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A Superior Precursor for Palladium(0)-Based Cross-Coupling and Other Catalytic Reactions

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The easily synthesized, easily handled compound Pd(η^3-1-PhC$_3$H$_4$)(η^5-C$_5$H$_5$) (**II**) reacts readily with mono- and bidentate tertiary phosphines to produce the corresponding bis-phosphine palladium(0) complexes in good yields; **II** is thus an excellent precursor, perhaps the most efficacious and reliable available, for the synthesis of palladium(0) cross-coupling catalysts.

Introduction

Palladium(0)-catalyzed Suzuki−Miyaura cross-coupling reactions have revolutionized methodologies for the formation of carbon−carbon bonds.[1] In the general case, an aryl halide ArX (X=Cl, Br, I) reacts catalytically with an arylborate species $[Ar'BY_3]^-$ (Y = halide, alkoxide, etc.) to form the coupled product Ar−Ar′, the most widely accepted catalytic cycle (Scheme 1) typically involving oxidative addition of ArX to a bis-phosphine palladium(0) compound PdL_2 (L = tertiary phosphines) followed by transmetalation and reductive elimination steps.[1]

Unfortunately bis-phosphine palladium(0) compounds are extremely air sensitive and hence difficult to synthesize and store, and preformed bis-phosphine compounds are therefore relatively rarely utilized. Instead a more readily accessible compound such as the relatively poor catalyst $Pd(PPh_3)_4$ is used,[2d,g,k,l] or the phosphine to be employed is added to solutions of precursor palladium(0) compounds such as Pd(dba)$_2$ and Pd$_2$(dba)$_3$ (dba=*trans*,*trans*-dibenzylideneacetone).[3] Regrettably it is now widely recognized that dba is not readily displaced and in fact impedes oxidative addition.[4]

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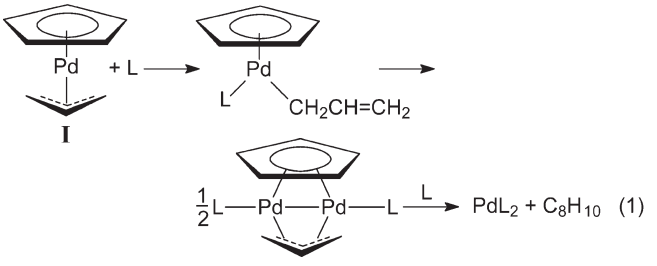
Catalyst solutions are alternatively generated by adding a phosphine to a suspension or solution of a palladium(II) compound such as $Pd(OAc)_2$ or $PdCl_2$, sometimes in the presence of a base, the assumption made being that the palladium(II) salts are efficiently reduced to the desired palladium(0) catalytic precursors.[1] Although suggestions of relevance for a number of reducing processes have appeared for palladium-based catalytic systems, there seems in fact to be a paucity of careful studies establishing the usefulness, general or specific, of any class of reducing agents. Indeed, for most of the phosphine/palladium catalyst systems used as cross-coupling catalysts, there is little or no evidence that reduction is effected either rapidly or completely.

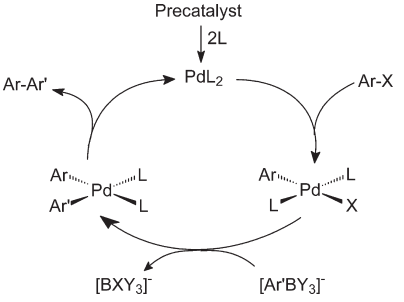
To develop mild conditions under which compounds of the specific stoichiometry PdL_2 may be generated unambiguously, quantitatively, and quickly, we have recently utilized $Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)$[5a] (**I**). This precursor, when heated in the absence of potential ligands, reductively eliminates $C_3H_5-C_5H_5$ as a mixture of isomers and deposits palladium metal.[6] It also reacts with phosphines L as in eq 1 to give, following reductive elimination of $C_3H_5-C_5H_5$, palladium(0) compounds of the types PdL_n ($n = 2-4$);[2f,h,m,p,7] σ-allyl compounds of the type $\eta^5\text{-}C_5H_5Pd(\eta^1\text{-}C_3H_5)L$ and dinuclear species of the type $Pd_2L_2(\mu\text{-}C_5H_5)(\mu\text{-}C_3H_5)$ have often been observed as intermediates.[8]



(1)

Although **I** had been used in this way previously to generate palladium(0) cross-coupling catalysts,[7] a systematic study to determine the optimal conditions for catalyst generation had not previously been carried out and we determined and reported the optimum (i.e., minimum temperature, maximum time required) conditions under which the representative, catalytically very important[1a,b,g,h] compounds PdL_2 (L = PCy_3,[2e,g] $PMeBu^t_2$,[2p] PBu^t_3[2f,m,o]) could be generated cleanly and essentially quantitatively.[9]

SCHEME 1



Unfortunately **I** has its own practical limitations. Although reported to be stable in air for days at room temperature,[5b] we have observed that storage at room temperature can result in the formation of black palladium metal within a day or two.[9] The compound is also very volatile, and attempts to remove solvents from it under reduced pressure often result in significant amounts of the deep red compound appearing in the condensate.[9] Thus **I** does not lend itself to uncomplicated, routine applications in the laboratory.

We therefore set out to investigate the use of the presumably less volatile 1-phenylallyl analogue, $Pd(\eta^3\text{-}1\text{-}PhC_3H_4)(\eta^5\text{-}C_5H_5)$ (**II**),[10a] which is also deep red and hence might be expected to have an electronic structure and reactivities similar to those of **I**. The literature description of **II** suggested that it is thermally more robust than is **I**, and we have found, gratifyingly, that the chemistry of this compound with tertiary phosphines is very similar to that of **I**. Indeed, **II** is not only more readily prepared, handled, and stored, but it is also found often to convert to palladium(0) compounds more rapidly than does **I**. We describe herein a series of experiments in which we explore the chemistry of **II** with a representative series of mono- and bidentate phosphines. We find that the reactions generally involve σ-allylic and dinuclear intermediates, analogous to those in eq 1, but that these convert readily and in good yields to palladium(0) complexes which are characterized both spectroscopically and by their proclivities to undergo oxidative addition reactions with iodobenzene as in Scheme 1. Overall, we find that the 1-phenylallyl derivative **II** is in many ways an ideal precursor for the synthesis of palladium(0) phosphine complexes.

Results and Discussion

The present research involved an assessment of the ease with which palladium(0) complexes PdL_n ($n = 1-3$; L = mono- and bidentate phosphines) can be synthesized via reactions of the potential 1-phenylallyl precursor **II** with the various phosphines. By analogy with the known chemistry of **I** (eq 1), we anticipated that the desired palladium(0) compounds would be formed as in eq 2 via σ-allylic and/or dinuclear intermediates, with concomitant reductive

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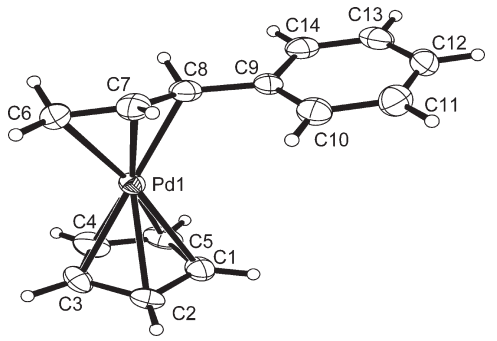
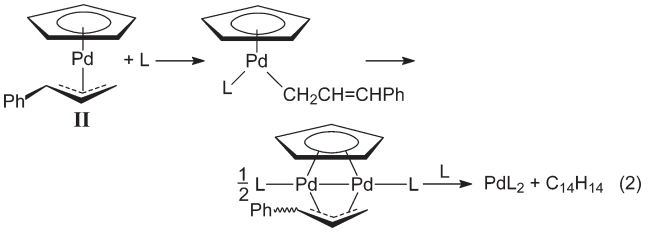


FIGURE 1. Molecular structure of **II** (50% probability level).

TABLE 1. Selected Bond Lengths (Å) for II

bond	bond length (Å)	bond	bond length (Å)
Pd(1)−C(7)	2.072(3)	C(1)−C(2)	1.398(4)
Pd(1)−C(6)	2.123(3)	C(1)−C(5)	1.433(5)
Pd(1)−C(8)	2.174(3)	C(2)−C(3)	1.406(4)
Pd(1)−C(3)	2.293(3)	C(3)−C(4)	1.425(4)
Pd(1)−C(4)	2.303(3)	C(4)−C(5)	1.388(5)
Pd(1)−C(5)	2.313(3)	C(6)−C(7)	1.408(4)
Pd(1)−C(1)	2.353(3)	C(7)−C(8)	1.400(4)
Pd(1)−C(2)	2.403(3)	C(8)−C(9)	1.476(4)

elimination of an isomeric mixture of hydrocarbon products $C_{14}H_{14}$.



However, we anticipated that the presence of the phenyl substituent on **II** would render this compound significantly less volatile than is **I**, and hence easier to prepare and purify. We also hoped that **II** would be thermally and oxidatively more stable than is **I**, but that it would at the same time react reasonably readily with nucleophiles as in eq 2.

Pd(η^3-1-PhC$_3$H$_4$)(η^5-C$_5$H$_5$) (II). Compound **II** was easily obtained in 78% yield as a red, crystalline solid by reaction of [Pd(μ-Cl)(η^3-1-PhC$_3$H$_4$)]$_2$ with NaC$_5$H$_5$,[10] and was characterized by ^{1}H and ^{13}C NMR spectroscopy (see the Experimental Section) and X-ray crystallography. While the structure of **II** has previously been described,[10a] the crystal used here was of a different space group and the previously reported[10a] disorder problem was not observed. The molecular structure is displayed in Figure 1 and selected bond lengths and angles are provided in Table 1. These data and their significance will be discussed below, and complete structural data for **II** are available in the Supporting Information.

Compound **II** was found to have minimal vapor pressure and is also sufficiently robust that it remains unchanged in appearance as a crystalline solid on standing in air at room temperature for several days. In addition, solutions in toluene-d_8 are stable at room temperature in air for at least 24 h, and thus **II** is much more easily synthesized and handled than is **I**.

TABLE 2. Reaction Conditions for the Formation of Pd(0)L$_n$ from II

		time to complete conversion to Pd(0) products[a]		
L	ratio L:Pd	25 °C	50 °C	75 °C
PPh_3	2	> 24 h	5 h < T < 20 h	30 min
$PMePh_2$	2	> 48 h	5 h < T < 24 h	30 min
PCy_3	2	> 48 h	5 h < T < 18 h	1 h
$PMeBu^t_2$	2	> 48 h	45 min	NI
PBu^t_3	2	5 h < T < 24 h	3 h	1 h
dppe	1	> 4 days	> 24 h	3 h
dppe	2	< 5 min	NI	NI
dppp	1	90 min	< 15 min	< 10 min
dppp	2	< 5 min	NI	< 5 min
dppf	1	> 24 h	NI	> 24 h
dppf	2	> 1 h	NI	< 1 h

[a] NI = not investigated

In Situ Generation of Palladium(0) Compounds from Reactions of II with PPh_3, $PMePh_2$, PCy_3, $PMeBu^t_2$, and PBu^t_3. Procedures generally involved treating toluene-d_8 solutions of **II** with the monodentate tertiary phosphines with a view to ascertaining the optimum conditions (minimum time at a reasonably low temperature) under which significant conversions to palladium(0) complexes Pd(0)L$_n$ can be achieved. Where possible, the progress of each reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy, disappearance from the ^{1}H NMR spectra of the strong, singlet η^5-C$_5$H$_5$ resonances of the starting material, and σ-allylic and dinuclear intermediates providing useful criteria with which to monitor the course of the reactions. (^{1}H NMR data for σ-allylic and dinuclear intermediates are listed in Tables 1 and 2 of the Supporting Information.) The identities of the palladium(0) products were further confirmed by oxidative additions with iodobenzene to give the readily identified compounds *trans*-PdPhIL$_2$. The reaction conditions employed and the times required for essentially complete conversions of **II** to palladium(0) products at various temperatures are listed in Table 2.

Table 3 presents ^{31}P chemical shift and ^{31}P−^{31}P coupling constant data for all of the phosphorus-containing species involved, the free phosphines, the σ-allylic and dinuclear intermediates formed as in eq 2, the palladium(0) compounds, and the products of oxidative addition of iodobenzene. Where solubility problems arose, aliquots of reaction mixtures at various stages of completion were taken to dryness and dissolved in C$_6$D$_6$ or CD$_2$Cl$_2$ for NMR studies.

Since the major catalytically active species in cross-coupling reactions are believed to be of the type PdL$_2$,[1] our initial experiments involved phosphine:Pd ratios of 2:1 although 3:1 complexes are known[9,12a] and some systems were also investigated at a phosphine:Pd ratio of 3:1. The ^{1}H NMR spectra of reaction mixtures involving the monodentate phosphines at 25 °C exhibited resonances which were assigned to σ-allylic intermediates on the basis of chemical shifts, coupling constants and 2D NMR experiments (Table 1 of the Supporting Information). The corresponding ^{31}P resonances were then identified by using decoupling experiments and correlations with the ^{1}H spectra. Identification of the ^{31}P resonances of the dinuclear species was a

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TABLE 3. ^{31}P NMR Data for the Free Phosphines, of the σ-Allylic and Dinuclear Intermediates, and of the Palladium(0) Compounds and the Phenylpalladium Products of Oxidative Addition[a]

	chemical shifts δ (lit.)				
phosphine (L)	free L	η^5-CpPd (η^1-PhC$_3$H$_4$)L	Pd$_2$L$_2$(μ-Cp) (μ-PhC$_3$H$_4$)	Pd(0)L$_n$	PdPhIL$_2$[b]
PPh_3	−4.9	45.7	24.3, 26.3 (J = 95 Hz) 22.9, 26.9 (J = 139 Hz)	23.7 (22.6,[12a] toluene-d_8, n = 3)	24.1 (24.3 in $CDCl_3$)[15a]
$PMePh_2$	−25.9	26.2	5.1, 7.5 (J = 107 Hz) 3.9, 6.7 (J = 136 Hz)	1.4 (−4.2,[12a] toluene-d_8, n = 4)	6.9 (11.3 in CD_2Cl_2)[15b]
PCy_3	9.9	55.8	27.1, 33.4 (J = 72 Hz) 22.4, 27.0 (J = 128 Hz)	40.2 (39.2,[9] toluene-d_8, n = 2)	(see text)
$PMeBu^t_2$	12.5	61.7		42.6 (41.9,[9] toluene-d_8, n = 2)	(see text)
PBu^t_3	62.2	97.4		84.8 (84.7,[9] n = 2)	
dppe	−11.6			33.7 (30.4,[12b] THF-d$_8$, n = 2)	34.9, 49.7 (J = 28 Hz) (33.9, 48.9, J = 28 Hz in THF-d_8)[15d]
dppp	−16.5			4.8 (4.0,[12b] THF-d_8, n = 2)	12.3, −8.8 (J = 53 Hz) (12.2, −7.9, J = 54 Hz in THF-d_8)[15e]
dppf	−16.2			8.1 (7.4,[12b] THF-d_8, n = 2)	26.1, 8.7 (J = 34 Hz) (26.2, 8.1, J = 35 Hz in THF-d_8)[15d]

[a] Spectra run in toluene-d_8 with the exception of the dppf compounds which are reported in C_6D_6 and the compounds PdPhIL$_2$ (L = PPh_3, $PMePh_2$, dppe, dppp) which are reported in CD_2Cl_2. [b] The monodentate ligands form *trans*-PdPhIL$_2$, the bidentate ligands *cis*-PdPhI(L-L).

trivial matter because the asymmetry of the 1-phenylallyl groups renders the two phosphines in these compounds nonequivalent as shown in eq 2. Thus the ^{31}P NMR spectra of reaction mixtures generally exhibited pairs of AB quartets of unequal intensity, tentatively attributed to the presence of *syn* and *anti* isomers. For the PPh_3, PCy_3, and $PMeBu^t_2$ systems, species exhibiting coupling constants $^3J_{PP}$ of 95, 72, and 103 Hz, respectively, appeared initially, but species exhibiting larger $^3J_{PP}$ coupling constants, 139, 129, and 136 Hz, respectively, persisted longer in solution.

Unfortunately, because of overlap both of the resonances of the various species with each other and with those of the isomeric products of reductive elimination, it was generally impossible to identify all of the resonances of the dinuclear species in ^{1}H NMR spectra of the reaction mixtures. In an attempt to gain structural information on one system, at least, a solution of **II** in hexanes was stirred for an hour at room temperature with 1 equiv of PPh_3. The resulting precipitate was filtered, washed with hexanes, and dried, and was found by ^{1}H NMR spectroscopy (toluene-d_8 at 25 °C) to consist of a mixture of comparable amounts of the *syn* and *anti* isomers of Pd$_2$(PPh$_3$)$_2$(μ-C$_5$H$_5$)(μ-PhC$_3$H$_4$), with only very weak resonances of the σ-allylic compound and the products of reductive elimination. Analysis of the ^{1}H NMR spectrum made it possible to identify the allylic ligands of the two isomers in the ^{1}H NMR spectrum (Table 2 of the Supporting Information) and to correlate them with the AB quartets in the ^{31}P NMR spectra. The AB quartet with the smaller of the two couplings was identified as the *syn* isomer and the AB quartet with the larger coupling was identified as the *anti* isomer based on $^3J_{HH}$ coupling constants and NOESY experiments. The assignments are further supported by the integration of the proton signals, and the J_{HH} and J_{PH} coupling constants were distinguished utilizing ^{1}H{^{31}P} NMR experiments. The J_{PH} couplings correspond well to other known Pd$_2$L$_2$(μ-C$_5$H$_5$)(μ-C$_3$H$_4$-R) complexes, with smaller J_{PH} couplings for *anti* protons and larger J_{PH} for *syn* protons.[8a,e]

Palladium(0) compounds of PPh_3,[11a] $PMePh_2$,[11a] PCy_3,[9] $PMeBu^t_2$,[9] and PBu^t_3[9] have all been characterized to some extent previously, and Pd(PBu^t_3)$_2$, Pd($PMeBu^t_2$)$_2$, and Pd(PCy_3)$_2$ were identified on the basis of the ^{31}P resonances which agreed well with literature data.[9] The chemical shift observed for the PPh_3 system is also in good agreement for the tris-phosphinepalladium(0) species, Pd(PPh$_3$)$_3$,[12a] but the chemical shift observed for the $PMePh_2$ system is some 5.6 ppm downfield from the resonance reported previously for Pd(PMePh$_2$)$_4$,[12a] the only known palladium(0) species of this ligand. The reason for the discrepancy may lie in the presence in solution of species with various coordination numbers (i.e., 2−4) and which are undergoing intermolecular ligand exchange. What is certain is that we did indeed generate a reactive complex of palladium(0) (see below).

Reactions of **II** with 2 molar equiv of the monodentate phosphines PPh_3, $PMePh_2$, and PCy_3 were slow at room temperature but conversions to palladium(0) products were complete within 1 h at 75 °C (Table 2) albeit with some precipitation of palladium black for the PPh_3 and $PMePh_2$ systems. In contrast, as can be seen, reactions of the bulkier phosphines $PMeBu^t_2$ and PBu^t_3 were found to be much faster. When 3 equiv of PPh_3 or $PMePh_2$ was employed, formation of palladium(0) compounds occurred at 25 °C within 90 and 10 min, respectively, with no observable precipitation of palladium black from either system. The ^{31}P NMR spectrum of the PPh_3 system exhibited a broad singlet at δ 22.8, consistent with the formation of Pd(PPh$_3$)$_3$.[12a] At −80 °C this singlet shifted upfield to δ 24.1 but remained

(11) (a) *Bruker AXS Crystal Structure Analysis Package*: Bruker AXS Inc., Madison, WI, 2000. *SHELXTL*, Version 6.14; Bruker AXS Inc., Madison, WI, 2005. *XPREP*, Version 2005/2; Bruker AXS Inc., Madison, WI, 2005. *SAINT*, Version 7.23A; Bruker AXS Inc., Madison,WI, 2006. *APEX2*, Version 2.0−2; Bruker AXS Inc., Madison, WI. (b) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, UK, 1974; Vol. 4, Table 2.2 A.

(12) (a) Mann, B. E.; Musco, A. *J. Chem. Soc., Dalton Trans.* **1975**, 1673. (b) Broadwood-Strong, G. T. L.; Chaloner, P. A.; Hitchcock, P. B. *Polyhedron* **1993**, *12*, 721.

broad, suggesting that an equilibrium between various Pd(PPh_3)$_n$ species and free PPh_3 may still exist but that exchange was rapid on the NMR time scale. The ^{31}P NMR spectrum of the Pd($PMePh_2$)$_n$ species displayed a broad singlet at δ −1.9, upfield from that produced from 2 equiv of $PMePh_2$. Low-temperature experiments revealed that the same species exist in both the 2 and 3 equiv systems, just in different proportions. At −80 °C, the main Pd($PMePh_2$)$_n$ resonance shifted to δ −1.3, with a weaker singlet at δ 2.8; both were broad.

Except for the PBu^t_3 system, where exchange between free and coordinated PBu^t_3 is sufficiently slow that separate ^{31}P resonances can be observed for PBu^t_3 and Pd(PBu^t_3)$_2$, ^{31}P NMR spectroscopy could not generally be used to assess yields because of rapid exchange between free ligands and the palladium(0) products; separate resonances were generally not observed. However, it was clear in all experiments that, from the very early stages, the ratio of palladium(0) species to free phosphine was high as the averaged chemical shifts observed were considerably closer to those of the ultimate palladium(0) products than to those of the free ligands. Because of exchange problems, the ^{1}H NMR spectra generally yielded little explicit information concerning the extent of formation of the palladium(0) products.

In Situ Generation of Palladium(0) Compounds from Reactions of II with dppe, dppp, and dppf. Bis-phosphinepalladium(0) compounds of dppe,[12b] dppp,[12b] and dppf[12b] have all been characterized previously, and the products obtained from **II** were readily identified spectroscopically. Procedures for the dppe, dppp, and dppf systems were generally the same as those with the monodentate phosphines, and involved treating toluene-d_8 solutions of **II** with solutions of the bidentate phosphines in 1:1 and 2:1 ligand:Pd ratios. Attempts to monitor the reactions by ^{1}H NMR spectroscopy proved futile as NMR spectra of the 1:1 reaction mixtures all exhibited plethorae of overlapping resonances while the 2:1 reactions were completed by the time the NMR spectra were run. However, ^{31}P NMR spectroscopy was very informative. As indicated in Table 2, the ^{31}P chemical shifts of the palladium(0) products formed in each case were very similar to those observed (different solvent) for the 2:1 complexes. The reactions of the 2:1 systems were much faster than were those of the 1:1 systems, but all reactions yielded only the 2:1 products as the major species. Palladium metal precipitated in the 1:1 but not the 2:1 systems.

Comparison of I and II As Precursors for the Generation of Pd(0)L$_n$ (L = PPh_3, PCy_3, $PMeBu^t_2$, PBu^t_3). Having established that **II** is not only easier to handle than is **I** but is also a useful precursor for the synthesis of palladium(0) compounds, we carried out experiments designed to compare directly the reactivities of the two compounds. Thus **I** and **II** were reacted under identical conditions (2:1 ratio, same temperature and concentrations in toluene-d_8) with each of the monodentate phosphines PPh_3, PCy_3, PBu^t_3, and $PMeBu^t_2$. To our surprise, PCy_3 and PBu^t_3 each reacted at comparable rates with both **I** and **II**, forming Pd(PCy_3)$_2$ and P(PBu^t_3)$_2$ within 1 h, respectively, while **II** reacted with PPh_3 to form Pd(PPh_3)$_3$ about twice as fast as did **I**. Furthermore, **II** reacted with $PMeBu^t_2$ to form Pd($PMeBu^t_2$)$_2$ within 45 min at 50 °C while **I** required an hour at 75 °C. Thus **II** is generally of comparable reactivity or is more reactive than is the less thermally stable **I**.

Wondering about the relatively high reactivity of the thermally more stable **II**, we compared the crystal structures of **I**[13a] and **II**. The structure of **I** was reported in 1968, albeit with no esd data and thus detailed comparisons of the two structures may not be warranted. However, **I** was found to assume essentially a sandwich structure with the angle between the planes of the allyl and cyclopentadienyl ligands being 19.5°. The two allylic C−C bond lengths (1.35, 1.36 Å) were identical within the limits of experimental error, and the Pd−C(1,3) distances (2.07, 2.10 Å) were found to be significantly longer than the Pd−C(2) distance (2.04 Å). The Pd−ring distances were longer (average 2.26 Å) but the C−C distances within the ring were normal (average 1.40 Å).

We find that **II** also assumes essentially a sandwich structure, with the angle between the planes of the allyl and cyclopentadienyl ligands being 19.93(22)° and with very similar allylic C−C bond lengths (1.408(4), 1.400(0) Å). However, compared with **I**, the structure of **II** appears to exhibit longer Pd−allyl (Pd−C(6) 2.123(3) Å, Pd−C(7) 2.072(3) Å, Pd−C(8) 2.174(3) Å) and longer Pd−ring bonds (2.293(3), 2.303(3), 2.313(3), 2.353(3), 2.403(3) Å), suggesting generally weaker Pd−ligand bonding in the more reactive **II**. However, as indicated above, the quality of the data for **I** is suspect and the differences may well not be significant.

Possibly pertinent, however, is the observation of pronounced asymmetry in the Pd−allyl bonding in **II**, with the Pd−C(8) bond being significantly longer (by 0.051 Å) than is the Pd−C(6) bond. While a difference of this magnitude for this ligand is not unexpected,[13b,c] the result here is that the metal in **II** binds less strongly at the substituted terminus and hence this position may be more susceptible to attack by phosphines. Thus we wondered if the greater reactivity of **II** might be rationalized in terms of a lower activation energy for initial phosphine attack to give, e.g., σ-allylic intermediates.

Direct NMR comparisons of the initial rates with which **I** and **II** react with phosphines under identical conditions showed, however, a lack of correlation with the comparative data in Table 2. Indeed, the identities of the initially formed intermediates varied, depending on the phosphine, suggesting that the reactions are very complicated and even that different mechanisms may be in play with the different ligand systems as has been noted for reactions of the compounds M(η^3-C_3H_5)(η^5-C_5H_5) (M = Ni, Pd) with phosphites P(OR)$_3$ (R = Et, Ph).[14] We suspect, therefore, that highly asymmetric η^3-allyl binding in the various intermediates may account for the high reactivity of **II**.

Oxidative Addition of PhI to PdL$_n$ Generated in Situ from II. As noted above, the ^{31}P chemical shifts of certain of the palladium(0) products differed somewhat from literature values, and while the differences could be attributed to combinations of solvent and temperature effects, experimental error, and/or the presence of small amounts of free ligands giving rise to exchange phenomena, we felt it prudent to demonstrate that our products would take part in the expected stereotypical

(13) (a) Minasyants, M. Kh.; Struchkov, Y. T. *J. Struct. Chem.* **1968**, *9*, 406. For recent examples of η^3-1-phenylallyl-Pd structures, see: (b) Marion, N.; Navarro, O.; Mei, J.; Stevens, E. D.; Scott, N. M.; Nolan, S. P. *J. Am. Chem. Soc.* **2006**, *128*, 4101. (c) Pérez, S.; López, C.; Bosque, R.; Solans, X.; Font-Bardía, M.; Roig, A.; Molins, E.; van Leeuwen, P. W. N. M.; van Strijdonck, G. P. F.; Freixa, Z. *Organometallics* **2008**, *27*, 4288.

(14) Harder, V.; Werner, H. *Helv. Chim. Acta* **1973**, *56*, 549.

oxidative addition reactions of iodobenzene to give high yields of the corresponding palladium(II) compounds *cis*- or *trans*-$PdPhIL_2$. Most of the latter are known compounds and were identified as such spectroscopically on the basis of appropriate phosphine ligand resonances and of readily distinguished Pd−Ph resonances and/or virtual triplet methyl and *tert*-butyl resonances in the ^1H NMR spectra.

The oxidative addition study involved reacting samples of newly formed PdL_2 in situ with 4 equiv of iodobenzene in toluene-d_8 at 25 °C, the reactions being deemed complete when the ^{31}P resonances of the PdL_2 species had converted completely to the resonances of the corresponding phenylpalladium(II) compound. For the PPh_3 system in the presence of both 2 and 3 equiv of ligand, a beige solid precipitated from the toluene-d_8 solution within minutes and its NMR spectrum had to be obtained in CD_2Cl_2 solution where a ^{31}P resonance at δ 24.1 was consistent with the formation of *trans*-$PdPhI(PPh_3)_2$.[15a] Oxidative addition was also successful with the $PMePh_2$ system in the presence of both 2 and 3 equiv of $PMePh_2$. As with $Pd(PPh_3)_3$, *trans*-$PdPhI(PMePh_2)_2$ precipitated from the toluene-d_8 solution within 3 h, and while the ^{31}P resonance chemical shift, δ 6.9, was significantly upfield from the literature reported value of δ 11.3[15b] (both in CD_2Cl_2), the identity of the species was confirmed by observation of a virtual methyl triplet for the $PMePh_2$ ligand at δ 1.65 (6H, J 3.1 Hz) and of Pd−Ph resonances at δ 6.59 (3H, m) and δ 6.78 (2H, m).

The formation of *trans*-$PdPhI(PCy_3)_2$ occurred within minutes at 25 °C, and although this compound has been reported previously,[7a,15c] no NMR data were provided. However, a dominant singlet in the ^{31}P NMR spectrum at δ 21.0 (toluene-d_8) is very similar to the chemical shift of the bromo analogue (δ 20.6).[15c] In addition, Pd−Ph resonances were observed at δ 6.87 (1H, t, J = 7.3 Hz), δ 6.99 (2H, t, J = 7.3 Hz), and δ 7.56 (2H, d, J = 7.3 Hz), similar to those of *trans*-$PdPdPhBr(PCy_3)_2$.[15c] The compound *trans*-$PdPhI(PMeBu^t{}_2)_2$ does not be appear to have been reported previously and thus no precedents for ^1H or ^{31}P NMR data could be found. Oxidative addition of iodobenzene to $Pd(PMeBu^t{}_2)_2$ occurred within minutes at 25 °C, producing a compound that was extremely soluble in all solvents tried and hence was difficult to purify. However, a single ^{31}P resonance was observed, at δ 27.2, as were Pd−Ph resonances at δ 6.87 (1H, tt, J = 7.2, 1.2 Hz), δ 6.92 (2H, t, J = 7.2 Hz), and δ 7.32 (2H, dd, J = 7.9, 1.2 Hz), and virtual Bu^t and Me triplets at δ 1.40 (36H, t, J = 6.8 Hz) and δ 0.23 (6H, t, J = 3.0 Hz), respectively, in the ^1H NMR spectra. These data are all consistent with identification of the product as *trans*-$PdPhI(PMeBu^t{}_2)_2$.

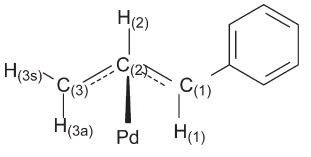
For all three bidentate ligands investigated, the oxidative addition reactions were relatively slow. Thus $Pd(dppe)_2$ and $Pd(dppp)_2$ required several minutes at 75 °C while $Pd(dppf)_2$, which was insoluble in toluene, was reacted in THF overnight at 25 °C. In all cases, the previously reported[15d,e] compounds *cis*-PdPhIL formed cleanly and were readily identified by the mutually coupled doublets in the ^{31}P NMR spectra. For L = dppe, Pd−Ph resonances at δ 6.66 (1H, m), δ 6.72 (2H, m), and δ 7.04 (2H, m) further confirmed the oxidative addition product. The Pd−Ph resonances for L = dppp and dppf were obscured by other Ph resonances.

Summary. The compound $Pd(\eta^3\text{-}1\text{-}PhC_3H_4)(\eta^5\text{-}C_5H_5)$ (**II**) is readily synthesized, purified, and stored, and reacts rapidly and cleanly with mono- and bidentate tertiary phosphines to produce the corresponding palladium(0) complexes which react in turn with iodobenzene to form in good yields the corresponding phenylpalladium(II) products of oxidative addition. Compound **II** thus avoids the disadvantages of previously used precursors such as $Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)$ (**I**) (thermally labile, highly volatile), $Pd(PPh_3)_{3,4}$ (low activity), $Pd(dba)_2$ or $Pd_2(dba)_3$ (dba is not completely replaced by tertiary phosphines and inhibits oxidative addition), and palladium(II) salts (the extent to which Pd(II) is reduced to Pd(0) is generally unknown), and is perhaps the most effective and reliable precursor available for the synthesis of a range of palladium(0) cross-coupling catalysts.

Experimental Section

All syntheses were carried out under a dry, deoxygenated argon atmosphere with standard Schlenk line techniques. Argon was deoxygenated by passage through a heated column of BASF copper catalyst and then dried by passing through a column of 4 Å molecular sieves. Handling and storage of air-sensitive compounds were carried out in a glovebox and NMR spectra were recorded on 500 or 600 MHz spectrometers. ^1H and ^{13}C NMR data were referenced to TMS via the residual proton signals of the deuterated solvents, ^{31}P NMR spectra with respect to external 85% H_3PO_4. For COSY experiments, the standard gradient enhanced COSY-90 protocol (256 increments, 1 scan per increment) was used. For NOESY experiments, the standard TPPI phase sensitive version (256 increments, 2 scans per increment) and gradient pulse were used during the mixing time (0.4 s). In many cases, yields of products were determined from the ^{31}P NMR spectra by using a solution of tetraoctylphosphonium bromide in a capillary as a standard.

Toluene-d_8 and benzene-d_6 were degassed under vacuum and dried by passage through a small column of activated alumina before being stored over 4A molecular sieves. The phosphines PPh_3, $PMePh_2$, PCy_3, $PMeBu^t{}_2$, $PBu^t{}_3$, 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp), and 1,1′-bis(diphenylphosphino)ferrocene (dppf) were used as received, while **I**[9] and **II**[10a] were prepared as in the literature. Compound **II**[10a] was readily recrystallized from hexanes, providing crystals suitable for X-ray crystallographic study. ^1H NMR spectrum (600 MHz, toluene-d_8) δ 2.16 (d, J = 10.5 Hz, 1H, H(3a)), 3.36 (d, J = 6.1 Hz, 1H, H(3s)), 3.84 (d, J = 9.8 Hz, 1H, H(1)), 5.14 (ddd, J = 6.1, 9.8, 10.5 Hz, 1H, H(2)), 5.63 (s, 5H, C_5H_5), 6.98−7.03 (m, 3H, Ph), 7.24−7.27 (m, 2H, Ph). ^{13}C NMR (toluene-d_8) δ 42.8 (C(3)), 68.3 (C(1)), 92.1 (C(2)), 95.2 (C_5H_5), 126.7 (*p*-C), 126.9 (*o*-C), 137.44 (*m*-C), 148.8 (*i*-C).



In Situ Generation of Pd(0)L_n from II. To maximize the precision with which reactants were combined in these experiments, standard solutions of **II** and of the various phosphines in toluene-d_8 were utilized. In a typical experiment, a solution of

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10 mg of **II** (3.4×10^{-5} mol) in 0.25 mL of toluene-d_8 was combined with a solution containing 6.8×10^{-5} mol of a phosphine L in 0.25 mL of toluene-d_8, and the mixture was monitored by ^{1}H and/or ^{31}P NMR spectroscopy at 25 °C for several hours or longer as necessary. Alternatively the sample was placed in an oil bath at 50 or 75 °C and periodically cooled to 25 °C for NMR spectra to be run. Reactions were carried out in this way with 2:1 ligand:Pd ratios of PPh_3, $PMePh_2$, PCy_3, $PMeBu^t_2$, PBu^t_3, dppe, dppp, and dppf, 3:1 ligand:Pd ratios of PPh_3 and $PMePh_2$, and 1:1 ligand:Pd ratios of dppe, dppp, and dppf. Table 2 summarizes the times required for essentially complete conversions of **II** and the various allylic intermediates to the palladium(0) products under these conditions.

Oxidative Addition of Iodobenzene to PdL$_n$ Generated in Situ from II. In a typical experiment, a palladium(0) compound was generated as above and a 4-fold molar excess of iodobenzene ($15\,\mu$L, 1.35×10^{-4} mol) was added to the solution. The reaction mixture was then monitored at 25 °C by ^{1}H NMR, ^{31}P NMR, COSY, and, when appropriate, ^{31}P−^{31}P correlation spectroscopy. For L=PPh_3 and $PMePh_2$, the 3:1 ligand:Pd systems were also investigated.

When L = PPh_3, $PMePh_2$, dppe, and dppp, the products precipitated from the toluene-d_8 solutions and were collected and redissolved in CD_2Cl_2 for identification. When L = PCy_3 and $PMeBu^t_2$, the products remained in solution and were identified and quantified directly; in these cases yields were found to be 99% based on a tetraoctylphosphonium bromide standard. When L = dppf, Pd(dppf)$_2$ precipitated over time from both toluene-d_8 and C_6D_6 solutions and was isolated and then reacted with PhI in THF. The solvent was removed under reduced pressure after 18 h of stirring at 25 °C and the residue was dissolved in C_6D_6.

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Supporting Information Available: ^{1}H NMR data for σ-allylic compounds η^5-CpPd(η^1-PhC_3H_4)L and dinuclear compounds $Pd_2L_2(\mu$-Cp)(μ-PhC_3H_4). Complete crystallographic details for Pd(η^3-1-PhC_3H_4)(η^5-C_5H_5) (**II**), showing thermal ellipsoid figures and complete numbering schemes, tables of positional thermal parameters, and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.