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Suzuki−Miyaura Cross-Coupling Reactions of Aryl Tellurides with Potassium Aryltrifluoroborate Salts

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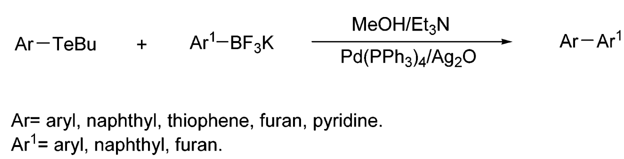

Palladium(0)-catalyzed cross-coupling between potassium aryltrifluoroborate salts and aryl tellurides proceeds readily to afford the desired biaryls in good to excellent yield. The reaction seems to be unaffected by the presence of electron-withdrawing or electron-donating substituents in both the potassium aryltrifluoroborate salts and aryl tellurides partners. Biaryls containing a variety of functional groups can be prepared. A chemoselectivity study was also carried out using aryl tellurides bearing halogen atoms in the same compound. In addition, this new version of the Suzuki−Miyaura cross-coupling reaction was monitored by electrospray ionization mass spectrometry where some reaction intermediates were detected and analyzed.

Introduction

Biaryl systems are an important class of compounds; they are involved in many applications, especially in the pharmaceutical chemistry. For example, in the sartan family of drugs for high blood pressure,[1] vancomycin antibiotics,[2] and flurbiprofen antiinflammatories,[3] biaryls comprise an important feature. Moreover, the aryl−aryl bond is present in numerous natural products as well as in biologically active agrochemicals.[4]

The main way to obtain biaryl compounds is the Suzuki cross-coupling reactions. Many protocols have been recently described.[5] The reaction is usually performed using a boronic acid or boronate ester and aryl halides or aryl triflates in the presence of a palladium catalyst, a ligand, and a base.[6] These conditions, however, can be changed in some cases. As an example, instead of aryl halides or triflates, aryldiazonium[7] or aryltrimethylammonium[8] salts can be used. In other cases, transition-metal

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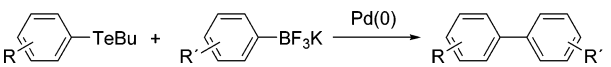
catalysts, such as nickel[8,9] or rhodium,[10] can substitute palladium as catalysts. Leadbeater et al. recently reported a "transition-metal-free" Suzuki cross-coupling reaction[11a] using microwave irradiation as an energy source and water as solvent. Recently,[11c] the author discovered that the sodium carbonate used as a base was contaminated with palladium (level of 50 ppb) and that this contaminant is responsible for the cross-coupling reaction. This alternative energy source was also studied by Yu et al.[12]

Boronic acids and boronate esters are the most commonly used derivatives in Suzuki cross-coupling reactions. Recently, Molander et al.[13] have explored the use of potassium organotrifluoroborate salts as an alternative to these boron reagents in Suzuki coupling reactions. These salts are readily prepared by the addition of an aqueous solution of inexpensive, widely available KHF_2 to a wide variety of organoboron intermediates.[14]

In the past decade, organotellurium chemistry was extensively explored, and many methods employing tellurium compounds have been developed.[15] Among these methods, organotellurium reagents were successfully used as the electrophilic reagent[16] in several metal-catalyzed cross-coupling reactions, such as Sonogashira,[17] Negishi,[18] Heck,[19] and Suzuki−Miyaura.[20].

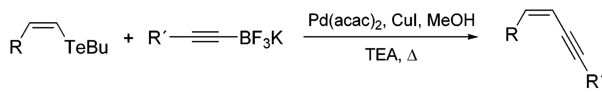
By taking advantage of the attractive features of potassium organotrifluoroborate salts and the organotellurium compounds in cross-coupling reactions, we report herein an efficient and chemoselective method for the synthesis of important biaryl compounds by the palladium-catalyzed cross-coupling reaction of aryl tellurides and potassium aryl trifluoroborate salts (eq 1).



(1)

Results and Discussion

Development. We initially focused our attention on the determination of the best experimental conditions for the reaction, electing to use 1-butyltellanyl-4-methoxybenzene **1a** and potassium phenyltrifluoroborate **2a** as standard reagents. First, we used a previous protocol described for Suzuki cross-coupling reactions between alkynyltrifluoroborate salts and vinylic tellurides[20] (eq 2). Regarding this, treatment of compound **1a** with **2a** in methanol at reflux temperature using Pd-$(acac)_2$ (15 mol %) as catalyst, in the presence of CuI (30 mol %) and triethylamine, afforded the corresponding 4-methoxybiphenyl **3a** in low yield (30%) (Table 1, entry 4).



(2)

In view of this result, we initiated an investigation to define the best catalyst. The reactions were monitored by the consumption of starting material and the appearance of the desired product by GC or GC−MS. As can be seen in Table 1, both Pd(0) and Pd(II) as well as the nickel catalyst were tested. The best result was reached when $Pd(PPh_3)_4$ with Ag_2O was used (Table 1, entry 8). The desired product **3a** was formed in 83% yield.

When $Pd(acac)_2$ and Ag_2O were used (Table 1, entry 5) the yield slightly increased in relation to when CuI (Table 1, entry 4) was used as the oxidant of palladium, but it remained less than when palladium(0) tetrakis(triphenylphosphine) was used as the catalyst. When $PdCl_2(dppf)\cdot CH_2Cl_2$ was used, product **3a** was obtained in 80% yield (Table 1, entry 7). We have tested palladium on charcoal (Table 1, entry 1) using sodium carbonate as the base and without an oxidant as described by Xu et al.,[21] but only traces of **3a** were detected by GC. When the nickel

TABLE 1. Study of Catalyst Effect on Cross-Coupling Reaction Using Aryl Telluride 1a and Potassium Phenyltrifluoroborate 2a

$$\underset{\substack{1\ \text{equiv.}\\ \mathbf{1a}}}{4\text{-MeO}(C_6H_4)\text{TeBu}} + \underset{\substack{1.2\ \text{equiv.}\\ \mathbf{2a}}}{\text{PhBF}_3\text{K}} \xrightarrow[\text{TEA, additive, MeOH, }\Delta]{\text{catalyst (10 mol\%)}} \underset{\mathbf{3a}}{4\text{-MeO}(C_6H_4)\text{−Ph}}$$

entry	catalyst	additive[a]	yield (%)
1	Pd/C		traces[b]
2	$PdCl_2$		<10
3	$NiCl_2(dppe)$	Ag_2O	nr
4	$Pd(acac)_2$	CuI	30
5	$Pd(acac)_2$	Ag_2O	55
6	Pd $(acetate)_2$	Ag_2O	43
7	$PdCl_2(dppf)\cdot CH_2Cl_2$	Ag_2O	80
8	$Pd(PPh_3)_4$	Ag_2O	83
9	$Pd(PPh_3)_4$	Ag_2O	80[c]
10	$Pd(PPh_3)_4$	Ag_2O	58[d]
11	$Pd(PPh_3)_4$	Ag_2O	40[e]
12	$Pd(PPh_3)_4$	Ag_2O	70[f]
13	$Pd(PPh_3)_4$	Ag_2O	65[g]
14	$Pd(PPh_3)_4$	Ag_2O	79[h]
15	$Pd_2(dba)_3\cdot CHCl_3$	Ag_2O	57

[a] 2 equiv was used. [b] Na_2CO_3 used as base. [c] 20 mol % of catalyst. [d] 5 mol % of catalyst. [e] 1 mol % of catalyst. [f] The reaction was performed at room temperature. [g] 1 equiv of **2a**. [h] 2 equiv of **2a**.

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TABLE 2. Study of Base Effect on Cross-Coupling Reaction Using Aryl Telluride 1a and Potassium Trifluoroborate 2a

$$\underset{\mathbf{1a}}{4\text{-MeO}(C_6H_4)\text{TeBu}} + \underset{\mathbf{2a}}{\text{PhBF}_3\text{K}} \xrightarrow[\text{Ag}_2\text{O, base}]{\text{Pd(PPh}_3)_4\text{, MeOH, }\Delta} \underset{\mathbf{3a}}{4\text{-MeO}(C_6H_4)\text{—Ph}}$$

entry	base	yield (%)
1		60
2	Et_3N	83
3	DIPEA	82
4	K_2CO_3	70
5	Cs_2CO_3	57
6	$EtNH_2$	traces
7	(*i*-Pr)$_2$NH	traces

TABLE 3. Study of the Effect of Additive on the Cross-Coupling Reaction Using Aryl Telluride 1a and Potassium Trifluoroborate 2a

$$\underset{\mathbf{1a}}{4\text{-MeO}(C_6H_4)\text{TeBu}} + \underset{\mathbf{2a}}{\text{PhBF}_3\text{K}} \xrightarrow[\text{2 equiv. additive, TEA}]{\text{Pd(PPh}_3)_4\text{, MeOH, }\Delta} \underset{\mathbf{3a}}{4\text{-MeO}(C_6H_4)\text{—Ph}}$$

entry	additive	yield (%)
1		n.r.
2	Ag_2O	83
3	Ag_2O	49[a]
4	Ag_2O	30[b]
5	AgOAc	76
6	CuI[c]	n.r.
7	CuI	n.r.

[a] 1 equiv of reoxidant was utilized. [b] 10 molar equiv of reoxidant was utilized. [c] This reaction was performed in the presence of atmospheric air.

complex, $NiCl_2$(dppe), was used as catalyst no reaction was observed (Table 1, entry 3). Other Pd(0) catalysts were used, e.g., $Pd_2(dba)_3{\cdot}CHCl_3$ (Table 1, entry 15), but the yield decreased in these cases.

The results of these studies indicated that the use of 20 and 10 mol % of $Pd(PPh_3)_4$, respectively, proved to be comparably effective (Table 1, entries 9 and 8). However, when the loading was dropped to 5 and 1 mol % (Table 1, entries 10 and 11), the yield noticeably decreased. The cross-coupling reaction between **1a** and **2a** was performed at room temperature (Table 1, entry 12), but the yield was less than when reflux temperature was applied (Table 1, entry 8). Only 90 min was required for total consumption of the starting material as monitored by GC.

The homocoupling reaction of phenyltrifluoroborate **2a** under these conditions was observed on a small scale. Because of this, the phenyltrifluoroborate **2a** loading was studied. The result of this study indicated that the use of 1.2 equiv of **2a** (Table 1, entry 8) is similar to that when 2 equiv of **2a** was used (Table 1, entry 14). However, when 1 equiv of **2a** was used (Table 1, entry 13), the yield decreased.

After the determination of the best catalyst, we studied the influence of the base. First, the reaction was carried out in the absence of base (Table 2, entry 1). Biaryl **3a** was obtained in satisfactory yield. Inorganic bases, such as potassium carbonate (Table 2, entry 4) and cesium carbonate (Table 2, entry 5), were used but led to a reduction in the yield of the desired product and to an increased formation of borate salt **3a** homocoupling product. Although the reaction yield remained high for the tertiary amines, e.g., triethylamine (TEA) or diisopropylethylamine (DIPEA) (Table 2, entries 2 and 3, respectively), when secondary or primary amines were used only traces of the product were detected by GC−MS analysis (Table 2, entries 6 and 7).

We observed that this cross-coupling reaction required the use of an additive for Pd(0) to Pd(II), as can be seen in Table 3. When the reaction was performed in the absence of additive (Table 3, entry 1) no reaction was observed. The best result was observed using 2 equiv of Ag_2O (Table 2, entry 2). When the reaction was carried out with 1 equiv of Ag_2O (Table 2, entry 3) or a catalytic amount (Table 2, entry 4) of Ag_2O, the desired product **3a** was obtained in lower yield. Silver acetate (Table 2, entry 5) and cuprous iodide (Table 2, entries 6 and 7) were tested also to improve the yield, but these additives were not good alternatives, especially when cuprous reagents were used wherein no reaction was observed.

The influence of the reaction solvent was also investigated. No reaction occurred in acetonitrile, and when THF−H_2O (20:1, v/v) was used the cross-coupling product was obtained in 63% yield. Thus, careful analysis of the optimized reaction revealed that the optimum conditions for the coupling were found to be the use of 1-butyltellanyl-4-methoxybenzene **1a** (0.5 mmol) and potassium phenyltrifluoroborate salt **2a** (1.2 equiv), $Pd(PPh_3)_4$ (10 mol %), Ag_2O (1 mmol), Et_3N (3 equiv) in MeOH at reflux temperature for 90 min. Using these reaction conditions, we were able to prepare the 4-methoxybiphenyl **3a** in 83% yield.

To demonstrate the efficiency of this cross-coupling reaction, we explored the generality of our method extending the coupling reaction to a variety of aryl tellurides **1a**−**n**. The results are summarized in Table 4. The Pd(0)-catalyzed Suzuki reaction proved to be exceptionally active. It is clear that this is a general method that tolerates both electron-withdrawing and electron-donating substituents. In addition, even an ortho-substituted telluride afforded the corresponding biphenyl compound in good yield (Table 4, entry 4). Unfortunately, this method was less effective for the reaction of heteroaryl tellurides. The reaction of 2-butyltellurium thiophene **1i** with **2a** afforded a 46% yield of the corresponding coupled product **3i** (Table 4, entry 9). However, the 2-butyltellanylfuran **1j** coupled with **2a** in 63% yield (Table 4, entry 10), while the 3-butyltellanylpyridine **1k** afforded the desired product **3k** in 65% yield (Table 4, entry 11).

Study of the Relative Reactivity of the Tellurium Moiety Compared to Halides in the Cross-Coupling Reaction. For substrates that contain more than one halide/triflate, the selective monofunctionalization through Suzuki cross-coupling can be a great tool in organic synthesis.[22] For previously described palladium catalysts, the general order of reactivity as follows: $I > Br \geq OTf \gg Cl$.[5] However, to the best of our knowledge, a chemoselective study between organotellurium compounds and substrates that contain halides or triflates in the structure have never been described.

As can be seen in Table 5, we have established that under the optimal conditions for Suzuki coupling as described above, the 1-butyltellanyl-4-chlorobenzene **1l** and 1-butyltellanyl-4-bromobenzene **1m** have reacted with highly selective monofunctionalization of difunctionalized arenes, affording the 4-chlorobiphenyl **3l** (Table 5, entry 1) and 4-bromobiphenyl **3m** (Table 5, entry 2), respectively, in high yields. Unfortunately, in the case of 1-butyltellanyl-4-iodobenzene **1n** the chemoselectivity seems not to be very effective; the 4-iodobiphenyl **3n** (Table 5; entry 3) was obtained only in 42% yield. This low

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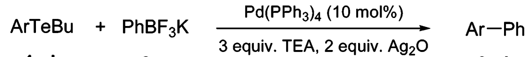
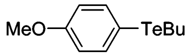
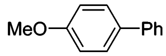
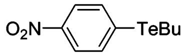
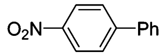
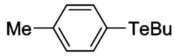
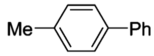
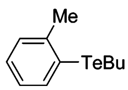
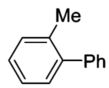
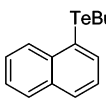
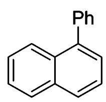
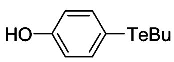
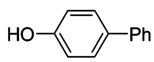
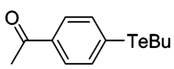
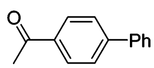
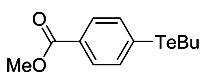
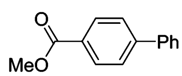
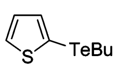
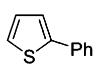
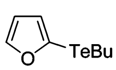
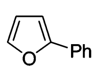
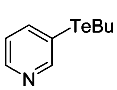
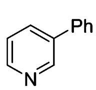
TABLE 4. Cross-Coupling Reaction of Aryl Tellurides 1 and Potassium Phenyltrifluoroborates 2



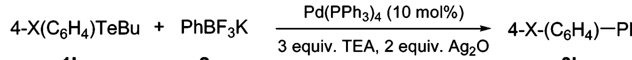
Entry	ArTeBu	Product	Yield (%)
1	 **1a**	 **3a**	82
2	 **1b**	 **3b**	89
3	 **1c**	 **3c**	80
4	 **1d**	 **3d**	74
5	 **1e**	 **3e**	79
6	 **1f**	 **3f**	92
7	 **1g**	 **3g**	80
8	 **1h**	 **3h**	83
9	 **1i**	 **3i**	46
10	 **1j**	 **3j**	63
11	 **1k**	 **3k**	65

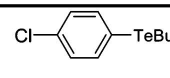
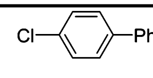
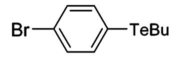
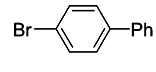
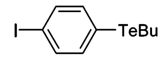
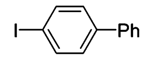
yield is due to coupling of **3n** with **2a** affording the terphenyl **4** (Scheme 1). It is important to point out that no telluro-substituted biphenyl **5** (Scheme 1) was detected by GC−MS.

To understand the scope of this reaction more clearly, we tested a variety of potassium aryltrifluoroborate salts **3** under the optimized procedure, and the results are summarized in Table 6. In the case of variation of the aryl tellurides **1**, the reaction proved to be a general method that tolerates both electron-rich and electron-deficient substituents in the aryltrifluoroborate **2b**−**d**.

ESI-MS Analysis of the Cross-Coupling Reaction. At the conclusion of the systematic study of this new version of the

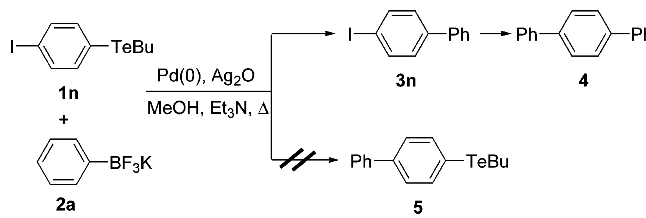
TABLE 5. Study of the Chemoselectivity on Cross-Coupling of Halo-Substituted Aryl Tellurides and Potassium Phenyltrifluoroborate 2a



Entry	4-X-ArTeBu	Product	Yield (%)
1	 **1l**	 **3l**	83
2	 **1m**	 **3m**	84
3	 **1n**	 **3n**	42[a]

[a] Terphenyl was formed in 15% isolated yield.

SCHEME 1



Suzuki−Miyaura cross-coupling reaction, we turned our attention to an investigation of this reaction in detail, taking advantage of the electrospray ionization mass spectrometry technique (ESI-MS) features. ESI-MS is a powerful tool for detection and characterization in the gas phase of charged and labile species in solution.[23] The mildness of ionization of this technique allows the detection and characterization of labile species and reaction intermediates proving to be very useful for probing mechanistic propositions of chemical reactions as already demonstrated in some representative early reports.[24] For this reason, we found that an ESI-MS analysis of this cross-coupling reaction can contribute to an understanding of the reactivity of RBF_3K reagents in this kind of reaction.

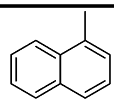
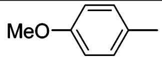
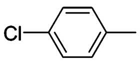
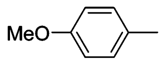
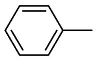
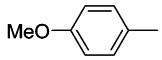
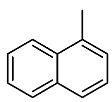
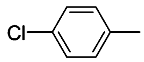
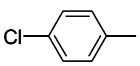
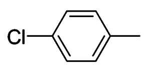
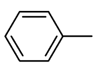
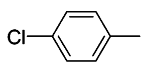
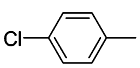
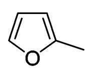
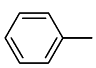
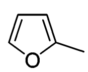
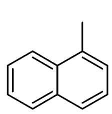
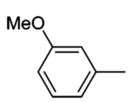
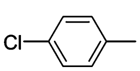
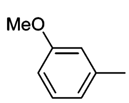
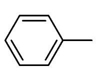
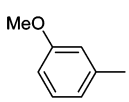
We began our study with a series of control experiments with the starting materials and each of these in combination with the catalyst. Species containing tellurium, palladium, phosphorus, and silver were detected by the characteristic isotopic distribution of these elements or their combination; isotopic abundance of the observed clusters was compared with calculated values. In the reaction monitoring, aliquots of 40 μL were taken from the reaction mixture and diluted in 960 μL of methanol containing 10 μL of formic acid for acid quenching.

(23) (a) Colton, R.; D'Agostino, A.; Traeger, J. C. *Mass Spectrom. Rev.* **1995**, *14*, 79. (b) Henderson, W.; Nicholson, B. K.; McCaffrey, L. J. *Polyhedron* **1998**, *17*, 4291.

(24) (a) Wilson, S. R.; Perez; Pasternak, A. *J. Am. Chem. Soc.* **1993**, *115*, 1994. (b) Furmeier, S.; Metzger, J. O. *J. Am. Chem. Soc.* **2004**, *126*, 14485. (c) Aliprantis, A. O.; Canary, J. W. *J. Am. Chem. Soc.* **1994**, *116*, 6985. (d) Aramendía, M. A.; Lafont, F.; Moreno-Mañas, M.; Pleixats, R.; Roglands, A. *J. Org. Chem.* **1999**, *64*, 3592. (e) Raminelli, C.; Prechtl, M. H. G.; Santos, L. S.; Eberlin, M. N.; Comasseto, J. V. *Organometallics* **2004**, *23*, 3990. (f) Chevrin, C.; Le Bras, J.; Henin, F.; Muzart, J.; Pla-Quintana, A.; Roglans, A.; Pleixats, R. *Organometallics* **2004**, *23*, 4796.

TABLE 6. Cross-Coupling Reaction of Various Aryl Telluride and Potassium Aryltrifluoroborates

$$\mathrm{ArTeBu} + \mathrm{Ar^1BF_3K} \xrightarrow[\text{3 equiv. TEA, 2 equiv. } Ag_2O \text{, MeOH, } \Delta]{Pd(PPh_3)_4 \text{ (10 mol\%)}} \mathrm{Ar{-}Ar^1}$$

Entry	Ar	Ar[1]	Product	Yield (%)
1	 **1e**	 **2b**	**3o**	87
2	 **1l**	 **2b**	**3p**	75
3	 **1o**	 **2b**	**3a**	81
4	 **1e**	 **2c**	**3q**	87
5	 **1l**	 **2c**	**3r**	94
6	 **1o**	 **2c**	**3l**	59
7	 **1l**	 **2d**	**3s**	52
8	 **1o**	 **2d**	**3j**	40
9	 **1e**	 **2e**	**3t**	79
10	 **1l**	 **2e**	**3u**	80
11	 **1o**	 **2e**	**3v**	78

The solutions of the potassium trifluoroborates (**2b** and **2c**) in methanol were monitored by ESI-MS-(−), which showed the presence of potassium-bound dimers [$ArBF_3^-\cdots K^+\cdots {}^-F_3BAr$] (Figure 1). The presence of these dimers is in agreement of an earlier observation of an 18-crown-6 potassium complex of a nitrile-functionalized alkyltrifluoroborate salt in solution and in the solid state.[25]

When the solutions of the tellurides were monitored, we were not able to observe the protonated tellurides (**1a**, **1b**, **1c**, and **1e**) as the major species in solution or its solvent adducts, as

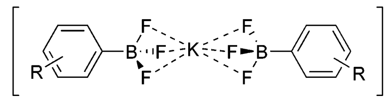


FIGURE 1. Potassium-bound aryltrifluoroborate dimers.

recently observed for vinylic tellurides,[25b] even when working at low *cone voltages* of 10−50 V in ESI-MS-(+) or ESI-MS-(−). The major species in solution of the arylic tellurides were the protonated telluroxide [ArTe(OH)Bu]$^+$, formed by air oxidation of the telluride, and the [ArTe]$^+$ cation. The methanolic solution of the palladium catalyst, [$Pd(PPh_3)_4$], showed an ESI-MS-(+) spectrum similar to that described in a preceding study of the palladium-catalyzed self-coupling of boronic acids.[25c] Next, we examined the interaction of the palladium catalyst with the aryltrifluoroborates and tellurides. These experiments showed that both reagents are able to undergo an oxidative addition with the palladium catalyst generating a [$(PPh_3)_2PdAr$]$^+$ species.

The reaction of telluride **1a** and the trifluoroborate salt **2c** was monitored at 5, 20, 40, and 60 min by ESI-MS-(+). At the beginning of the reaction, the silver cations [$Ag(PPh_3)$]$^+$ (**4**) of *m*/*z* 368 and [$Ag(PPh_3)_2$·MeOH]$^+$ (**5**) of *m*/*z* 662 were detected, after acid quench with formic acid. The products of the oxidative addition of telluride **1a** with the palladium catalyst were [*p*-MeO(C_6H_4)PdTeBu·H]$^+$ (**6**) of *m*/*z* 400 and {[*p*-MeO(C_6H_4)]-Pd(TeBu)(MeOH)(PPh_3)]}$^+$ (**7**) of *m*/*z* 692 and traces of the palladium bis-aryl adducts [(*p*-MeOC_6H_4)$_2$Pd(PPh_3)$_2$]$^+$ (**8**) of *m*/*z* 844 and [(*p*-MeOC_6H_4)(*p*-Cl C_6H_4)Pd(PPh_3)$_2$]$^+$ (**9**) of *m*/*z* 848. The latter cation is less stable than the former, probably by the stabilization conferred by two methoxy groups in comparison with a chlorine group (Figure 2). During the course of the reaction, a variation of the relative abundance of the observed species was noted where the silver cations were always present in solution and the oxidative addition products could not be detected.

The ESI-MS-(+) spectra of the cross-coupling reaction shows the presence of intermediates involved in the catalytic cycle of the coupling reaction (**6**−**9**) and also the silver cations **4** and **5** because different aryl derivatives of the telluride and the trifluoroborate salt were used. The obtained results suggest that the oxidative addition of the telluride is preferred over that of trifluoroborate salt. The product of the transmetalation of **2c** to the oxidative addition product of the telluride is likely to be a labile, transient species due to their low concentration in the reaction media. The role of Ag_2O cannot be solely attributed to that of an oxidant additive in the reaction because the presence of the triphenylphosphine cations **4** and **5** suggests an interaction of silver and the palladium catalyst or its intermediates leading to soluble triphenylphosphine silver salts. This proposition is supported by a demonstration of the interaction of soluble silver salts with palladium complexes wherein the silver salt can assist the halide removal and it can also assist the removal of complexed tertiary phosphines to promote the catalytic cycle.[26] These findings support the catalytic cycle depicted in Figure 3. In the proposed catalytic cycle, the aryl telluride oxidatively

(25) (a) Fei, Z.; Zhao, D.; Geldbach, T. J.; Scopelliti, R.; Dyson, P. J. *Eur. J. Inorg. Chem.* **2005**, 860. (b) Raminelli, C.; Prechtl, M. H. G.; Santos, L. S.; Eberlin, M. N.; Comasseto, J. V. *Organometallics* **2004**, *23*, 3990. (c) Aramedía, M. A.; Lafont, F.; Moreno-Mañas, M.; Pleixats, R.; Roglands, A. *J. Org. Chem.* **1999**, *64*, 3592.

(26) Kayaki, Y.; Shimizu, I.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1140.

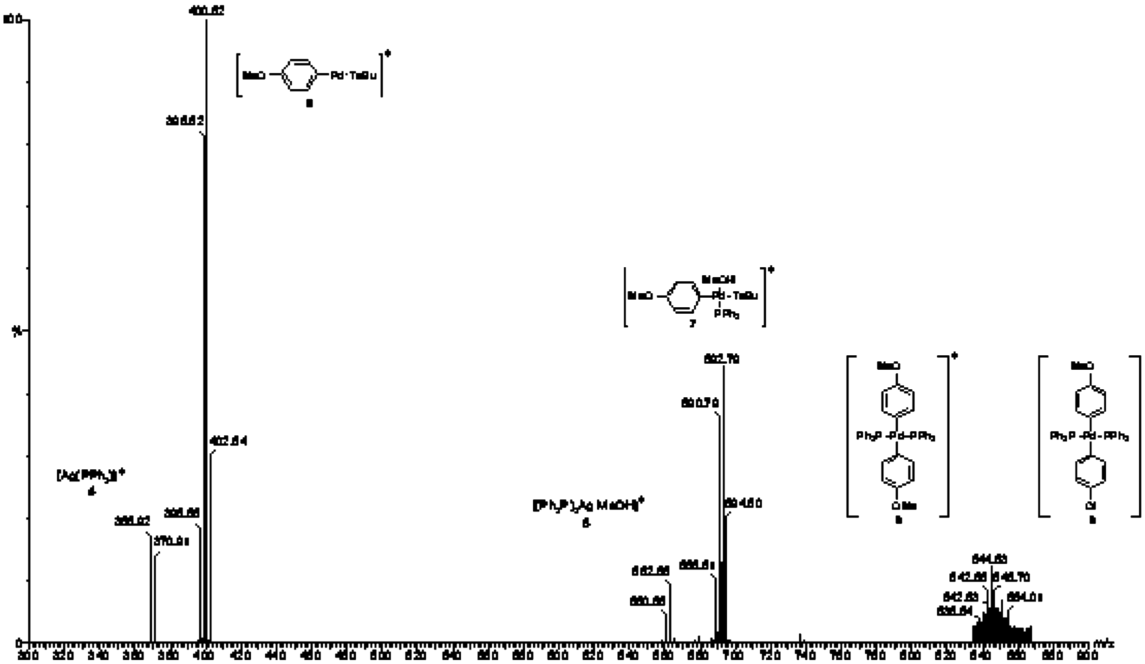


FIGURE 2. ESI-MS(+) spectrum of the reaction between telluride **1a** and trifluoroborate **2c** under cross-coupling reaction conditions.

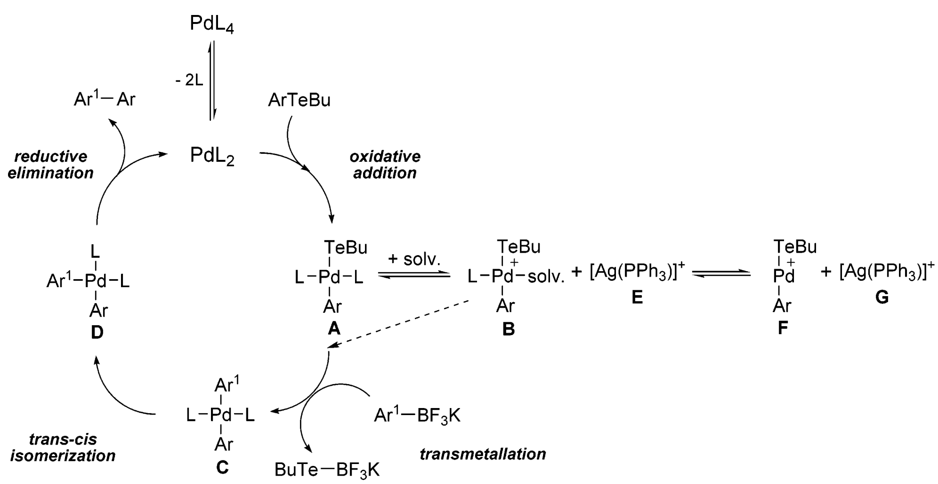


FIGURE 3. Proposed catalytic cycle of the cross-coupling reaction based on the ESI-MS observations.

adds to the PdL_2 species leading to the tellurated palladium intermediate **A** that can exchange one ligand by a solvent molecule yielding the detected species **B**. In the transmetalation step of the catalytic cycle, both species **A** or **B** can react with the aryltrifluoroborate where the tellurium moiety would be combined to the borate as its aryl group is transferred to palladium forming to the detected bis-arylated palladium intermediate **C**. At the end of the reaction, a black powder of indeterminate composition was formed and only traces of dibutyltelluride was observed by GC−MS analysis, with these observations the fate of tellurium and the trifluoroborate could not be rationalized. The labile *trans* intermediate **C** should isomerize to the *cis* intermediate **D,** which suffers the reductive elimination readily since its abundance in the solution is very low; in this way, the bis-arylic product is formed regenerating the starting zerovalent palladium catalyst. As pointed below, the role of silver oxide can be attributed to the removal of phosphine ligands of the catalyst or from one of the catalytic intermediates formed in the course of the reaction; such a process could therefore occur with the catalytic intermediate **A** leading to the mono- and diphosphino silver complexes **E** and **G** and the tellurated palladium species **B** and **F**, the main palladium species observed in the ESI-MS−(+) spectrum (Figure 2).

Conclusion

In summary, we have developed general and high-yielding methods for accomplishing Suzuki cross-coupling reactions between aryl tellurides and potassium aryltrifluoroborate salts. The use of potassium aryltrifluoropotassium salts makes this method useful and attractive for the synthesis of biaryl compounds. One feature of this method was the tolerance of a variety of functional groups, either electron-withdrawing or electron-donating substituents in both substrates. The Suzuki−Miyaura cross-coupling reaction was highly chemoselective, and we have demonstrated that aryl tellurides are more reactive than aryl halides under these conditions.

Experimental Section

Representative Procedure of Suzuki–Miyaura Cross-Coupling Reaction. To a suspension of butyl(4-methoxyphenyl)tellane (**1a**) (0.146 g, 0.5 mmol), potassium phenyltrifluoroborate (**2a**) (0.110 g, 0.6 mmol), $Pd(Ph_3P)_4$ (0.058 g, 0.05 mmol), and silver(I) oxide (0.232 g, 1 mmol) in 3 mL of methanol was added triethylamine (0.2 g, 2 mmol), and the reaction mixture was stirred and heated at reflux for 90 min and then cooled to room temperature and diluted with ethyl acetate (30 mL). The organic layer was washed with saturated solution of NH_4Cl (2 × 10 mL) and water (2 × 10 mL), dried over $MgSO_4$, and concentrated under vacuum. Purification by silica gel chromatography (eluting with hexane/ethyl acetate 9.5:0.5) yielded 4-methoxybiphenyl (**3a**)[1] (0.076 g, 83%): white solid; ^1H NMR (300 MHz, $CDCl_3$) δ ppm 7.52 (t, *J* 8.6 Hz, 4H), 7.39 (t, *J* 7.8 Hz, 2H), 7.28 (t, *J* 7.2 Hz, 1H), 6.95 (d, *J* 8.7 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 159.1, 140.8, 133.7, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3; MS *m/z* 185 (10), 184 (100), 169 (67), 152 (21), 76 (61).

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Supporting Information Available: Experimental procedures, ^1H and ^{13}C NMR spectra for compounds listed in Tables 4–6, and ESI-MS-(+), ESI-MS-(−), and ESI-MS/MS spectra of the studied species and reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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