capillary. For the imaging-plate apparatus the acquisition time was 3600–7200 seconds (distance between source and detector: 150 mm, diameter of plate: 300 mm).

Precursor **1**: m.p.:151.5 °C; ^{29}Si NMR (CP MAS): $\delta = 8.06$.

Hybrid material **2**: ^{29}Si NMR (CP MAS): $\delta = -50.8(T^1)$, $-59.5(T^2)$, $-68.8(T^3)$; CP MAS NMR spectroscopy is not always quantitative, however, single-pulse experiments did not reveal any significant variation in relative peak intensity from the CP MAS NMR spectra in the case of alkylene-bridged polysilsesquioxanes with structure similar to **2**.[21, 22] Elemental analysis calcd for $O_{1.5}SiCH_2(C_6H_4)_2CH_2SiO_{1.5}$: C 59.1, H 4.2, Cl 0 %; found: C 55.2, H 4.9, Cl 0.66 %.

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A More Efficient Catalyst for the Carbonylation of Chloroarenes**

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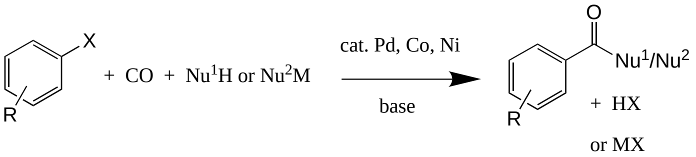
Matthias Beller*

Dedicated to Professor K. Barry Sharpless
on the occasion of his 60th birthday

Palladium-catalyzed C–C bond formation with aryl halides is, at the moment, one of the most important organometallic reactions used in synthetic organic chemistry.[1] However, the palladium-catalyzed carbonylation[2] has been investigated far less intensively than the well known Heck, Suzuki, or Stille reactions, although it offers the practical preparation of a broad spectrum of aromatic carboxylic acid derivatives from simple, commercially available building blocks (Scheme 1).[3]



X = I, Br, Cl, N_2^+, OSO_2R', ArI^+, IO_2, SO_2Cl

M = Na, K, BR'_2, AlR'_2, SnR'_3, SiR'_3

Nu^1 = OH, OR', NR'_2, F, Cl, SR'; Nu^2 = H, alkyl, aryl, CN, alkenyl, alkinyl, $R'CO_2$

Scheme 1. Carbonylation of aryl–X compounds.

Of the aryl halides aryl chlorides, because of their ready availability and low cost, are particularly interesting starting materials for "refinement". These substrates are, however, comparatively inert towards conventional palladium–aryl phosphane catalysts because the dissociation energy of the $C(sp^2)$–Cl bond is relatively large (402, 339, and 272 kJ mol^{-1} for PhCl, PhBr, and PhI, respectively, at 298 K). Whereas significant progress has been made in recent years in the activation of chloroarenes for Suzuki, Heck, and other similar reactions,[4, 5] the efficient carbonylation of chloroarenes remains a problem without a general solution. The crux of the problem is the coordination of CO to the metal center, the π-acceptor character of this ligand reduces the activity of the

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palladium complex towards oxidative insertion into the C−Cl bond. An additional difficulty is that the agglomeration of Pd atoms and the formation of clusters, which deactivates the catalyst, proceeds particularly readily in the presence of CO.[6] This problem *cannot* be solved through the use of sterically demanding monodentate ligands, so successfully employed in the reactions named above.

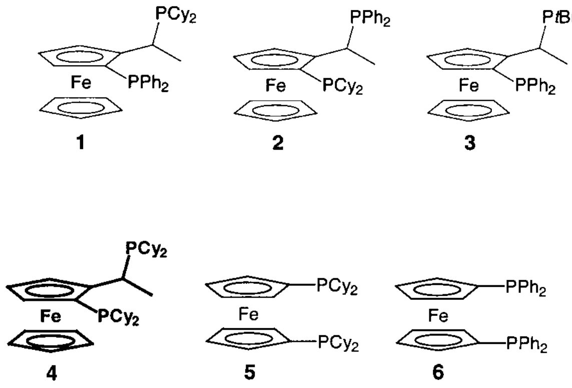
To date, the only successful palladium-catalyzed carbonylation, in good yield, of unactivated chloroarenes was with the 1,3-bis(diisopropylphosphanyl)propane (dippp) ligand used by Milstein and co-workers[7]. The drawbacks with this ligand are its difficult synthesis and the high sensitivity of the pyrophoric phosphane. In addition, no catalyst productivities (TON = turnover number) > 100 are reported for this system. Other catalyst systems give less than satisfying yields ($< 40\%$) and/or catalytic productivities (TON < 40) in the carbonylation of unactivated chloroarenes.[8]

Herein we describe a new palladium catalyst system that allows an efficient carbonylation of electron poor, neutral, and electron rich aryl chlorides in good to very good yields. With regard to catalytic productivity, all the results reported so far for the carbonylation of aryl chlorides are surpassed by at least an order of magnitude. Advantageously the ligands used are relatively air stable and commercially available.

To develop a generally applicable catalyst system for the carbonylation of unactivated aryl chlorides we have chosen the alkoxycarbonylation of chlorobenzene as a model reaction system. Our previous catalyst system ([$PdCl_2(PhCN)_2$]/dppb; P:Pd = 8:1; dppb = 1,4-bis(diphenylphosphanyl)butane), optimized for 4-bromoacetophenone[9] and diverse activated chloroheteroarenes,[10] served as the starting point for these investigations. Preliminary experiments with 0.5 mol% Pd catalyst showed that at reaction temperatures from 145 to 160 °C and CO pressures of 3 to 20 bar, the alkoxycarbonylation of chlorobenzene did not proceed with any significant level of conversion. Also, palladium-complex catalysts with sterically demanding, basic, monodentate phosphane ligands, such as tricyclohexylphosphane, tri-*tert*-butylphosphane, *n*-butyldiadamantylphosphane, gave unsatisfying yields of product ($< 20\%$).

To impede the formation of less-active palladium carbonyl complexes we decided to study the effects of chelating phosphane ligands. With this aim in mind ferrocenylphosphanes[11] struck us as being particularly interesting in that this class of ligand can be prepared from simple precursors allowing modular modification of the final, comparatively stable ligands. The best known example of the basic ferrocenylphosphanes is Josiphos (**1**) which is used in the elegant Novartis process for the large-scale industrial preparation of the agrochemical Metolachlor.[12]

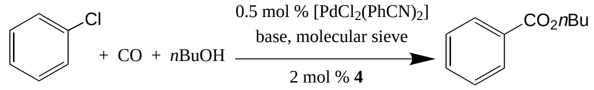
The alkoxycarbonylation of chlorobenzene with CO and *n*-butanol in the presence of 0.5 mol% [$PdCl_2(PhCN)_2$]/**1** at just 145 °C indeed gave a yield of 49%. With the Pd–Josiphos catalyst the catalyst productivity (TON = 98) and the catalytic activity (turnover frequency (TOF) = 6.5 h^{-1}) are already comparable with the best result reported for the alkoxycarbonylation of chlorobenzene.[7] On the basis of this promising start further 1,2- and 1,1′-disubstituted ferrocenylphosphanes **2**–**6** were tested in the model reaction (Scheme 2).



Scheme 2. The ferrocenylphosphanes used. Cy = cyclohexyl.

The best results were delivered by a catalyst based on the ligand 1-[2-(dicyclohexylphosphanyl)ferrocenyl]ethyldicyclohexylphosphane (**4**). Under the reaction conditions given above this ligand gave a conversion of 78% and a yield of 67% of the target product *n*-butyl benzoate. To further improve the selectivity and catalytic productivity of the carbonylation reaction the [$PdCl_2(PhCN)_2$]/**4** system was studied more closely (Table 1).

Table 1. Investigation of the alkoxycarbonylation of chlorobenzene in the presence of [$PdCl_2(PhCN)_2$]/**4**.[a]



Entry	T [°C]	p [bar]	mol% Pd	P:Pd	Equiv. base	Conversion [%][b]	Ester yield [%][b]	Selectivity [%][c]
1	145	3	0.5	8	3 NaOAc	78	67	86
2	145	1	0.5	8	3 NaOAc	97	73	75
3	145	1	0.5	16	3 NaOAc	100	72	72
4	145	1	0.5	8	1 NaOAc	97	81	84
5[d]	145	3	0.5	8	3 Na_2CO_3	100	99	99
6[d]	145	1	0.5	8	3 Na_2CO_3	100	97	97
7[d]	130	1	0.5	8	3 Na_2CO_3	85	79	93
8[d]	145	1	0.05	80[14]	3 Na_2CO_3	100	78	78

[a] 7 mmol chlorobenzene, 14 mL *n*-butanol, molecular sieves 4 Å, 18 h. [b] Determined by GC with diethylene glycol di-*n*-butylether as the internal standard. [c] Selectivity = yield of ester/conversion. [d] 16 h.

In the presence of NaOAc (OAc = acetate) as base and reducing the CO pressure from 3 to 1 bar lead to almost quantitative conversion (Table 1, entries 2 and 3), and *n*-butyl benzoate was obtained in 72 – 73 % yield. The only by-product detected was benzoic acid, generated from hydrolysis of the product ester. This by-product is formed by attack of the acetate on the palladium – acyl complex and subsequent hydrolysis, and through transesterification of the acetic acid formed (from HCl and NaOAc). Consequently reducing the amount of NaOAc (Table 1, entry 4) gives a significantly higher yield of the desired ester. By employing Na_2CO_3 as the base (Table 1, entries 5 – 8) the carbonylation proceeded with quantitative conversion and excellent selectivity (> 99 %) under 1 as well as 3 bar of CO. Although we chose a general reaction time of 16 h for the conversion, concentration–time profiles of the model reaction show that under the optimized conditions the conversion is complete in 5 to 6 h (under 1 bar CO). When the reaction temperature is reduced to 130 °C then the conversion is reduced to 85 %, however, the yield of the desired product is still almost 80 %.

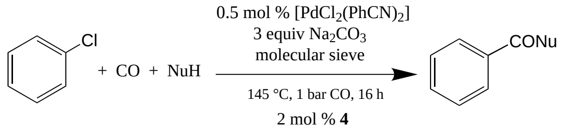
To the best of our knowledge these reactions represent the first alkoxycarbonylation of unactivated chloroarenes that give good yields under 150 °C.[13] The catalyst productivities of the $[PdCl_2(PhCN)_2]$/**4** system significantly surpass all the literature values. In the presence of only 0.05 mol % $[PdCl_2(PhCN)_2]$[14] 78 % *n*-butyl benzoate is still formed, which corresponds to a TON of 1560 and a catalytic activity (TOF) of around 100 h^{-1}.

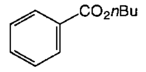
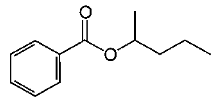
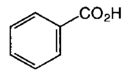
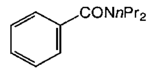
After developing an efficient catalyst system for the model reaction we were interested in the reaction of chlorobenzene and CO with other nucleophliles, as well as the alkoxycarboxylation of different chloroarenes. In all the reactions the standard conditions were as described above (0.5 mol % Pd, P:Pd = 8:1, 3 equivalents of Na_2CO_3, molecular sieves (4 Å), 145 °C, 1 bar CO, 16 h). The results are summarized in Tables 2 and 3.

Whereas with secondary alcohols noticeably lower yields (58 %) of carbonylation products and selectivities (81 %) were obtained, with water the reaction proceeded smoothly and carboxylic acids were obtained directly in 84 % yield. This observation is of particular interest for the fine chemicals industry where free acids are the most interesting products. In addition the carbonylation of chlorobenzene with di-*n*-propylamine proceeds in good yield to the corresponding benzamide (70 %). In this case the isolated by-products were benzoic acid (16 %) and dimethylbenzamide (7 %).

All the reactions of the various aryl chlorides with CO and *n*-butanol (Table 3) gave quantitative conversions. 2-Chlorofluorobenzene and 4-chlorotoluene give the corresponding carbonylation products in excellent yield (98 – 100 %; Table 3, entries 1 and 2). Also deactivated N-heteroaryl chlorides react in good yield, for example, 3-chloropyridine in 72 % yield to nicotinate. The electron rich and sterically demanding 2-chloroanisol gave the desired product in near to quantitative yield (95 %; Table 3, entry 4). Surprisingly the reaction of 3-chloroanisol is noticeably less selective and the corresponding ester is only obtained in 80 % together with 15 % *m*-methoxybenzoic acid. Use of 4-chlorophenyl ethyl acetate delivers 4-(butoxycarbonyl)phenyl butyl acetate also in 80 % yield. These results show that even the labile phenyl ethyl acetate unit is easily tolerated under the reaction conditions however, it does undergo transesterification.

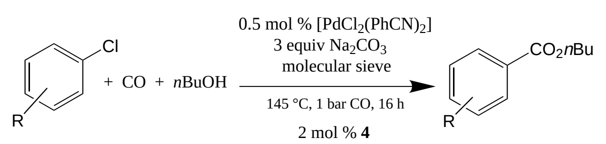
Table 2. Carbonylation of chlorobenzene with various nucleophiles.[a]

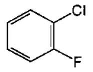
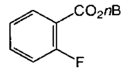
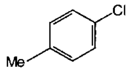
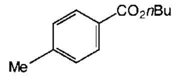
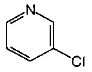
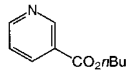
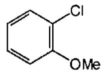
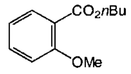
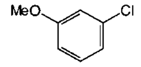
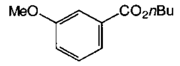
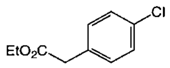
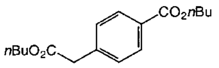


Entry	Nucleophile	Conversion	Product	Yield [%][b]	Selectivity [%][c]
1[d]	*n*BuOH	100		97 (85)	100
2[e]	2-pentanol	85		58 (40)	81
3[f]	H_2O	95		84 (84)	100
4[g]	nPr_2NH	100		94 (65)	75

[a] 7 mmol chlorobenzene. [b] Yield (GC) of all carbonylation products (ester or amide + acid). GC yield of the product was determined with with diethylene glycol di-*n*-butylether as the internal standard. Yield of the isolated products in parentheses. [c] Chemoselectivity = GC yield of the product/total yield of carbonylation products. [d] 14 mL *n*-butanol. [e] 17 mL 2-pentanol. [f] 2.7 mL water, 11.3 mL dioxane. [g] 3 mL di-*n*-propylamine, 9 mL *N*,*N*-dimethylformamide.

Table 3. Butoxycarbonylation of various chloroarenes.[a]



Entry	Chloroarene	Conversion [%]	Product	Yield [%][b]	Selectivity [%][c]
1		100		100 (76)	95
2		100		98 (80)	92
3		100		> 72 (67)	100
4		100		95 (91)	100
5		100		95 (68)	84
6		> 99		93 (68)	86

[a] 7 mmol chloroarene, 14 mL *n*-butanol. [b] Total yield (GC) of carbonylation products (ester + acid). GC yield of the product was determined with diethylene glycol di-*n*-butylether as the internal standard. Yield of the isolated product in parentheses. [c] Chemoselectivity = GC yield of the ester/total yield of carbonylation products.

Experimental Section

General procedure for the alkoxycarbonylation of chloroarenes: the corresponding chloroarene (7 mmol), *n*-butanol (14 mL), $[PdCl_2(PhCN)_2]$ (13.4 mg, 0.035 mmol, 0.5 mol%), and ligand **4** (84.9 mg, 0.140 mmol, 2 mol%) were added to a Schlenk flask under argon (orange solution). Sodium carbonate (2.226 g, 21 mmol, 3 equiv) and molecular sieves (4 Å, ca. 3 g) were added to the reaction autoclave. Following evacuation and replacement with argon (three cycles) the reaction mixture was transferred with a PVC hose (∅ ≈ 2 mm) under a slight excess pressure of argon from the Schlenk flask into the autoclave. The autoclave was closed and heated to the reaction temperature (145 °C). The reaction pressure (1 bar CO) was held constant by means of a CO reservoir, connected to the autoclave by a pressure regulator. After 16 h reaction time the autoclave was cooled to room temperature and the yellow orange mixture diluted with dichloromethane (70 mL). After washing with water (70 mL) the aqueous phase was extracted with dichloromethane (2 × 20 mL), and the combined organic phases were dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The crude product was then purified by column chromatography (silica gel, EtOAc/hexane).

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[13] In a long reaction time experiment on the alkoxycarbonylation of chlorobenzene with 5 mol% Pd catalyst a conversion of 48% (selectivity 91%) was reached after 5 days even at a reaction temperature of 90 °C.

[14] A P:Pd ratio of 80:1 was chosen for these experiments to maintain a ligand concentration 2 mol%. In earlier work on carbonylation reactions we showed that for the stabilization of the Pd catalyst the ligand concentration and not the ligand:palladium ratio is important.[9]

Synthesis, Structure, and Reactivity of a Diphosphadiferratetrahedrane with a Fe–Fe Double Bond[**]

Christine Eichhorn, Otto J. Scherer,* Thorsten Sögding, and Gotthelf Wolmershäuser

Dedicated to Professor Marianne Baudler
on the occasion of her 80th birthday

Whereas in the chemistry of acetylene complexes of iron, compound **1** containing a C_2Fe_2 tetrahedrane framework and a Fe–Fe double bond was prepared and crystallographically characterized already in 1976,[1] for the iso(valence)electronic and isolobal ($\mathrm{HC} \underset{\circ}{\longleftrightarrow} \mathrm{P}$, $\mathrm{HC{\equiv}CH} \mathrel{\hat{=}} \mathrm{:P{\equiv}P:}$) diphosphadiferratetrahedranes only the complex **2** with a Fe–Fe single bond and additional P-coordination is known.[2]

Diphosphadimetallatetrahedranes of the type $[\{L_nM\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}P_2)]$ (L_nM = 15 valence-electron(VE) fragment)[3] synthesized to date all display M–M single bonds, and with six skeleton electron pairs (SEPs) for the tetrahedral M_2P_2 framework are considered as *nido* clusters. According to theoretical investigations a decrease (5 SEPs) as well as an increase (7 SEPs) in the number of electrons in the skeleton lead to changes of the M_2P_2 framework.[4]

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[+] Crystal structure analysis.

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