the question, deuterated phosphine complex $Pd[P(C_6D_5)_3]_2(Ph)I$ was prepared.[5] Heating the compound in THF at 50 °C led to exchange between the phenyl and the deuterated phenyls with a degree of migration of 6.3:1.[9] This value was obtained from measuring the relative intensity in the ^1H NMR spectrum[10] of the exchange mixture and is consistent with the expected value of 6:1 calculated on the basis of a random distribution of all the phenyl groups.

There are indications that the exchange products such as **3a** and $Pd[PPh_2(C_6H_4\text{-}p\text{-}OCH_3)]_2(Ph)I$ (**3b**) further undergo exchanges to yield complexes containing coordinated $PPh(C_6H_4\text{-}p\text{-}CH_3)_2$ and $PPh(C_6H_4\text{-}p\text{-}OCH_3)_2$, respectively. In the ^1H NMR spectrum of the exchange products of **1a**, a small doublet at 7.07 ppm (overlapped with the doublet at 7.10 ppm)[11] and a singlet at 2.32 ppm are likely due to the meta and methyl protons of the tolyl group in the coordinated $PPh(C_6H_4\text{-}p\text{-}CH_3)_2$ on the basis of the observation that the corresponding chemical shifts of $Pd[PPh(C_6H_4\text{-}p\text{-}CH_3)_2]_2(Ph)I$ also appear at the same frequencies. Similar results were also observed in the exchange products of **1b**. Further proof for the presence of $PPh(C_6H_4\text{-}p\text{-}OCH_3)_2$ was obtained by the addition of dppe (1.1 equiv) to the exchange products of **1b** followed by separation on silica gel. Three phosphines, PPh_3, $PPh_2(C_6H_4\text{-}p\text{-}OCH_3)$, and $PPh(C_6H_4\text{-}p\text{-}OCH_3)_2$, in a 9:7:1 ratio were isolated.[12]

The exchange reaction is sensitive to air and free phosphine. In the presence of air, an unknown decomposition is dominant and only a complete degassing of the solution prior to heating can stop the side reaction. While the presence of 0.1 equiv of $Pd(PPh_3)_4$ did not influence the exchange rate, the addition of 1 equiv of PPh_3 to the solution of **1** led to a nearly total inhibition of the aryl exchange. Thus, it is reasonable to assume that the dissociation of a phosphine from **1** to give a three-coordinate intermediate is a necessary step for the exchange reaction. Oxidative addition of a P–Ar bond to the metal center in the same intermediate to yield a transient Pd(IV) species, followed by migration of the aryl group originally bound to the palladium to the phosphorus, would complete the exchange reaction.

Although aryl–aryl exchange had not been observed previously, one-way aryl migration from coordinated phosphine to the metal center was implicated in several cobalt-,[13] nickel-,[14] and palladium-mediated[15] reactions. Examples on the closely related oxidative addition of triarylphosphine to low-valent transition-metal complexes were also known.[16] In addition, ortho metalation[17] and the related ortho hydrogen exchange of coordinated triarylphosphine were extensively investigated.[18]

In conclusion, we have demonstrated a facile two-way aryl migration between the metal center and coordinated phosphine in Pd(II) complexes. The generality and detailed mechanism of the exchange in palladium as well as in nickel and platinum systems is currently under investigation. The effect of this reaction on the catalytic reaction is which **1** is involved as catalyst intermediate is also being explored, and the results will be reported shortly.

Acknowledgment. We thank the National Science Council of the Republic of China for support of this research.

(9) The $^{31}P\{^1H\}$ NMR spectrum of the heated solution showed that only a new signal at 22.8 ppm in addition to the original resonance at 22.7 ppm was observed. The new signal was assigned as the signal of coordinated $P(C_6D_5)_2(C_6H_5)$ from the aryl–aryl exchange of $Pd[P(C_6D_5)_3]_2(Ph)I$. For comparison, the ^{31}P resonance of the coordinated PPh_3 in $Pd(PPh_3)_2(Ph)I$ appears at 23.3 ppm. These results indicate that the exchange is a clean reaction.

(10) The resonances of the phenyl bound to palladium appear at 6.59 (d), 6.33 (t), and 6.21 (t) ppm, while the corresponding values of the phenyl bound to phosphorus come at 7.51 (dd), 7.32 (t), and 7.26 (t) ppm.

(11) Both doublets were well separated in acetone-d_6.

(12) To the exchange product mixture (0.23 g, 0.27 mmol) of **1b** was added dppe (0.12 g, 0.30 mmol). The resulting solution was separated on TLC using ethyl acetate/hexane (1/30) as the eluent to give 70.7 mg (0.27 mmol) of PPh_3, 61.0 mg (0.21 mmol) of $PPh_2(C_6H_4\text{-}p\text{-}OCH_3)$, and 9.4 mg (0.03 mmol) of $PPh(C_6H_4\text{-}p\text{-}OCH_3)_2$. The total yield of these monodentate phosphines was 94%. All these species were characterized by NMR and mass spectroscopy.

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Palladium-Catalyzed Coupling of Alkenyl Iodonium Salts with Olefins: A Mild and Stereoselective Heck-Type Reaction Using Hypervalent Iodine

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Hypervalent iodine reagents have been used for carbon–carbon coupling.[1] We now report a palladium-catalyzed variation of this process with phenyl(alkenyl)iodonium salts and various alkenes as exemplified in eq 1. Both Kitamura, Stang et al.,[2] and Ochiai[3] have demonstrated Pd-catalyzed carbonylation of phenyl(alkynyl)- and phenyl(alkenyl)iodonium systems. However extension to olefination is novel and of considerable synthetic potential.[4]

The present coupling reaction (eq 1, Table I) shares in common with the obviously related Heck reaction[5] high yields and transstereoselectivity. A key distinguishing advantage of the hypervalent iodine reaction is that it proceeds at room temperature. Thus polymerization of activated olefins at temperatures in excess of 100 °C as practiced in the Heck reaction is obviated, and this is exemplified by the success with acrolein as an olefinic component[5] (entry 6). Styrene (entries 5 and 9) is noteworthy in that,

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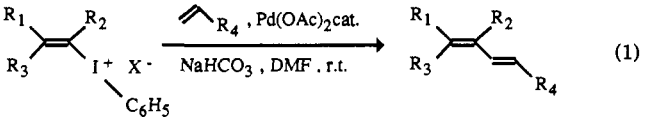
Table I. Alkenyliodonium Salt–Olefin Palladium-Catalyzed Coupling

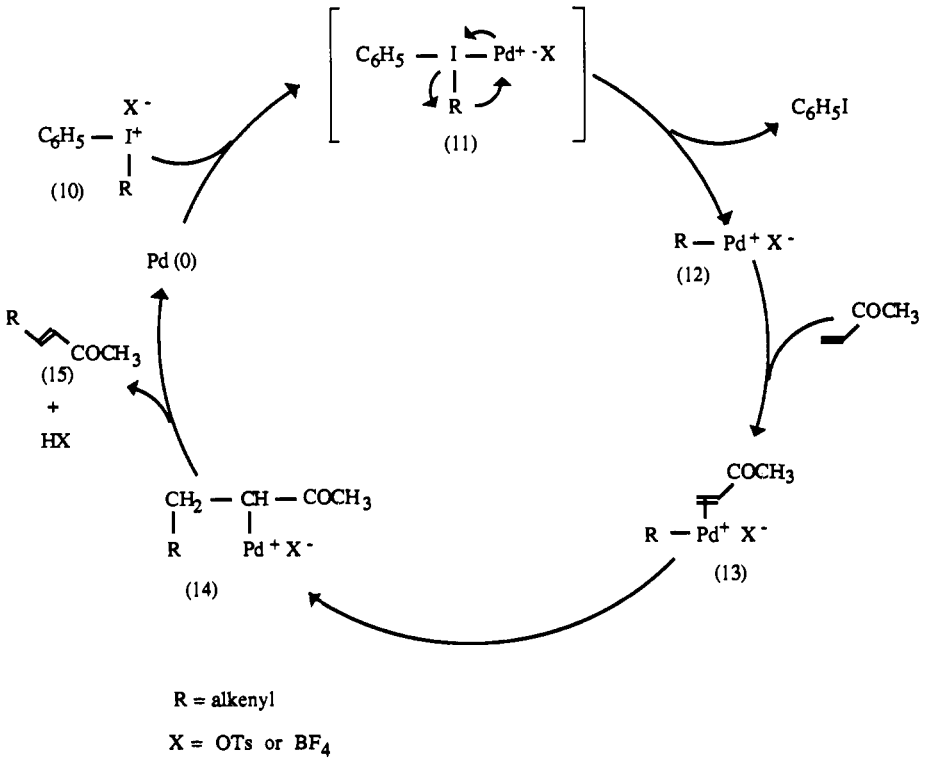


(1)

entry	alkenyliodonium salt	R_1	R_2	R_3	X^-	R_4	time (h)	product[a]	yield[b] (%)
1	**1**	C_6H_5	H	H	BF_4	$COCH_3$	1.5–2	**2a**	73
2	**1a**	C_6H_5	H	H	OTs	$COCH_3$	1.25	**2a**	72
3	**1**	C_6H_5	H	H	BF_4	CO_2CH_3	1–1.5	**2b**	68
4	**1a**	C_6H_5	H	H	OTs	CO_2CH_3	1.5	**2b**	75
5	**1a**	C_6H_5	H	H	OTs	C_6H_5	3.5	**2c**	71
6	**1**	C_6H_5	H	H	BF_4	CHO	1	**2d**	75
7	**3**	1-cyclohexenyl		H	BF_4	$COCH_3$	1.5–2	**4a**	85
8	**3**	1-cyclohexenyl		H	BF_4	CO_2CH_3	1.25	**4b**	80
9	**3**	1-cyclohexenyl		H	BF_4	C_6H_5	12	**4c**	74
10	**5**	OTs	H	H	OTs	$COCH_3$	0.75	**6a**	68
11	**5**	OTs	H	H	OTs	CO_2CH_3	6	**6b**	60
12	**7** (*E*)[c]	OTs	H	*n*-Bu	OTs	$COCH_3$	0.75	**8a**	83
13	**7** (*E*)[c]	OTs	H	*n*-Bu	OTs	CO_2CH_3	1.25	**8b**[d]	75
14	**9** (*Z*)[c]	*n*-Bu	H	OTs	OTs	$COCH_3$	0.5	**10a** (*Z*,*E*:*E*,*E*,3.6:1)[e]	71[f]
15	**9** (*Z*)[c]	*n*-Bu	H	OTs	OTs	CO_2CH_3	1–1.5	**10b** (*Z*,*E*:*E*,*E*,4:1)[e]	64[f]

[a] Characterized through IR, ^1H, and ^{13}C NMR and mass (CI and/or EI) spectroscopy. [b] In a typical reaction, to a stirred mixture of 0.5 mmol alkenyliodonium salt, 5 mol % $Pd(OAc)_2$, was added 5 mmol $NaHCO_3$ in 2 mL of DMF, under Ar, was added 2.5 mmol (excess) of olefin. [A 2:1 ratio of olefin to iodonium salt can be used for activated olefins (e.g., methyl vinyl ketone) without an appreciable effect, but for less active olefins (e.g., styrene) a longer reaction time is needed]. Almost in all cases precipitation of Pd black was observed at the end of the time period given in Table I. Saturated aqueous NH_4Cl was added to the reaction mixture and was followed by extraction with EtOAc. The organic layer was dried with Na_2SO_4, dried under vacuum and purified by flash chromatography (gradient elution, hexanes/ethyl acetate) to give the pure product. [c] Determined from NOE experiments. [d] A trace of the *Z*,*E* isomer was also observed in the ^1H NMR spectra. [e] ^1H NMR ratio. [f] Total yield.

Scheme I



R = alkenyl

X = OTs or BF_4

while it is a useful Heck component, no coupling with the Stille vinyl triflate variation occurs.[6]

The range of alkenyliodonium components (Table I) includes cyclohexenyl (entries 7–9), vinyl tosyloxy (entries 10 and 11), and 2-(tosyloxy)hexenyl (entries 12–15). The high yields, invariable transstereoselectivity, and mild conditions in terms of reaction time and temperature are significant. Vinyl tosyloxy diene products (**6a–10b**, Table I) suggest the potential of these compounds for further synthetic transformations.

The requisite alkenyliodonium salts are readily prepared by the method of Ochiai et al.[3] with the stereoselective reaction of alkenyl trimethylsilanes with $(C_6H_5IO)n/BF_3{\cdot}OEt_2/NaBF_4$ or NaOTs. The stereoisomeric **7** and **9** as well as **5** are made by the method of Koser in which the parent alkyne (in the case of **5**, trimethylsilylacetylene) is reacted with $C_6H_5I(OH)OTs$.[7]

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In considering a general mechanism (Scheme I), it is possible that initially the highly electrophilic alkenyliodonium salt (**10**) reacts with the catalytic species Pd(0) [generated from the reduction of Pd(II) under the reaction conditions[5a]] followed immediately by the reductive elimination of iodobenzene and ligand coupling to yield an alkenyl palladium intermediate (**10** → **11** → **12**). Addition of this to the olefin (via the formation of a π-complex—(**12** → **13** → **14**), followed by reductive elimination would yield the coupled product (**14** → **15**) and Pd(0). Alternatively, it is possible that the initial step is a transmetalation between the alkenyliodonium salt and the palladium(II) catalyst which would also yield an alkenyl palladium intermediate similar to **12**. In fact, similar transmetalations[8] have been proposed for palladium-catalyzed coupling reactions of organomercury(II) compounds[9,5a] and organothallium(III) compounds.[10]

In summary, we consider the process reported herein to be a valuable addition to the Heck-type method because of its mild conditions, the wide range of structural types available, and its ease of operation.

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Supplementary Material Available: Experimental and spectroscopic data for compounds **5**, **7**, **9**, **4a,b**, **6a,b**, **8a,b**, and **10a,b** and NOE data (6 pages). Ordering information is given on any current masthead page.

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Flexible Strategy to Polyfunctional Cyclopentanes. A Synthesis of Mannostatin A

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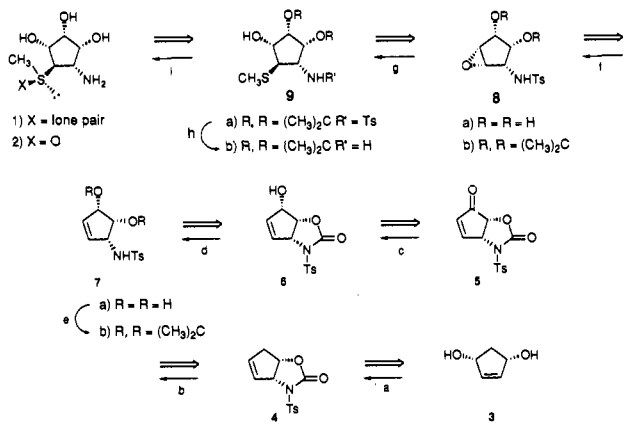
Particular interest has focused on glycosidase inhibitors as potential antiviral agents as well as antimetastatic, antitumor proliferative, or immunoregulatory agents.[1,2] Mannosidase inhibitors in particular have been promulgated as potential anti-HIV agents.[3] Great excitement and activity have revolved around the syntheses of several such inhibitors including nojirimycin,[4] swainsonine,[5,6] castanospermine,[6,7] and 1,5-dideoxy-1,5-imino-D-mannitol.[8] Mannostatin A (**1**) and B (**2**), isolated from *Streptoverticillium verticillus*, are highly specific nontoxic nanomolar inhibitors of α-D-mannosidase and represent the only known carbocyclic, naturally occurring mannosidase inhibitors.[9,10] The density of functionality and rich stereochemistry make such molecules extremely challenging targets for total synthesis. We record a highly flexible strategy for controlled introduction of heteroatoms around a cyclopentane nucleus, an increasingly important goal because of the growing number of cyclopentane analogues of carbohydrates as glycosidase inhibitors.

Scheme I outlines our retrosynthetic analysis, for which the key challenge is the chemo-, regio-, and diastereoselectivity of introduction of three different heteroatom functions on each carbon of a cyclopentane. While an asymmetric version of this synthesis is readily available via one of the scalemic analogues of **3** which derives from enzyme-catalyzed hydrolysis,[11] we chose to attempt to streamline the route by focusing on introducing the chirality

Scheme I. Retrosynthesis and Synthesis of Mannostatin A[a]



[a] (a) TsNCO (2 equiv), THF, add 1.8 mol % $[(iC_3H_7O)_3P]_4Pd$, reflux, 97%; (b) SeO_2, Na_2HPO_4, quartz sand, diglyme, 170 °C, followed by Dess–Martin periodinane, $NaHCO_3$, CH_2Cl_2, room temperature, 65%; (c) $NaBH_4$, $CeCl_3$, CH_3OH, C_2H_5OAc, −5 °C, 83%; (d) K_2CO_3, CH_3OH–H_2O, room temperature, 95%; (e) $(CH_3)_2C(OCH_3)_2$, $(CH_3)_2CO$, CSA, room temperature, 93%; (f) CF_3CO_3H, Na_2HPO_4, CH_2Cl_2, 90%; (g) CH_3SLi, THF, −78 °C to room temperature, 78%; (h) Na, NH_3, 97%; (i) 60% aqueous CF_3CO_2H, 60 °C, 86%.

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