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Palladium-catalyzed or -promoted reductive carbon–carbon coupling. Effects of phosphines and carbon ligands

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Abstract

The reaction of $Cl_2Pd(PEt_3)_2$ with 2 equiv of (E)-t-BuCH=CHLi, t-BuC≡CLi, or MeLi gives the corresponding $R^1_2Pd(PEt_3)_2$ in a nearly quantitative yield without producing R^1R^1, where R^1 = (E)-t-BuCH=CH, t-BuC≡C, or Me. The reaction of PhLi or PhZnCl gives $Ph_2Pd(PEt_3)_2$ and biphenyl in approximately 90 and 10% yields, respectively. On the other hand, the corresponding reaction of $Cl_2Pd(PPh_3)_2$ produces R^1R^1 in > 95% yield within 1 h in each case. Attempts to detect $R^1_2Pd(PPh_3)_2$ have failed. Their formation as unstable intermediates may be inferred from those cases where PEt_3, $PPhMe_2$, and PPh_2Me are used. The ease of formation of R^1R^1 is inversely proportional to the basicity of PR_3, i.e., $PEt_3 < PPhMe_2 < PPh_2Me < PPh_3$. Although $Me_2Pd(PEt_3)_2$ is *cis*, all the other $R^1_2Pd(PEt_3)_2$ and $R^1R^2Pd(PEt_3)_2$ prepared in this study are *trans*. All but one are stable for 3 h at 22 °C. *trans*-[(E)-n-HexCH=CH]PhPd$(PEt_3)_2$, however, undergoes a slow reductive elimination to give (E)-n-HexCH=CHPh in 70% within 12 h at room temperature. Biphenyl and [(E)-t-BuCH=CH]$_2$ can be produced in high yields based on Pd via the corresponding $R^1_2Pd(PR_3)_2$, where PR_3 is PEt_3, $PPhMe_2$, or PPh_2Me, through the use of 8 equiv. of R^1Li. Similar acceleration effects have also been observed in the reaction of $R^1R^2Pd(PR_3)_2$ with an excess of R^1Li, R^2I, or PR_3. However, the reductive elimination reactions of (p-Tol)PhPd$(PEt_3)_2$ promoted by p-TolLi and PhI give significant amounts of homo-coupled products. These results can be explained in terms of various associative mechanisms that have previously been proposed. The reaction of aryl- or alkenyl-zinc chlorides with aryl or alkenyl iodides catalyzed by "$Pd(PR_3)_2$" can give the desired cross-coupled products in ≥ 60% yields. However, only "$Pd(PPh_3)_2$" leads to uniformly high cross/homo ratios. With PEt_3, PPh_2Me, and $PPhMe_2$, cross-homo scrambling occurs to considerable extents, although the reaction of t-BuC≡CZnCl with PhI catalyzed by

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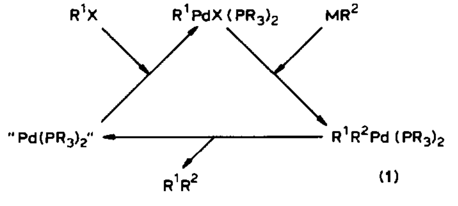
"$Pd(PEt_3)_2$" is exceptional. The high cross/homo ratio observed with PPh_3 is consistent with some dissociative mechanisms but does not appear to be consistent with any associative mechanisms.

Introduction

The Pd-promoted coupling reaction has proved to be a selective and versatile method for carbon–carbon bond formation [1]. Although the feasibility of the three steps in a proposed mechanism shown in Scheme 1 has been demonstrated under stoichiometric conditions [2], various aspects of the reaction, especially the mechanism of reductive elimination of $R^1R^2Pd(PR_3)_2$ (**1**), continue to provide puzzles to be clarified. In addition to a dissociative mechanism [3,4,5b–5d] via $R^1R^2Pd(PR_3)$ (**2**), a mechanism involving palladium(IV) intermediates [5], such as $R^1_2R^2PdI(PR_3)_2$ (**3**), has been proposed. Its plausibility has however been questioned in some cases, and an alternate ligand exchange mechanism has been proposed [4b]. Acceleration of the *trans*-to-*cis* isomerization via a palladate of the type $[R^1_2R^2Pd(PR_3)_2]^-$ (**4**) has also been reported [4a,5c].

Essentially all of the previous studies on the mechanism of reductive elimination have dealt with relatively stable and readily characterizable $R^1R^2Pd(PR_3)_2$ under stoichiometric conditions. However, our recent investigation [6] indicates that, in many synthetically attractive cases, the reductive elimination of presumed intermediates **1** is faster than their formation. It is therefore possible that some of those mechanistic schemes established for relatively slow reductive elimination reactions may not be relevant in many of the synthetically attractive cases. We have further observed that the reductive elimination of **1** can be subject to inhibition by strongly basic organometallic reagents, such as organolithiums. Thus, for example, reductive elimination of $(t\text{-BuC}{\equiv}C)_2Pd(PPh_3)_2$ (**5**) to produce $t\text{-BuC}{\equiv}CC{\equiv}CBu\text{-}t$ (**6**) is strongly inhibited by the action of $t\text{-BuC}{\equiv}CLi$ through the formation of $Li_2Pd(C{\equiv}CBu\text{-}t)_4$ (**7**) [7].

One of the two main objectives of this investigation is to systematically examine the effects of PR_3, where PR_3 is PPh_3, $PMePh_2$, PMe_2Ph, or PEt_3, and of the carbon group R^1 on the ease and nature of reductive elimination of $R^1_2Pd(PR_3)_2$ (**8**) under stoichiometric conditions. The other goal is to examine the effects of an excess of an organic halide or an organolithium on the reductive elimination of $R^1_2Pd(PR_3)_2$ or $R^1R^2Pd(PR_3)_2$ in the hope of probing the mechanism of reductive elimination under catalytic conditions.



Scheme 1

Results and discussion

Essentially all of the previous mechanistic studies of reductive elimination of diorganopalladium derivatives [2–5] have dealt with those in which at least one of the carbon ligands is an sp^3 hybridized carbon group, such as methyl, alkyl, or benzyl. Thus, information on many synthetically attractive cases where both of the carbon groups of **1** are aryl, alkenyl, and/or alkynyl was lacking. We therefore undertook to examine the reactions of $Cl_2Pd(PR_3)_2$, where PR_3 was PPh_3, PPh_2Me, $PPhMe_2$, or PEt_3, with PhLi, (*E*)-t-BuCH=CHLi, and t-BuC≡CLi. The reactions of $Cl_2Pd(PR_3)_2$ with MeLi, which have been investigated in detail by other workers [4a,5b], were also included for comparison.

To probe the effects of PR_3 and the organic ligands (R^1) on the ease of reductive elimination from $R^1_2Pd(PR_3)_2$ (**8**), the above-described reactions were first carried out in a 1/2 molar ratio [$Cl_2Pd(PR_3)_2/R^1Li$] in THF at 22°C, and the yields of R^1R^1 were determined by GLC and/or ^1H NMR at 1 and 3 h. Of the $Cl_2Pd(PR_3)_2$ complexes prepared by treating either $PdCl_2$ or Li_2PdCl_4 with PR_3, $Cl_2Pd(PPh_3)_2$ and $Cl_2Pd(PEt_3)_2$ were known to be *trans* based on their IR and/or ^{31}P NMR [8]. Although $Cl_2Pd(PPhMe_2)_2$ and $Cl_2Pd(PPh_2Me)_2$ were reported to be 67/33 and 55/45 mixtures of the *cis* and *trans* isomers, respectively [8], in CH_2Cl_2, the ^{31}P NMR spectra of these compounds prepared by treating $PdCl_2$ with the corresponding phosphines in benzene indicated that the samples used in this study were nearly 100% *trans* in THF.

The experimental data summarized in Table 1 indicate that the ease of formation of R^1R^1, as judged by their yields after 1 and 3 h, is inversely proportional to the basicity of PR_3, i.e., $PEt_3 < PPhMe_2 < PPh_2Me < PPh_3$ [9]. The high contrast between PEt_3 and PPh_3 is especially noteworthy. Treatment of $Cl_2Pd(PEt_3)_2$ with 2 equiv. of R^1Li, where R^1 = (*E*)-t-BuCH=CH, t-BuC≡C, or Me, in THF (−78°C to room temperature) leads to the formation in a nearly quantitative yield of $R^1_2Pd(PEt_3)_2$, which does not give R^1R^1 in any detectable amount over 3 h at 22°C. The reaction of $Cl_2Pd(PEt_3)_2$ with 2 equiv. of PhLi also gives $Ph_2Pd(PEt_3)_2$. However, its formation is accompanied by that of biphenyl (8–9%). These compounds have been characterized by ^1H and ^{31}P NMR, and the spectral data are summarized in Table 2. Of the four, $Me_2Pd(PEt_3)_2$ has been previously reported by

Table 1

Effects of phosphines and organolithiums on the ease of reductive elimination from $R^1_2Pd(PR_3)_2$ [a]

$Cl_2Pd(PR_3)_2$	pK_a [b] of PR_3	Yield [c] of R^1R^1 obtained from R^1Li (%)							
		PhLi		(*E*)-t-BuCH=CHLi		t-BuC≡CLi		MeLi	
		1 h	3 h	1 h	3 h	1 h	3 h	1 h	3 h
$Cl_2Pd(PEt_3)_2$	8.65	8	9	< 2	< 2	< 2	< 2	< 2	< 2
$Cl_2Pd(PPhMe_2)_3$	6.50	32	37	85	85	< 5	< 5	< 5	< 5
$Cl_2Pd(PPh_2Me)_2$	4.65	63	66	95	95	< 5	< 5	15	40
$Cl_2Pd(PPh_3)_2$	2.71	> 95	> 95	> 95	> 95	> 95	> 95	> 95	> 95

[a] The reaction of $Cl_2Pd(PR_3)_2$ and R^1Li was carried out in a 1/2 molar ratio in THF at 22°C. [b] Ref. 9.
[c] By GLC and/or ^1H NMR.

Table 2

Characterization of $R^1_2Pd(PEt_3)_2$ and $R^1R^2Pd(PEt_3)_2$ by ^1H and ^{31}P NMR

R^1	R^2	^1H NMR		^{31}P NMR
		PCH_2CH_3	Others	
Ph [a]	–	0.95 (quin. [b], J 8 Hz)	Ph, 6.5–7.7 (m, 10 H)	12.7 (s)
(E)-t-BuCH=CH	–	1.05 (quin., J 8 Hz)	t-Bu, 0.94 (s, 18 H)	13.9 (s)
t-BuC≡C	–	1.15 (quin., J 8 Hz)	t-Bu, 1.17 (s, 18 H)	19.3 (s)
Me [c]	–	not observed [b]	Me, −0.14 (q, 6 H)	13.0 (s)
Ph	p-Tol	1.08 (quin., J 8 Hz)	2.45 (s, 3H), 6.9–7.8 (m, 9H)	12.8 (s)
Ph	(E)-1-Octenyl	not observed	4.91 (dt, J 13.8 and 6.0 Hz, 1H), 5.17 (d, J 13.8 Hz, 1 H)	12.5 (s)
Ph	t-BuC≡C	1.08 (quin., J 8 Hz)	1.24 (s, 9H), 7.0–7.6 (m, 5H)	15.9 (s)
Ph	Me	not observed	−0.6 (t, 6H)	16.7 (s)

[a] Ref. 10. [b] Ref. 4a. [c] A ca. 6/1 mixture of *cis*-$Me_2Pd(PEt_3)_2$ and $LiMe_3PdPEt_3$.

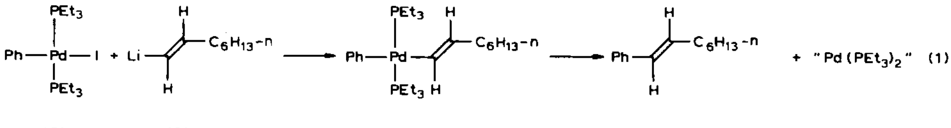
other workers [5b,10], and our data are consistent with those for *cis*-$Me_2Pd(PEt_3)_2$. The apparent quintets [4a] for the methyl groups of PEt_3 in $Ph_2Pd(PEt_3)_2$, [(E)-t-BuCH=CH]$_2$Pd(PEt$_3$)$_2$ and (t-BuC≡C)$_2$Pd(PEt$_3$)$_2$ at 0.95 (J 8 Hz), 1.05 (J 8 Hz), and 1.15 (J 8 Hz) ppm, respectively, indicate that these three compounds are *trans*. There is no indication for the presence of the *cis* isomer.

The use of organozinc chlorides, readily prepared by treating the corresponding organolithiums with dry $ZnCl_2$, leads to essentially the same products. Thus, the reaction of $Cl_2Pd(PEt_3)_2$ with 2 equiv. of PhZnCl and t-BuC≡CZnCl in THF afforded in > 90% yields $Ph_2Pd(PEt_3)_2$ and (t-BuC≡C)$_2$Pd(PEt$_3$)$_2$, respectively, whose ^1H NMR spectra were virtually identical with those in Table 2. The yields of biphenyl and t-BuC≡CC≡CBu-t were ca. 10 and < 5%, respectively, after 3 h at room temperature.

In sharp contrast, the reaction of $Cl_2Pd(PPh_3)_2$ with the four organolithium reagents gives the expected coupling products (R^1R^1) in > 95% yields within 1 h. All attempts to detect $R^1_2Pd(PPh_3)_2$ by ^1H NMR have failed except for the case of $Me_2Pd(PPh_3)_2$ [5b]. The formation of $R^1_2Pd(PPh_3)_2$ may, however, be inferred from those cases where PEt_3, $PPhMe_2$, and PPh_2Me are involved. For example, the reaction of 2 equiv. of t-BuC≡CLi with $Cl_2Pd(PR_3)_2$ containing these three phosphines rapidly and quantitatively produces *trans*-(t-BuC≡C)$_2$Pd(PR$_3$)$_2$. The ^1H NMR signals for the t-Bu and P-bound Me groups of the complexes containing $PPhMe_2$ and PPh_2Me appear at 1.05 (s, 18 H), 1.87 (t, J 3 Hz, 12H) and 0.83 (s, 18 H), 2.17 (t, J 4 Hz, 6H), respectively. These complexes also show ^{31}P NMR singlets at −5.9 and 7.5 ppm, respectively. These results suggest that the reaction of t-BuC≡CLi (2 equiv.) with $Cl_2Pd(PPh_3)_2$ must also give (t-BuC≡C)$_2$Pd(PPh$_3$)$_2$ as an unstable intermediate, which must rapidly decompose to give **6** via reductive elimination. We tentatively conclude that the reaction of $Cl_2Pd(PR_3)_2$ with 2 equiv. of R^1Li rapidly gives $R^1_2Pd(PR_3)_2$ as either unstable intermediates or stable products with all four organolithiums and all four phosphines employed in this study.

Reductive elimination from diorganopalladium species under stoichiometric conditions

We then turned our attention to the question of whether diorganopalladium species, e.g., $R^1_2Pd(PR_3)_2$ and $R^1R^2Pd(PR_3)_2$, containing two unsaturated organic groups can indeed serve as precursors to coupling products, i.e., R^1R^1 and R^1R^2, under stoichiometric conditions. We have therefore sought a case in which either $R^1_2Pd(PR_3)_2$ or $R^1R^2Pd(PR_3)_2$ forms quantitatively as a readily characterizable species and cleanly decomposes at a convenient rate under thermal conditions such that the reaction can be directly monitored by ^1H NMR. None of the 16 cases shown in Table 1 readily satisfy the above conditions. We have however found that the 1/1 reaction of preformed *trans*-$PhPdI(PEt_3)_2$ (**9**) [11] with (*E*)-1-octenyllithium (**10**) does. The preparation of **9** was performed by treating $Cl_2Pd(PEt_3)_2$ with 2 equiv. of n-BuLi followed by addition of PhI. The ^1H NMR signals for the α and β alkenyl protons of **10** appeared at 6.38 (d, *J* 21.5 Hz) and 6.00 (dt, *J* 21.5 and 4.5 Hz) ppm, respectively. The phenyl protons of **9** appeared as 2 multiplets at 7.0–7.45 and 7.45–7.7 ppm. These two reactants were mixed in THF first at −78° C, and the mixture was then warmed to room temperature. After 1 h at room temperature, its ^1H NMR spectrum indicated that the alkenyl proton signals had shifted to 5.17 (d, *J* 14 Hz) and 4.91 (dt, *J* 14 and 6 Hz) ppm without any significant change in signal pattern. Although the Ph proton signals had remained in the 6.95–7.6 ppm region, the signal pattern had significantly changed. Importantly, no signals assignable to either **10** or the expected product **11**, which shows its alkenyl proton signals at 6.3–6.6 (m) ppm, were discernible. The ^{31}P NMR signal for **9** at 13.87 (s) ppm also shifted cleanly to 12.50 (s) ppm upon treatment of **9** with **10** within 1 h at room temperature. Over 6–12 h at room temperature, the multiplet for the alkenyl protons of **11** completely replaced the alkenyl proton signals for **12**, indicating that **12** must have undergone a slow reductive elimination to product **11** and "$Pd(PEt_3)_2$". The ^{31}P NMR sharp singlet at 12.50 ppm for **12** was replaced by a broad singlet at 9.7 ppm assignable to "$Pd(PEt_3)_2$", which presumably is $(LiCl)_nPd(PEt_3)_2$, where $n = 1$ or 2, in analogy with $(LiCl)_nPd(PPh_3)_2$ [12]. The yield of **11** by ^1H NMR was ca. 70%. Although the overall transformation can be readily accommodated by eq. 1, a more detailed examination of the reaction by ^1H NMR indicates that the alkenyl proton signals undergo highly complex changes between 1 and 6 h. Since **12** is expected to undergo a series of transformations, such as decomplexation, complexation, and *trans–cis* isomerization, the observed ^1H NMR data are not unreasonable. At present, however, they are not fully interpretable.



(1)

(9) (10) (12) (11)

The reaction of **9** with one equiv. of PhLi, *p*-TolLi, t-BuC≡CLi, or MeLi similarly produced in quantitative yield *trans*-$Ph_2Pd(PEt_3)_2$ (**13**), *trans*-Ph(*p*-Tol)$Pd(PEt_3)_2$ (**14**), *trans*-Ph(t-BuC≡C)$Pd(PEt_3)_2$ (**15**), or *trans*-$PdMePd(PEt_3)_2$ (**16**). Their ^1H and ^{31}P NMR data are summarized in Table 2. Unlike **12**, however, **13**–**16** did not give the expected coupling products in more than 2% yields over 24 h at 22° C. The results indicate that alkenyl groups participate in reductive elimina-

Table 3

Effects of excess quantities of organolithiums on the ease of reductive elimination from $R^1_2Pd(PR_3)_2$ [a]

$Cl_2Pd(PR_3)_2$	Yield [b] of R^1R^1 (%)					
	PhLi		(*E*)-t-BuCH=CHLi		t-BuC≡CLi	
	4 equiv.	8 equiv.	4 equiv.	8 equiv.	4 equiv.	8 equiv.
$Cl_2Pd(PEt_3)_2$	41(43 [c])	70(73 [c])	94	98	< 5	6
$Cl_2Pd(PPhMe_2)_2$	84	–	> 95	> 95	–	36(35 [c])
$Cl_2Pd(PPh_2Me)_2$	97	–	> 95	> 95	–	32(35 [c])

[a] The reaction of $Cl_2Pd(PR_3)_2$ with R^1Li was carried out in THF for 3 h at 22° C. [b] By GLC and/or ^1H NMR. [c] A preformed $R^1_2Pd(PR_3)_2$ was treated with 2 or 6 equiv. of R^1Li.

tion more readily than aryl, alkynyl, or alkyl groups. It is not clear, however, why **12** is seemingly more reactive than $[(E)\text{-t-BuCH=CH}]_2Pd(PEt_3)_2$.

As in the preparation of symmetrical $R^1_2Pd(PEt_3)_2$, the use of organozinc chlorides leads to the same mixed diorganopalladium derivatives. Thus, the reaction of **9** with *p*-TolZnCl in THF gave in ≥ 90% yield **14**, whose ^1H NMR spectrum was virtually identical with that of the sample prepared from *p*-TolLi. The yield of *p*-TolPh was < 5%.

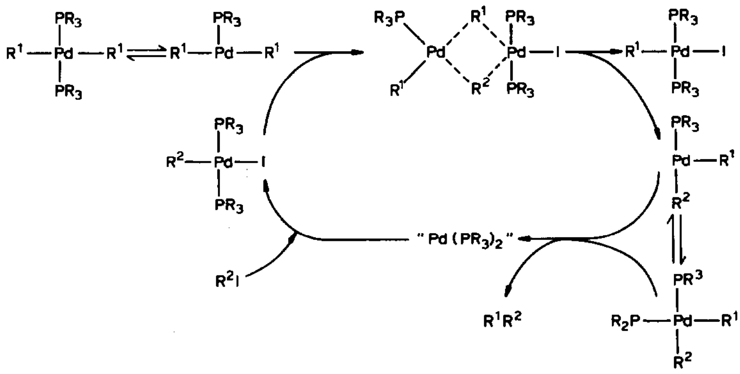
Effects of excessive amounts of organometals and organic halides on the reductive elimination of diorganopalladium species

Under catalytic conditions, the presumed diorganopalladium intermediates are transformed into the desired coupling products in the presence of excessive amounts of organometals and organic halides. Furthermore, some free phosphine molecules liberated under catalytic conditions may exert influences on the reductive elimination of diorganopalladium species. Acceleration of reductive elimination of diorganopalladium species containing one or two alkyl groups by organic halides [5], organolithiums [4a,5c], and phosphines [5c] has indeed been observed in some cases.

To probe the effects of excessive quantities of organometallic reagents, we treated $Cl_2Pd(PR_3)_2$, where PR_3 was PEt_3, $PPhMe_2$, or PPh_2Me with 4 or 8 equiv. of PhLi, (*E*)-t-BuCH=CHLi, or t-BuC≡CLi. In order to probe the effect of countercations, the reaction of $Cl_2Pd(PEt_3)_2$ with 4 or 8 equiv. of PhZnCl was also carried out. The experimental results are summarized in Table 3.

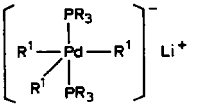
These results indicate that the desired coupling products (R^1R^1) are obtained in high yields based on Pd from the reactions involving PhLi and (*E*)-t-BuCH=CHLi. Similarly, the use of 4 and 8 equivalents of PhZnCl leads to the formation of biphenyl in 35 and 52% yields, respectively. The effect of an excess of t-BuC≡CLi depends on PR_3. With PEt_3, acceleration of the formation of t-BuC≡CC≡CBu-t has been observed only to a very minor extent, and a strong inhibition of reductive elimination has been observed with PPh_3 (vide supra) [7]. On the other hand, acceleration of reductive elimination to a modest extent occurs with Pd complexes containing $PPhMe_2$ and PPh_2Me.

The mode of acceleration by organometals is unclear. As suggested previously [4a,5c], however, it is likely that $R^1_2Pd(PR_3)_2$ reacts with R^1Li to give palladates, such as **17**, which can, in principle, promote reductive elimination either directly from $R^1_2Pd(PR_3)_2^-$ or via *trans*-to-*cis* isomerization of $R^1_2Pd(PR_3)_2$. Addition of 2



Scheme 2

and 6 equiv. of PhI to $Ph_2Pd(PEt_3)_2$ also accelerates the formation of biphenyl. Thus, its yields after 3 h at room temperature are 30 and 51%, respectively. The results appear to be consistent with the intermediacy of a hexacoordinate complex **18** [5]. Very recently, however, an alternate mechanism involving dissociation of $R^1_2Pd(PR_3)_2$ followed by intermolecular exchange of carbon ligands was proposed to account for the accelerating effect of R_2X (Scheme 2) [4b].



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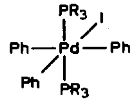


(18)

The corresponding reactions of *trans*-Ph(*p*-Tol)Pd(PEt$_3$)$_2$ (**14**) with *p*-TolLi and PhI are particularly informative. Addition of 6 equiv. of *p*-TolLi to **14** induces in 1 h the formation of PhTol-*p* and bis(*p*-tolyl) in 17 and 15% yields, respectively, along with a trace of biphenyl, while addition of 6 equiv. of PhI to **14** gives in 1 h PhTol-*p* and biphenyl in 8 and 38% yields, respectively, along with a trace of bis(*p*-tolyl). In either case, the product yields do not significantly increase after 1 h. Thus, at least in aryl–aryl coupling, acceleration by an aryllithium or an aryl halide is accompanied by extensive cross-homo scrambling.

We have also examined the effects of an excess of PEt_3 on the reductive elimination of *trans*-[(*E*)-n-HexCH=CH]PhPd(PEt$_3$)$_2$ (**12**). Whereas **12** gives a < 5% yield of the expected coupling product **11** in 1 h, addition of 1 and 8 equiv. of PEt_3 leads to the formation of **11** in 83 and 91% yields, respectively. No additional investigation of the effects of phosphines has been made in the present study, however.

Mechanism of the palladium-catalyzed carbon–carbon coupling

We have so far dealt with Pd-promoted carbon–carbon coupling reactions that are stoichiometric in Pd. Essentially all of the reactions examined in the previously reported mechanistic studies are also stoichiometric in Pd. Consequently, little is firmly known about the actual mechanisms of the Pd-catalyzed carbon–carbon coupling reactions, especially those which display high reaction rates, product

Table 4

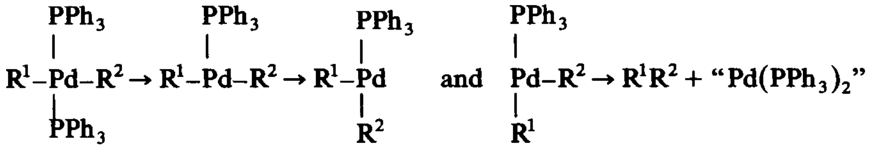
The reaction of organozinc chlorides with organic iodides catalyzed by "$Pd(PR_3)_2$" in THF [a]

R^1 of R^1I	R^2 of R^2ZnCl	PR_3 of "$Pd(PR_3)_2$"	Reaction time (h)	Yield [b] (mmol×100)			$\frac{R^1R^2}{R^1R^1+R^2R^2}$
				R^1R^2	R^1R^1	R^2R^2	
Ph	*p*-Tol	PPh_3	0.1	95	<1	<1	>48
Ph	*p*-Tol	PPh_2Me	1	86	8	6	6.1
Ph	*p*-Tol	$PPhMe_2$	1	62	15	11	2.4
Ph	*p*-Tol	PEt_3	6	60	13	11	2.5
Ph	(*E*)-1-Octenyl	PPh_3	0.1	85	<1	4	>17
Ph	(*E*)-1-Octenyl	PEt_3	3 [c]	65	3	9	5.4
(*E*)-1-Octenyl	Ph	PEt_3	1	64	8	15	2.8
(*E*)-1-Hexenyl	(*E*)-1-Octenyl	PPh_3	0.1	85	4	1	17
(*E*)-1-Hexenyl	(*E*)-1-Octenyl	PEt_3	1	71	8	7	4.7
Ph	t-BuC≡C	PPh_3	0.1	92	<1	<1	>46
Ph	t-BuC≡C	PEt_3	12 [c]	92	<1	<1	>46

[a] Unless otherwise mentioned, the reaction was run in a 1/1 molar ratio at 22° C in the presence of 5 mol % of a Pd catalyst prepared by treating $Cl_2Pd(PR_3)_2$ with 2 equiv. of n-BuLi. [b] The reaction was run on a 1 mmol scale. The yield was determined by GLC and is indicated in mmol×100. [c] At 50° C.

yields, and cross/homo ratios. Although investigation of such synthetically attractive Pd-catalyzed carbon–carbon coupling reactions remains exceedingly difficult, we have nonetheless hoped to gain some insights into the matter. We have therefore carried out the cross-coupling reactions of unsaturated organozinc chlorides, i.e., *p*-TolZnCl, (*E*)-n-HexCH=CHZnCl, and t-BuC≡CZnCl, with unsaturated organic iodides, i.e., PhI and (*E*)-n-BuCH=CHI, in the presence of Pd catalysts generated by treating $Cl_2Pd(PR_3)_2$ (5 mol%) with n-BuLi (10 mol%). Although organolithiums are very convenient for preparing $R^1_2Pd(PR_3)_2$ and $R^1R^2Pd(PR_3)_2$, they are generally unsuitable for the Pd-catalyzed cross coupling due to competitive lithium–halogen exchange, which leads to cross-homo scrambling. On the other hand, essentially no zinc–iodine exchange occurs among the above-mentioned reagents at room temperature.

The reaction of *p*-TolZnCl with PhI in a 1/1 molar ratio in the presence of 5 mol% of "$Pd(PR_3)_2$" generated in situ by treating $Cl_2Pd(PR_3)_2$, where $PR_3 = PPh_3$, PPh_2Me, $PPhMe_2$, or PEt_3, was carried out in THF at 22° C, and the yields of the cross- and homo-coupling products were determined by GLC. The results summarized in Table 4 indicate that, although the desired cross-coupling product, i.e., *p*-TolPh, is produced in good to excellent yields in all four cases, the cross/homo ratio, i.e., $R^1R^2/(R^1R^1 + R^2R^2)$, is satisfactory (48) only when $Cl_2Pd(PPh_3)_2$ is used as a precatalyst. With $Cl_2Pd(PPhMe_2)_2$ and $Cl_2Pd(PEt_3)_2$, the cross/homo ratios are only 2.4 and 2.5, respectively. These latter results are consistent with those mechanisms discussed above in which reductive elimination is promoted by organometals, and/or organic halides, although the exact courses of these reactions are still unclear. On the other hand, the clean formation of *p*-TolPh in 95% yield in the reaction catalyzed by "$Pd(PPh_3)_2$" appears to be incompatible with any associative mechanisms including that shown in Scheme 2, since any of them is expected to produce extensively cross-homo scrambled products in the *p*-Tol–Ph coupling. Associative mechanisms relevant to the present discussion may be defined as those in which interaction of organopalladium intermediates with species containing either R^1 or R^2 group is significant. We suggest that the reaction of *p*-TolZnCl with PhI catalyzed by "$Pd(PPh_3)_2$" does not involve to any significant extent acceleration of reductive elimination by either *p*-TolZnCl or PhI and that the high cross/homo ratio displayed by the reaction seems to be best accommodated by a dissociative mechanism, such as that shown in eq. 2.



$$\underset{PPh_3}{\overset{PPh_3}{R^1\text{-}Pd\text{-}R^2}} \rightarrow \overset{PPh_3}{R^1\text{-}Pd\text{-}R^2} \rightarrow R^1\text{-}\underset{R^2}{\overset{PPh_3}{Pd}} \quad \text{and} \quad \underset{R^1}{\overset{PPh_3}{Pd}}\text{-}R^2 \rightarrow R^1R^2 + \text{“}Pd(PPh_3)_2\text{”} \qquad (2)$$

The results summarized in Table 4 also indicate that, regardless of R^1 and R^2, the cross/homo ratios are uniformly high ($\geqslant 17$) in those cases where "$Pd(PPh_3)_2$" is used as a catalyst. On the other hand, when "$Pd(PEt_3)_2$" is used as a catalyst, the cross/homo ratios are low (< 5) in the alkenyl–alkenyl, alkenyl–aryl, and aryl–aryl coupling, although it is high (46) in the alkynyl–aryl coupling. Here again, we attribute the generally low cross/homo ratios observed with PEt_3 to some associative mechanisms. Since *trans*-[(*E*)-t-BuC≡C]PhPd$(PEt_3)_2$ itself is thermally stable, its reductive elimination must be assisted by some reagents present in the reaction mixture, and such processes must be associative. The origin of the high cross/homo ratio (46) is however unclear. Despite relatively low cross/homo ratios and mechanistic uncertainties, it is nonetheless useful to note that even those cases which are catalyzed by "$Pd(PEt_3)_2$" give the cross-coupled products in $\geqslant 60\%$ yields.

Conclusion

The reaction of $Cl_2Pd(PR_3)_2$ and $R^2PdI(PR_3)_2$ with organolithiums (R^1Li) can produce $R^1_2Pd(PR_3)_2$ and $R^1R^2Pd(PR_3)_2$, respectively, as either stable products or intermediates under stoichiometric conditions. With PPh_3, it has not been possible to detect $R^1_2Pd(PPh_3)_2$ and $R^1R^2Pd(PPh_3)_2$, and their formation as unstable intermediates can only be inferred from those cases where PEt_3, $PPhMe_2$, and PPh_2Me are used.

The ease of formation of R^1R^1 from $Cl_2Pd(PR_3)_2$ and 2 equiv. of R^1Li is inversely proportional to the basicity of PR_3, i.e., $PEt_3 < PPhMe_2 < PPh_2Me < PPh_3$.

Aryl–aryl, aryl–alkenyl, and alkenyl–alkenyl coupling can be achieved in high yields based on Pd even with PEt_3, $PPhMe_2$, and PPh_2Me, provided that an excess of R^1Li is used. Similar acceleration effects have also been observed with an excess of R^2I or PR_3. With alkynyllithiums, however, inhibition of reductive elimination has been observed with PPh_3 and PEt_3. The reductive elimination reaction of $R^1R^2Pd(PEt_3)_2$ promoted by R^1Li or R^2I tends to give significant amounts of homo-coupled products. These results can be explained in terms of various associative mechanisms that have previously been proposed.

Finally, the reaction of aryl- or alkenyl-zinc chlorides with aryl or alkenyl iodides catalyzed by "$Pd(PR_3)_2$" can give the desired cross-coupled products in $\geqslant 60\%$ yields. However, only "$Pd(PPh_3)_2$" leads to uniformly high cross/homo ratios. The high cross/homo ratios, especially in the cases of aryl–aryl and alkenyl–alkenyl coupling, are not readily accommodated by any of the associative mechanisms discussed herein but are consistent with some dissociative mechanisms. With the other phosphines, i.e., PEt_3, $PPhMe_2$, and PPh_2Me, significant amounts of homo-coupled products are generally produced, although the reaction of t-BuC≡CZnCl with PhI catalyzed by "$Pd(PEt_3)_2$" displays a cross/homo ratio of 46.

Experimental

All organometallic reactions were run under an inert atmosphere of nitrogen. Unless otherwise stated, chemicals obtained from commercial sources were used without further purification. Tetrahydrofuran (THF) and ether were dried over sodium and benzophenone. Zinc chloride was flame-dried in vacuo. Gas-liquid chromatographic analyses (GLC) were performed on SE-30 columns using appropriate linear and saturated hydrocarbons as internal standards. NMR spectra were obtained using Perkin–Elmer R32, Varian CFT-20, and Varian XL-200 spectrometers. Dichlorobis(triphenylphosphine)palladium, dichlorobis(diphenylmethylphosphine)palladium, dichlorobis(dimethylphenylphosphine)palladium, and dichlorobis(triethylphosphine)palladium were prepared by the reaction of the corresponding phosphine with a suspension of anhydrous palladium chloride in benzene at 60 °C [13]. *trans*-Iodo(phenyl)bis(triphenylphosphine)palladium was prepared according to a literature procedure [14]. (*E*)-1-Octenyl iodide, (*E*)-1-hexenyl iodide, and (*E*)-3,3-dimethyl-1-butenyl iodide were prepared from the corresponding alkynes via hydroalumination-iodinolysis [15]. Phenyllithium and methyllithium were available commercially (Aldrich).

Reaction of $Cl_2Pd(PR_3)_2$ with various organolithiums or organozinc chlorides

(a) Reaction of $Cl_2Pd(PPh_3)_2$ with phenyllithium: Representative procedure. To a mixture of $Cl_2Pd(PPh_3)_2$ (0.35 g, 0.50 mmol) and THF (5 ml) cooled to −78 °C was added 0.5 ml of a THF solution of phenyllithium (2.0 *M*, 1.0 mmol). The mixture was stirred for 10 min at −78 °C and then for 1 h at room temperature. The reaction mixture was quenched with 2*N* HCl and analyzed by GLC using undecane as an internal standard. Biphenyl, which was identified by co-injection with an authentic sample, was formed in 95% yield.

Unless otherwise mentioned, the following experiments were carried out according to the above representative procedure, and the results are summarized in Table 1.

(b) Reaction of $Cl_2Pd(PR_3)_2$ with methyllithium. This reaction was followed by monitoring the disappearance of the palladium-methyl protons in the ^{1}H NMR [4a,5b].

(c) Reaction of $Cl_2Pd(PR_3)_2$ with organozinc chlorides. This reaction was carried out according to the representative procedure described above except that organozinc chlorides, prepared by treatment of the corresponding organolithiums with 1 molar equiv of $ZnCl_2$, were used as the organometallic reagents.

The homo-coupled products have yielded the following data.

(3E,5E)-2,2,7,7-Tetramethyl-3,5-octadiene [16]. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 1.00 (s, 18H), 5.4–6.1 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$ Me_4Si): δ 29.5, 33.0, 126.2, 144.0 ppm.

2,2,7,7-Tetramethyl-3,5-octadyne [17]. M.p. 130–131 °C (lit. [17] m.p. 129.5–131.5 °C); ^{1}H NMR ($CDCl_3$, Me_4Si): δ 1.25 (s, 18H) ppm.

Characterization of $R^1_2Pd(PEt_3)_2$ and $R^1R^2Pd(PEt_3)_2$ by ^1H NMR. The solvent of each reaction mixture obtained according to the representative procedure described above was removed under reduced pressure, and its ^{1}H NMR was taken in CH_2Cl_2, $CDCl_3$, or THF-d_8. The results are summarized in Table 2.

Characterization of $R^1_2Pd(PEt_3)_2$ and $R^1R^2Pd(PEt_3)_2$ by ^{31}P NMR. In each case, the reaction mixture obtained according to the representative procedure described above was directly subjected to ^{31}P NMR measurements. The chemical shift values are relative to external 85% phosphoric acid. The results are summarized in Table 2.

trans-Iodo(phenyl)bis(triethylphosphine)palladium [11]. To a mixture of 207 mg (0.5 mmol) of dichlorobis(triethylphosphine)palladium and 5 ml of THF was added 0.75 ml (1.6 *M*, 1.2 mmol) of n-BuLi at −78 °C. The mixture was stirred at −78 °C for 1 h, followed by addition of 143 mg (0.7 mmol) of iodobenzene. After stirring the reaction mixture for 1 h at room temperature, *trans*-iodo(phenyl)bis(triethylphosphine)palladium was formed in 89% yield. The mixture was evaporated to dryness, extracted with pentane, treated with charcoal, and filtered. Crystallization gave yellow crystals of *trans*-iodo(phenyl)bis(triethylphosphine)palladium [11]: m.p. 105.0–105.5 °C (decomp); IR (crystals) 2960 (m), 1530 (m), 1450 (m), 1410 (m), 1032 (s), 762 (s), 736 (s), 721 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si); δ 1.07 (quint, *J* 8 Hz, 18H), 1.5–1.9 (m, 12H), 6.9–7.5 (m, 5H) ppm; ^{31}P NMR (THF, 85% H_3PO_4); δ 11.77 (s) ppm.

Reaction of iodo(phenyl)bis(triethylphosphine)palladium with (E)-1-octenyllithium. To a mixture of 54.7 mg (0.1 mmol) of $PhPd(PEt_3)I$ and 0.3 ml of THF in a 5-mm NMR tube was added 0.2 ml (0.5 *M*, 0.1 mmol) of (*E*)-1-octenyllithium at −78 °C. The reaction mixture was warmed to room temperature and monitored by ^{1}H and ^{31}P NMR. Before mixing the reagents, the ^{1}H NMR spectrum of (*E*)-1-octenyllithium showed signals for the α and β alkenyl protons at 6.38 (d, *J* 21.5 Hz) and 6.00 (dt, *J* 21.5 and 4.5 Hz) ppm, and the phenyl protons of $PhPd(PEt_3)I$ (**9**) appeared as 2 multiplets at 7.0–7.45 and 7.45–7.7 ppm, while the ^{31}P NMR spectrum of **9** showed a singlet at 11.78 ppm. After 1 h, the ^{1}H NMR spectrum of the reaction mixture indicated that the alkenyl proton signals had completely shifted to 5.17 (d, *J* 14 Hz) and 4.91 (dt, *J* 14 and 6 Hz) ppm without any major change in the signal pattern. Although the phenyl proton signals had remained in the 6.95–7.6 ppm region, the signal pattern had significantly changed. No signals assignable to either (*E*)-1-octenyllithium or the expected product, i.e., (*E*)-1-octenylbenzene (**11**) which would show its alkenyl proton signals at 6.3–6.6 (m) ppm, were discernible. The ^{31}P NMR spectrum at this point showed a singlet at 13.87 ppm. The alkenyl proton signals slowly and gradually underwent highly complex changes mainly between 1 and 6 h, which are not fully interpretable. After 6–12 h, the only alkenyl proton signals observable were those of **11** at 6.3–6.6 ppm, and the ^{31}P NMR spectrum of the reaction mixture showed only a broad singlet at 9.69 ppm. The yield of **11** by both ^{1}H NMR and GLC was ca. 70%.

(E)-1-Octenylbenzene (**11**) [18]. IR (neat): 3020 (m), 2950 (s), 2920 (s), 2850 (s), 1595 (m), 1480 (m), 960 (s), 735 (s), 690 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.90 (t, *J* 6 Hz, 3H), 1.35 (b.s. 8H), 2.1–2.5 (m, 2H), 6.0–6.7 (m, 2H), 7.1–7.8 (m, 5H) ppm.

Reaction of $Cl_2Pd(PR_3)_2$ with excessive amounts of organometals. These reactions were carried out according to the representative procedure described above except that excessive amounts of organometals were used. The experimental results are summarized in Table 3.

Reaction of $R^1R^2Pd(PEt_3)_2$ with excessive amounts of organometals, organic halide and PEt_3

*(a) Reaction of trans-Ph(p-Tol)Pd(PEt_3)$_2$ (**14**) with an excess of p-tolyllithium: Representative procedure.* To the THF solution of *trans*-Ph(*p*-Tol)Pd(PEt_3)$_2$ (**14**) obtained according to the representative procedure described above was added 6 equiv. of *p*-tolyllithium in THF at room temperature. The mixture was stirred at room temperature for 1 h, quenched with 2*N* HCl, and analyzed by GLC using undecane as an internal standard. The products were identified by co-injection with their authentic samples. PhTol-*p* and bis(*p*-tolyl) were formed in 17 and 15% yields, respectively, along with a trace of biphenyl. The product yields did not increase after two additional hours.

*(b) Reaction of trans-Ph(p-Tol)Pd(PEt_3)$_2$ (**14**) with an excess of PhI.* This reaction was carried out according to the representative procedure except that 6 equiv. of PhI was used. PhTol-*p* and biphenyl were formed in 8 and 38% yield, respectively, along with a trace of bis(*p*-tolyl). The product yield did not increase after two additional hours.

*(c) Reaction of trans-[(E)-1-Oct]PhPd(PEt_3)$_2$ (**12**) with an excess of PEt_3.* To the THF solution of *trans*-[(*E*)-1-Oct]PhPd(PEt_3)$_2$ (**12**) obtained according to the representative procedure described above was added 1 or 8 equiv. of PEt_3 in THF. Addition of 1 and 8 equiv. of PEt_3 leads to the formation of (*E*)-1-octenylbenzene (**11**) in 83 and 91% yields, respectively after 1 h.

Reaction of organozinc chlorides with organic iodides catalyzed by "Pd(PR_3)$_2$"

(a) Reaction of p-tolylzinc chloride with phenyl iodide catalyzed by "Pd(PPh_3)$_2$": Representative procedure. To a mixture of 0.218 g (1.0 mmol) of *p*-tolyl iodide and 2 ml of ether was added 1.3 ml (1.60 *M*, 2.0 mmol) of t-butyllithium at −78°C. The mixture was stirred for 1 h at −78°C and then for 1 h at room temperature. The reaction mixture was evaporated, and the residue was dissolved in 2 ml of THF. This solution of *p*-tolyllithium was added to 0.273 g (2.0 mmol) of dry zinc chloride and 2 ml of THF. The mixture was stirred for 1 h at room temperature. This solution, in turn, was added to the THF solution of "Pd(PPh_3)$_2$" prepared by the reaction of $Cl_2Pd(PPh_3)_2$ (35.0 mg, 0.05 mmol) in 2 ml of THF with 0.063 ml (1.60 *M*, 0.1 mmol) of n-BuLi, 0.204 g (1.0 mmol) of phenyl iodide, and 1 ml of THF. The mixture was stirred at room temperature for 0.1 h, quenched with 2*N* HCl, and analyzed by GLC using undecane as an internal standard. 4-Methylbiphenyl, which was identified by co-injection with an authentic sample, was formed in 95% yield. The amounts of biphenyl and bis(*p*-tolyl) were < 0.01 mmol each.

Unless otherwise mentioned, the following experiments were carried out according to the above representative procedure, and the results are summarized in Table 4.

(b) Reaction of (E)-1-octenylzinc chloride with phenyl iodide catalyzed by "Pd(PEt_3)$_2$". This reaction was carried out on a 1 mmol scale according to the representative procedure described above except that the reaction temperature was 50°C. After 3 h, (*E*)-1-octenylbenzene was formed in 65% yield, with 10% of PhI remaining unreacted. The amounts of (7*E*,9*E*)-7,9-hexadecadiene and biphenyl were 0.09 and 0.03 mmol, respectively.

(c) Reaction of 3,3-dimethylbutynylzinc chloride with phenyl iodide catalyzed by "Pd(PEt_3)$_2$". This reaction was carried out according to the representative

procedure described above except that the reaction temperature was 50 ° C. After 12 h, 3,3-dimethylbutynylbenzene was formed in 92% yield. The amounts of biphenyl and 2,2,7,7-tetramethyl-3,5-octadyne were < 0.01 mmol each (1 mmol scale run).

The spectral data of the coupling products are listed below.

4-Methylbiphenyl [19]. ^{1}H NMR (CDCl$_3$, Me$_4$Si): δ 2.38 (s, 3H), 7.2–7.8 (m, 9H) ppm.

4,4'-Dimethylbiphenyl [19]. ^{1}H NMR (CDCl$_3$, Me$_4$Si): δ 2.37 (s, 6H), 7.13 (d, J 8 Hz, 4H), 7.49 (d, J 8 Hz, 4H) ppm.

(5E,7E)-5,7-Tetradecadiene [20]. IR (neat): 2900 (s), 1460 (s), 1375 (s), 727 (m) cm^{-1}: ^{1}H NMR (CDCl$_3$, Me$_4$Si): δ 0.90 (t, J 6 Hz, 6H), 1.1–1.7 (m, 12H), 1.8–2.4 (m, 4H), 5.2–6.7 (m, 4H) ppm.

(7E,9E)-7,9-Hexadecadiene [21]. IR (neat): 2960 (s), 2920 (s), 2850 (s), 1460 (m), 1375 (m), 980 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$, Me$_4$Si): δ 0.88 (t, J 6 Hz, 6H), 1.25 (b.s. 16H), 1.8–2.4 (m, 4H), 4.8–6.2 (m, 4H) ppm.

(5E,7E)-5,7-Dodecadiene [21]. IR (neat): 2960 (s), 2920 (s), 2850 (s), 1460 (m), 1375 (m), 985 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$, Me$_4$Si): δ 0.88 (t, J 6 Hz, 6H), 1.1–1.8 (m, 8H), 1.85–2.5 (m, 4H), 5.3–6.4 (m, 4H) ppm.

3,3-Dimethylbutynylbenzene [22]. IR (neat) 2965 (s), 1595 (m), 1470 (m), 1360 (m), 1285 (m), 1195 (m), 750 (s), 690 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$, Me$_4$Si): δ 1.28 (s, 9H), 7.15–7.8 (m, 5H) ppm.

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