ak**)
14	H (**1a**)	OPh (**2l**)	99	95 (**3 al**)
15	H (**1a**)	Ph (**2 m**)	> 99	98 (**3am**)

[a] Reaction conditions: precursor: 0.01 mmol, ligand: 0.02 mmol, substrate 1 mmol, nucleophile: 2 mmol, Et_3N: 1.2 mmol, toluene: 10 mL, p(CO) = 120 bar, T = 120 °C, reaction time: 48 h.
[b] Determined by GC.
[c] Isolated yields.

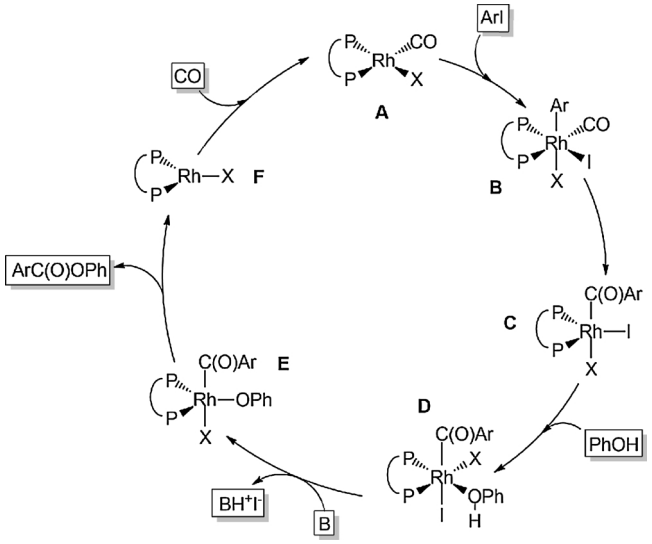


Fig. 1. Proposed mechanism of aryloxycarbonylation with carbon monoxide.

toluene or DMF gave low conversion and negligible yields of the corresponding ester (entries 1, 2). That is, in most cases not the ester formation but the side reactions, such as hydrodeiodination of the substrate and acid formation were also favoured. Numerous optimization reactions were conducted with different solvents and bases. Na_2CO_3 provided much better results than that of obtained in the presence of triethyl amine, and the introduction of drying agent ($MgSO_4$) also enhanced the chemoselectivity supressing the hydrolysis of the target esters. It should be also noted, that the addition of copper (I)-chloride considerably increased the reaction rate. The same phenomenon was described with palladium systems, where copper(I) plays important role on forming active catalytic species by removing phosphine ligands from palladium complexes [29]. In case of increased ligand/precursor ratio (see optimised conditions later) the potential formation of bis-diphosphine rhodium complexes can reduce the number of catalytically active species. It is conceivable that copper(I) can create vacant sites by receiving these additional ligands from rhodium enhancing the activity.

Precursor or ligand change did not resulted in any improvement in both activity and selectivity, even the best performance ligand under high pressure conditions, XANTPHOS showed moderate efficiency on paraformaldehyde-mediated carbonylation (entry 6). However, increasing the precursor-ligand ratio from 1 to 5 using DPPP, the side reactions can be supressed (entry 7). In order to increase the dissolution of the *in situ* forming formaldehyde, ethyl acetate was added to the reaction mixture as a co-solvent (entries 8–13) resulting in significantly better by using increased ligand ratio. Interestingly, only DPPP ligand showed acceptable performance under the selected reaction conditions (entry 8). In the presence of DPPF or DPPB still low ester yields can be obtained with slightly increased selectivity. Further increase of ethyl acetate ratio caused very low catalyst activity (entry 13). It is worth noting, that the $Rh(CO)_2(acac)$ precursor gave poorer results contrary to reactions under CO pressure (entry 3, 12).

The optimized procedure was applied to the phenoxycarbonylation of *para*-substituted iodoarenes (**1a–h**) and phenols (**2a–m**) (Table 4). Unfortunately, any substitution on the iodobenzene ring dramatically decreases the ester yield under the selected reaction conditions. Conversion values also decreased in numerous cases, but side reaction, namely hydrodeiodination obviously dominated against the carbonylation reaction (entries 1–7). This reductive pathway was described by other authors earlier [25], and efficient palladium-catalysed hydrodehalogenation with paraformaldehyde was also published by Lee and co-workers [32]. Beside the reduction of aryl halide, oxidation of the alcohol nucleophile was suggested providing aldehyde or formate as products.

Contrary to iodoarene substitution, no such negative effect was observed using various phenol derivatives (entries 8–14). The transformed amount of the substrate varied in wide range from 49% to total conversion, without any correspondence with the character of the substituents. Most of the nucleophiles gave lower conversions than the parent phenol, except fluoro and bromo substituted derivatives showed exceeded results (entries 8 and 10). The chemoselectivity of the carbonylation reaction was over 88% in all cases, in addition exclusive ester formation occurred with chloro, phenoxy and phenyl substituted phenols (entries 9, 13, 14 respectively).

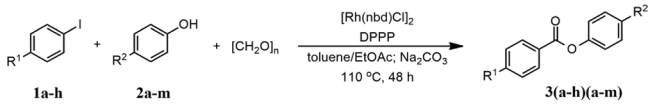
On the basis of our experiments and reported results [18,30–32], a plausible reaction mechanism can be proposed for the aryloxycarbonylation of iodoarenes, and for the reduction path via rhodium hydride intermediate (Fig. 2). First, the depolymerisation of paraformaldehyde occurs at elevated temperature to produce formaldehyde, which can undergo an oxidative addition with rhodium(I) species (**F**). The forming (hydrido)(acyl)rhodium(III) complex (**G**) can react further in two directions. Reductive elimination of H_2 gives the carbonyl-rhodium complex (**A**), which is the key intermediate of the phenoxycarbonylation pathway (cycle II). Upon this way, the formed carbonyl-rhodium complex can follow the route described earlier (Fig. 1), via aryl iodide addition (**B**), CO insertion (**C**) and by the attack of the nucleophile (**D**).

Table 3
Optimization of the phenoxycarbonylation reaction in the presence of paraformaldehyde.[a].

Entry	Precursor	Ligand (eq.)	Solvent	Conversion[b] [%]	Ester yield[b] [%]
1	$[Rh(nbd)Cl]_2$	DPPP (2)	Toluene	45	19
2	$[Rh(nbd)Cl]_2$	DPPP (2)	DMF	29	2
3	$Rh(CO)_2(acac)$	DPPB (1)	Toluene	32	15
4	$[Rh(nbd)Cl]_2$	DPPB (2)	Toluene	47	15
5	$[Rh(nbd)Cl]_2$	DPPF (2)	Toluene	44	14
6	$[Rh(nbd)Cl]_2$	XANTPHOS (2)	Toluene	24	11
7	$[Rh(nbd)Cl]_2$	DPPP (5)	Toluene	26	26
8	$[Rh(nbd)Cl]_2$	DPPP (2)	EtOAc:Toluene (6:4)	40	25
9[c]	$[Rh(nbd)Cl]_2$	DPPP (5)	EtOAc:Toluene (6:4)	76	76
10[c]	$[Rh(nbd)Cl]_2$	DPPB (5)	EtOAc:Toluene (6:4)	38	25
11[c]	$[Rh(nbd)Cl]_2$	DPPF (5)	EtOAc:Toluene (6:4)	43	18
12[c]	$Rh(CO)_2(acac)$	DPPB (2.5)	EtOAc:Toluene (6:4)	22	11
13[c]	$[Rh(nbd)Cl]_2$	DPPP (5)	EtOAc:Toluene (8:4)	5	5

[a] Reaction conditions: precursor: 0.01 mmol, substrate 0.5 mmol, phenol: 3 mmol, solvent: 10 mL, paraformaldehyde: 16 mmol, Na_2CO_3: 1.5 mmol, $MgSO_4$: 1.25 mmol, temperature: 100 °C, reaction time: 24 h. Mixed solvent (entries 7–12) are given in v/v%.
[b] Determined by GC.
[c] 1.0 mmol CuCl was used.

Table 4
Phenoxycarbonylation reaction with substituted iodoarenes and phenols.[a].



Entry	R^1 (iodoarene)	R^2 (phenol)	Conv.[b] [%]	Yield[b] (ester) [%]
1	F (**1b**)	H (**2a**)	28	19 (**3ba**)
2	Cl (**1c**)	H (**2a**)	67	3 (**3ca**)
3	Br (**1d**)	H (**2a**)	> 99	6 (**3 da**)
4	Me (**1e**)	H (**2a**)	43	35 (**3ea**)
5	*t*Bu (**1f**)	H (**2a**)	40	13 (**3fa**)
6	Ac (**1 g**)	H (**2a**)	> 99	2 (**3ga**)
7	Ph (**1 h**)	H (**2a**)	89	9 (**3 ha**)
8	H (**1a**)	F (**2b**)	> 99	86 (**3ab**)
9	H (**1a**)	Cl (**2c**)	51	51 (**3ac**)
10	H (**1a**)	Br (**2d**)	87	83 (**3ad**)
11	H (**1a**)	CF_3 (**2i**)	49	43 (**3ai**)
12	H (**1a**)	*i*Pr (**2 j**)	65	61 (**3aj**)
13	H (**1a**)	OPh (**2l**)	61	61 (**3 al**)
14	H (**1a**)	Ph (**2 m**)	58	58 (**3am**)

[a] Reaction conditions: precursor: 0.01 mmol, ligand: 0.05 mmol, substrate 0.5 mmol, nucleophile: 3 mmol, toluene: 4 mL, EtOAc: 6 mL, Na_2CO_3: 1.5 mmol, $MgSO_4$: 1.25 mmol, CuCl: 1.0 mmol.
[b] Determined by GC.

As another option, the release of CO provides the dihydrido-rhodium species ($\mathbf{H_A}$), which can be responsible for the reduction of the iodoarenes (cycle I, path A). Further possible way can be proposed with the formation of (formyl)(phenoxy)-rhodium complex ($\mathbf{H_B}$), which assumes the reductive elimination of phenyl formate as side product (path B). Both mechanisms lead to the (hydrido)(aryl) species (**I**), to get the hydrodehalogenated product and the initial unsaturated complex (**F**).

4. Summary

Rhodium-catalysed phenoxycarbonylation of aryl iodides were conducted under carbon monoxide atmosphere and with paraformaldehyde as CO surrogate. Under optimized reaction conditions both strategies proved to be appropriate for the synthesis of various phenyl esters. Increased reactivity can be observed by the substitution

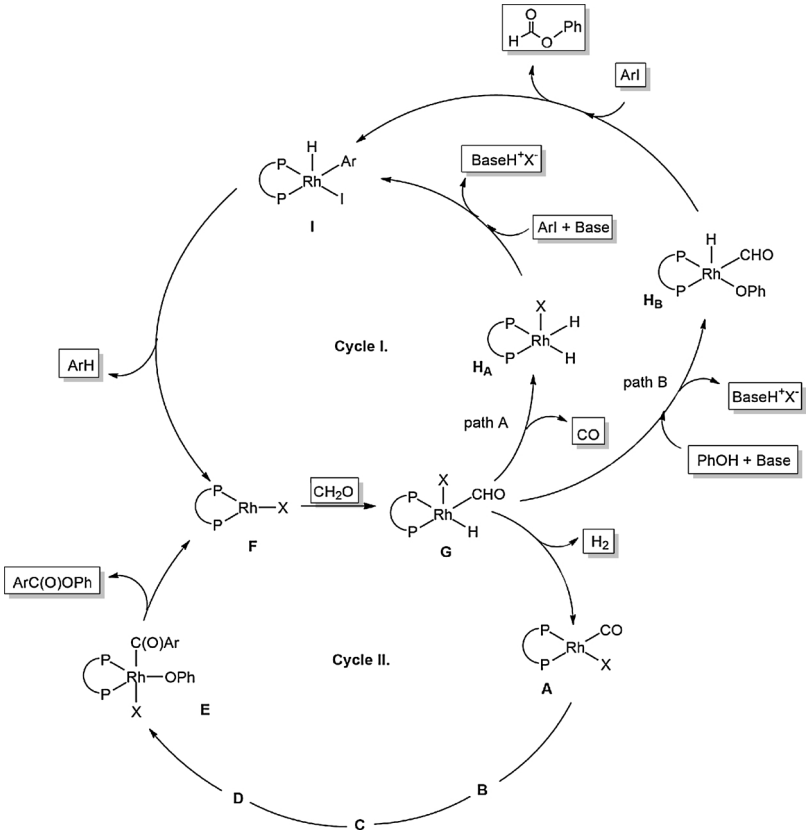


Fig. 2. Proposed reaction mechanism of aryloxycarbonylation and hydrodeiodination with formaldehyde. (**B**, **C** and **D** catalytic intermediates are identical with those depicted in Fig. 1).

of both the substrate and the nucleophile in the presence of carbon monoxide. Paraformaldehyde mediated carbonylations showed different dependence. Considering the electronic properties of the substituents of phenol no definite effect observed on carbonylation reaction. Surprisingly, iodoarene substitution switches the reaction to hydrodehalogenation pathway providing arenes instead of the target ester compounds.

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