

Palladium Catalysed Electrosynthesis using Aryl Trifluoromethanesulfonates (Triflates). Synthesis of Biaryls and Aromatic Carboxylic Acids

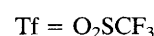
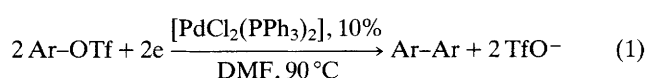
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The palladium(II) complex $[\text{PdCl}_2(\text{PPh}_3)_2]$ catalyses the electrosynthesis of biaryls from aryl triflates whereas, in the presence of carbon dioxide, this complex catalyses the electrosynthesis of aromatic carboxylic acids.

The synthesis of biaryls from aryl halides is a well known reaction catalysed by nickel^{1,2} or palladium³ complexes, in the presence of a chemical reducer such as zinc powder¹ or upon electrochemical reduction.^{2,3} The electrosynthesis of aromatic acids from aryl halides and carbon dioxide can also be catalysed by nickel⁴ or palladium⁵ complexes. Since palladium complexes can activate aryl triflates,⁶⁻⁸ we have investigated the reactivity of aryl triflates in the presence of a catalytic amount of palladium complexes under reducing conditions and observed that this reaction afforded biaryls. Aromatic carboxylic acids were synthesized when the reduction was performed in the presence of carbon dioxide.

Whereas the direct electrochemical reduction of aryl triflates[†] in the absence of any catalyst mainly provided the corresponding phenol, the presence of a catalytic amount of a palladium(II) complex modified the reactivity of the aryl triflates, thus providing the corresponding biaryl [Table 1; eqn. (1)]. By this new reaction, biaryls can be synthesized from phenols *via* the triflates by activation of the Ar–O bond. This reaction, not yet optimized, also produced some arene⁹ and phenol, but the latter can be easily recycled back to the initial aryl triflate. The reaction was regiospecific and was compatible with functional substituents of the aryl group. An attempt to perform this reaction in the presence of zinc powder as the reducer led to lower selectivity and yield.



In the presence of carbon dioxide, the formation of the biaryl was totally inhibited (except for the cyano substituted compound) and the reaction afforded the aromatic carboxylic acid as the main product (Table 2). Aryl triflates normally react with nucleophiles in the presence of a palladium catalyst.^{6,8} By supplying electrons to the system electrochemically, it has been possible to invert their reactivity so that they

Table 1 Electrosynthesis of biaryls from aryl triflates catalysed by $[\text{PdCl}_2(\text{PPh}_3)_2]$ [see eqn. (1)]

Ar-OTf ^a	T/°C	Yield (%) ^b		
		Ar-Ar	ArH	ArOH
1-Naphthyl-OTf ^c	20	0	13	86
1-Naphthyl-OTf	20	20	23	64
1-Naphthyl-OTf	60	40 (34)	33 (32)	28 (27)
1-Naphthyl-OTf	90	50	36	13
Ph-OTf ^d	90	76	—	10
<i>p</i> -NCC ₆ H ₄ -OTf	90	70 (55)	0	15
<i>p</i> -CF ₃ C ₆ H ₄ -OTf	90	68 (45)	—	5
<i>p</i> -ClC ₆ H ₄ -OTf	90	(57)	0	8
<i>o</i> -ClC ₆ H ₄ -OTf	90	(34)	0	26

[†] The potentials of the irreversible reduction peak (E_{pc}) of 1-naphthyl-OTf, Ph-OTf, *p*-NCC₆H₄-OTf, *p*-CF₃C₆H₄-OTf, *p*-ClC₆H₄-OTf and *o*-ClC₆H₄-OTf are, respectively: -1.95, -2.63, -1.8, -2.21, -2.5 and -2.45 vs. SCE. They were determined in DMF (containing 0.3 mol dm⁻³ Bu₄NBF₄) at a gold disk electrode, at a scan rate of 0.2 V s⁻¹.

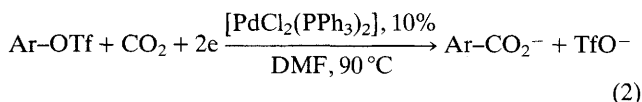
^a ArOTf/catalyst: 1 mmol/0, 1 mmol except c and d. ^b Yields are based on ArOTf which had been completely converted and were determined by ¹H NMR spectroscopy (250 MHz) using CHCl₂CHCl₂ as internal standard (isolated yield of pure product is given in parentheses). ^c No catalyst present. ^d ArOTf/catalyst: 10 mmol/1 mmol.

Table 2 Palladium catalysed^a electrosynthesis of aromatic acids from aryl triflates and carbon dioxide at 90 °C [see eqn. (2)]

ArOTf	Yield (%) ^c		
	<i>E/V</i> ^b vs. SCE	Ar-CO ₂ H	ArOH
Ph-OTf ^d	-2.0	88	0
Ph-OTf ^e	-2.0	59 (96)	0
<i>p</i> -MeC ₆ H ₄ -OTf ^e	-2.0	75	0
<i>p</i> -EtO ₂ CC ₆ H ₄ -OTf ^e	-1.6	(52)	(28)
<i>p</i> -CF ₃ C ₆ H ₄ -OTf ^e	-1.6	64	(4)
<i>p</i> -ClC ₆ H ₄ -OTf ^e	-2.0	71	0
<i>p</i> -NCC ₆ H ₄ -OTf ^e	-1.4	(23) ^f	(22)

^a Catalyst = [PdCl₂(PPh₃)₂] except for first entry. ^b Electrolysis potential. ^c Isolated yields based on ArOTf which had been completely converted; yields determined by ¹H NMR spectroscopy (250 MHz) of the crude mixture, using CHCl₂CHCl₂ as internal standard, are given in parentheses. ^d Stoichiometric reaction ArOTf-Pd(PPh₃)₄: 1 mmol/1 mmol. ^e ArOTf/[PdCl₂(PPh₃)₂]: 1 mmol/0.1 mmol. ^f formation of 47% of 4,4'-NCC₆H₄-C₆H₄CN also.

reacted with electrophiles such as carbon dioxide. This is a unique route for the synthesis of aromatic acids from carbon dioxide and phenols *via* the triflates, by substitution at the Ar-O bond.† The electrocarboxylation was regiospecific and was compatible with functional substituents of the aryl group.



Our studies so far have shown that [PdCl₂(PPh₃)₂] was the best catalyst for formation of biaryls or carboxylic acids. The palladium(II) complex [PdCl₂(PPh₃)₂] was reduced at the beginning of the electrolysis [*E*_{pc} -0.90 V vs. standard calomel electrode (SCE)]. The electrogenerated palladium(0) [Pd⁰(PPh₃)₂] could be detected and characterized by its oxidation peak (*E*_{pa} -0.02 V vs. SCE)¹¹ which disappeared in the presence of ten equivalents of the aryl triflate. This suggests that the first step of the electrosynthesis of the biaryl or of the carboxylic acid is an oxidative addition of the aryl triflate with a palladium(0) complex which affords the corresponding *σ*-arylpalladium complex.⁸ The latter can be reduced‡ more easily than the aryl triflate† and its reduction in the presence of the aryl triflate affords the biaryl whereas its reduction in the presence of carbon dioxide affords the corresponding carboxylic acid.

The electrosynthesis of biaryls was performed in a divided cell [50 ml of anhydrous dimethylformamide (DMF) containing Bu₄NBF₄ (0.3 mol dm⁻³) as supporting electrolyte] at a controlled potential (the reduction potential of the ArPdOTfL₂ complex§). The cathode was of carbon cloth and the anode a magnesium rod. The reaction was monitored by HPLC. After exhaustive electrolysis that consumed between one and two Faradays per mole of aryl triflate, the mixture was

hydrolysed with aqueous HCl and extracted with diethyl ether. The mixture was analysed by ¹H NMR (250 MHz) spectroscopy. The pure biaryl was obtained after flash chromatography (eluent: light petroleum-ethyl acetate).

The electrosynthesis of the aromatic carboxylic acids was performed under the same conditions but in the presence of bubbling carbon dioxide. The electrolysis consumed 2.2 Faradays per mole of aryl triflate. The mixture was hydrolysed with aqueous HCl, extracted with diethyl ether and analysed by ¹H NMR (250 MHz) spectroscopy. The crude product was treated with aqueous NaOH (1 mol dm⁻³) that solubilized the carboxylate. After extraction with diethyl ether, the aqueous solution of the carboxylate was treated with aqueous HCl, affording the pure acid. The biaryls and carboxylic acids were characterized by ¹H NMR (250 MHz) spectroscopy, mass spectrometry and comparison with authentic samples. The optimization and the scope of these new reactions are under investigation.

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‡ Potassium or sodium phenoxides can be carboxylated by carbon dioxide by the Kolbe Schmitt reaction but this reaction affords aromatic acids in which the carboxylic group is substituted in the *ortho* or *para* position relative to the phenoxy group.¹⁰ The phenoxide produced during the electrolysis (Table 2) was not carboxylated according to the Kolbe Schmitt reaction, mainly because it was present as the tetrabutylammonium salt.¹⁰

§ The reduction potentials (*E*_{pc}) of the Ar-Pd-OTf(PPh₃)₂ complex corresponding to 1-naphthyl-OTf, Ph-OTf, *p*-NCC₆H₄-OTf, *p*-CF₃C₆H₄-OTf, *p*-ClC₆H₄-OTf and *o*-ClC₆H₄-OTf are respectively: -1.89, -2.5, -1.75, -2.0, -2.41 and -2.26 V vs. SCE. They were determined in DMF (containing 0.3 mol dm⁻³ Bu₄NBF₄) at a gold disk electrode, at a scan rate of 0.2 V s⁻¹.