

Activation of Aryl and Vinyl Triflates by Palladium and Electron Transfer – Electrosynthesis of Aromatic and α,β -Unsaturated Carboxylic Acids from Carbon Dioxide

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The electrochemical reduction of aryl and vinyl triflates in the presence of CO_2 and a catalytic amount of palladium results in the formation of aromatic and α,β -unsaturated carboxylic acids. Aryl and vinyl triflates usually undergo palladium-catalysed cross-coupling reactions with nucleophiles. Their reactivity has been reversed in the

presence of an electron source, so that they react with electrophiles such as CO_2 . The reaction proceeds through an activation of the C–O bond of the aryl or vinyl triflate by oxidative addition to a palladium(0) complex, followed by an activation by electron transfer of the thus formed aryl- or vinylpalladium(II) complexes.

Introduction

Aryl and vinyl triflates usually undergo cross-coupling reactions with *nucleophiles* in the presence of catalytic amounts of palladium complexes, affording substituted arenes or alkenes.^[1] The reactions proceed by nucleophilic attack on the aryl- or vinylpalladium(II) complexes formed by oxidative addition of the aryl^[2] or vinyl^[3] triflates to the palladium(0) complex. In 1992, we reported that it was possible to invert the reactivity of aryl triflates and to make them to react with *electrophiles* in the presence of an electron source and a palladium catalyst.^{[4][5]} We reported a similar reactivity for vinyl triflates in 1997.^[6] In the absence of any electrophile other than the aryl or vinyl triflate itself, homocoupling reactions were observed affording biaryls^[7] or conjugated dienes,^[6] respectively. In the presence of carbon dioxide as the electrophile, aromatic carboxylic acids^[4] and α,β -unsaturated carboxylic acids^[6] were synthesized in good yields with $\text{PdCl}_2(\text{PPh}_3)_2$ as the catalyst. We now wish to report more details concerning the carboxylation reaction.

Results and Discussion

Palladium-Catalysed Electrosynthesis of Aromatic Carboxylic Acids from Aryl Triflates and Carbon Dioxide

As we have previously reported,^[4] aryl triflates, ArOTf , are electroactive compounds (Table 1). Their electrochemical reduction leads, after hydrolysis, to a mixture of phenol Ar-OH and arene Ar-H , as illustrated in Table 2 (entry 1) for 1-naphthyl triflate. When the electrolysis was performed at the controlled potential of -2.0 V at room temperature in DMF, 1-naphthol was formed as the major compound (86% yield), showing that the cleavage of the O–S bond (Eq. 2) in the intermediate radical anion $\text{Ar-O-SO}_2\text{CF}_3^{\bullet-}$

formed by the first electron transfer (Eq. 1), is highly favoured compared to the cleavage of the Ar-O bond (Eq. 3).

Mechanism of the electrochemical reduction of aryl triflates is depicted in Eqs. 1–7.^[7]

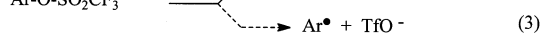
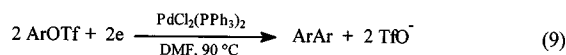
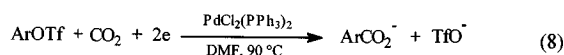


Table 1. Reduction peak potentials of aryl triflates and arylpalladium(II) chloride complexes (Scheme 1, eq. a)

Ar–	Ar–OTf $E_{\text{Red}}^{\text{p}}[\text{a}]$	Ar–Pd–Cl(PPh ₃) ₂ $E_{\text{Red}}^{\text{p}}[\text{a}]$
<i>p</i> -CN–C ₆ H ₄ –	–1.80	–1.75
<i>p</i> -TfO–C ₆ H ₄ –	–2.24	–2.15
<i>p</i> -CF ₃ –C ₆ H ₄ –	–2.21	–2.00
<i>p</i> -EtO ₂ C–C ₆ H ₄ –	–1.82	–1.75
<i>p</i> -Cl–C ₆ H ₄ –	–2.50	–2.41
<i>p</i> -Br–C ₆ H ₄ –	–2.44	–2.16
<i>p</i> -F–C ₆ H ₄ –	–2.54	–2.54
C ₆ H ₅ –	–2.63	–2.20
<i>p</i> -Me–C ₆ H ₄ –	–2.71	–2.53
<i>p</i> -MeO–C ₆ H ₄ –	–2.67	– ^[b]
<i>p</i> - <i>t</i> Bu–C ₆ H ₄ –	–2.74	–2.68
<i>o</i> -Me–C ₆ H ₄ –	–2.70	–2.46
1-naphthyl–	–1.95	–1.89
2-naphthyl–	–2.01	–1.90

[a] Volts vs. SCE; reduction peak potentials were determined at a steady gold disc electrode (i.d. 0.5 mm) at a scan rate of 0.2 V s^{-1} in DMF containing *n*Bu₄NBF₄ (0.3 M) at 20°C. – [b] No reaction at 20°C.

As a consequence, when the electrochemical reduction of 1-naphthyl triflate was performed in the presence of carbon dioxide at -2.0 V (Table 2, entry 2), only a small amount of the desired 1-naphthoic acid was formed by carboxylation of the electrogenerated 1-naphthyl anion (Eq. 6); 1-naphthol was still the major product of the reaction (Eqs. 4, 5). A possible side reaction, namely the carboxylation of the electrogenerated 1-naphthoxide anion to afford 1-hydroxynaphthalene-2-carboxylic acid as in a Kolbe-Schmitt reaction did not take place.^[8] The introduction of a palladium catalyst such as $\text{PdCl}_2(\text{PPh}_3)_2$ resulted in the exclusive formation of the desired 1-naphthoic acid (Table 2, entry 3, Eq. 8) at a potential of -1.7 V, which is less negative than the reduction potential of 1-naphthyl triflate (-1.95 V).

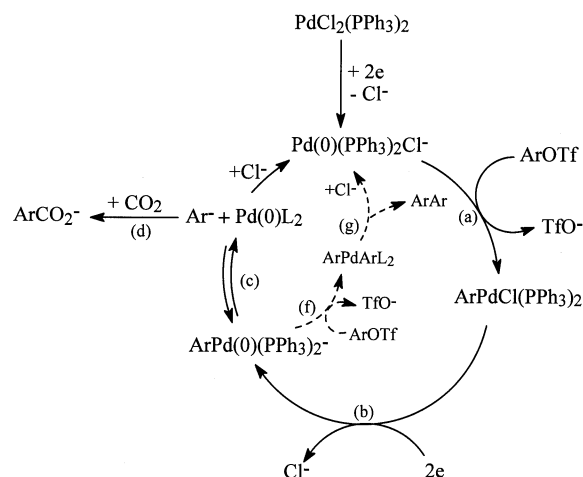


Moreover, no 1,1'-binaphthyl was detected, which was the major compound formed when the electrolysis was carried out in the absence of CO_2 (Table 2, entry 4, Eq. 9).^[7]

This shows that the Pd-catalysed carboxylation (Eq. 8) is considerably more efficient than the Pd-catalysed homocoupling (Eq. 9).

The mechanism of the Pd-catalysed carboxylation of aryl triflates (Scheme 1) can be described with reference to the mechanism of the Pd-catalysed homocoupling of aryl triflates that we have described previously.^[7] The precursor $\text{PdCl}_2(\text{PPh}_3)_2$ is reduced to a palladium(0) complex ligated by one chloride ion: $\text{Pd}^0(\text{PPh}_3)_2\text{Cl}^-$.^[9] This complex then undergoes an oxidative addition with the aryl triflate (eq. a in Scheme 1), resulting in the formation of a neutral complex $\text{ArPdCl}(\text{PPh}_3)_2$,^[2] which is more easily reduced than the starting aryl triflate (see Table 1). The electrochemical reduction of neutral $\text{ArPdX}(\text{PPh}_3)_2$ complexes consumes two electrons per mol (eq. b in Scheme 1) and affords an anionic arylpalladium(0) complex $\text{ArPd}^0(\text{PPh}_3)_2^-$, which is in rapid equilibrium with the free anion Ar^- and $\text{Pd}^0(\text{PPh}_3)_2$ (eq. c).^[10] It has been established that the carboxylation proceeds from the anion Ar^- (eq. d),^[10] whereas $\text{ArPd}^0(\text{PPh}_3)_2^-$ complexes are able to undergo oxidative ad-

Scheme 1. Mechanism of the palladium-catalyzed electrocarboxylation of aryl triflates



dition with aryl triflates, ultimately leading to the corresponding biaryl ArAr ^[7] (eqs. f and g in Scheme 1).^[11]

For example, $p\text{-CF}_3\text{-C}_6\text{H}_4\text{-OTf}$, 3 mmol dm^{-3} , in DMF (containing $n\text{Bu}_4\text{NBF}_4$, 0.3 M) was reduced at $E_{\text{R}0} = -2.0$ V (Figure 1a), whereas the reduction of CO_2 took place at -2.32 V. When the reduction was performed with a stoichiometric mixture of $p\text{-CF}_3\text{-C}_6\text{H}_4\text{-OTf}$ and $\text{PdCl}_2(\text{PPh}_3)_2$, we first observed the reduction peak of $\text{PdCl}_2(\text{PPh}_3)_2$ at $E_{\text{R}1} = -0.74$ V (Figure 1b). This complex was then reduced to a palladium(0) complex $\text{Pd}^0(\text{PPh}_3)_2\text{Cl}^-$, which underwent an oxidative addition with the aryl triflate (eq. a in Scheme 1). The oxidative addition was attested by the quasi-absence of the oxidation peak of $\text{Pd}^0(\text{PPh}_3)_2\text{Cl}^-$, which is usually observed on the reverse scan at $E_{\text{O}1} = +0.08$ V (Figure 1c). Since the electrogenerated palladium(0) species, $\text{Pd}^0(\text{PPh}_3)_2\text{Cl}^-$, was ligated by one chloride ion, the oxidative addition resulted in the formation of a neutral complex, $p\text{-CF}_3\text{-C}_6\text{H}_4\text{-PdCl}(\text{PPh}_3)_2$.^[2] This complex was reduced at $E_{\text{R}2} = -1.83$ V, i.e. it was more easily reduced than the starting aryl triflate (Figure 1b). The cyclic voltammogram exhibited a third reduction peak at $E_{\text{R}3} = -2.12$ V (Figure 1b), which was assigned to the dimer $p\text{-4,4'-CF}_3\text{-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-CF}_3$ (Eq. 9). The magnitude of the reduction peak R_2 grew as the concentration of the aryl triflate was increased (Figure 1d), indicating a catalytic reaction

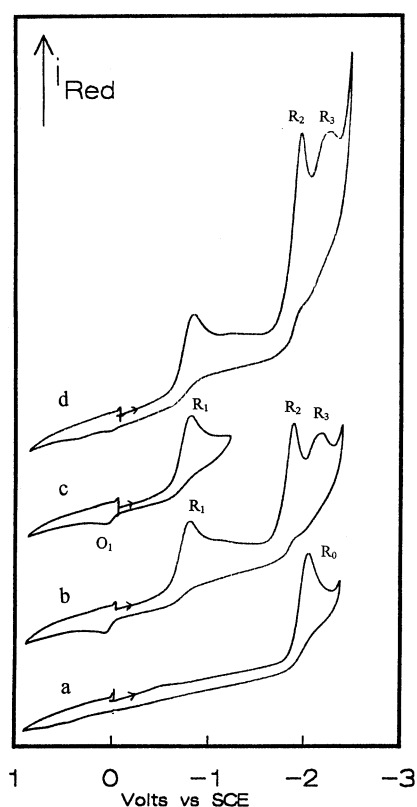
Table 2. Uncatalysed and palladium-catalysed electrochemical reduction of 1-naphthyl triflate;^[a] Ar = 1-naphthyl

Entry	Catalyst (10%)	CO_2 [atm]	$E^{[b]}$ [V]	T [$^\circ\text{C}$]	F/mol ^[c]	Ar-OH (%) ^[d]	Ar-H (%) ^[d]	Ar-CO ₂ H (%) ^[d]	Ar-Ar (%) ^[d]
1	no	no	-2.0	20	2.0	86	13	—	0
2	no	1	-2.0	20	2.2	80	0	13	0
3	$\text{PdCl}_2(\text{PPh}_3)_2$	1	-1.7	90	2.2	0	0	83 ^[e]	0
4	$\text{PdCl}_2(\text{PPh}_3)_2$	no	-1.7	90	1.5	13	33	—	50

^[a] 1 mmol of 1-naphthyl triflate in 50 ml of DMF containing $n\text{Bu}_4\text{NBF}_4$ (0.3 M); divided cell. — ^[b] Electrolysis potential vs. SCE. — ^[c] Faradays per mol = number of electrons per mol involved in the electrolysis. — ^[d] Yields are relative to that obtained with 1-naphthyl triflate, which was completely converted; values were determined from the crude mixture after work-up by $^1\text{H-NMR}$ spectroscopy using $\text{CHCl}_2\text{CHCl}_2$ as internal standard. — ^[e] Isolated yield.

leading to the biaryl (Eq. 9).^[7] In the presence of CO₂, the reduction of *p*-CF₃-C₆H₄-PdCl(PPh₃)₂ at R₂ afforded the carboxylic acid, *p*-CF₃-C₆H₄-CO₂H.

Figure 1. Cyclic voltammetry performed in DMF (containing *n*Bu₄NBF₄, 0.3 M) at a stationary gold disc electrode (i.d. = 0.5 mm) at a scan rate of 50 mVs⁻¹ at 20°C; (a) *p*-CF₃-C₆H₄-OTf, 3 mmol dm⁻³; (b) PdCl₂(PPh₃)₂, 3 mmol dm⁻³ and *p*-CF₃-C₆H₄-OTf, 3 mmol dm⁻³; (c) same solution as in (b) but the direction of the scan has been reversed just after the reduction of PdCl₂(PPh₃)₂ at -1.2 V. (d) PdCl₂(PPh₃)₂, 3 mmol dm⁻³ and *p*-CF₃-C₆H₄-OTf, 6 mmol dm⁻³



The carboxylation reaction is in fact more efficient than the dimerization, since the oxidative addition of ArPd⁰(PPh₃)₂⁻ with ArOTf (Scheme 1, eq. f) is considerably slower than the nucleophilic attack of the anion Ar⁻ on CO₂ (eq. d). Indeed, this anion is very basic as it is generated in the absence of any stabilizing cation, the only cation present being the *n*Bu₄N⁺ of the supporting electrolyte. The rate-determining step of the Pd-catalysed carboxylation is the first chemical step (Scheme 1, eq. a), i.e. the oxidative addition of the aryl triflate to the palladium(0) complex. The rate constant of the oxidative addition has been estimated by cyclic voltammetry as 5.5 M⁻¹ s⁻¹ for 1-naphthyl triflate at 20°C.^{[7][12]}

The electrolyses were performed in DMF in a divided cell, at the reduction potentials of the arylpalladium(II) complexes, which were found to be more easily reduced than the precursor aryl triflates (Table 1). The reactions were performed at 90°C to accelerate the rate of the oxidative addition. Even though the solubility of CO₂ at 90°C is most probably less than that at room temperature, the reaction works equally well at low CO₂ concentration because

the carboxylation step (Scheme 1, eq. d) is not the rate-determining step. As illustrated in Table 3, a wide variety of aromatic carboxylic acids, substituted by electron donor or acceptor groups, has been synthesized by electrocarboxylation of aryl triflates with CO₂ under atmospheric pressure. The main by-products were phenols, which could easily be recycled to the aryl triflates.

The electrocarboxylation proved to be regiospecific and compatible with most functional substituents on the aryl ring (e.g. CN, CF₃, CO₂Et, Cl, F). However, the reaction failed when starting from *p*-NO₂-C₆H₄-OTf, due to preferential reduction of the nitro group. Moreover, no carboxylation occurred when the substituent was too strongly donating (entry 15). In such cases, direct reduction of the aryl triflate to the corresponding phenol was observed, as the oxidative addition was too slow. Indeed, we have reported previously that the oxidative addition of aryl triflates to palladium(0) complexes is favoured when the aryl triflates are substituted by electron-withdrawing groups (Hammett correlation with a positive value of ρ).^[2] With *p*-Br-C₆H₄-OTf as the substrate, some *para*-terephthalic acid was formed after consumption of 2e per mol (entry 7), showing that the palladium(0) underwent a competitive oxidative addition into both the Ar-Br and Ar-OTf bonds. We have previously established that palladium(0) complexes ligated by PPh₃ are only 1.7 times more reactive towards ArOTf than towards ArBr.^{[2][13]} With the bromide substituent in the *ortho* position, double carboxylation was not observed, but reduction of the C-Br bond to C-H took place instead (entry 17). On the other hand, oxidative addition of palladium(0) complexes with aryl chlorides is known to be very slow, which is why a good compatibility was observed in the case of *p*-Cl-C₆H₄-OTf (entry 9). Attempts to use NiCl₂(dppe) as a catalyst resulted in lower yields when the substituent was an acceptor such as an ester group (entry 5), whereas this complex proved to be an efficient catalyst in cases with donor substituents (compare entries 15 and 16). In an experiment aimed at elucidating the mechanism of the Pd-catalysed carboxylation, electrolysis was performed in the presence of a stoichiometric amount of Pd⁰(PPh₃)₄, the oxidative addition of which to ArOTf, in the absence of any chloride ions, affords a cationic complex ArPd^{II}(PPh₃)₂⁺.^[2] The high yield of the reaction (entry 12) demonstrates that the carboxylation can also take place by the reduction of cationic arylpalladium(II) complexes.^[14]

Thus, by supplying electrons, it is possible to invert the reactivity of aryl triflates, thereby causing them to react with an electrophile such as carbon dioxide.^[15] To date, this represents a unique route for the synthesis of aromatic carboxylic acids from carbon dioxide and phenols via the triflate derivatives, by substitution at the Ar-O bond (Eq. 10).

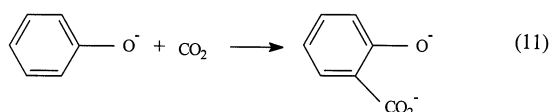
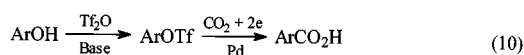
Indeed, reaction of phenoxide with carbon dioxide as in the Kolbe-Schmitt reaction (Eq. 11) results in the formation of the *ortho*-carboxylated phenols without, of course, any activation of the Ar-O bond.

Our process is an alternative to the electrocarboxylation of aryl halides, in the absence^[16] or the presence of pal-

Table 3. PdCl₂(PPh₃)₂-catalysed electrocarboxylation of aryl triflates in DMF at 90 °C (Eq. 8)^[a]

Entry	Ar-OTf	E ^[b] [V]	F/mol ^[c]	Ar-CO ₂ H (%) ^[d]	Ar-OH (%) ^[d]
1	<i>p</i> -CN-C ₆ H ₄ -OTf	-1.6	1.9	<i>p</i> -CN-C ₆ H ₄ -CO ₂ H, 35 ^[e]	22
2	<i>p</i> -CF ₃ -C ₆ H ₄ -OTf	-1.6	2.1	<i>p</i> -CF ₃ -C ₆ H ₄ -CO ₂ H, 64 [50]	4
3	<i>p</i> -CH ₃ CO-C ₆ H ₄ -OTf	-1.4	2.2	<i>p</i> -CH ₃ CO-C ₆ H ₄ -CO ₂ H, 22	48
4	<i>p</i> -EtO ₂ C-C ₆ H ₄ -OTf	-1.6	2.1	<i>p</i> -EtO ₂ C-C ₆ H ₄ -CO ₂ H, 52	28
5	<i>p</i> -EtO ₂ C-C ₆ H ₄ -OTf ^[f]	-1.6	1.3	<i>p</i> -EtO ₂ C-C ₆ H ₄ -CO ₂ H, 10	47
6	<i>p</i> -TfO-C ₆ H ₄ -OTf	-1.8	3.7	<i>p</i> -CO ₂ H-C ₆ H ₄ -CO ₂ H, [71]	0
7	<i>p</i> -Br-C ₆ H ₄ -OTf	-1.8	2.0	<i>p</i> -Br-C ₆ H ₄ -CO ₂ H, 46 + <i>p</i> -CO ₂ H-C ₆ H ₄ -CO ₂ H, 31	0
8	<i>p</i> -Br-C ₆ H ₄ -OTf	-1.8	4.0	<i>p</i> -CO ₂ H-C ₆ H ₄ -CO ₂ H, 63 + C ₆ H ₅ -CO ₂ H, 26	0
9	<i>p</i> -Cl-C ₆ H ₄ -OTf	-2.0	3.0	<i>p</i> -Cl-C ₆ H ₄ -CO ₂ H, [71]	0
10	<i>p</i> -F-C ₆ H ₄ -OTf	-2.0	2.3	<i>p</i> -F-C ₆ H ₄ -CO ₂ H, [92]	0
11	C ₆ H ₅ -OTf	-2.0	2.3	C ₆ H ₅ -CO ₂ H, [96]	0
12	C ₆ H ₅ -OTf ^[g]	-2.0	2.3	C ₆ H ₅ -CO ₂ H, [88]	0
13	<i>p</i> -CH ₃ -C ₆ H ₄ -OTf	-2.0	2.2	<i>p</i> -CH ₃ -C ₆ H ₄ -CO ₂ H, [75]	0
14	<i>p</i> -MeO-C ₆ H ₄ -OTf	-2.1	2.2	<i>p</i> -MeO-C ₆ H ₄ -CO ₂ H, 13	49
15	<i>p</i> - <i>t</i> Bu-C ₆ H ₄ -OTf	-2.4	3.0	<i>p</i> - <i>t</i> Bu-C ₆ H ₄ -CO ₂ H, 0	100
16	<i>p</i> - <i>t</i> Bu-C ₆ H ₄ -OTf ^[h]	-1.9	2.1	<i>p</i> - <i>t</i> Bu-C ₆ H ₄ -CO ₂ H, [45]	17
17	<i>o</i> -Br-C ₆ H ₄ -OTf	-1.6	2.8	C ₆ H ₅ -CO ₂ H, [41]	0
18	<i>o</i> -CH ₃ -C ₆ H ₄ -OTf	-1.8	2.6	<i>o</i> -CH ₃ -C ₆ H ₄ -CO ₂ H, 44	33
19	2-naphthyl-OTf	-1.8	2.2	2-naphthyl-CO ₂ H, [95]	0

^[a] ArOTf/PdCl₂(PPh₃)₂: 1 mmol/0.1 mmol in 50 ml of DMF containing *n*Bu₄NBF₄ (0.3 M); divided cell. – ^[b] Electrolysis potential in volts vs. SCE. – ^[c] Faradays per mol = number of electrons involved in the electrolysis. – ^[d] Yields are relative to initial ArOTf; values were determined from the crude mixture after work-up by ¹H-NMR spectroscopy using CHCl₂CHCl₂ as internal standard; isolated yields are given in brackets. – ^[e] Formation of 47% of 4,4'-CN-C₆H₄-C₆H₄-CN. – ^[f] NiCl₂(dppe) as catalyst; ArOTf recovered: 26%. – ^[g] Stoichiometric reaction ArOTf/Pd(PPh₃)₄: 1 mmol/1 mmol. – ^[h] NiCl₂(dppe) as catalyst; ArOTf recovered: 22%.



ladium^{[10][17]} or nickel complexes^{[18][19]} as catalysts. However, the challenge is higher for aryl triflates than for aryl halides since the latter can be reduced, after cleavage of the Ar-Br bond, to the anion Ar⁻, which then reacts with CO₂. As shown above, the reduction of aryl triflates is a more complex process since a carbanion Ar⁻ cannot be quantitatively generated by cleavage of the Ar-O bond, and thus a catalyst is required. It is only in the presence of palladium that activation of the Ar-O bond takes place, leading to an Ar-Pd^{II} complex, which is the source of the anion Ar⁻ after activation by electron transfer.

Application to the Synthesis of Substituted 1,3,5-Triarylbenzene Derivatives from 4-Hydroxyacetophenone

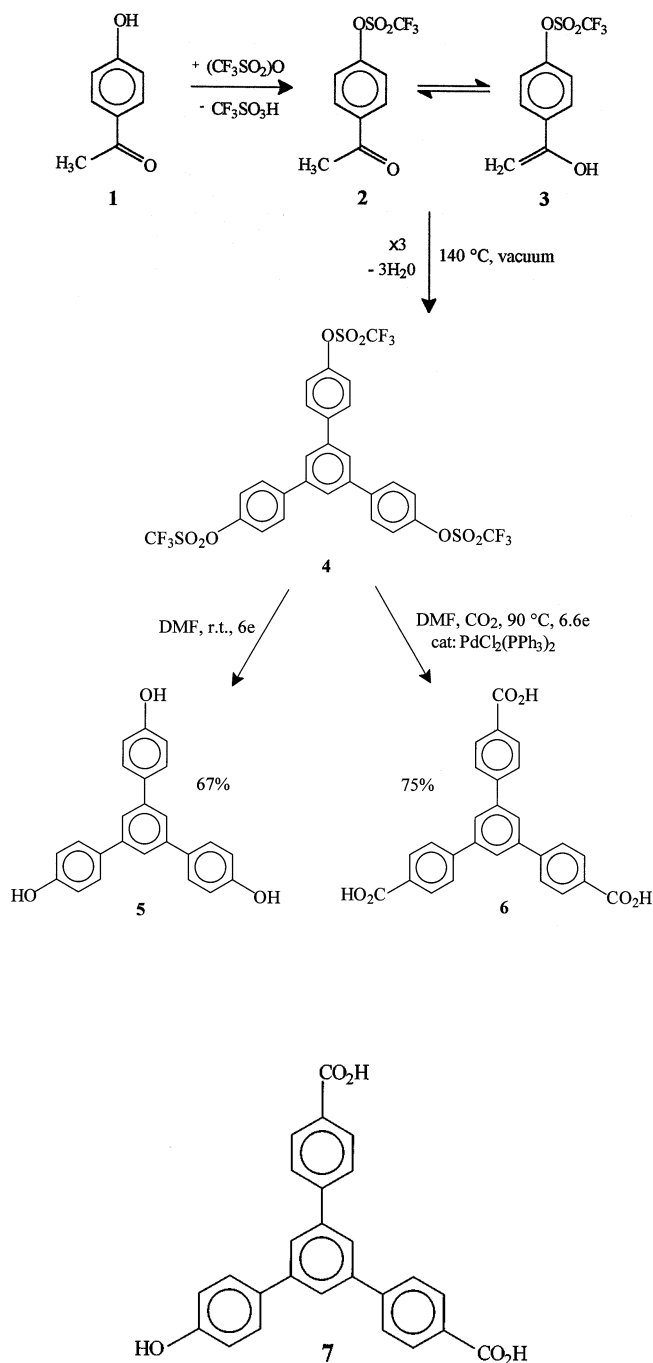
In an attempt to synthesize 4-(trifluoromethylsulfonyl-oxo)acetophenone (**2**) by treating triflic anhydride with 4-hydroxyacetophenone (**1**), we found that a modification of the reported procedure^[20] and of the usual work-up^[23] (i.e. heating the crude product at 140–150 °C in vacuo) did not result in the formation of the desired aryl triflate **2**. Instead, a new compound was isolated as white crystals in 97% yield and was characterized as 1,3,5-tris[4-(trifluoromethylsulfonyloxy)phenyl]benzene (**4**). The ¹H-NMR spectrum of the

initial product immediately after extraction and prior to heating in vacuo exhibited, besides the signals characteristic of compound **2**,^[24] additional signals attributable to the enol **3**.^[25] The tautomeric equilibrium between the ketone and the enol was probably due to some traces of acid^[26] originating from the acidic work-up. Under these conditions, the formation of compound **4** is a condensation of three molecules of the ketone **2** via the enol, with the concurrent elimination of three molecules of water in vacuo.^[27]

Since we were developing new reactions of aryl triflates through activation of the Ar-O bond by palladium complexes and electron transfer, we took the opportunity to transform compound **4** into functional terphenylene derivatives that might represent new materials or be precursors of new materials. Compound **4** was found to be reducible in DMF at *E*_{red} = -1.67, -1.85, and -1.97 V vs. SCE (at a gold disc electrode with a scan rate of 0.2 Vs⁻¹). An electrolysis performed at -1.9 V afforded, after consumption of 6 electrons per mol, a white solid that was isolated in 67% yield and characterized as 1,3,5-tris(4-hydroxyphenyl)benzene (**5**) (Scheme 2). All attempts to synthesize compound **5** by the direct condensation of compound **1** in acidic media were unsuccessful.^[28]

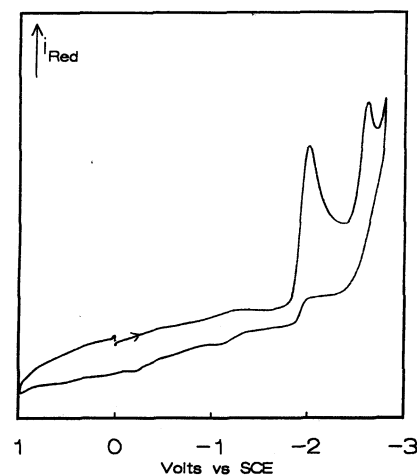
An electrolysis of compound **4** performed at -1.6 V, in the presence of gaseous carbon dioxide and 30% of PdCl₂(PPh₃)₂ according to Eq. 8, afforded, after consumption of 6.6 electrons per mol, a white solid that was isolated in 75% yield and characterized as 1,3,5-tris(4-carboxyphenyl)benzene (**6**) (Scheme 2). When the electrosynthesis was performed with only 10% of the catalyst, compound **6** was obtained in 43% yield along with a by-product which was isolated and characterized as compound **7** (34% yield).

Scheme 2



In conclusion, it is possible to synthesize new 1,3,5-triarylbenzene derivatives possessing triflate, carboxyl, and/or hydroxy groups as substituents. Some functionalized derivatives of 1,3,5-triarylbenzene (terphenylene) have been shown to be precursors of discotic liquid crystals and of materials possessing self-assembling properties.^[29] Compounds **5–7** can be easily transformed into esters or ethers and are thus potential precursors of liquid crystals.^[30] They can be used as reticulating agents for polymers.^[31] More-

Figure 2. Cyclic voltammetry of vinyl triflate **8b**, 3 mmol dm^{-3} in DMF (containing $n\text{Bu}_4\text{NBF}_4$, 0.3 M) at a stationary gold disc electrode (i.d. = 0.5 mm) at a scan rate of 50 mVs^{-1} at $20\text{ }^\circ\text{C}$



over, they may have interesting properties with regard to nonlinear optics.^[32]

Palladium-Catalysed Electrosynthesis of α,β -Unsaturated Carboxylic Acids from Vinyl Triflates and Carbon Dioxide

Vinyl triflates **8** are electroactive compounds (Table 4).^[6] Their electrochemical reduction affords, after hydrolysis, the ketone **9** in almost quantitative yield (Table 5, entries 1–2).^[33] The cyclic voltammogram of compound **8b** (Figure 2), obtained at a scan rate of 50 mVs^{-1} , exhibits two

Table 4. Reduction peak potentials of vinyl triflates and vinylpalladium(II) chloride complexes (Scheme 4, eq. a)

Vinyl-OTf 8	Vinyl-OTf 8 $E_{\text{red}}^{\text{[a]}}$	Vinyl-Pd-Cl(PPh ₃) ₂ $E_{\text{red}}^{\text{[a]}}$
	-1.94	-1.92
8a		
	-2.16	-2.08
8b		
	-2.91	-2.10
8c		
	-2.94	-2.20
8d		
	-2.95	-2.15
8f		
	-2.95	-2.20
8g		

^[a] Volts vs. SCE; reduction peak potentials were determined at a steady gold disc electrode (i.d. 5 mm) at a scan rate of 0.2 V s^{-1} in DMF containing $n\text{Bu}_4\text{NBF}_4$ (0.3 M) at $20\text{ }^\circ\text{C}$.

Table 5. Uncatalysed and PdCl₂(PPh₃)₂-catalysed electrochemical reduction of vinyl triflates in DMF at 20°C^[a]

entry	vinyl-OTf 8	catalyst %	CO ₂ atm.	E ^[b] volts	F/ mol ^[c]	ketone 9 % isolated ^[d]	diene 14 % isolated ^[d]	vinyl-CO ₂ H 15 % isolated ^[d]
1		0	0	-2.8	2.1	 9d (86)	0	—
2		0	0	-2.6	2.1	 9f (98)	0	—
3		0	1	-2.6	4.0	 9f (46) ^[e]	0	0
4		10	0	-2.0	1.1	0	 14f (96)	—
5		10	1	-2.0	2.4	0	0	 15f (85)
6		0	1	-2.0	2.7	 9b (3) ^[f]	0	0
7		10	1	-1.6	2.0	0	0	 15b (60)

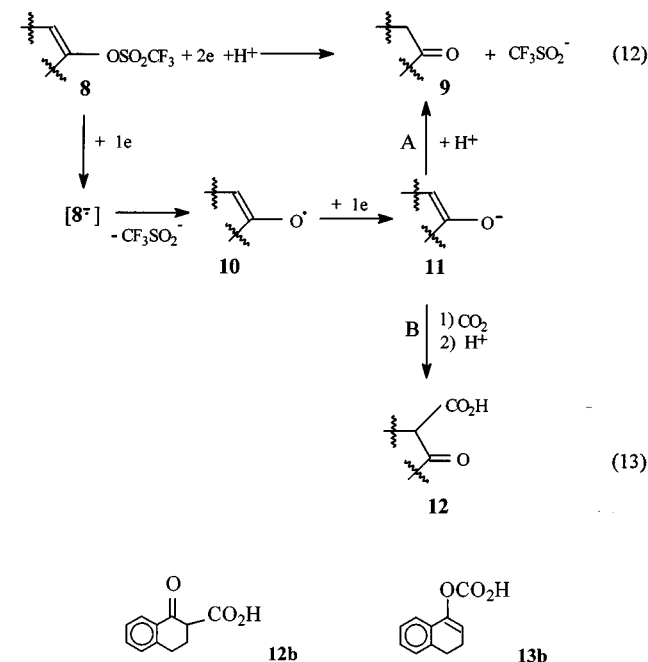
^[a] 1 mmol of vinyl triflate **8** in 50 ml of DMF containing *n*Bu₄NBF₄ (0.3 M); divided cell. — ^[b] Electrolysis potentials in volts vs. SCE. — ^[c] Faradays per mol = number of electrons involved in the electrolysis. — ^[d] Yields are related to the vinyl triflate completely converted. — ^[e] 49% of recovered **8f**. — ^[f] Formation of **12b** (51%), **13b** (25%).

successive reduction peaks. The first one, at -2.02 V, characterizes the two-electron reduction of the vinyl triflate **8b**, while the second one, at -2.62 V, characterizes the reduction of the α -tetralone **9b**, identified by comparison with an authentic sample. Similar behaviour was observed in the case of **8a**, where a second reduction peak was detected at -2.61 V and assigned to acetophenone.

The first electron transfer affords a radical anion **8^{•-}** (Scheme 3). After cleavage of the O-S bond, a vinyloxy radical **10** is formed, which is more easily reduced than the vinyl triflate. Its reduction furnishes the enolate **11** and, after protonation, the ketone **9** (route A), with the overall process consuming 2 electrons per mol (Eq. 12). Thus, as in the case of aryl triflates, electrochemical reduction of vinyl triflates results in an activation and cleavage of the O-S bond of the triflate group.

The electrochemical reduction of vinyl triflates **8** in the presence of carbon dioxide is a complex process. As illustrated in Table 4, the vinyl triflates **8** considered in this work can be divided in two groups, depending on the value of their reduction potential relative to that of CO₂ (-2.32 V, determined at a gold disc electrode at a scan rate of 0.2 Vs⁻¹). Vinyl triflates **8a, b** possessing a double bond conjugated to a phenyl group are more easily reduced than CO₂. In such cases, it is possible to selectively reduce the vinyl triflates **8a, b** without reducing CO₂. For example, the electrolysis of **8b**, performed in the presence of CO₂ in a divided cell, afforded the ketone **9b**, the β -oxocarboxylic acid **12b**, and the carbonate **13b** (Table 5, entry 6). Compound **12b**

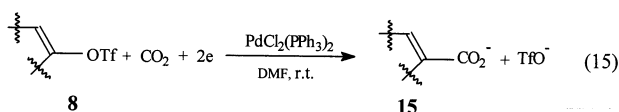
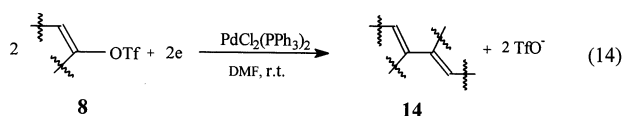
Scheme 3. Mechanism of the electrochemical reduction of vinyl triflates



was formed by carboxylation of the electrogenerated enolate **11**, as illustrated in Scheme 3 (route B, Eq. 13), while compound **13b** probably resulted from the carboxylation of the enolate at the oxygen atom.

The non-conjugated vinyl triflates **8c–f** are reduced at very negative potentials (Table 4), at around -3 V vs. SCE, and are thus less easily reduced than CO_2 (-2.32 V). Consequently, in these cases, electrolyses performed at the reduction potentials of **8c–f** also involved the reduction of CO_2 . An electrolysis of **8f**, performed in a divided cell at a controlled potential of -2.9 V, afforded, after consumption of 4 electrons per mol, the ketone **9f** in 46% yield. Some 49% of the vinyl triflate **8f** was recovered (Table 5, entry 3) and no reaction of the electrogenerated enolate with CO_2 was observed.^[6] The consumption of more than 2 electrons per mol of **8f** converted indicates that reduction of CO_2 occurred concurrently with that of **8f**, and that the direct reduction of **8f** to ketone **9f** was not affected by the reduction of CO_2 . Tokuda has recently reported that β -oxocarboxylic acids **12** are formed exclusively in good yields, even from vinyl triflates that are less easily reduced than CO_2 .^[34] The success of this reaction is due to the presence of magnesium salts released by oxidation of the magnesium anode during the electrolyses, which were carried out in undivided cells.^[34]

However, in none of these cases were α,β -unsaturated carboxylic acids **16** produced, since activation of the C–O bond of the vinyl triflates could not be achieved by simple electron transfer. This reaction requires activation of the C–O bond by a transition metal. In the presence of a catalytic amount of $\text{PdCl}_2(\text{PPh}_3)_2$, the formation of ketone **9** was completely inhibited and a conjugated diene **14** was obtained in quantitative yield (Table 5, entry 4, Eq. 14). This shows that activation of the C–O bond of the vinyl triflate via a palladium complex occurred, thereby preventing the direct reduction of the vinyl triflate to the corresponding ketone.



The electrochemical reduction performed in the presence of $\text{PdCl}_2(\text{PPh}_3)_2$ and carbon dioxide resulted in the formation of α,β -unsaturated carboxylic acids **15** (Eq. 15, Table 5, entries 5, 7).^[6]

We note from Table 5 (entries 4, 5, 7) that the Pd-catalysed homocoupling (Eq. 14) and carboxylation (Eq. 15) were performed at a less negative potential than the reduction potential of the vinyl triflates, and that this potential is also less negative than that of CO_2 . The values of the electrolysis potentials were determined by cyclic voltamme-

try, which has provided a mechanistic insight into the Pd-catalysed carboxylation (Scheme 4).

Scheme 4

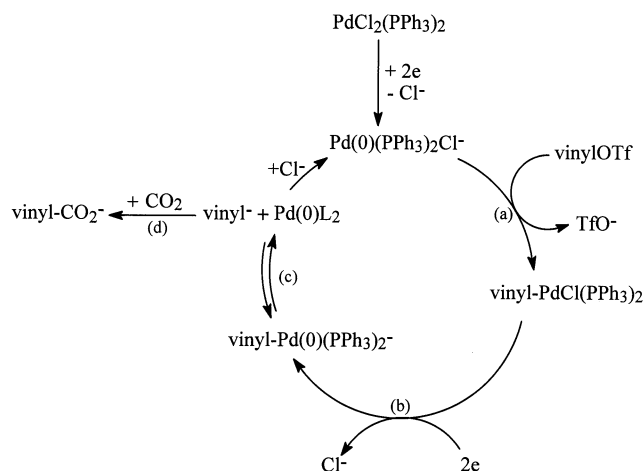
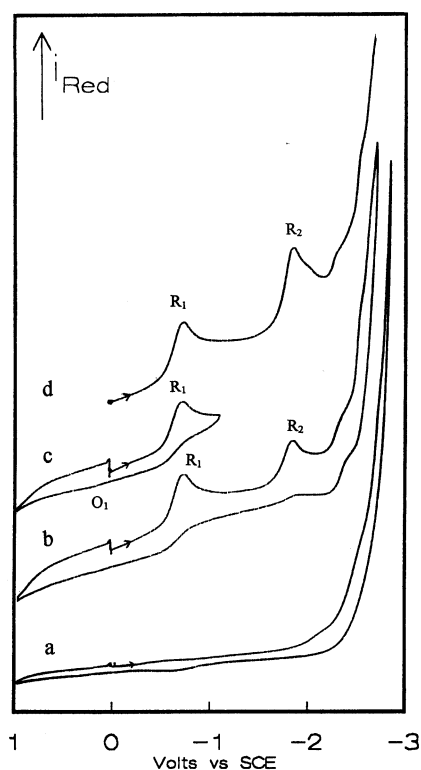


Figure 3a shows the cyclic voltammogram obtained for the reduction of compound **8d** (3 mmol dm^{-3} in DMF containing $n\text{Bu}_4\text{NBF}_4$, 0.3 M) at a scan rate of 50 mV s^{-1} . Under these conditions, the reduction peak of **8d** was not detected before the reduction of the solvent.^[35] In the presence of $\text{PdCl}_2(\text{PPh}_3)_2$, 3 mmol dm^{-3} , the reduction peak R_1 of $\text{PdCl}_2(\text{PPh}_3)_2$ was first observed at $E_{R1}^p = -0.74$ V (Figure 3b), followed by a second reduction peak at $E_{R2}^p = -1.90$ V (Figure 3b). $\text{PdCl}_2(\text{PPh}_3)_2$ was reduced to a palladium(0) complex $\text{Pd}^0(\text{PPh}_3)_2\text{Cl}^-$, which underwent an oxidative addition with compound **8d** (eq. a in Scheme 4). Indeed, the oxidation peak O_1 , characteristic of the electrogenerated complex $\text{Pd}^0(\text{PPh}_3)_2\text{Cl}^-$, was not observed on the reverse scan of Figure 3c. Stille has established that the oxidative addition of vinyl triflates to palladium(0) complexes yields cationic σ -vinylpalladium(II) complexes, whereas neutral σ -vinylpalladium(II) chloride complexes are formed when the oxidative addition is performed in the presence of chloride anions.^[3] Thus, in the present case, the oxidative addition to the electrogenerated chloride-ligated $\text{Pd}^0(\text{PPh}_3)_2\text{Cl}^-$ led to a neutral σ -vinylpalladium(II) chloride complex (Scheme 4, eq. a). This complex was reduced at R_2 , i.e. at a less negative potential than the reduction potential of the vinyl triflate **8d**. The magnitude of the reduction peak R_2 grew as the concentration of the vinyl triflate was increased (Figure 3d), indicating a catalytic reaction leading to the conjugated diene (Eq. 14). The α,β -unsaturated carboxylic acid was produced when the reduction was performed at R_2 in the presence of CO_2 (Eq. 15). The mechanism of the carboxylation step can reasonably be described as depicted in Scheme 4, by analogy with the mechanism outlined above for the aryl triflates (Scheme 1). Thus, initial activation of the vinylpalladium(II) chloride complex by electron transfer affords a vinyl anion, which is then able to react with CO_2 (eqs. b–d). In all cases investigated here, the σ -vinylpalladium(II) complexes were found to be more easily reduced than the precursor vinyl triflate (Table 4). Thus, the electrosyntheses of the α,β -unsaturated

Figure 3. Cyclic voltammetry performed in DMF (containing $n\text{Bu}_4\text{NBF}_4$, 0.3 M) at a stationary gold disc electrode (i.d. = 0.5 mm) at a scan rate of 50 mVs^{-1} at 20°C : (a) vinyl triflate **8d**, 3 mmol dm^{-3} ; (b) $\text{PdCl}_2(\text{PPh}_3)_2$, 3 mmol dm^{-3} and **8d**, 3 mmol dm^{-3} ; (c) same solution as in (b) but the direction of the scan has been reversed just after the reduction of $\text{PdCl}_2(\text{PPh}_3)_2$ at -1.2 V . (d) $\text{PdCl}_2(\text{PPh}_3)_2$, 3 mmol dm^{-3} and **8d**, 6 mmol dm^{-3} .



carboxylic acids **15** were performed at the reduction potential of the vinylpalladium(II) complexes, i.e. at a potential less negative than that of the vinyl triflates, thereby avoiding their direct reduction to enolates, which are source of ketones or α -oxocarboxylic acids. Moreover, the σ -vinylpalladium(II) complexes were more easily reduced than CO_2 . The reduction of CO_2 did not occur during the electrolyses and the carboxylation could proceed normally. Carboxylations were performed with cyclic and linear vinyl triflates (Table 6) and were regiospecific. Most electrolyses were performed in divided cells, although they could be performed in an undivided cell, provided that a sacrificial anode was used (compare entries 2–4 of Table 6). Vinyl triflates are more reactive than aryl triflates since their electrocarboxylation could be performed by bubbling CO_2 at room temperature, rather than at 90°C as in the case of the aryl triflates. This enhanced reactivity is probably due to a faster oxidative addition of the palladium(0) complex with vinyl triflates than with aryl triflates. Attempts to carboxylate a vinyl trifluoroacetate derivative such as compound **16c**, which would be expected to be less reactive in the oxidative addition than the triflate derivative, were indeed unsuccessful (Table 6, entry 9).

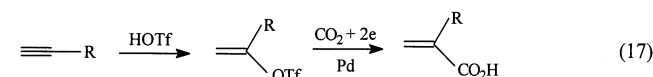
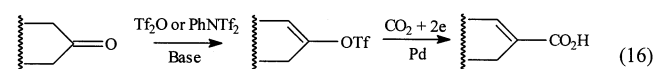
Vinyl triflates are synthesized by two different routes. Cyclic vinyl triflates (compounds **8b**, **c**, **f**, **g**) are synthesized by reaction of ketone enolates with a triflating reagent,^[36]

Table 6. $\text{PdCl}_2(\text{PPh}_3)_2$ -catalysed electrocarboxylation of vinyl triflates in DMF at 20°C (Eq. 15)^[a]

Entry	vinyl-OTf 8	CO_2 atm	$E^{[b]}$ Volt	$F/\text{mol}^{[c]}$	vinyl- CO_2H 15 (% isolated) ^[d]
1		1	$-1.7^{[e]}$	2.1	 15a (32)
2		1	$-1.6^{[e]}$	2.0	 15b (60)
3		1	$-1.6^{[f]}$	2.0	 15b (75)
4		1	$-1.6^{[g]}$	2.0	 15b (0) ^[h]
5		1	$-2.0^{[e]}$	2.2	 15c (80)
6		1	$-2.2^{[e]}$	2.3	 15d (70) ^[i]
7		1	$-2.0^{[e]}$	2.4	 15f (85)
8		1	$-2.0^{[e]}$	2.1	 15g (86)
9		1	$-1.6^{[e]}$	2.1	 15c (0) 9c (71)

[a] Vinyl-OTf **8**/ $\text{PdCl}_2(\text{PPh}_3)_2$: 1 mmol/0.1 mmol in 50 ml of DMF containing $n\text{Bu}_4\text{NBF}_4$ (0.3 M). – [b] Electrolysis potential in volts vs. SCE. – [c] Faradays per mol = number of electrons involved in the electrolysis. – [d] Yields are relative to the vinyl triflate that was totally converted. – [e] Divided cell. – [f] Undivided cell with a magnesium sacrificial anode. – [g] Undivided cell with $\text{Li}_2\text{C}_2\text{O}_4$ as compound oxidized at a platinum anode. – [h] 71% of **8b** recovered. – [i] Formation of 8% of 1-hexene.

whereas linear vinyl triflates (compounds **8a**, **d**) are synthesized by addition of HOTf to alkynes.^[37]



This work shows that cyclic ketones and alkynes are transformed into α,β -unsaturated carboxylic acids in the presence of CO_2 , a palladium catalyst, and an electron source, via the vinyl triflates (Eqs. 16 and 17). These new reactions offer an alternative route to the palladium-catalysed synthesis of α,β -unsaturated carboxylic acids from vinyl triflates and carbon monoxide under basic con-

ditions.^[38] Uncatalysed electrocarboxylation of vinyl halides has recently been reported by Tokuda.^[39] However, this reaction is restricted to phenyl-substituted vinyl bromides, i.e. to vinyl halides that are easily reduced to the vinylic anion, which then reacts with CO₂. For alkyl-substituted vinyl bromides, i.e. those which are not electroreducible, a nickel catalyst is required.^[40] Our reaction is more general in the sense that it is not restricted to phenyl-substituted vinyl triflates. Moreover, as in the case of aryl triflates, the challenge is higher since we react vinyl triflates the direct electrochemical reduction of which does not lead to vinyl anions by cleavage of the C–O bond, but rather to enolates by cleavage of the O–S bond of the triflate group. When vinyl triflates are generated from terminal alkynes, our process has the advantage of selectively affording the α,β -unsaturated carboxylic acids in which the carboxyl group resides at the more substituted position (Eq. 17). Nickel-catalysed electrocarboxylation of terminal alkynes has been reported.^[41] However, this reaction is not selective and affords a mixture of two α,β -unsaturated acids.

Conclusion

Aryl and vinyl triflates usually react with nucleophiles in the presence of a palladium catalyst. By supplying electrons, their reactivity has been reversed so that they react with electrophiles such as carbon dioxide, affording aromatic and α,β -unsaturated carboxylic acids, respectively.

Carboxylations generally proceed in one of two ways: Uncatalysed carboxylations proceed by nucleophilic attack of CO₂ by a carbanion (e.g. a Grignard reagent), whereas catalysed carboxylations usually proceed through activation of CO₂ by a transition metal complex.^[42] Our work is representative of a third route, which proceeds by a double activation. Indeed, the carboxylation reaction requires a transition metal, but this is responsible for the activation of the C–O bond of the aryl or vinyl triflate by an oxidative addition. This first activation affords an aryl- or vinylpalladium(II) complex, activation of which by electron transfer is required so as to generate an aryl or vinyl carbanion able to react with CO₂. The process is of particular interest since aryl or vinyl carbanions cannot be directly generated by reduction of aryl or vinyl triflates in the absence of a catalyst.

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Experimental Section

IR (KBr pellets): Nicolet Impact 400D. – NMR: Bruker AM 400 (400 MHz and 100.6 MHz for ¹H and ¹³C, respectively, with TMS as internal standard), Bruker AC 250 (250 MHz and 62.9 MHz for ¹H and ¹³C, respectively, with TMS as internal standard). – MS: Nermag R 10-10C.

Materials: The aryl triflates listed in Tables 2 and 3 were synthesized from commercial phenols according to published procedures.^{[21][36a]}

1,3,5-Tris[4-(trifluoromethylsulfonyloxy)phenyl]benzene (4): To a solution of 2.0 g (14.7 mmol) of 4-hydroxyacetophenone (**1**) in 150 ml of CH₂Cl₂ at –50°C, was added 2.16 ml (31.3 mmol) of triethylamine and 4.37 g (15.5 mmol) of trifluoromethanesulfonic anhydride. The solution was stirred for 1 h at –50°C, then for 8 h at room temperature, and then added to aqueous HCl (1 M). The organic phase was dried and the dichloromethane was evaporated. The ¹H-NMR spectrum of the crude product revealed, besides the signals of compound **2**,^[24] the presence of 7.5% of enol **3**.^[25] The crude product was then heated at 140–150°C in vacuo for 1.5 h to afford brown crystals, which were recrystallised from ethanol. 3.56 g (97%) of white crystals were collected, m.p. 153°C. When the enol was not present in the ¹H-NMR spectrum, 0.045 g (0.3 mmol) triflic acid was added to the crude product and the resulting mixture was treated as above. – ¹H NMR (250 MHz, CDCl₃): δ = 7.42 (d, J = 8.5 Hz, 6 H, *m*-H), 7.75 (s, 3 H, central *H*), 7.76 (d, J = 8.5 Hz, 6 H, *o*-H). – ¹³C NMR (62 MHz, CDCl₃): δ = 118.74 (q, J_{CF} = 315 Hz), 121.90 (d), 125.82 (d), 129.09 (d), 140.84 (s), 141.02 (s), 149.29 (s). – IR (KBr): $\tilde{\nu}$ = 1611, 1510 cm^{–1} (C=C), 1420, 1214, 614 (SO₂CF₃), 848, 751, 721 (CH). – MS (70 eV); m/z (%): 750 [M⁺], 617 (100) [M – SO₂CF₃], 484 [M – 2 SO₂CF₃], 351 [M – 3 SO₂CF₃]. – C₂₇H₁₅F₉O₉S₃ (749.97): calcd. C 43.20, H 2.02; found C 43.38, H 2.08.

Cyclic vinyl triflates **8b**, **c**, **f**, **g** were synthesized from commercial cyclic ketones;^[36] acyclic vinyl triflates **8a**, **d** from commercial alkynes.^[37]

Electrochemical Set-up and Procedure for Cyclic Voltammetry and Electrolyses: Cyclic voltammetry was performed with a home-made potentiostat and a PAR Model 175 wave-form generator. The cyclic voltammograms were recorded with a Nicolet 3091 digital oscilloscope. Experiments were carried out in a three-electrode cell connected to a Schlenk line. The counterelectrode consisted of a platinum wire of ca. 1 cm² macroscopic surface area. The reference was a saturated calomel electrode (Tacussel) separated from the solution by a bridge filled with 3 ml of a solution of *n*Bu₄NBF₄ (0.3 M) in DMF. 20 ml of DMF containing *n*Bu₄NBF₄ (0.3 M) was poured into the cell, 0.06 mmol of the appropriate aryl or vinyl triflate was added, and cyclic voltammetry was performed with a stationary disc electrode [a gold disc made from a cross section of wire (i.d. 0.5 mm) sealed into glass] at a scan rate of 0.05 Vs^{–1} or 0.2 Vs^{–1}. 42 mg (0.06 mmol) of PdCl₂(PPh₃)₂ was then added and cyclic voltammetry performed once more.

The electrolyses were performed at a controlled potential using a Tacussel PJT 35-2 potentiostat in a divided three-electrode cell with the two compartments separated by a sintered-glass frit. The cathodic compartment contained 50 ml of anhydrous DMF with *n*Bu₄NBF₄ (0.3 M) and was equipped with a carbon-cloth cathode (10 cm², Carbone Lorraine). The anodic compartment contained 5 ml of DMF with *n*Bu₄NBF₄ (0.3 M) and was equipped with a magnesium rod. The reference was a saturated calomel electrode separated from the solution by a bridge filled with 3 ml of a solution of *n*Bu₄NBF₄ (0.3 M) in DMF.

Typical Procedure for the Electroreduction of Aryl Triflates in the Absence of CO₂ and Catalyst – Preparation of 1,3,5-Tris(4-hydroxyphenyl)benzene (**5**): 0.375 g (0.5 mmol) of compound **4** was placed in the cathodic compartment. The electrolysis was performed at room temperature at a controlled potential of –1.9 V vs. SCE and was terminated when the current dropped to about 5% of its initial value. 6 F/mol were passed through the cell. The contents of the cathodic compartment were then added to aqueous HCl (1 M) and after leaving the mixture overnight, it was extracted with diethyl ether. After evaporation of the solvent from the com-

bined ether extracts, 0.119 g (67%) of white, greasy crystals was isolated. – ^1H NMR (250 MHz, $[\text{D}_4]\text{methanol}$): δ = 7.03 (d, J = 8 Hz, 6 H, *o*-H), 7.69 (d, J = 8 Hz, 6 H, *m*-H), 7.73 (s, 3 H, central H), 9.47 (s, 3 H, OH) – ^{13}C NMR (62.9 MHz, $[\text{D}_4]\text{methanol}$): δ = 115.11 (d), 122.45 (d), 127.74 (d), 132.56 (s), 141.80 (s), 156.73 (s). – MS (70 eV); m/z (%): 354 (100) $[\text{M}^+]$, 338.^[27b]

Typical Procedure for the Palladium-Catalysed Electrocarboxylation of Aryl Triflates – Preparation of 4-Fluorobenzoic Acid: The cathodic compartment was charged with 0.244 g (1 mmol) of 4-fluoro(trifluoromethylsulfonyloxy)benzene followed by 0.07 g (0.1 mmol) of $\text{PdCl}_2(\text{PPh}_3)_2$. Carbon dioxide was then bubbled into the cathodic compartment and the electrolysis was conducted at 90°C at a controlled potential of –2 V, until the current dropped to 5% of its initial value. The electrolysis consumed 2.3 F/mol of 4-fluoro(trifluoromethylsulfonyloxy)benzene. The mixture was then hydrolysed overnight with aqueous HCl (1 M). After extraction with diethyl ether and evaporation of the solvent, the crude product was analysed by ^1H -NMR spectroscopy, which revealed the presence of some phosphane oxide. The crude product was then treated with an aqueous solution of NaOH (1 M) so as to solubilize the corresponding carboxylate salt. After washing with diethyl ether, the basic aqueous solution was treated with aqueous HCl (1 M) and extracted with diethyl ether, to afford 0.129 mg of pure 4-fluorobenzoic acid. – ^1H NMR (250 MHz, CDCl_3): δ = 7.17 (t, J_{HH} = 9 Hz, J_{HF} = 9 Hz, 2 H, *o*-H vs. F), 8.15 (dd, J_{HH} = 9 Hz, J_{HF} = 5.5 Hz, 2 H, *m*-H vs. F). – MS (70 eV); m/z (%): 140 $[\text{M}^+]$, 123 (100) $[\text{M} - 17]$, 95 $[\text{M} - 45]$.

1-Naphthoic acid, 4-cyanobenzoic acid, 4-trifluoromethylbenzoic acid, 4-acetylbenzoic acid, para-terephthalic acid, 4-bromobenzoic acid, 4-chlorobenzoic acid, 4-fluorobenzoic acid, benzoic acid, 4-methylbenzoic acid, 4-methoxybenzoic acid, 4-tert-butylbenzoic acid, 2-bromobenzoic acid, 2-methylbenzoic acid, and 2-naphthoic acid were characterized by ^1H -NMR (250 MHz) spectroscopy, mass spectrometry, and by comparison of their analytical data with those of commercial samples. *para-Terephthalic acid monoethyl ester* was characterized by ^1H -NMR (250 MHz) spectroscopy and mass spectrometry, and by comparison of its analytical data with those reported in the literature.^[43]

1,3,5-Tris(4-carboxyphenyl)benzene (6): 0.75 g (1 mmol) of compound **4** was placed in the cathodic compartment, followed by 0.21 g (0.3 mmol) of $\text{PdCl}_2(\text{PPh}_3)_2$, and carbon dioxide was bubbled through the catholyte. The electrolysis was performed at 90°C at a controlled potential of –1.6 V vs. SCE and was terminated when the current dropped to 5% of its initial value. 6.6 F/mol were passed through the cell. The catholyte was then added to aqueous HCl (1 M) and the mixture was left overnight. A white precipitate was formed, which was filtered off and washed with dichloromethane, to give 0.328 g (75%) of **6**, m.p. 235°C. – ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$): δ = 8.262 (d, J = 7.5 Hz, 6 H, *m*-H), 8.291 (d, J = 7.5 Hz, 6 H, *o*-H), 8.305 (s, 3 H, central H). – ^{13}C NMR (100.6 MHz, $[\text{D}_6]\text{DMSO}$): δ = 125.61 (d), 127.45 (d), 129.94 (d), 130.04 (s), 140.76 (s), 143.87 (s), 167.19 (s). – IR (KBr): $\tilde{\nu}$ = 3600–2400 cm^{-1} (OH), 1680 (C=O), 1600, 1560, 1420 (C=C), 1290 (C–O), 850, 765, 700 (CH). – MS (70 eV); m/z (%): 439 (100) $[\text{M} + 1]$. – $\text{C}_{27}\text{H}_{18}\text{O}_6$ (438.11): calcd. C 73.97, H 4.14; found C 73.75, H 4.38.

1,3-Bis(4-carboxyphenyl)-5-(4-hydroxyphenyl)benzene (7): The procedure used was as that described for the synthesis of compound **6**, but the electrolysis was performed in the presence of 0.07 g (0.1 mmol) of $\text{PdCl}_2(\text{PPh}_3)_2$. 6.2 F/mol were passed through the cell. The catholyte was then added to aqueous HCl (1 M). A white precipitate was formed, which was filtered off, and a ^1H -NMR spectrum of the crude product was recorded. This revealed the

presence of the two compounds **6** and **7**. They were separated by treating the mixture with dichloromethane. Compound **6** is insoluble in dichloromethane, whereas compound **7** is freely soluble. Thus, filtration afforded 0.188 g (43%) of pure compound **6**. Evaporation of dichloromethane from the filtrate afforded 0.139 g (34%) of pure compound **7** as white crystals. – ^1H NMR (250 MHz, $[\text{D}_6]\text{acetone}$): δ = 6.93 (dd, J = 7 Hz, J = 1.5 Hz, 2 H, *o*-H vs. OH), 7.65 (m, 2 H), 7.80 (m, 2 H, *m*-H vs. OH), 7.89 (m, 5 H), 8.03 (d, J = 7 Hz, 4 H, *o*-H vs. CO_2H). – IR (KBr): $\tilde{\nu}$ = 3600–3000 cm^{-1} (OH), 1620 (C=O), 1475, 1430 (C=C), 1090 (C–O), 750, 740, 705, 690 (CH). – MS (70 eV); m/z (%): 410 (100) $[\text{M}^+]$, 393 $[\text{M} - \text{OH}]$, 384.

Typical Procedure for the Palladium-Catalysed Electrocarboxylation of Vinyl Triflates – Preparation of 6-Methylcyclohex-1-ene-1-carboxylic Acid (15g): The cathodic compartment was charged with 0.244 g (1 mmol) of **8g**, followed by 70 mg (0.1 mmol) of $\text{PdCl}_2(\text{PPh}_3)_2$, and carbon dioxide was bubbled through the catholyte. The electrolysis was conducted at room temperature at a controlled potential of –2 V, until the current dropped to 5% of its initial value. The mixture was then hydrolysed overnight with aqueous HCl (1 M). After extraction with diethyl ether and evaporation of the solvent, the crude product was analysed by ^1H -NMR spectroscopy. The signals of the α,β -unsaturated carboxylic acid were detected, but the compound was shown to be contaminated with some triphenylphosphane oxide. The carboxylic acid was purified by solubilization in aqueous NaOH (1 M). After washing with diethyl ether, the basic aqueous phase was treated with aqueous HCl (1 M). The acidic aqueous phase was then extracted with diethyl ether. Evaporation of the solvent from the combined extracts afforded 120 mg (86%) of pure **15g** as white crystals, m.p. 102°C. – ^1H NMR (250 MHz, CDCl_3): δ = 1.04 (d, J = 7 Hz, 3 H, CH_3), 1.45–1.60 (m, 4 H, CH_2CH_2), 2.06–2.17 (m, 2 H, $\text{CH}_2\text{CH}=\text{C}$), 2.54–2.67 (m, 1 H, CHCH_3), 7.03 (t, 1 H, J = 4 Hz, =CH), 11.60 (br. s, 1 H, OH). – ^{13}C NMR (62.9 MHz, CDCl_3): δ = 16.99, 20.10, 26.12, 27.40, 29.43, 134.69, 142.17, 173.14. – IR (KBr pellet): $\tilde{\nu}$ = 3200–2700 cm^{-1} (O–H), 2965 (=CH), 2945, 2918, 2870 (CH), 1677 (C=O), 1635 (C=C), 1422, 1274, 1251 (CO), 1068, 939. – MS (70 eV); m/z (%): 140 $[\text{M}^+]$, 125 $[\text{M} - \text{CH}_3]$, 95 (100) $[\text{M} - \text{CO}_2\text{H}]$.^[44]

The isolated α,β -unsaturated carboxylic acids *2-phenylacrylic acid (15a)*,^[45] *3,4-dihydronaphthalene-1-carboxylic acid (15b)*,^[46] *4-tert-butyl-cyclohex-1-enecarboxylic acid (15c)*,^[47] *2-butylacrylic acid (15d)*,^[48] and *4-phenylcyclohexyl-1-enecarboxylic acid (15f)*^[38] were characterized by ^1H -NMR (250 MHz) spectroscopy, mass spectrometry, and by comparison of their analytical data with those reported in the literature.

The α -oxocarboxylic acid, *1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid (12b)* was characterized by ^1H -NMR (250 MHz) spectroscopy.^[49]

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- [24] 4-(Trifluoromethylsulfonyloxy)acetophenone (**2**): ¹H NMR (250 MHz, CDCl₃): δ = 2.64 (s, 3 H, CH₃), 7.39 (d, *J* = 8.7 Hz, 2 H, arom. H), 8.07 (d, *J* = 8.7 Hz, 2 H, arom. H), identical to that reported by Stille.^[22]
- [25] 1-[4-(Trifluoromethylsulfonyloxy)phenyl]ethanol (**3**), not isolated but identified in the ¹H-NMR spectrum of compound **2** (7.5%): ¹H NMR (250 MHz, CDCl₃): δ = 5.50 (d, *J* = 4.2 Hz, 1 H, =CH *cis* vs. OH), 5.68 (d, *J* = 4.2 Hz, 1 H, =CH *trans* vs. OH), 6.99 (br. s, 1 H, OH), 7.36 (d, *J* = 8.9 Hz, 2 H, arom. H), 7.65 (d, *J* = 8.9 Hz, 2 H, arom. H).
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