Intramolecular Transmetalation of Arylpalladium(II) and Arylplatinum(II) Complexes with Silanes and Stannanes

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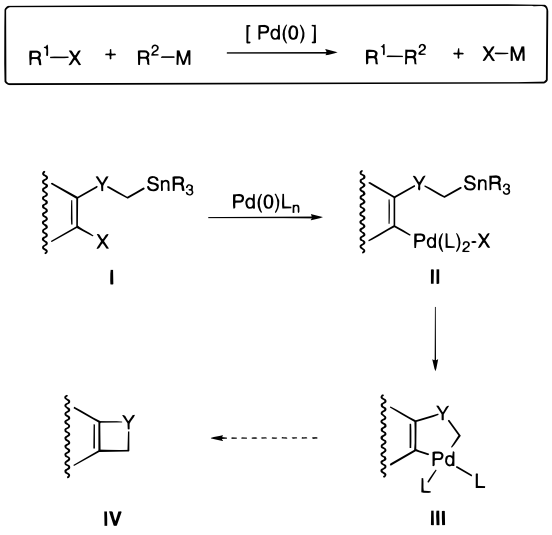
The oxidative addition of *o*-$(Me_2RSiCH_2O)C_6H_4I$ (R = Me, Ph, F) to palladium(0) complexes $[Pd(PPh_3)]$, $[Pd(dba)(AsPh_3)_2]$ (dba = dibenzylideneacetone), and $[Pd(dba)(L_2)]$ [L_2 = 1,1′-bis(diphenylphosphino)ferrocene (dppf), 2,2′-bipyridine (bpy), *o*-phenanthroline (phen)] leads to the corresponding complexes *o*-$(Me_2RCH_2O)C_6H_4Pd(L_2)I$ (L = PPh_3, $AsPh_3$; L_2 = dppf, bpy, phen). This Pd(II)/Si transmetalation, the key step in the Hiyama cross-coupling reaction, proceeds smoothly with different fluorides as the promoters. Additionally, silver and potassium carbonate promote the transmetalation by the likely formation of an intermediate with a Pd−O bond. The related Pt(II)/Sn and Pt(II)/Si transmetalation leads to the formation of stable oxaplatinacycles. In contrast with the requirement of additives for the Pd(II)/Si transmetalation, the transmetalation of Pt(II) complexes proceeds directly in the absence of additives. Additionally, $[Pt(PPh_3)]_4$ was shown to behave as a moderate catalyst for the cross-coupling of two aryl triflates with ethenyltributylstannane to form the corresponding styrenes.

Introduction

Transmetalation of stannanes with organopalladium(II) complexes is a key step in the Stille[1] cross-coupling reaction, which allows for the efficient formation of carbon−carbon bonds in an almost general way (Scheme 1, M = SnR_3).[2] However, the toxicity of the byproducts R_3SnX is a limitation for the application of this reaction to the large-scale preparation of valuable organic compounds.[3] Organosilanes, which are considerably less toxic than organostannanes,[4] also react with organic electrophiles in the presence of a palladium catalyst (Hiyama reaction).[5] However, silanes are relatively poor nucleophilic organometallic reagents[6,7] and require the addition of stoichiometric amounts of fluoride salts in their reactions.[5,8,9] It has been proposed that the acceleration observed in the presence of fluoride is the result of the formation of a pentacoordinated fluorosilane intermediate, more nucleophilic toward the organopalladium in the rate-determining transmetalation step.[4,5,10] Alternatively, fluoride anion may shift the

Scheme 1



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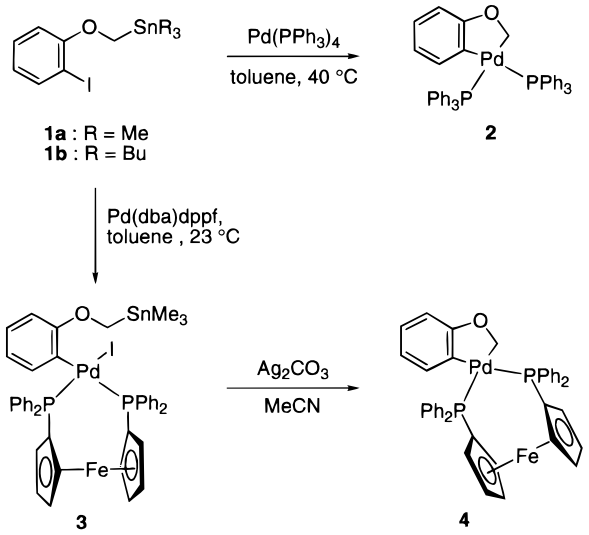
transmetalation equilibrium by the formation of a strong Si−F bond.[4] Fluorides also enhance the reactivity of alkenyl- and arylboronic acids in the cross-coupling with organic electrophiles (Suzuki reaction) by the likely formation of a reactive fluoroborate.[11−13] Fluoride anion can also promote the reduction of phosphine palladium(II) complexes to palladium(0), which is initiated by the nucleophilic attack of fluoride on the coordinated phosphine.[14] Alternatively, AgF has been found to yield arylpalladium fluorides.[15] Recently it has been demonstrated that NaOH, a commonly used additive in the Suzuki reaction,[11] also promotes the Hiyama reaction.[16,17]

We have recently reported that derivatives **I** (X = Br, I) undergo oxidative addition to [Pd(PPh$_3$)$_4$] to give intermediate complexes **II**, which suffered a rapid transmetalation to form palladacycles **III**.[18] The isolated palladacycles **III** are stable species which do not reductively eliminate due to the high ring strain of the four-membered ring heterocycles **IV**. This truncated intramolecular Stille coupling process was first demonstrated with iodoarylstannanes **1a,b**, which cleanly react with [Pd(PPh$_3$)$_4$] to afford the parent oxapalladacycle **2** (Scheme 2).[18] Interestingly, arylpalladium(II) complex **3**, an intermediate of type **II**, could be isolated as a stable yellow solid from the oxidative addition of **1a** to the palladium(0) complex [Pd(dba)dppf].[18b,19] This aryliodopalladium(II) complex underwent smooth transmetalation in the presence of Ag_2CO_3 to form palladacycle **4**.[18b] We have recently also found that, by using silanes instead of stannanes, the oxidative addition intermediates can be obtained as stable compounds in a general way, making it possible to systematically study the transmetalation step of the synthetically important Hiyama cross-coupling reaction, isolated from the oxidative addition and reductive elimination steps.[20] Herein we describe the use of substrates related to **1** as tools for the comparative study on the transmetalation of organosilanes with Pd(II) and Pt(II) as well as the related transmetalation of stannanes with Pt(II).[21−23]

Scheme 2



Results and Discussion

Transmetalation of Silanes with Pd(II). Silanes **5** and **6** were prepared by alkylation of *o*-iodophenol in the presence of K_2CO_3 as the base with iodomethyltrimethylsilane (92% yield) and chloromethyldimethylphenylsilane (81% yield), respectively. Fluorosilane **7** was prepared by selective cleavage of the phenylsilicon bond of **6** by reaction with HBF_4 (82% yield).[24] Thioether **8** was prepared by reaction of *o*-bromothiophenol with iodomethyltrimethylsilane in 93% yield. Similarly, germane **9** was obtained in 73% yield by alkylation of *o*-iodophenol with iodomethyltrimethylgermane.[25]

Silane **5** reacted smoothly with [Pd(PPh$_3$)$_4$] in toluene at 40 °C to give oxidative addition product **10** (88%). A similar reaction of silane **7** with [Pd(PPh$_3$)$_4$] in THF at 23 °C gave **11** (82%). Synthesis of complexes **12**−**14**

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(19) Abbreviations: dba = dibenzylideneacetone; dppf = 1,1′-bis(diphenylphosphino)ferrocene; bpy = 2, 2′-bipyridine; phen = 1, 10-phenanthroline; TASF = tris(dimethylamino)sulfonium difluorotrimethylsilicate; TBAF = tetrabutylammonium fluoride.

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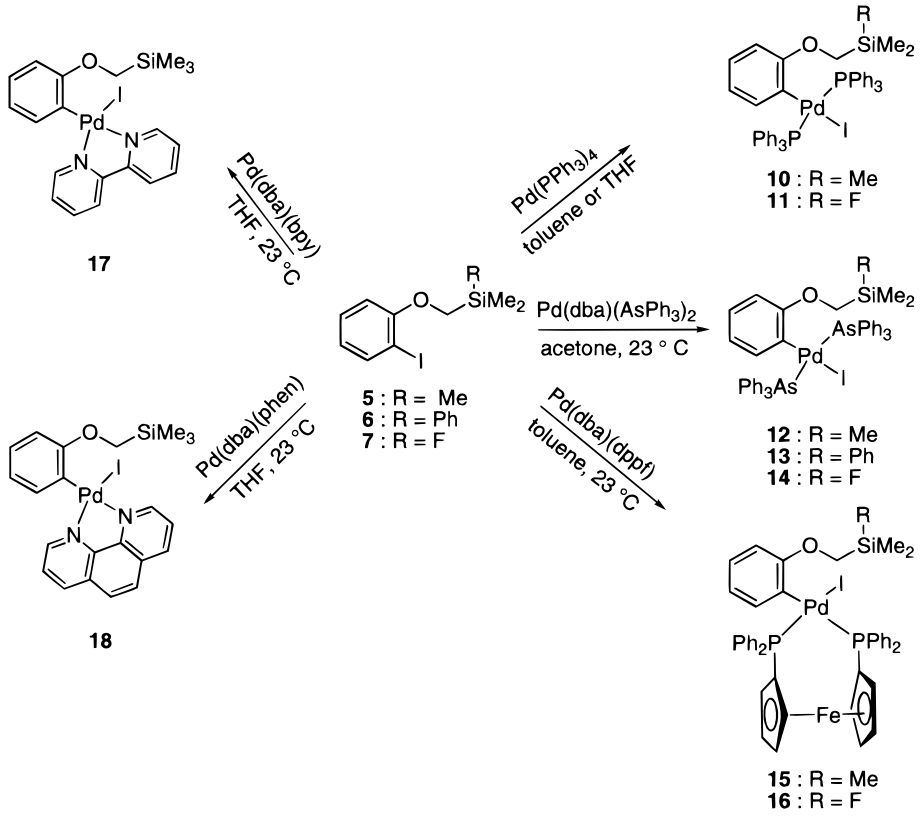
Scheme 3



with two $AsPh_3$ ligands was carried out by reaction of silanes **5**−**7** with $[Pd(dba)(AsPh_3)_2]$[26] in acetone at 23 °C (59−88%) (Scheme 3). However, no reaction was observed after treatment of **5**−**7** with $[Pd(dba)(SbPh_3)_2]$ or $[Pd(dba)(BiPh_3)_2]$ prepared in situ from $[Pd_2(dba)_3$·dba] and $SbPh_3$ or $BiPh_3$.[26] On the other hand, silanes **5** and **7** reacted smoothly with [Pd(dba)(dppf)][27] in toluene at 23 °C to afford complexes **15** (76%) and **16** (43%), respectively. Similarly, reaction of **5** with [Pd(dba)(bpy)] or [Pd(dba)(phen)][19,26] in THF at 23 °C gave **17** (78%) and **18** (66%), respectively. In contrast with these results, thiosilane (**8**) led only to decomposition products after treatment with $[Pd(dba)(AsPh_3)_2]$. Germane **9** also failed to give stable oxidative addition complexes with $[Pd(PPh_3)_4]$ or $[Pd(dba)(AsPh_3)_2]$, leading instead to uncharacterized mixtures of products and black palladium precipitates.[28]

The arylpalladium(II) complexes of Scheme 3 were obtained as yellow-brown solids which were fully characterized spectroscopically. Complexes **10**−**14**, with two mutually trans phosphines or arsines, show the CH_2 hydrogens at 2.5−2.7 ppm in the ^1H NMR spectra as singlets or doublets coupled with ^{19}F. On the other hand, complexes **15**−**18** bearing a cis bidentate ligand show the characteristic diastereotopic CH_2 hydrogens around 2.8−3.8 ppm with $^2J(^1H-^1H) = 12.5-13.0$ Hz.

Palladium(II) complexes **10**−**18** are stable compounds which do not suffer intramolecular Pd/Si transmetalation after being heated at 50 °C for 17 h ($CDCl_3$ or CD_3CN solutions). Furthermore, trimethylsilyl derivatives **10** and **15** failed to undergo transmetalation in the presence of fluoride anion as the promoter (Table 1, entries 1−3, 13−15). However, the desired transmetalation could be achieved from the complexes **12**−**14** bearing triphenylarsine as the ligand for palladium.[29]

Table 1. Transmetalation of Complexes 10−15 Promoted by Fluorides

entry	Ar-Pd-I	additive[a]	reaction time (h)	palladacycle	yield (%)[c]
1	**10**	TASF			*d*
2	**10**	TBAF[b]			*d*
3	**10**	KF			*d*
4	**12**	TASF	51	**19**	22
5	**12**	TBAF	51	**19**	80
6	**12**	KF			*d*
7	**13**	TASF			*d*
8	**13**	TBAF	51	**19**	67
9	**13**	KF	51	**19**	14
10	**14**	TASF	1	**19**	100
11	**14**	TBAF	1	**19**	100
12	**14**	KF	51	**19**	25
13	**15**	TASF			*d*
14	**15**	TBAF			*d*
15	**15**	KF			*d*

[a] 2 equiv of additive in MeCN at 23 °C. [b] MeOH was used as the solvent. [c] Yields were determined by integration of the ^1H NMR spectra. [d] No reaction was observed after 24−48 h.

(26) This complex was prepared in situ by reaction of $[Pd_2(dba)_3$·dba] with 2 equiv of $AsPh_3$. For the preparation of similar complexes: (a) Takahashi, Y.; Ito, T.; Sakai, S.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1970**, 1065. (b) Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253. (c) Amatore, C.; Jutand, A.; Khalil, F.; M'Barki, M. A.; Mottier, L. *Organometallics* **1993**, *12*, 3168.

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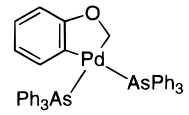
Thus, addition of TASF or TBAF[19] to **12** led to formation of palladacycle **19** (entries 4 and 5). Less soluble KF failed to promote this transmetalation (entry 6). Phenylsilane **13** also reacted in the presence of TBAF or KF (entries 8 and 9). The more favorable cleavage of the alkyl−Si in **13** in the presence of the usually more reactive phenyl−Si bond is another example of endocyclic restriction[30] in the intramolecular transmetalation reaction.[18] Fluorosilyl derivative **14** was the most reactive complex in the presence of fluorides. Thus, **14** gave **19** in almost quantitative yield after treatment with 1 equiv of TASF or TBAF (entries 10 and 11). In general, best results were obtained by using commercially available TBAF hydrate as the fluoride source. No attempt was made to increase the reactivity of this fluoride by drying or by using other commercially available sources. KF was only able to promote the reactions of complexes **13** and **14** to give oxapalladacycle **19** in poor yields (entries 9 and 12). Similar results were obtained with the more soluble CsF.



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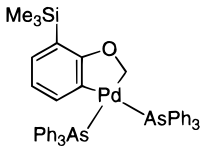

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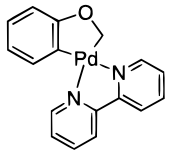

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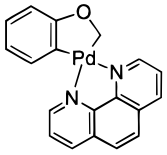

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Although the above results demonstrate that the addition of fluoride is a convenient method for the activation of silanes toward transmetalation with Pd(II) compounds,[5,8] we also tried to promote this reaction by increasing the electrophilicity of the palladium center by removal of the iodide ligand. However, all the experiments carried out with **12** by using silver salts such as AgOTf, $AgBF_4$, AgOTs, Ag_2SO_4, and $AgNO_3$ gave negative results, leading to extensive decomposition of **12** or recovery of the starting complex. Interestingly, the use of Ag_2CO_3 as the additive led to the desired transmetalation under smooth conditions. Thus, complex **11** led readily to palladacycle **2** after being treated with Ag_2CO_3 in acetonitrile solution for 1 h at room temperature (Table 2, entry 2). Complex **12** also reacted with Ag_2CO_3 in acetonitrile at 50 °C to give the corresponding palladacycle **19**. In addition, an equimolar amount of silyl-substituted complex **20** was obtained in this experiment (Table 2, entry 4). A similar result was obtained by using Ag_2O as the additive (Table 2, entry 6). The formation of an equimolar quantity of **19** and **20** suggests that a binuclear palladium complex with a carbonate or oxide bridge is formed which is cleaved by a trimethylsilyl electrophile. Significantly, the presence of silver ion was not essential for these reactions since the transmetalation of **12** to **19** could be cleanly triggered by the addition of K_2CO_3 in acetonitrile (Table 2, entry 5). Experiments carried out with complex **12** in the presence of Ag_2CO_3 (acetonitrile, 20 °C) showed that addition of excess $AsPh_3$ (10 equiv) almost completely suppressed the transmetalation reaction. NaOH and Na_2HPO_4 also promoted the transmetalation of **12** in acetonitrile (23 °C), albeit quite inefficiently (≤8% yields).[31] Reaction of **13** with Ag_2CO_3 or K_2CO_3 also led to **19** (Table 2, entries 7 and 8). As expected, fluorodimethylsilyl complexes **14** and **16** underwent smooth transmetalation in the presence of Ag_2CO_3 to give oxapalladacycles **19** or **4** (Table 2, entries 9 and 12). However, trimethylsilyl derivative **15** failed to react under these conditions (Table 2, entry 11). The lack of reactivity of complexes **10** and **15** in the presence of fluoride (Table 1, entries 1−3 and 13−15) or Ag_2CO_3 (Table 2, entries 1 and 11) is probably due to the stronger coordination ability of PPh_3 and dppf toward Pd(II). Interestingly, trimethylsilyl derivatives **17** and **18**, bearing bidentate pyridine-type ligands, reacted smoothly in the presence of Ag_2CO_3 to give palladacycles **21** and **22**, respectively (Table 2, entries 13 and 14).

Table 2. Transmetalation of Complexes 10−18 Promoted by Ag(I) or K_2CO_3 as Additives

entry	Ar-Pd-I	additive[a]	*T* (°C)	reaction time (h)	palladacycle	yield (%)[b]
1	**10**	Ag_2CO_3	50			*c*
2	**11**	Ag_2CO_3	23	1	**2**	94
3	**11**	K_2CO_3	23			*c*
4	**12**	Ag_2CO_3	50	24	**19** + **20**	95[d]
5	**12**	K_2CO_3	50	5	**19**	100
6	**12**	Ag_2O	50	6	**19** + **20**	(100)[d]
7	**13**	Ag_2CO_3	23	51	**19**	(100)
8	**13**	K_2CO_3	50	44	**19**	(20)
9	**14**	Ag_2CO_3	23	2	**19**	90 (100)
10	**14**	K_2CO_3	23	43	**19**	(27)
11	**15**	Ag_2CO_3	50			*c*
12	**16**	Ag_2CO_3	23	1	**4**	100
13	**17**	Ag_2CO_3	50	32	**21**	100
14	**18**	Ag_2CO_3	50	32	**22**	100

[a] 2 equiv of additive in MeCN. [b] Isolated yields. Numbers in parentheses are for yields determined by ^1H NMR. [c] No reaction was observed after 24−48 h. [d] A 1:1 mixture of **19** and **20**.

The activation observed with the carbonates suggests that an arylpalladium carbonato complex[32,33] or a palladium oxo complex[11b,c,34] is involved as the reactive species in the transmetalation. Nevertheless, the high reactivity of fluorosilanes **14** and **16** in their reactions with Ag_2CO_3 or K_2CO_3 suggests that the silane is also activated by the carbonate to form a pentacoordinated silicon species. Formation of a reactive palladium oxo or hydroxo intermediate is probably involved in the activation promoted by Ag_2O, NaOH, or Na_2HPO_4. Interestingly, formation of complexes with a Pd−O bond

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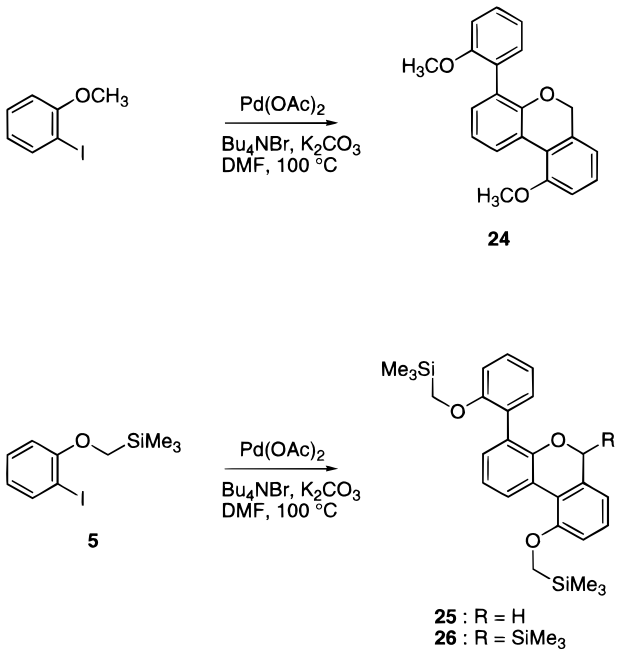
(31) On the other hand, $Na_3BO_3 \cdot 4H_2O$, Na_3PO_4, NaH_2PO_4, and $(NaO)_3PS \cdot 12H_2O$ failed to promote the transmetalation.

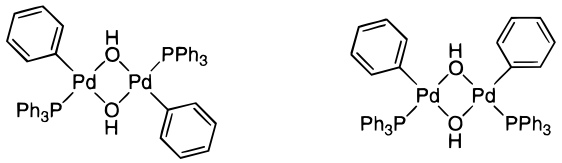
(32) For the formation of bis(triphenylphosphino)carbonatopalladium(II): Nyman, C. J.; Wymore, C. E.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 561.

(33) Reaction of Ag_2CO_3 with dichloro(diphosphine)platinum(II) complexes leads to (diphosphine)carbonatoplatinum(II) complexes: (a) Andrews, M. A.; Gould, G. L.; Voss, E. J. *Inorg. Chem.* **1996**, *35*, 5740. (b) Andrews; M. A.; Gould, G. L:, Klooster, W. T.; Koenig, K. S.; Voss, E. J. *Inorg. Chem.* **1996**, *35*, 5478 and references therein.

Scheme 4

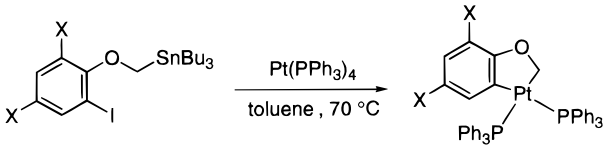


has been proposed to accelerate the Pd/B transmetalation in the Suzuki coupling reaction.[11] Indeed, preliminary results show that hydroxo complexes **23** (as a mixture of trans and cis isomers)[34c] react with tributylvinylstannane in $CDCl_3$ at room temperature to yield styrene.



Recently, Dyker reported a remarkable palladium-catalyzed synthesis of dibenzo[*b*,*d*]pyrane (**24**) from *o*-iodoanisole (Scheme 4)[35] which presumably takes place through palladacycle intermediates such as **2** as a result of an activation of the methoxy C−H bond by palladium[35,36] Therefore, it was of some interest to determine if a silane such as **5** would afford the corresponding dibenzo[*b*,*d*]pyranes **25** or **26** by a process initiated by C−Si or C−H activation by palladium(II). In the event, heating of **5** at 100 °C in DMF with Pd(OAc)$_2$ as the catalyst in the presence of Bu_4NBr and K_2CO_3 led to **25**, isolated in 20% yield after repeated chromatographic purifications. No reaction was observed by using palladium(0) complexes such as [Pd(PPh$_3$)$_4$], [Pd(dba)AsPh$_3$], or [Pd(dba)dppf] as the catalysts. Formation of **25** reveals that this transformation proceeds by a Pd(II)/Si transmetalation through a complex similar to **2** and **19** in which palladium(II) is probably coordinated with two molecules of DMF.

Transmetalation of Silanes and Stannanes with Pt(II). The oxidative addition of aryl iodides to platinum(0) is known to provide the corresponding arylplatinum(II) complexes.[37] In the event, when solutions of iodoaryl stannanes **1b** or **27** and [Pt(PPh$_3$)$_4$][38] were heated at 40−70 °C in toluene, oxaplatinacycles **28** (85% yield) and **29** (46% yield) were cleanly obtained (eq 1). No intermediate arylplatinum(II) complex could be observed upon performing the reactions at lower temperatures and/or shorter reaction times, which demonstrates that the Pt(II)/Sn transmetalation is faster than the oxidative addition of the aryl iodides to platinum(0) coordinated to PPh$_3$.



Platinacycles **28** and **29** are white solids which can be purified by chromatography on silica gel without decomposition. Their structures were determined by NMR. Thus, the ^{1}H NMR spectrum of **28** is similar to that of **2** and shows the aryl hydrogens between 5.99 and 6.92 ppm as multiplets coupled to ^{31}P, with the expected satellites due to the coupling with ^{195}Pt. The CH_2 hydrogens appeared as a dd ($^3J(^{31}P-^1H) = 4.4$ and 2.9 Hz) with $^2J(^1H-^{195}Pt) = 49.5$ Hz. The $^{13}C\{^1H\}$ NMR spectrum of **28** showed the CH_2 carbon at $\delta = 85.99$ ppm as a dd due to the coupling with two distinct phosphines ($^2J(^{13}C-^{13}C) = 93.8$, 5.3 Hz) with the corresponding coupling to ^{195}Pt ($^1J = 683.2$ Hz). The $^{31}P\{^1H\}$ NMR spectrum showed a resonance at $\delta = 28.36$ ppm as a singlet, although the corresponding ^{195}Pt satellites appeared as a pair of doublets corresponding to ^1J couplings of two different ^{31}P with ^{195}Pt of 2146 and 1888 Hz and $^2J(^{31}P-^{31}P) = 14.2$ Hz.[39] The $^{31}P\{^1H\}$ NMR of **29** showed an AB pattern ($\delta = 27.54$ and 27.02 ppm, $^2J(^{31}P-^{31}P) = 15.5$ Hz) corresponding to different phosphine ligands further coupled with ^{195}Pt ($^1J = 1860$ and 2267 Hz). The $^2J(^{31}P-^{31}P)$ of 14−15 Hz in oxaplatinacycles **28** and **29** is smaller than that found for the oxapalladacycles (25.6 Hz for **2**).[18]

In analogy with what was observed in the case of silanes, we had expected to isolate the corresponding oxidative addition products in the reaction of silane **5** with platinum(0) complexes. However, reaction of **5** with [Pt(PPh$_3$)$_4$] in toluene at 70 °C led exclusively to the slow formation of oxaplatinacycle **28** (isolated in 45% yield) (eq 2). On the other hand, treatment of **5** with

(34) Hydroxo palladium complexes: (a) Bushnell, G. W.; Dixon, K. R.; Hunter, R. G.; McFarland, J. J. *Can. J. Chem.* **1972**, *50*, 3694. (b) López, G.; Ruiz, J.; García, G.; Vicente, C.; Martí, J. M.; Santana, M. D. *J. Organomet. Chem.* **1990**, *393*, C53. (c) Grushin, V. V.; Alper, H. *Organometallics* **1993**, *12*, 1890. (d) Grushin, V. V.; Bensimon, C.; Alper, H. *Organometallics* **1993**, *12*, 2737. (e) Ruiz, J.; Rodríguez, V.; López, G.; Chaloner, P. A.; Hitchcok, P. B. *J. Organomet. Chem.* **1996**, *523*, 23. (f) Ruiz, J.; Cutillas, N.; Sampedro, J.; López, G.; Hermoso, J. A.; Martínez-Ripoll, M. *J. Organomet. Chem.* **1996**, *526*, 67. (g) Grushin, V. V.; Alper, H. *Organometallics* **1996**, *15*, 5242. (h) Kuznetsov, V. F.; Bensimon, C.; Facey, G. A.; Grushin, V. V.; Alper, H. *Organometallics* **1997**, *16*, 97.

(35) (a) Dyker, G. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1023. (b) Dyker, G. *J. Org. Chem.* **1993**, *58*, 6426. (c) Dyker, G. *Chem. Ber.* **1994**, *127*, 739.

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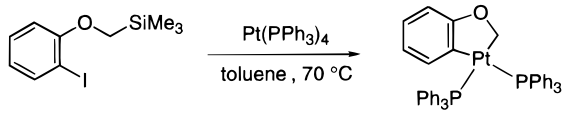
(38) Ugo, R.; Cariati, F.; La Monica, G. *Inorg. Synth.* **1990**, *28*, 124.

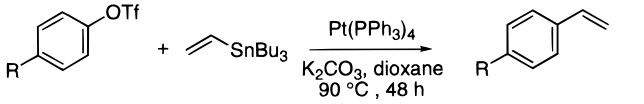
(39) For the relation between $^1J(^{119}Pt-^{31}P)$ and the Pt−P distance in Pt(II) complexes: Mather, G. G.; Pidcock, A.; Rapsey, G. J. N. *J. Chem. Soc., Dalton Trans.* **1973**, 2095.

$[Pt(dba)(AsPh_3)_2]$, prepared in situ from $[Pt(dba)_2]$[40] and $AsPh_3$, in acetone or THF led only to the recovery of the starting materials. Oxaplatinacycle **28** was the only new platinum complex observed in the reaction of **5** with $[Pt(PPh_3)_4]$, which indicates that, in contrast with what was observed in the Pd(II)/Si transmetalation, the related Pt(II)/Si transmetalation is a facile process which takes place in the absence of any additive.



5 **28**

The results shown in eqs 1 and 2 suggest that platinum(0) could catalyze the coupling of stannanes or silanes with organic electrophiles. However, preliminary results show that the reactions are rather slow under catalytic conditions, probably due to an inefficient oxidative addition reaction. Thus, the coupling of aryl triflates **30** and **31** with tributylvinylstannane could be catalyzed by $[Pt(PPh_3)_4]$ (5 mol %) in the presence of K_2CO_3 to give styrenes **32** and **33** (eq 3), although the reaction is much slower than that catalyzed by the analogous Pd complex.[41]



30 : R = COMe
31 : R = OMe

32 : R = COMe (37%)
33 : R = OMe (30%)

Conclusions

The system that we have developed for the study of the Stille reaction[18] makes it possible also to study the effect of ligands and additives on the Pd(II)/Si transmetalation, isolated from the oxidative addition and reductive elimination steps. We have found that the intramolecular transmetalation of alkylsilanes with arylpalladium complexes, the key step in the Hiyama coupling reaction, requires the addition of F^- or CO_3^{2-} as promoters. Additionally, the use of $AsPh_3$ as the ligand for palladium(II) substantially accelerates the Pd(II)/Si transmetalation step. Among the tested bidentate ligands, best results were obtained with pyridine-type ligands (bpy and phen), which allow for the efficient transmetalation of the less reactive trimethylsilyl derivatives. On the other hand, additives which may favor formation of cationic arylpalladium(II) complexes do not promote the intramolecular transmetalation. The higher reactivity of phenyl- and fluorosilanes in the transmetalation reactions with fluorides and carbonates as the additives suggests that the silane is activated by formation of a more nucleophilic pentacoordinated Si(IV) species. However, formation of palladium(II)−oxygen bond[11] by reaction of the arylpalladium(II) iodide with the carbonates cannot be excluded as a key step in the Pd(II)/Si transmetalation.

The Pt(II)/Sn and Pt(II)/Si transmetalations also take place, leading to the formation of oxaplatinacycles. Interestingly, the Pt(II)/Si transmetalation takes place readily in the absence of additives. A platinum analogue of the Stille and related cross-coupling reactions could be possible by using the adequate platinum(0) complexes as catalyst.

Despite much mechanistic work on cross-coupling reactions,[1,2,42−44] some recent results indicate that these reactions may proceed by a variety of mechanisms. Thus, for example, coupling of an alkynylstannane with aryl iodides with a palladium catalyst with a bidentate ligand has been recently proposed to proceed by a mechanism which involves an oxidative addition of the alkynylstannane to the palladium(0) complex, followed by reaction of an $Ar-Pd-SnBu_3$ complex with ArI.[45] Additionally, several aspects of the key transmetalation step[46] are not clearly understood. Thus, inversion[47] or retention[48,49] of the configuration of alkylstannanes or silanes has been found to depend on the presence of additives, solvent polarity, and temperature.[50] On the other hand, alkylboranes have been recently reported to transmetalate with retention of configuration in the presence of hydroxide anion.[11b,c] Efforts directed to study the stereochemistry of the Pd(II)/Sn or Pd(II)/Si transmetalation step by using a system related to that outlined in Scheme 1 are underway.

Experimental Section

Only the most significant IR frequencies are given. Elemental analyses were performed at the SIdI (UAM). All reactions were carried out under an atmosphere of Ar. Solvents were purified and dried by standard methods. Chromatographic purifications were carried out with flash grade silica gel.

The following palladium and platinum complexes were prepared according to the known procedures: $[Pd(PPh_3)_4]$,[51] $[Pd_2(dba)_3dba]$,[26] [Pd(dba)(*o*-phen)],[26] [Pd(dba)(bpy)],[26] $[Pd(dba)(AsPh_3)_2]$,[26] [Pd(dba)(dppf)],[27] $[Pt(PPh_3)_4]$,[37] $[Pt(dba)_2]$,[38] and palladium complexes **23**.[34c] Stannanes **1b** and **27** were

(40) Moseley, K.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1974**, 169.
(41) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478.
(42) Brown, J. M.; Cooley, N. A. *Chem. Rev.* **1988**, *88*, 1031.
(43) Stille, J. K. In *The Chemistry of the Metal−Carbon Bond*; Hartley, F. R., Patai, S. Eds.; Wiley: Chichester, 1985; Vol. 2, Chapter 9.
(44) Lead recent references: (a) Stang, P. J.; Kowalski, M. H.; Schiavelli, M. D.; Longford, D. *J. Am. Chem. Soc.* **1989**, *111*, 3347. (b) Brown, J. M.; Hii, K. K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 657. (c) Amatore, C.; Broeker, G.; Jutand, A.; Khalil, F. *J. Am. Chem. Soc.* **1997**, *119*, 5176. (d) Casado, A. L.; Espinet, P. *Organometallics* **1998**, *17*, 954. (e) For a recent discussion of the role of phosphines on the reductive elimination step: Vicente, J.; Arcas, A.; Bautista, D.; Jones, P. G. *Organometallics* **1997**, *16*, 2127. (g) For a study on the mechanism of coupling of alkynylcopper(I) complexes with palladium(II) complexes (Sonogashira reaction): Osakada, K.; Sakata, R.; Yamamoto, T. *Organometallics* **1997**, *16*, 5354.
(45) Shirakawa, E.; Yoshida, H.; Hiyama, T. *Tetrahedron Lett.* **1997**, *38*, 5177.
(46) (a) Louie, J.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 11598. (b) Morita, D. K.; Stille, J. K.; Norton, J. R. *J. Am. Chem. Soc.* **1995**, *117*, 8576. (c) Vedejs, E.; Haight, A. R.; Moss, W. O. *J. Am. Chem. Soc.* **1992**, *114*, 6556.
(47) Labadie, J. W.; Stille, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 6129.
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(49) For the coupling of organostannanes with organic iodides mediated by copper: (a) Allred, G. D.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1996**, *118*, 2748. (b) Zhang, S.; Zhang, D.; Liebeskind, L. S. *J. Org. Chem.* **1997**, *62*, 2312. (c) Coupling mediated by Cu(I) or Mn(II): Kang, S.-K.; Kim, J.-S.; Choi, S.-C. *J. Org. Chem.* **1997**, *62*, 4208.
(50) Hatanaka, Y.; Hiyama, T. *J. Am. Chem. Soc.* **1990**, *112*, 7793.
(51) Cotton, F. A. *Inorg. Synth.* **1972**, *13*, 121.

prepared according to our previously described method.[18] Triflates **29** and **30** were prepared according to the described procedure.[41] (Iodomethyl)trimethylgermane was synthesized from ICH_2ZnI, $GeCl_4$, and MeMgBr:[25] ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.08 (s, 2H), 0.27 (s, 9H).

(2-Iodophenoxymethyl)trimethylsilane (5). A mixture of *o*-iodophenol (1.00 g, 4.54 mmol) and K_2CO_3 (850 mg, 6.16 mmol) was stirred at 23 °C in DMF (10 mL). After 30 min, iodomethyltrimethylsilane (975 mg, 4.54 mmol) was added, and the resulting mixture was heated at 70 °C for 17 h. After being cooled to room temperature and undergoing extractive workup (1:1 hexanes−Et_2O), the residue was chromatographed (hexane) to give **5** as a colorless oil (1.28 g, 92%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.81 (d, J = 7.5 Hz, 1H), 7.37 (t, J = 8.6 Hz, 1H), 7.0 (d, J = 8.6 Hz, 1H), 6.75 (t, J = 7.5 Hz, 1H), 3.69 (s, 2H), 0.29 (br s, 9H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$; DEPT) δ 159.60 (C), 139.08 (CH), 129.29 (CH), 121.97 (CH), 111.11 (CH), 86.55 (C), 62.20 (CH_2), −3.00 (3 × CH_3). Anal. Calcd for $C_{10}H_{15}IOSi$: C, 39.22; H, 4.93. Found: C, 39.66; H, 4.87.

Dimethyl(2-iodophenoxymethyl)phenylsilane (6). A mixture of *o*-iodophenol (500 mg, 2.27 mmol) and K_2CO_3 (471 mg, 3.41 mmol) was stirred at 23 °C in DMF (10 mL). After 30 min, chloromethyldimethylphenylsilane (382 mg, 2.06 mmol) in DMF (10 mL) was added, and the resulting mixture was heated at 60 °C for 24 h. After being cooled to room temperature and undergoing extractive workup (1:1 hexanes−Et_2O), the residue was chromatographed (hexane) to give **6** as a colorless oil (614 mg, 81%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.75 (dd, J = 7.7, 1.6 Hz, 1H), 7.70−7.66 (m, 2H), 7.43−7.38 (m, 3H), 7.28 (br t, J = 8.6 Hz, 1H), 6.90 (dd, J = 7.9 1.0, Hz, 1H), 6.68 (br t, J = 7.9 Hz, 1H), 3.79 (s, 2H), 0.52 (s, 6H); ^{13}C-{^{1}H} NMR (50 MHz, $CDCl_3$) δ 159.42, 139.05, 136.35, 133.98, 129.48, 129.30, 127.88, 122.07, 111.02, 86.46, 61.54, −4.40. Anal. Calcd for $C_{15}H_{17}IOSi$: C, 48.92; H, 4.65. Found: C, 49.22; H, 4.53.

Fluoro(2-iodophenoxymethyl)dimethylsilane (7). To a solution of silane **6** (964 mg, 2.62 mmol) in CH_2Cl_2 (20 mL) at 0 °C was added HBF_4 (0.72 mL, 54% solution in Et_2O, 4.9 mmol), and the resulting mixture was stirred at this temperature for 24 h. After extractive workup (CH_2Cl_2/H_2O), **7** was obtained as a very pale yellow oil (664 mg, 82%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.76 [dd, J(^{1}H−^{1}H) = 8.5, 1.5 Hz, 1H], 7.30 [td, J(^{1}H−^{1}H) = 7.7, 1.5 Hz, 1H], 6.91 [(dd, J(^{1}H−^{1}H) = 8.0, 1.0 Hz, 1H], 6.72 [td, J(^{1}H−^{1}H) = 8.5, 1.5 Hz, 1H], 3.74 [d, ^3J(^{1}H−^{19}F) = 3.9 Hz, 2H], 0.49 [d, ^3J(^{1}H−^{19}F) = 7.2 Hz, 6H]; ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 158.91, 139.17, 129.41, 122.47, 111.07, 86.31, 60.16 [dd, ^2J(^{13}C−^{19}F) = 20.0 Hz], −2.46 [d, ^2J(^{13}C−^{19}F) = 14.1 Hz]. This compound suffered some decomposition after chromatography (3:1 hexanes−EtOAc) to give a product whose mass spectrum showed peaks corresponding to the siloxane $(RMe_2Si)_2O$ (R = *o*-$IC_6H_4OCH_2$).

(2-Bromothiophenoxymethyl)trimethylsilane (8). A suspension of 2-bromothiophenol (500 mg, 2.64 mmol) and K_2CO_3 (547 mg, 3.96 mmol) in DMF (10 mL) was stirred at 23 °C for 30 min. A solution of iodomethyltrimethylsilane (566 mg, 2.64 mmol) in DMF (5 mL) was then added, and the mixture was stirred at 60 °C for 24 h. After being cooled to 23 °C, the mixture was partitioned between water and 1:1 hexanes−Et_2O. The organic extract was dried (Na_2SO_4 and $MgSO_4$), and the solvent was evaporated. The residue was chromatographed (hexane) to give **8** as a colorless oil (680 mg, 94%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (dd, J = 8.0, 1.3 Hz, 1H), 7.33−7.25 (m, 2H), 6.99 (ddd, J = 7.9, 6.8, 2.1 Hz, 1H), 2.12 (s, 2H), 0.22 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 141.17, 132.28, 127.42, 125.22, 125.16, 121.09, 17.90, −1.64. Anal. Calcd for $C_{10}H_{15}BrSSi$: C, 43.63; H, 5.49. Found: C, 43.49; H, 5.37.

(2-Iodophenoxymethyl)trimethylgermane (9). A suspension of 2-iodophenol (318 mg, 1.56 mmol) and K_2CO_3 (294 mg, 2.13 mmol) in DMF (25 mL) was stirred at 25 °C for 20 min. A solution of (iodomethyl)trimethylgermane (366 mg, 1.42 mmol) in DMF (10 mL) was added, and the mixture was stirred at 60 °C for 21 h. After being cooled to 23 °C, the mixture was partitioned between water and hexane. The organic extract was dried (Na_2SO_4 and $MgSO_4$) and evaporated. Chromatography (hexane) gave **9** as a colorless oil (363 mg, 73%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.76 (dd, J = 7.6, 1.6 Hz, 1H), 7.32 (td, J = 7.3, 1.6 Hz, 1H), 6.93 (dd, J = 8.2, 1.3 Hz, 1H), 6.69 (td, J = 7.6, 1.5 Hz, 1 H), 3.87 (s, 2H), 0.37 (s, 9H); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 159.54, 139.17, 129.29, 122.07, 111.30, 86.53, 63.00, −3.05; EI-MS *m*/*z* (relative intensity) 353 (M^+ + 2, 4), 351 (M^+, 5), 350 (M^+ − 1, 2), 349 (M^+ − 2, 4), 347 (M^+ − 4, 2), 337 (13), 335 (10), 297 (9), 295 (8), 237 (50), 236 (20), 235 (67), 233 (54), 121 (20), 119 (100), 117 (75), 115 (56). Anal. Calcd for $C_{10}H_{15}GeIO$: C, 34.24; H, 4.31. Found: C, 33.70; H, 4.93.

***trans*-Bis(triphenylphosphine)iodo[2-(trimethylsilylmethoxy)phenyl]palladium (10).** To a partial solution of $[Pd(PPh_3)_4]$ (1.03 g, 0.89 mmol) in toluene (3 mL) was added silane **5** (300 mg, 0.98 mmol), and the mixture was stirred at 40 °C for 3 h. The resulting solid was filtered and washed with Et_2O to give **10** as a yellow solid (670 mg, 88%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.57−7.17 (m, 30H), 6.82 [dq, J(^{1}H−^{1}H) = 9.7 Hz, J(^{1}H−^{1}H) = J(^{1}H−^{31}P) = 1.8 Hz, 1H], 6.47 [t, J(^{1}H−^{1}H) = 7.5 Hz, 1H], 6.17 [t, J(^{1}H−^{1}H) = 7.2 Hz, 1H], 5.79 [dd, J(^{1}H−^{1}H) = 8.1 Hz, J(^{1}H−^{1}H) = 1.2 Hz, 1H], 2.51 (s, 2H), 0.16 (s, 9H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$; DEPT) δ 161.65 [t, J(^{13}C−^{31}P) = 2.6 Hz; C], 144.71 [t, J(^{13}C−^{31}P) = 3.7 Hz; C], 134.96 [t, ^2J(^{13}C−^{31}P) = 6.3 Hz, PPh_3; CH], 134.31 [t, J(^{13}C−^{31}P) = 4.1 Hz; CH], 132.23 [t, ^1J(^{13}C−^{31}P) = 23 Hz, PPh_3; C], 129.56 (br s, PPh_3; CH), 127.47 [t, ^3J(^{13}C−^{31}P) = 5.1 Hz, PPh_3; CH], 124.09 (s; CH), 119.43 (s; CH), 110.18 (s; CH), 59.47 (s; CH_2), −2.33 (s; CH_3); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$) δ 23.06. Anal. Calcd for $C_{46}H_{45}IOP_2PdSi$: C, 58.95; H, 4.83. Found: C, 58.92; H, 4.63.

***trans*-Bis(triphenylphosphine)[2-(fluorodimethylsilylmethoxy)phenyl]iodopalladium (11).** A mixture of silane **7** (80 mg, 0.26 mmol) and $[Pd(PPh_3)_4]$ (271 mg, 0.24 mmol) in THF (5 mL) was stirred at 23 °C for 18 h. The solvent was evaporated, and the residue was triturated with Et_2O to give **11** as a yellow solid (181 mg, 82%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.54−7.43 (m, 12H), 7.40−7.16 (m, 18H), 6.89−6.81 (m, 1H), 6.46 (br t, J = 7.3 Hz, 1H), 6.20 (br t, J = 7.2 Hz, 1H), 5.58 (br d, J = 7.4 Hz, 1H), 2.57 [d, ^3J(^{1}H−^{19}F) = 6.1 Hz, 2H], 0.40 [d, ^3J(^{1}H−^{19}F) = 7.5 Hz, 6H]; ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 160.78 (br s), 145.16 (br s), 134.88 [t, ^2J(^{13}C−^{31}P) = 5.3 Hz; PPh_3], 134.09 (br s), 132.12 [t, ^1J(^{13}C−^{31}P) = 24.2 Hz; PPh_3], 129.56 (s; PPh_3), 127.49 [br d, ^3J(^{13}C−^{31}P) = 5.2 Hz; PPh_3], 124.10, 119.87, 110.46, 57.62 [d, ^2J(^{13}C−^{19}F) = 18.6 Hz], −2.16 [d, ^2J(^{13}C−^{19}F) = 14.7 Hz]; ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 Hz) δ 23.09. Anal. Calcd for $C_{45}H_{42}FIOP_2PdSi$: C, 57.43; H, 4.50. Found: C, 57.78; H, 4.61.

***trans*-Bis(triphenylarsine)iodo[2-(trimethylsilylmethoxy)phenyl]palladium (12).** A mixture of $[Pd_2(dba)_3dba]$ (625 mg, 0.54 mmol) and $AsPh_3$ (990 mg, 3.24 mmol) in acetone (15 mL) was stirred at 23 °C for 3 h, yielding $[Pd(dba)(AsPh_3)_2]$. To this suspension was added silane **5** (500 mg, 1.63 mmol) and toluene (20 mL), and the mixture was heated at 40 °C for 17 h. The resulting solution was filtered through Celite, and the solvent was evaporated. The residue was triturated with Et_2O to give **12** as a yellow solid (720 mg, 65%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.44−7.16 (m, 30H), 6.71 (dd, J = 7.5, 1.5 Hz, 1H), 6.49 (t, J = 7.5 Hz, 1H), 6.16 (t, J = 7.2 Hz, 1H), 5.70 (d, J = 8.0 Hz, 1H), 2.48 (s, 2H), 0.06 (s, 9H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$; DEPT) δ 162.35 (C), 136.26 (C), 135.74 (CH), 134.22 (CH; $AsPh_3$), 134.0 (C; $AsPh_3$), 129.31 (CH; $AsPh_3$), 128.07 (CH; $AsPh_3$), 124.49 (CH), 119.27 (CH), 111.42 (CH), 59.45 (CH_2), −2.53 (CH_3). Anal. Calcd for $C_{46}H_{45}As_2IOPdSi$: C, 53.89; H, 4.42. Found: C, 53.79; H, 4.15.

***trans*-Bis(triphenylarsine)[2-dimethylphenylsilylmethoxy)phenyl]iodopalladium (13).** A mixture of $[Pd_2(dba)_3dba]$ (335 mg, 0.29 mmol) and $AsPh_3$ (375 mg, 1.22 mmol) in acetone

(20 mL) was stirred at 23 °C for 3 h, yielding [Pd(dba)($AsPh_3$)$_2$]. To this suspension was added silane **6** (322 mg, 0.87 mmol) in acetone (5 mL), and the resulting mixture was stirred at 23 °C for 20 h. The solvent was evaporated, and the residue was triturated with Et_2O to give **13** as a brown solid (426 mg, 67%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.49−7.13 (m, 35H), 6.71 (dd, J = 7.2, 1.5 Hz, 1H), 6.49 (td, J = 8.3, 1.4 Hz, 1H), 6.18 (td, J = 7.4, 1.0 Hz, 1H), 5.73 (br d, J = 8.3 Hz, 1H), 2.69 (s, 2H), 0.39 (s, 6H); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 162.41, 137.20, 136.12, 135.96, 134.20, 133.98, 133.70, 129.31, 128.61, 128.07, 127.89, 124.55, 119.41, 111.69, 58.88, −3.88. Anal. Calcd for $C_{51}H_{47}As_2IOPdSi$: C, 56.35; H, 4.36. Found: C, 55.82; H, 4.35.

***trans*-Bis(triphenylarsine)[2-(fluorodimethylsilylmethoxy)phenyl]iodopalladium (14).** A mixture of [Pd_2(dba)$_3$dba] (586 mg, 0.51 mmol) and triphenylarsine (655 mg, 2.14 mmol) in acetone (20 mL) was stirred at 23 °C for 3 h, yielding [Pd(dba)($AsPh_3$)$_2$]. To this suspension was added silane **7** (474 mg, 1.53 mmol) in acetone (5 mL), and the mixture was stirred at 23 °C for 24 h. The solvent was evaporated, and the residue was triturated with Et_2O to give **14** as a yellow solid (622 mg, 59%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.46−7.19 (m, 30 H), 6.77 (br d, J = 7.5 Hz, 1H), 6.50 (br t, J = 7.3 Hz, 1H), 6.21 (br t, J = 7.4 Hz, 1H), 5.64 (br d, J = 8.0 Hz, 1H), 2.58 [d, $^3J(^1H-^{19}F)$ = 5.5 Hz, 2H], 0.39 [d, $^3J(^1H-^{19}F)$ = 7.5 Hz, 6H];^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 161.44, 136.79, 135.66, 134.09, 133.92, 129.29, 128.05, 124.50, 119.76, 110.80, 57.67 [d, $^2J(^{13}C-^{19}F)$ = 19.1 Hz], −2.34 [d, $^2J(^{13}C-^{19}F)$ = 14.4 Hz]. Anal. Calcd for $C_{45}H_{42}As_2FIOPdSi$: C, 52.52; H, 4.11. Found: C, 52.50; H, 4.14.

[1,1′-Bis(diphenylphosphino)ferrocene]iodo[2-(trimethylsilylmethoxy)phenyl]palladium (15). To a suspension of [Pd(dba)(dppf)] (70 mg, 78.2 mmol) in toluene (10 mL) was added a solution of silane **5** (25 mg, 81.6 mmol) in toluene (3 mL). The resulting suspension was stirred at 23 °C for 17 h. The solvent was evaporated, and the residue was triturated with Et_2O to give **15** as a red solid (60 mg, 76%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.19−7.95 (m, 6H), 7.51−7.45 (m, 6H), 7.42−7.28 (m, 2H), 7.16−7.03 (m, 3H), 6.87−6.82 (m, 2H), 6.80−6.63 (m, 2H), 6.54−6.38 (m, 2H), 6.01−5.95 (m, 1H), 5.10 (br s, 1H), 4.59 (br s, 1H), 4.30 (br s, 2H), 4.09 (br s, 2H), 3.69 (br s, 1H), 3.57 (br s, 1H), 3.29 [d, $^2J(^1H-^1H)$ = 12.9 Hz, 1H], 2.86 [d, $^2J(^1H-^1H)$ = 12.9 Hz, 1H], 0.30 (s, 9H); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$) δ 26.35 [d, $J(^{31}P-^{31}P)$ = 30.8 Hz, 1P], 8.91 [d, $J(^{31}P-^{31}P)$ = 30.8 Hz, 1P]. Anal. Calcd for $C_{44}H_{43}FeIOP_2PdSi$: C, 54.65; H, 4.48. Found: C, 54.49; H, 4.59.

[1,1′-Bis(diphenylphosphino)ferrocene][2-(dimethylfluorosilylmethoxy)phenyl]iodopalladium (16). A mixture of silane **7** (76 mg, 0.22 mmol) and [Pd(dba)(dppf)] (200 mg, 0.22 mmol) in toluene (6 mL) was stirred at 23 °C for 24 h. The solvent was evaporated, and the residue was triturated with 20:1 hexanes−Et_2O to give **16** as a yellow solid (95 mg, 43%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22−8.16 (m, 2H), 8.04−7.93 (m, 4H), 7.56−7.39 (m, 6H), 7.33−7.28 (m, 3H), 7.18−7.11 (m, 1H), 7.08−7.03 (m, 1H), 6.88−6.82 (m, 2H), 6.75−6.68 (m, 2H), 6.53−6.43 (m, 2H), 5.93−5.88 (m, 1H), 5.21 (br s, 1H), 4.61 (br s, 1H), 4.29 (br s, 2H), 4.14−4.07 (m, 2H), 3.64−3.58 (m, 2H), 3.35 [dd, $^2J(^1H-^1H)$ = 13.0 Hz, $^3J(^1H-^{19}F)$ = 10.7 Hz, 1H], 3.01 [br d, $^2J(^1H-^1H)$ = 13.0 Hz, 1H], 0.64 [d, $^3J(^1H-^{19}F)$ = 7.6 Hz, 3H], 0.40 [d, $^3J(^1H-^{19}F)$ = 7.4 Hz, 3H]; ^{31}P NMR (121.4 MHz, $CDCl_3$) δ 27.05 (d, J = 31.0 Hz, 1P), 9.22 (d, J = 31.0 Hz, 1P). Anal. Calcd for $C_{43}H_{40}FFeIOP_2PdSi$: C, 53.19; H, 4.15. Found: C, 53.26; H, 4.35.

***cis*-Iodo[2-(trimethylsilylmethoxy)phenyl](2,2′-bipyridine-N^1,$N^{1'}$)palladium (17).** A suspension of silane **5** (51 mg, 0.17 mmol) and [Pd(dba)(bpy)] (75 mg, 0.15 mmol) in THF (7 mL) was stirred at 23 °C for 16 h. The solvent was evaporated, and the residue was triturated (3:1 hexanes−Et_2O) to give **17** as a yellow solid (66 mg, 78%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.71 (d, J = 5.4 Hz, 1H), 8.08−7.92 (m, 4H), 7.72 (d, J = 5.1 Hz, 1H), 7.53 (td, J = 5.4, 1.5 Hz, 1H), 7.41 (dd, J = 8.1, 1.7 Hz, 1H), 7.31 (td, J = 5.5, 1.4 Hz, 1H), 6.99 (td, J = 7.8, 1.4 Hz, 1H), 6.75−6.68 (m, 2H), 3.70 (part A of an AB system, J = 12.5 Hz, 1H), 3.41 (part B of an AB system, J = 12.5 Hz, 1H), −0.14 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$; DEPT) δ 162.89 (C), 155.58 (C), 153.63 (C), 152.80 (CH), 150.09 (CH), 138.55 (CH), 138.47 (CH), 131.80 (C), 128.90 (CH), 126.57 (CH), 126.09 (CH), 124.29 (CH), 122.00 (CH), 121.62 (CH), 119.64 (CH), 110.77 (CH), 60.91 (CH_2), −3.12 (CH_3); EI-MS m/z (relative intensity) 261 (7), 179 (32), 156 (100), 135 (44), 78 (26), 73 (23) [the molecular ion was not observed]. Anal. Calcd for $C_{20}H_{23}IN_2OPdSi\cdot H_2O$: C, 40.94; H, 4.29; N, 4.77. Found: C, 41.07; H, 3.99; N, 4.91.

***trans*-Iodo[2-(trimethylsilylmethoxy)phenyl](1,10-phenanthroline-N^1,N^{10})palladium (18).** A suspension of silane **5** (293 mg, 0.96 mmol) and [Pd(dba)(phen)] (500 mg, 0.96 mmol) in THF (25 mL) was stirred at 23 °C for 18 h. The solvent was evaporated, and the residue was triturated with Et_2O to give **18** as a brown solid (372 mg, 66%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.95 (m, 1H), 9.00 (m, 1H), 8.47 (m, 1H), 7.98−7.80 (m, 1H), 7.67−7.55 (m, 2H), 7.48−7.40 (m, 2H), 7.35−7.21 (m, 2H), 6.86−6.75 (m, 2H), 3.78 (part A of an AB system, J = 12.8 Hz, 1H), 3.45 (part B of an AB system, J = 12.8 Hz, 1H), −0.24 (s, 3H); EI-MS m/z (relative intensity) 466 (<1), 180 (100), 154 (17), 131 (25), 77 (28) [the molecular ion was not observed]. Anal. Calcd for $C_{22}H_{23}IN_2OPdSi$: C, 44.57; H, 3.91. Found: C, 44.97; H, 4.10.

Bis(triphenylarsine)(methyleneoxy-1,2-phenylene)palladium (19). Method a. A mixture of **12** (175 mg, 0.17 mmol) and Ag_2CO_3 (94 mg, 0.34 mmol) in MeCN (10 mL) was heated at 50 °C for 24 h. The solvent was evaporated, and the residue was partially dissolved in CH_2Cl_2 and filtered through Celite. The filtrate was evaporated to give a 1:1 mixture of **19** and **20** (139 mg, 95%). Repeated trituration with Et_2O, Et_2O−hexane, and hexane led to **19** as the less soluble palladacycle in Et_2O and **20** as the less soluble palladacycle in hexane.

Method b. A mixture of **12** (20 mg, 0.019 mmol) and K_2CO_3 (5 mg, 0.039 mmol) in MeCN (10 mL) was heated at 80 °C for 18 h. The solvent was evaporated, and the residue was partially dissolved in CH_2Cl_2 and filtered through Celite. The filtrate was evaporated, and the residue was triturated with 1:1 Et_2O−hexane to give **19** as a white solid (15 mg, quantitative).

Method c. A mixture of **14** (25 mg, 0.024 mmol) and Ag_2CO_3 (14 mg, 0.049 mmol) in MeCN (6 mL) was stirred at 23 °C for 1 h. Workup as above yielded **19** (14 mg, 70%). Complex **19** was identical to that prepared before by ligand exchange reaction from palladacycle **2**.[18]

Bis(triphenylarsine)(methyleneoxy-1,2-(6-trimethylsilyl)phenylene)palladium (20): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.32−7.02 (m, 31H), 6.85 (t, J = 7.3 Hz, 1H), 6.06 (t, J = 7.3 Hz, 1H), 5.43 (s, 2H), 0.14 (s, 9H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$; DEPT) δ 171.86 (C), 142.68 (CH), 136.08 (C), 134.54 (C; $AsPh_3$), 134.28 (CH; $AsPh_3$), 133.62 (CH; $AsPh_3$), 131.04 (CH), 129.45 (CH; $AsPh_3$), 129.14 (CH; $AsPh_3$), 128.46 (CH; $AsPh_3$), 128.30 (CH; $AsPh_3$), 116.93 (C), 116.70 (CH), 90.13 (CH_2), −0.82 (CH_3) (the ipso C of one of the $AsPh_3$ ligands was not observed). This compound was contaminated with variable amounts of **19**.

Bis(triphenylphosphine)(methyleneoxy-1,2-phenylene)-palladium (2). A mixture of **11** (20 mg, 0.021 mmol) and Ag_2CO_3 (12 mg, 0.043 mmol) in MeCN (3 mL) was heated at 50 °C for 5 h. The solvent was evaporated, and the residue was partially dissolved in CH_2Cl_2 and filtered through Celite. The filtrate was evaporated, and the residue was triturated with Et_2O to give **2** (15 mg, 94%). Complex **2** was identical with that prepared before by Pd/Sn transmetalation.[18]

[1,1′-Bis(diphenylphosphino)ferrocene](methyleneoxy-1,2-phenylene)palladium (4). A mixture of **16** (18 mg, 0.02 mmol) and Ag_2CO_3 (10 mg, 0.04 mmol) in MeCN (3 mL) was

stirred at 23 °C for 15 h. The solvent was evaporated, and the residue was suspended in CH_2Cl_2, filtered through Celite, and evaporated. The residue was triturated with hexane to give **4** as an orange solid (15 mg, quantitative) identical with the complex prepared before from the corresponding stannane.[18]

(Methyleneoxy-1,2-phenylene)(2,2′-bipyridine-*N*¹,*N*¹′)-palladium (21). A suspension of **17** (15 mg, 0.03 mmol) and Ag_2CO_3 (10 mg, 0.04 mmol) in MeCN (2 mL) was stirred at 50 °C for 32 h. The solvent was evaporated, and the residue was partially dissolved in CH_2Cl_2 and filtered through Celite. The solvent was evaporated, and the residue was triturated with Et_2O to give **21** as an orange solid (10 mg, quantitative): ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.14 (d, J = 5.4 Hz, 1H), 8.17 (d, J = 5.4 Hz, 1 H), 8.06 (d, J = 7.9 Hz, 2H), 7.94 (qd, J = 7.5, 1.3 Hz, 2H), 7.71−7.09 (m, 4H), 6.99 (td, J = 7.6, 1.5 Hz, 1H), 6.73 (br t, J = 7.6 Hz, 1H), 6.00 (s, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 174.85, 154.63, 150.74, 150.45, 148.87, 140.47, 140.03, 138.35, 134.51, 126.47, 126.07, 125.72, 122.78, 122.00, 117.46, 107.93, 83.08; EI-MS *m*/*z* (relative intensity) 277 (1), 262 (<1), 156 (100), 128 (22), 78 (33) [the molecular ion was not observed]. This complex was isolated contaminated with traces of minor bipyridine palladium complexes, and an analytically pure sample could not be obtained.

(Methyleneoxy-1,2-phenylene)(1,10-phenanthroline-*N*¹,*N*¹⁰)palladium (22). A suspension of **18** (15 mg, 0.03 mmol) and Ag_2CO_3 (10 mg, 0.04 mmol) in MeCN (2 mL) was stirred at 50 °C for 32 h. The solvent was evaporated, and the residue was partially dissolved in CH_2Cl_2 and filtered through Celite. The solvent was evaporated, and the residue was triturated with Et_2O to give **22** as a yellow solid (10 mg, quantitative): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.56 (dd, J = 5.0, 1.5 Hz, 1H), 8.63 (dd, J = 4.9, 1.4 Hz, 1H), 8.47 (m, 2H), 7.95 (part A of an AB system, J = 8.8 Hz, 1H), 7.93 (part B of an AB system, J = 8.8 Hz, 1H), 7.92 (dd, J = 8.3, 5.0 Hz, 2H), 7.59 (dd, J = 7.1, 1.4 Hz, 1H), 7.03 (td, J = 7.5, 1.5 Hz, 1H), 6.79 (m, 2H), 6.25 (s, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 175.05, 150.36, 150.21, 148.54, 146.38, 146.27, 140.24, 137.36, 137.25, 134.55, 129.78, 127.28, 126.86, 125.83, 124.95, 124.88, 117.40, 108.05, 83.03; IR (KBr) ν 3040 (w), 2890 (w), 2820 (w), 1505 (m), 1465 (m), 1415 (s), 1275 (s), 960 (m), 840 (s), 750 (m), 720 (m) cm^{-1}; MS−FAB *m*/*z* (relative intensity) 395 (30), 394 (11), 393 (36), 392 (M^+, 29), 391 (19), 290 (50), 289 (58), 288 (78), 287 (38), 285 (90), 284 (70), 181 (100). Anal. Calcd for $C_{19}H_{14}N_2OPd\cdot0.5H_2O$: C, 56.81; H, 3.76; N, 6.97. Found: C, 56.96; H, 3.51; N, 6.96.

[10-Trimethylsilylmethoxy-4-(2-trimethylsilylmethoxy)phenyl]-6*H*-dibenzo[*b*,*d*]pyran (25). A mixture of silane **5** (612 mg, 2 mmol), $Pd(OAc)_2$ (18 mg, 0.08 mmol), K_2CO_3 (1.10 g, 8 mmol), and Bu_4NBr (645 mg, 2 mmol) in DMF (10 mL) was stirred at 100 °C for 3 d. After being cooled to room temperature, the mixture was partitioned between water and Et_2O. The organic extract was filtered through silica gel and evaporated, and the residue was chromatographed (50:1 hexanes−EtOAc) to give **25** as a colorless oil (63 mg, 20%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.50 (dd, J = 8.1, 1.6 Hz, 1H), 7.44−7.07 (m, 8H), 6.85 (d, J = 7.5 Hz, 1H), 5.01 (s, 2H), 3.81 (s, 2H), 3.66 (s, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$; DEPT) δ 158.81 (C), 158.40 (C), 152.80 (C), 134.67 (C), 131.03 (CH), 130.78 (CH), 128.48 (CH), 128.14 (CH), 128.04 (CH), 127.93 (C), 127.12 (C), 121.99 (C), 120.02 (CH), 119.82 (CH), 119.46 (C), 116,70 (CH), 111.58 (CH), 111.40 (CH), 68.91 (CH_2), 61.98 (CH_2), 61.46 (CH_2), −2.91 (CH_3), −3.36 (CH_3); EI-MS *m*/*z* (relative intensity) 462 (M^+, 100), 375 (5), 307 (12), 154 (59), 136 (51), 107 (16), 73 (76), 59 (65); EI−HRMS calcd for $C_{27}H_{34}O_3Si_2$ (obsd), 462.2046 (462.2050).

(Methyleneoxy-1,2-phenylene)bis(triphenylphosphine)-platinum (28). Method a. A suspension of **1b** (462 mg, 0.88 mmol) and [$Pt(PPh_3)_4$] (1.000 g, 0.80 mmol) in toluene (25 mL) was heated at 70 °C for 48 h. After being cooled to room temperature, the mixture was filtered off, and the solid was washed with Et_2O to give **28** as a white solid (56 mg, 85%). Further purification of samples of **28** contaminated with other Pt(II) complexes could be carried out by partial dissolution in CH_2Cl_2, followed by filtration and evaporation of the solvent.

Method b. A suspension of **5** (31 mg, 0.10 mmol) and [$Pt(PPh_3)_4$] (127 mg, 0.10 mmol) in toluene (4 mL) was heated at 70 °C for 54 h. After being cooled to room temperature, the mixture was filtered off, and the solid was washed with Et_2O to give **28** (38 mg, 45%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54−7.35 (m, 14H), 7.32−7.21 (m, 2H), 7.20−7.14 (m, 8H), 7.08−7.02 (m, 6H), 6.84−6.80 (m, 3H, satellites of ^{195}Pt as multiplets at 6.92−6.87 and 6.79−6.71), 6.06−5.99 (m, 1H), 5.14 [dd, $^3J(^1H-^{31}P)$ = 4.4, 2.9 Hz, $^2J(^1H-^{195}Pt)$ = 49.5 Hz, 2H]; ^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$) δ 174.31 [$^3J(^{13}C-^{31}P)$ = 4.0 Hz, $^2J(^{13}C-^{195}Pt)$ = 78.5 Hz], 142.63 [dd, $^2J(^{13}C-^{31}P)$ = 101.2, 4.8 Hz], 140.95 [t, $^3J(^{13}C-^{31}P)$ = 4.7 Hz, $^2J(^{13}C-^{195}Pt)$ = 48.1 Hz], 135.56−135.19 (m, PPh_3), 134.55−134.28 (m, PPh_3), 134.10 [d, $^1J(^{13}C-^{31}P)$ = 53.7 Hz, PPh_3], 131.90 [d, $^1J(^{13}C-^{31}P)$ = 48.2 Hz, PPh_3], 129.94 (PPh_3), 129.59 (PPh_3), 127.79 [d, $^3J(^{13}C-^{31}P)$ = 9.9 Hz, PPh_3], 127.48 [d, $^3J(^{13}C-^{31}P)$ = 9.5 Hz, PPh_3], 125.50, 116.53 [t, $^4J(^{13}C-^{31}P)$ = 4.9 Hz, $^3J(^{13}C-^{195}Pt)$ = 47.9 Hz], 108.05 [$^4J(^{13}C-^{195}Pt)$ = 23.1 Hz], 85.99 [dd, $^2J(^{13}C-^{31}P)$ = 93.8, 5.3 Hz, $^1J(^{13}C-^{195}Pt)$ = 683.2 Hz]; ^{31}P NMR (121.4 MHz, $CDCl_3$) δ 28.36 [s, $^1J(^{31}P-^{195}Pt)$ = 2146, $^2J(^{31}P-^{31}P)$ = 13.9 Hz, $^1J(^{31}P-^{195}Pt)$ = 1888, $^2J(^{31}P-^{31}P)$ = 14.6 Hz, 2P]; EI-MS *m*/*z* (relative intensity) 826 (M^+, <1), 277 (2), 262 (100), 261 (13), 184 (15), 183 (69), 108 (32); EI−HRMS calcd for $C_{43}H_{36}PP_2{}^{195}Pt$ (obsd), 825.1889 (825.1903). Anal. Calcd for $C_{43}H_{36}OP_2Pd\cdot H_2O$: C, 61.21; H, 4.54. Found: C, 61.04; H, 4.70.

[(3,5-Dichloro-1,2-phenylen)oxymethylen]bis(triphenylphosphine)platinum (29). A suspension of **27** (190 mg, 0.32 mmol) and [$Pt(PPh_3)_4$] (400 mg, 0.32 mmol) in toluene (7 mL) was heated at 40 °C for 67 h. After being cooled to room temperature, the mixture was filtered off, and the solid was washed with Et_2O to give **29** as a white solid (132 mg, 46%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48−7.00 (m, 30H), 6.84 (d, J = 2.3 Hz, 1H), 6.52 [dt, $^4J(^1H-^1H)$ = 2.3 Hz, $^4J(^1H-^{31}P)$ = 2.3, 7.1 Hz, $^3J(^1H-^{195}Pt)$ = 48.9 Hz, 1H], 5.23 [dd, $^3J(^1H-^{31}P)$ = 4.6, 3.5 Hz, $^2J(^1H-^{195}Pt)$ = 46.3 Hz, 2H]; ^{31}P NMR (121.4 MHz, $CDCl_3$) δ 27.54 [d, $^2J(^{31}P-^{31}P)$ = 15.5 Hz, $^1J(^{31}P-^{195}Pt)$ = 1860 Hz, 1P], 27.02 [d, $^2J(^{31}P-^{31}P)$ = 15.5 Hz, $^1J(^{31}P-^{195}Pt)$ = 2267 Hz, 1P]; EI-MS *m*/*z* (relative intensity) 729 (<1), 262 (100), 183 (73), 152 (11), 108 (34), 107 (2) [the molecular ion was not observed]. An analytically pure sample could not be obtained.

Platinum Catalyzed Coupling of Aryl Triflates. To a suspension of [$Pt(PPh_3)_4$] (23 mg, 0.018 mmol) and K_2CO_3 (105 mg, 0.74 mmol) in 1,4-dioxane (4 mL) was added triflate **30** or **31** (0.37 mmol) and ethenyltributylstannane (177 mg, 0.56 mmol). The mixture was stirred at 90 °C for 48 h. After being cooled to room temperature, the mixture was partitioned between water and Et_2O. The organic extract was washed with 10% aqueous HCl and water, dried ($MgSO_4$), and evaporated. Chromatography (50:1 hexanes−EtOAc) gave styrenes **32** (20 mg, 37%) or **33** (15 mg, 30%), identical with compounds prepared before.[41]

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Supporting Information Available: NMR spectra for **7**, **9**, **20**, **21**, **25**, and **29** (6 pages). See any current masthead page for ordering and Internet access instructions.

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