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The palladium(II) / carbon monoxide-mediated biaryl formation from aryltellurium trihalides

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Abstract

Treatment of aryltellurium trihalides ($ArTeX_3$: Ar = Ph, 4-BrC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-$BuOC_6H_4$, 4-$PhOC_6H_4$, 2-naphthyl; X = Cl, Br) with a palladium(II) salt in acetonitrile at 25 °C affords, in good yields (29–78%), the corresponding biaryls (ArAr) either in the atmosphere or under 1 atm CO. The presence of CO accelerates this aromatic coupling significantly to produce some active palladium carbonyl species, the formation of which was confirmed by IR spectroscopy of Li_2PdCl_4 in acetonitrile solution under CO; a strong sharp absorption and a weaker sharp one appeared at 2140 and 1908 cm^{-1}, respectively, attributable to the $\nu(C{\equiv}O)$ of the $(Pd{-}C{\equiv}O)$ species. Treatment with alkali after reaction was essential to producing the biaryls.

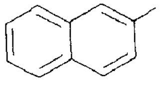
Introduction

We have shown that the treatment of various diorganyl tellurides with carbon monoxide (CO) in the presence of stoichiometric and catalytic amounts of palladium(II) salts gave the corresponding carboxylic acids or esters [1,2]. By contrast, the corresponding biaryls, instead of the expected benzoic acid derivatives, were obtained from phenyltellurium and 4-methoxyphenyltellurium trichlorides under the same conditions. Results of this study have been reported briefly [1]. We have investigated further the formation of this biaryl in order to find its scope and limitations and to clarify the active species for the coupling. The results are described here.

Results and discussion

Treatment of various readily available aryltellurium trichlorides (**1**) with palladium(II) chloride and lithium chloride in acetonitrile at 25 °C for 20 h under one atmosphere of CO, followed by alkaline hydrolysis by addition of 0.5 *N* aqueous NaOH, gave the corresponding biaryls **2** in good yields together with minor amounts of the corresponding acids **3**. Treatment with alkali caused the precipitation of a black solid, and was essential for obtaining **2** and **3** because neither could be isolated after treatment of the reaction mixture with brine. Although the aromatic coupling proceeded even in air in some cases, carbon monoxide accelerated the reaction significantly. Thus, **1a** and **1b** scarcely gave the biaryls **2a** and **2b** in air, and although the aryltellurium trichlorides having an electron-donating substituent such as **1d**–**1g** gave nearly the same yields of coupling products irrespective of the presence or absence of CO, an appreciable difference was observed in the product yield for short reaction times; i.e., after 10 min the yield of **2d** obtained from **1d** in air was about one-third of that when the reaction was carried out under CO. In regard to palladium(II) salts lithium chloropalladate

$$\underset{(\mathbf{1})}{\mathrm{ArTeCl_3}} \xrightarrow[\substack{(2)\ 0.5\ N\ \text{aq. NaOH} \\ (3)\ \mathrm{H_3O^+}}]{(1)\ \mathrm{Li_2PdCl_4/CO/MeCN}} \underset{(\mathbf{2})}{\mathrm{ArAr}} + \underset{(\mathbf{3})}{\mathrm{ArCO_2H}}$$

(**a**: Ar = Ph; **b**: Ar = 4-BrC$_6$H$_4$; **c**: Ar = 4-MeC$_6$H$_4$; **d**: Ar = 4-MeOC$_6$H$_4$;
e: Ar = 4-BuOC$_6$H$_4$; **f**: Ar = 4-PhOC$_6$H$_4$; **g**: Ar = )

derived from a mixture of PdCl$_2$ and LiCl was effective, but the coupling was not catalytic in the palladium(II) salt even in the presence of copper(II) chloride or with *p*-benzoquinone as reoxidant. The commercially available palladium powder and palladium black were also effective for aromatic coupling, but their reactivity was lower than that of the divalent palladium salt even under ultrasonic irradiation. Tetrakis(triphenylphosphine)palladium did not show any activity. Typical results are shown in Table 1. This aromatic coupling system is far more efficient than that of PdCl$_2$/NaOAc/AcOH at reflux temperature in which only 3% yield of **2d** was obtained from **1d** [3]. When equimolar amounts of phenyltellurium tribromide and **1d** were treated with lithium chloropalladate under CO for 20 h, cross-coupling occurred to give a mixture of **2a**, 4-methoxybiphenyl, and **2d** in a ratio of 1/2/0.8 in 79% total yield (see Experimental).

In order to throw some light on the reaction scheme and the active species engaged in the coupling under CO the following experiments were carried out and compared.

(a) A mixture of PdCl$_2$ and LiCl (1/2) was stirred in acetonitrile under 1 atm CO for 0.5 h with 3,3′,4,4′-tetramethylbiphenyl (as an internal standard for GLC analysis) and then **1d** was added to the mixture in air with stirring. An aliquot was pipetted off after appropriate intervals, which was treated with 0.5 *N* aq. NaOH, and subjected to GLC.

(b) Alternatively, an acetonitrile solution of **1d** containing the same internal standard was stirred under 1 atm CO for 0.5 h and then a mixture of PdCl$_2$ and LiCl (1/2) was added in air with stirring. Aliquots removed were treated as in (a). The yields of **2d** in the initial stages of both reactions were plotted against reaction time after the addition of the second reactant (Fig. 1). As Fig. 1 shows, in reaction a

Table 1

Palladium(II) mediated biaryl formation from aryltellurium(IV) trihalides [a]

Tellurium compound (1 mmol)	Palladium compound [b] (mmol)		Atmosphere (1 atm)	Product and yield (%) [c]	
				2	**3**
1a	Li_2PdCl_4	(1)	CO	72	5
1a	Li_2PdCl_4	(1)	air	trace	–
1a	Li_2PdCl_4	(0.5)	CO	51	3
1a	Li_2PdCl_4	(0.1)	CO	12	trace
1a	Pd powder	(1)	CO	28	14
$PhTeBr_3$	Li_2PdCl_4	(1)	CO	64	4
1b	Li_2PdCl_4	(1)	CO	13	11
1b	Li_2PdCl_4	(1)	air	0	–
1c	Li_2PdCl_4	(1)	CO	72	0
1d	Li_2PdCl_4	(1)	CO	67	4
1d	Li_2PdCl_4	(1)	air	54	–
1d [d]	Li_2PdCl_4	(1)	CO	26	trace
1d [d]	Li_2PdCl_4	(1)	air	8	–
1d	Na_2PdCl_4	(1)	CO	46	trace
1d	$Pd(OAc)_2$	(1)	CO	27	2
1d	Li_2PdCl_4	(0.05) [e]	CO	9	0
1d	Li_2PdCl_4	(0.1) [f]	CO	5	trace
1d	$Pd(PPh_3)_4$	(1)	CO	0	0
1d	Pd powder	(1) [g]	CO	30	trace
1d	Pd black	(1)	CO	14	21
1d	Pd black	(1) [g]	CO	16	19
1e	Li_2PdCl_4	(1)	CO	44 [h]	trace
1e	Li_2PdCl_4	(1)	air	26 [h]	–
1f	Li_2PdCl_4	(1)	CO	30 [h]	trace
1f	Li_2PdCl_4	(1)	air	29 [h]	–
1g	Li_2PdCl_4	(1)	CO	73 [h]	18 [h]
1g	Li_2PdCl_4	(1)	air	78 [h]	–

[a] Carried out in MeCN (10 ml) at 25 °C for 20 h (unless otherwise stated), and treated with 0.5 *N* aqueous NaOH after the reaction. [b] Li_2PdCl_4 denotes a 1/2 mixture of $PdCl_2$ and LiCl. [c] Determined by GLC; 0.5 mmol of **2** and 1 mmol of **3** (as methyl ester) correspond to 100% yield, respectively. [d] Reaction time; 10 min. [e] $CuCl_2$(2 mmol) was added. [f] *p*-Benzoquinone (2 mmol) was added. [g] Under ultrasonic irradiation. [h] Isolated yield.

the aromatic coupling is quite fast and is almost complete after 1 min, while in reaction b coupling is slower and the yield of **2d** increases only gradually. This fact observation indicates that CO produces some active palladium species from Li_2PdCl_4 in acetonitrile, and does not form the active species together with **1**. In fact, the possibility of the formation of the active palladium species was confirmed by measurement of the IR spectra of several acetonitrile solutions. Thus, neither an acetonitrile solution of **1a** or of **1d** stirred in air or 1 atm CO for 20 h nor an acetonitrile solution containing lithium chloropalladate under nitrogen showed absorptions in the range 2200–1800 cm^{-1}, whereas an acetonitrile solution of lithium chloropalladate under CO showed a strong sharp band at 2140 cm^{-1} after 30 min of stirring, and another weaker absorption at 1908 cm^{-1} after 20 h of stirring. Since the absorptions of terminal $\nu(C{\equiv}O)$ of metal carbonyls are known to appear at 2125–1850 cm^{-1} [4] and a very strong absorption at 1975 cm^{-1} is

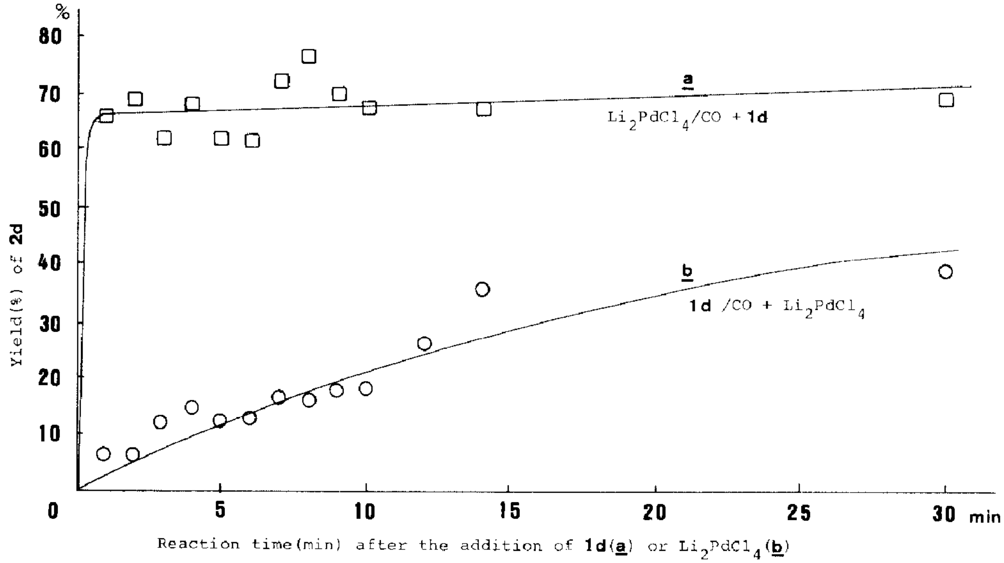


Fig. 1. Effect of the order in which substrates are added on yield of **2d**. Reactions: (a) **1d** was added to Li_2PdCl_4/CO/MeCN system after 0.5 h stirring; (b) Li_2PdCl_4 was added to **1d**/CO/MeCN system after 0.5 h stirring.

reported for $Pd_2(CO)_2Cl$ in Nujol [5] *, the data shown above clearly indicate the presence of a palladium carbonyl species which is more active than lithium chloropalladate itself for aromatic coupling of **1**.

We tentatively propose the Scheme 1 as a possible reaction pathway for the aromatic coupling reaction under CO, although we could not detect spectroscopically the species **A-D** **. The step for **A** has found a precedent in the reaction between **1** and $Ni(CO)_4$ for which the formation of a Te–Ni bond was proposed [6]. The aryl migration step from **A** to **B**, or the Te–Pd transmetallation, has been shown to occur in several palladium(II)-mediated and -catalyzed carbonylations of organotellurium compound, and in the reaction of $PdCl_2$-organic telluride complex with CO [1,2]. The step from **B** to **C** is regarded as the reductive elimination of $TeCl_4$ from a palladium(IV) intermediate **B**; such an elimination also has several precedents, one of which is the reductive elimination of ethane from a palladium(IV) intermediate formed on *trans* addition of CD_3I to *cis*-$PdMe_2L_2$ [7]. Disproportionation of **C** then occurs to give the diarylpalladium complex **D** [8], which is stabilized by coordination with $TeCl_4$. Alkaline treatment of **D** liberates a reactive diarylpalladium which immediately gives the corresponding biaryl **2**. The reaction of **C** with C(Ar′) derived from $Ar'TeCl_3$ results in the formation of a cross-coupling product (ArAr′). Tellurium tetrachloride seems to stabilize organopalladium compounds by

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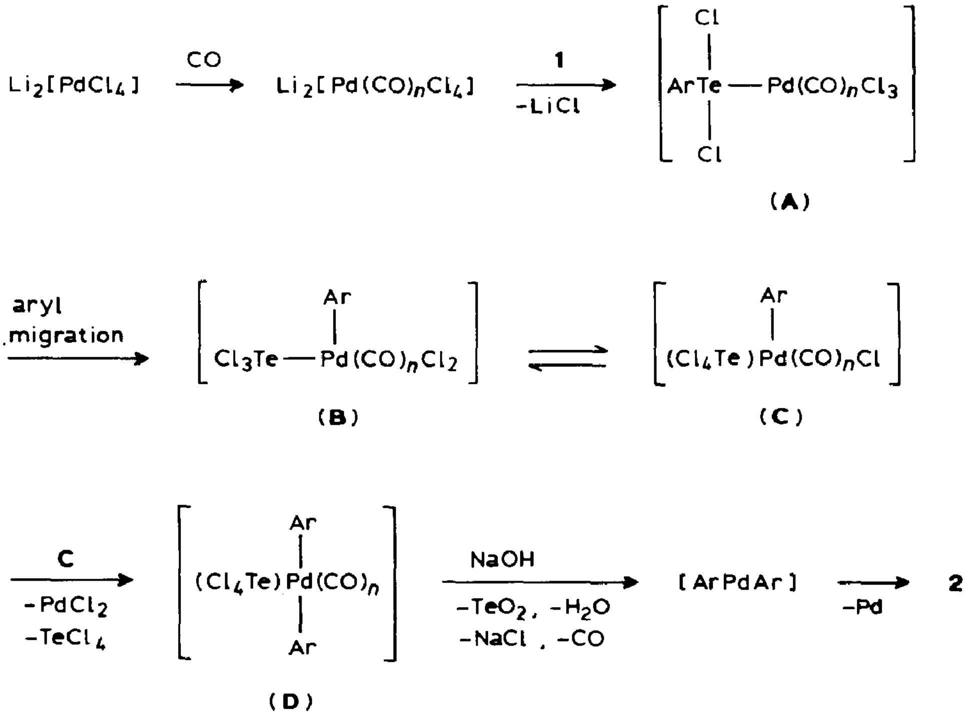
* An acetonitrile solution of $Pd_2(CO)_2Cl$, prepared separately by a published method [5], showed a sharp absorption at 1980 cm^{-1} in its IR spectrum. Treatment of **1d** with a stoichiometric amount of $Pd_2(CO)_2Cl$ (of unknown purity) in acetonitrile in air at 25 °C for 20 h gave **2d** in 30% yield, and no **3d** was formed.

** IR measurement of an acetonitrile solution containing **1a** and Li_2PdCl_4 stirred for 20 h under 1 atm CO showed only strong sharp band at 2140 cm^{-1} similar to that observed at the acetonitrile solution of Li_2PdCl_4/CO.



Scheme 1

coordination via chlorine or tellurium and, thus, we have already shown that the acylpalladium species containing an organotellurium compound such as ditelluride, telluride, or organotellurenyl halide as ligand were stable and resistant to methanolysis, such that alkaline hydrolysis was necessary to obtain the carboxylic acids [1].

Why **3** is scarcely formed is not yet clear, but one possibility is that the aryl transfer from palladium to carbon of CO ligand to give an acylpalladium species slows down because of coordination by the electron-withdrawing moiety, $TeCl_4$, to palladium. The aromatic coupling as well as carbonylation also proceeds, albeit less effectively, when Pd powder or Pd black are used (see above). In this case palladium may react with **1** to give aryltellurenyl chloride (ArTeCl) which then reacts with palladium followed by detelluration to afford the ArPdCl species. This species gives **2** as well as **3**. The reaction of ArTeCl with CO in the presence of palladium to give aromatic carboxylic acids has been proposed in palladium(II)-mediated carbonylation of organotellurides [2].

This palladium(II)/CO-mediated aromatic coupling is quite characteristic of aryltellurium trihalides, since it is known that arylmetal compounds usually afford carbonylation products under such conditions [9,10]. We also confirmed that the treatment of the phenylthallium compound ($PhTl(OAc)ClO_4 \cdot H_2O$) [11] and phenylmercury chloride under the conditions shown in Table 1 (1 atm CO, 2 h) yielded benzoic acid (68% yield) and a mixture of benzophenone (88%) and benzoic acid (9%), respectively, biphenyl being scarcely formed in both cases. In air, both organometallic compounds gave only biphenyl in high yields as expected [9,10] even without alkaline treatment after the reaction.

In summary, a good yield of biaryl was obtained by treatment of the readily available aryltellurium trihalides with a palladium(II) salt in acetonitrile at 25 ° C, the presence of CO at atmospheric pressure accelerates this aromatic coupling significantly by producing active palladium carbonyl complexes. Alkaline treatment was essential after the reaction probably to liberate a reactive diarylpalladium, from some tellurium species-coordinated stable diarylpalladium(II) intermediate, which would then give biaryl.

Experimental

^{1}H NMR spectra of $CDCl_3$ solutions of the samples were recorded on Hitachi Perkin–Elmer R600 (60 MHz) and Varian VXR 200 (200 MHz) spectrometers. IR spectra were recorded with a JASCO IR-810 infrared spectrophotometer as solutions in cells of 0.2 mm thickness. GLC analyses (1 m × 0.5 cm columns packed with 5% Silicone DC QF-1 and 5% EGSS-X on Chromosorb-W 60–80 mesh) were performed on a Yanaco G 2800 instrument with flame-ionization detectors and N_2 as carrier gas using a suitable internal standard. All column chromatographies were performed using Wakogel C-200 (100–200 mesh). For preparative chromatography plates precoated with Merck silica gel 60 F_{254} of 2-mm thickness were used. Melting points were determined with a Yanaco MP-S3 micro melting point determination apparatus, and were uncorrected.

Materials

Solvent acetonitrile was freshly distilled from CaH_2 prior to use. The other organic compounds and the inorganic metal salts, $TeCl_4$, LiCl, $PdCl_2$, $Pd(OAc)_2$, Na_2PdCl_4, Pd black, Pd powder, and $Pd(PPh_3)_4$ were all commercial products and used without any purification. Phenylthallium acetate perchlorate monohydrate was prepared by a published method [11]. Aryltellurium trichlorides (**1a** [12], **1b** [13], **1c** [13], **1d** [13], **1e** [14], **1f** [15], **1g** [16]) were prepared by the direct telluration of aromatic compounds by $TeCl_4$, whereas phenyltellurium tribromide was obtained from the reaction of diphenyl ditelluride with bromine [17]. The authentic samples of the biaryls (**2a**–**2c**), the 4-methoxybiphenyl and methyl esters (**3a**–**3d**, **3g**) for GLC analysis were commercial products. Compound **2d** was prepared by $Pd(PPh_3)_4$-catalyzed coupling of 4-iodoanisole with 4-methoxyphenylmagnesium bromide in THF; m.p. 179 ° C (from THF), lit., m.p. 173 ° C [18]. Other biaryls were isolated as white leaflets and identified as follows: **2e**, m.p. 145–146 ° C (from MeCN), lit., m.p. 145–146 ° C [19], ^{1}H NMR; δ(H) (200 MHz) 0.98 (6H, t, J 7.2 Hz), 1.50 (4H, m), 1.79 (4H, m), 3.99 (4H, t, J 6.4 Hz), 6.94 (4H, d, J 8.9 Hz), 7.45 (4H, d, J 8.8 Hz); **2f**, m.p. 151–152 ° C (from MeCN), Anal. Found: C, 85.26; H, 5.49. $C_{24}H_{18}O_2$ calcd.: C, 85.18; H, 5.36%; **2g**, m.p. 177–182 ° C (from MeCN), lit., m.p. 184–185 ° C [16].

Coupling of aryltellurium trichlorides

A typical procedure is described for the reaction of phenyltellurium trichloride (**1a**) under 1 atm CO atmosphere. Anhydrous lithium chloride (0.085 g, 2 mmol), palladium chloride (0.177 g, 1 mmol), and **1a** (0.311 g, 1 mmol) were placed in a two-necked 50-ml round bottom flask with a septum inlet and a three-way stopcock.

The system was then flushed with CO from a CO balloon connected to the flask at 25 ° C, and dry acetonitrile (10 ml) was added by a syringe. The resulting brown heterogeneous solution was stirred for 20 h at 25 ° C, during which it turned yellow brown and became homogeneous. It was poured into aqueous 0.5 *N* NaOH solution (100 ml) and a black precipitate formed immediately. The precipitate was filtered (Celite) and the filtrate was extracted with diethyl ether (3 × 50 ml). GLC analysis of the extract revealed the presence of biphenyl (**2a**) (benzophenone as an internal standard). The aqueous layer was separated off, acidified with HCl, and then extracted with diethyl ether (3 × 50 ml). After the extract had been treated with diazomethane, the product was found to be methyl benzoate (**3a**) by GLC.

Cross-coupling experiment

The same procedure, but using phenyltellurium tribromide (0.446 g, 1 mmol), **1d** (0.346 g, 1 mmol), palladium chloride (0.418 g, 2.35 mmol), lithium chloride (0.175 g, 4.13 mmol), and acetonitrile (20 ml), gave **2a** (0.210 mmol), 4-methyoxybiphenyl (0.414 mmol), **2d** (0.166 mmol), methyl benzoate (0.061 mmol), and methyl 4-methoxybenzoate (trace) (by GLC analysis, benzyl phenyl ketone and methyl phenylacetate as an internal standard respectively for cross-coupling products and methyl esters).

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