C–C Coupling

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Phosphane-Functionalized Cycloheptatrienyl–Cyclopentadienyl Titanium Sandwich Complexes: Phosphorus Ligands with an Integrated Reducing Agent for Palladium(0) Catalyst Generation**

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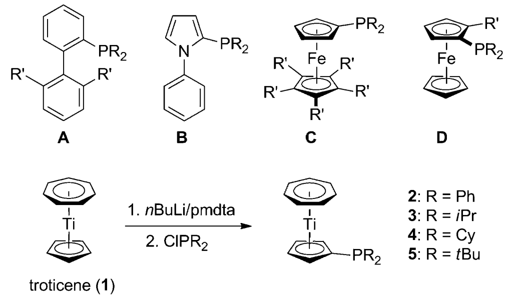
The Nobel prize winning[1] palladium-catalyzed cross-coupling methodology has become ubiquitous and indispensable for the formation of carbon–carbon and carbon–heteroatom bonds in organic synthesis and materials science.[2,3] The most common ligands employed in combination with a suitable palladium(0) or palladium(II) complex are phosphane-based, with Buchwald's biaryl and Beller's N-arylpyrrolyl (or indolyl) dialkylphosphanes of the type **A** and **B**, respectively, representing particularly prominent classes of electron-rich phosphorus ligands (Scheme 1).[4,5] Ferrocenyl mono- and diphosphanes have also become firmly established as ancillary ligands for transition metal catalyzed cross-couplings,[6] and sterically demanding phosphanes such as **C** and **D** have been used for numerous C–C, C–N, and C–O bond forming reactions.[7,8]



Scheme 1. Selected monophosphane ligands for palladium-catalyzed cross-coupling reactions. Preparation of troticenyl phosphanes. Cy = cyclohexyl, pmdta = *N*,*N'*,*N'*,*N''*,*N''*-pentamethyldiethylenetriamine.

Another class of phosphorus ligands derived from the cycloheptatrienyl–cyclopentadienyl (Cht-Cp) titanium sandwich moiety (troticene; **1**) was recently introduced by our group,[9] and the troticenyl monophosphanes **2** (R = Ph) and **3** (R = *i*Pr) were initially prepared by the reduction of the corresponding half-sandwich complexes $[(\eta^5\text{-C}_5\text{H}_4\text{PR}_2)\text{TiCl}_3]$ with magnesium in the presence of cycloheptatriene.[10] These phosphanes can be accessed more conveniently by treatment of troticene (**1**) with *n*-butyl lithium in the presence of *N*,*N'*,*N'*,*N''*,*N''*-pentamethyldiethylenetriamine (pmdta), and the resulting lithium complex $[(\eta^7\text{-C}_7\text{H}_7)\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{Li}\cdot\text{pmdta})]$ allows selective phosphane functionalization of **1** at the five-membered ring by reaction with chlorophosphanes (ClPR_2; Scheme 1).[11]

With **2** and **3** in hand, a few rhodium(I), platinum(II), and gold(I) complexes were isolated and structurally characterized,[10,11] and none of them showed any evidence for secondary interactions involving the titanium atom, despite a valence electron count of 16 for the sandwich moiety. In contrast, weak intramolecular interactions were found for metal complexes of the heavier group 4 analogues $[(\eta^7\text{-C}_7\text{H}_7)\text{M}(\eta^5\text{-C}_5\text{H}_4\text{PR}_2)]$ (M = Zr, Hf; R = Ph, *i*Pr), which can also dimerize in the solid state through weak intermolecular phosphorus–metal contacts.[10,12] These findings are in agreement with the reactivity of the unaltered Cht-Cp sandwich complexes $[(\eta^7\text{-C}_7\text{H}_7)\text{M}(\eta^5\text{-C}_5\text{H}_5)]$ (M = Ti, Zr, Hf), where only the zirconium and hafnium derivatives are susceptible to coordination of additional two-electron-donor ligands such as isocyanides, phosphanes, and N-heterocyclic carbenes.[9,13,14] In view of these results, we envisaged that troticenyl phosphanes might act as innocent ligands in organotransition-metal catalysis, with the sandwich moiety merely acting as a more bulky ferrocene analogue.[15] This assumption, however, was drastically refuted by the study reported herein.

Since cyclohexyl (Cy) and *tert*-butyl (*t*Bu) groups represent the favorite substituents (R) in the ligands **A**–**D**, the corresponding phosphanes **4** and **5** were synthesized as green crystalline solids in approximately 80 % yield according to the established procedure by use of ClPCy_2 and $\text{ClP}t\text{Bu}_2$, respectively (Scheme 1).[11] The ^{1}H and ^{13}C NMR spectra are in agreement with exclusive substitution at the Cp ring, and the ^{31}P NMR spectra give rise to signals at $\delta = -4.7$ (**4**) and 32.2 ppm (**5**), which is in agreement with the values reported for the analogous ferrocenes $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\eta^5\text{-C}_5\text{H}_4\text{PR}_2)]$ (M = Cy, *t*Bu).[7b,16] The molecular structures of **4** and **5** were additionally confirmed by X-ray diffraction analysis (Figure 1). Both compounds crystallize with four independent molecules in the asymmetric unit with very similar structural characteristics (see the Supporting Information), which closely resemble those in many other troticene derivatives.[9–11]

To exploit the potential of **4** and **5** as ancillary ligands in metal-catalyzed reactions, the Suzuki–Miyaura coupling

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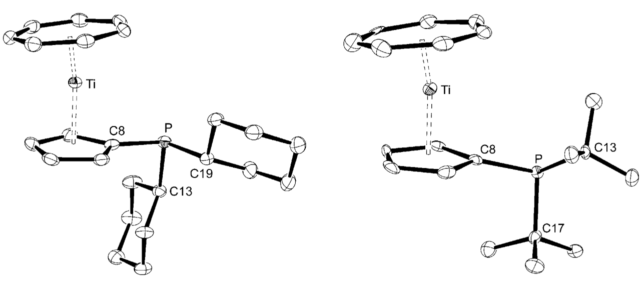
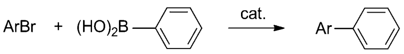


Figure 1. ORTEP drawings of one of the four independent molecules of **4** (left) and **5** (right) with thermal displacement parameters drawn at 50% probability.[31]

between aryl bromides and phenyl boronic acid was chosen as a test reaction. Initial screening of various bases and palladium precursors (see the Supporting Information) indicated optimum performance for palladium(II) acetate, [Pd(OAc)$_2$], in toluene together with potassium hydroxide as the base. Under the reaction conditions summarized in Table 1 (toluene, $T = 100$ °C, 1 mol% Pd, L:Pd ratio = 2), very rapid conversions and high yields of isolated products were obtained for less sterically demanding, unactivated aryl bromides (reaction times ca. 1 min, entries 1–4). Fast coupling was also observed for the more hindered substrates such as mesityl and 2,4,6-triisopropylphenyl bromide (entries 5 and 8), thus providing high yields (≥ 90%) in the case of **4**. For the last two substrates, the reactions were also accomplished in a satisfactory manner upon lowering the catalyst concentration to 0.1 (entries 6 and 9) and 0.01 mol% (entries 7 and 10), and it is particularly noteworthy that 2,4,6-triisopropyl-1,1′-biphenyl was isolated, after 60 minutes, in 94% yield in the presence of 0.1 mol% Pd(OAc)$_2$, thus indicating remarkably fast coupling in comparison with related catalyst systems.[4b]

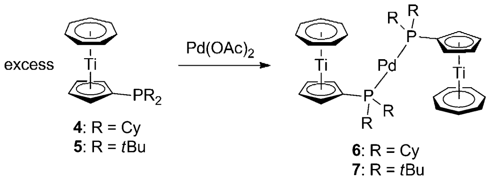
Table 1: Suzuki–Miyaura coupling of aryl bromides with phenyl boronic acid catalyzed by Pd(OAc)$_2$ in combination with the troticenyl phosphanes **4** or **5**.[a]



Entry	Ar	*t* [min]		Conv. [%]		Yield [%]	
		4	**5**	**4**	**5**	**4**	**5**
1	Ph	1	1	100	100	93	90
2	4-MeC$_6$H$_4$	1	1	100	100	90	88
3	4-MeOC$_6$H$_4$	1	1	100	100	92	98
4	4-*t*BuC$_6$H$_4$	1	1	100	100	95	88
5	2,4,6-Me$_3$C$_6$H$_2$	5	5	97	98	90	80
6[b]		5	10	99	99	95	95
7[c]		60	20	72	97	69	92
8	2,4,6-*i*Pr$_3$C$_6$H$_2$	60	10	99	91	99	81
9[b]		60	60	98	76	94	74
10[c]		180	180	71	74	69	70

[a] Pd(OAc)$_2$ (10^{-5} mol, 1 mol%), **4** or **5** (2×10^{-5} mol, 2 mol%), ArBr (1 mmol), PhB(OH)$_2$ (2 mmol), KOH (2 mmol), toluene (1.5 mL), *n*-decane (0.050 mL), $T = 100$ °C. The conversion was monitored by GC with *n*-decane as an internal standard. The yields were determined after isolation of the pure products by column chromatography. [b] 0.1 mol% Pd(OAc)$_2$. [c] 0.01 mol% Pd(OAc)$_2$.

We assumed that the short reaction times in Table 1 indicate fast generation of a catalytically active species and therefore sought to isolate the palladium(0) complexes from the reactions of Pd(OAc)$_2$ with two equivalents of either **4** or **5** in toluene; the complexes [Pd(**4**)$_2$] (**6**) and [Pd(**5**)$_2$] (**7**) resulted as dark green solids in approximately 50% yield after stirring at room temperature for 3 hours (Scheme 2). The formation of **6** and **7** was unequivocally confirmed by NMR spectroscopy, for example, by observation of the ^{31}P NMR chemical shifts at significantly lower field in comparison with those of the free ligands (**6**: $\delta = 23.8$ ppm, $\Delta\delta = 28.5$ ppm; **7**: $\delta = 57.9$ ppm, $\Delta\delta = 25.7$ ppm).



Scheme 2. Preparation of palladium(0) diphosphane complexes.

The molecular structures were additionally established by X-ray diffraction analyses, thus revealing the expected formation of linear diphosphane complexes with Pd-P bond lengths similar to those reported for other [Pd(PR$_3$)$_2$] systems (Figure 2).[17] Both structures exhibit a couple of unremarkable intramolecular C-H···Pd van der Waals contacts of about 2.9 Å, with the shortest distances involving the C$_7$H$_7$ ring in **6** (Pd-H7 = 2.84 Å) and a *tert*-butyl group in **7** (Pd-H40B = 2.89 Å).[17b–d] The structural parameters of the troticene units in **6** and **7** are similar to those in the free phosphane ligands **4** and **5** and in other troticene derivatives.[9–11]

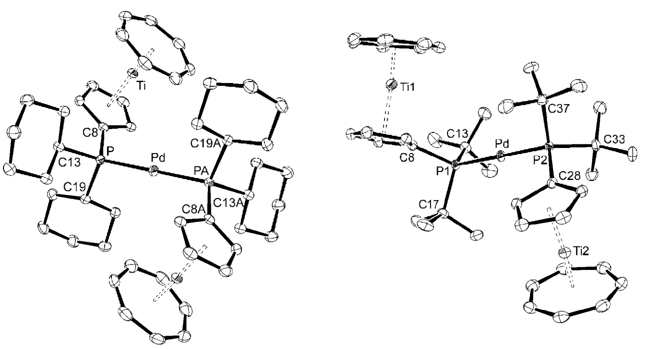
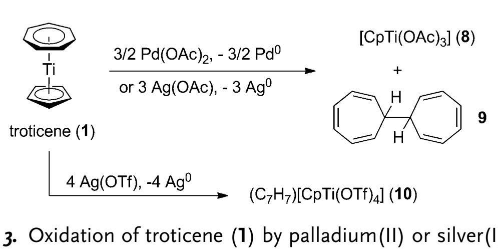


Figure 2. ORTEP drawings of **6** (left) and **7** (right) with thermal displacement parameters drawn at 50% probability. **6** displays crystallographic inversion symmetry. Selected bond lengths [Å] and angles [°] for **6**: Pd–P 2.2648(4), P-Pd-PA 180.0; for **7**: Pd–P1 2.2682(5), Pd–P2 2.2760(5), P1-Pd-P2 179.06(2).[31]

It should be noted that numerous complexes of the type [Pd(PR$_3$)$_2$] were previously prepared by the reaction of tertiary phosphanes with palladium(0) complexes such as [Pd(dba)$_2$] or [Pd$_2$(dba)$_3$] (dba = dibenzylideneacetone)[17bc,18] or with suitable palladium(II) precursors such as [Pd(η^3-C_3H_5)(η^5-C_5H_5)],[19] [Pd(η^3-1-PhC_3H_4)(η^5-C_5H_5)],[17e] [(tmeda)PdMe_2],[20] [Pd(η^3-2-methylallyl)Cl]$_2$,[21] and [(η^2:η^2-1,5-octadiene)PdBr_2],[22] which provide palladium(0) by reductive elimination steps. For palladium(II) salts such as Pd(OAc)$_2$, however, the phosphane itself has to act as the reducing agent with formation of the corresponding phosphane oxide.[23] The system Pd(OAc)$_2$/PPh_3 was particularly well studied, and it was suggested that the intermediate palladium(II) complex [Pd(OAc)$_2$(PPh_3)$_2$] slowly rearranges through an intramolecular mechanism to form initially the palladate(0) [Pd(PPh_3)(OAc)]$^-$ and the phosphonium ion [Ph_3P(OAc)]$^+$, which are subsequently converted into the catalytically active species [Pd(PPh_3)$_2$(OAc)]$^-$ and Ph_3PO by reaction with excess phosphane or residual water, respectively. In contrast, a very recent study involving [Pd(OAc)$_2$(PCy_3)$_2$] showed that this complex cannot be reduced to [Pd(PCy_3)$_2$] in the presence of an excess of PCy_3, but follows a base-promoted pathway to form Cy_3PO and a monophosphane-palladium(0) species, which is trapped in the presence of PhBr and water to form the dinuclear acetato- and hydroxo-bridged complex [{(Cy_3P)Pd(Ph)}$_2$(μ-OAc)(μ-OH)].[24]

To elucidate a possible mechanism for the palladium reduction by **4** and **5**, the reaction of Pd(OAc)$_2$ with two equivalents of the phosphane ligand was monitored by NMR spectroscopy in [D_8]toluene solution. The ^{31}P NMR spectra showed rapid formation of the corresponding palladium(0) complexes with no indication of phosphane oxide formation, while the ^{1}H NMR spectrum showed characteristic multiplets in a 2:2:2:1 ratio at $\delta = 6.54$, 6.11, 5.22 and 2.03 ppm, which point to the formation of a cycloheptatriene species. It was therefore supposed that the redox process for palladium(0) generation might involve the troticene rather than the phosphane moiety. Accordingly, **1** was treated with excess Pd(OAc)$_2$ in CH_2Cl_2, thus instantaneously furnishing a brownish precipitate of elemental palladium. Filtration and evaporation of the reaction mixture gave a yellow solid, from which 7,7′-bi-1,3,5-cycloheptatriene (**9**; ditropyl) was isolated by extraction with *n*-pentane,[25] and the remaining solid was identified as practically pure [(η^5-C_5H_5)Ti(OAc)$_3$] (**8**) by NMR spectroscopy and X-ray structure determination (Scheme 3).[26]



Scheme 3. Oxidation of troticene (**1**) by palladium(II) or silver(I) acetate and by silver trifluoromethanesulfonate (AgOTf).

Since it has been demonstrated several times that the substantially covalently bound Cht ligand in **1** is better conceived as a −3 ligand rather than a +1 ligand,[9] the formation of **8** and **9** can be formally described as an oxidation process, in which the trinegative Cht ligand delivers three electrons to afford the neutral C_7H_7 radical and subsequently its dimer (C_7H_7)$_2$ (**9**). Hence, assignment of a formal +4 oxidation state to the titanium atom in **1** gives a tricationic (CpTi)$^{3+}$ fragment, which furnishes **8** by coordination of three acetate ions. This oxidation can also be accomplished with silver(I) acetate, which reacts cleanly with **1** in a 1:3 ratio as shown in Scheme 3. It should be noted that comparison of the formal redox potential of the tropylium ion $C_7H_7^+$ (e. g. $E^{0\prime} = -0.65$ V in CH_3CN)[27] with those of the Ag^+/Ag and Pd^{2+}/Pd couples suggests that further oxidation of ditropyl (**9**) should occur in the presence of Ag(OAc) or Pd(OAc)$_2$. However, this process, which involves C–C bond cleavage, seems to be unfavorable under these reaction conditions, since no indication of 2,4,6-cycloheptatrienyl acetate[28] formation was found by treatment of **9** (or **1**) with a large excess of metal acetate.

In contrast, four-electron oxidation of **1** can indeed be accomplished by use of silver(I) trifluoromethanesulfonate (triflate) [AgOTf], in CH_2Cl_2, and tropylium tetrakis(trifluoromethanesulfonato)titanate(IV) (**10**) can be isolated in high yield (81%, Scheme 3). This salt is composed of (C_7H_7)$^+$ cations and [CpTi(OTf)$_4$]$^-$ anions, and the structure of the latter is best described as a pseudosquare pyramid with the η^5-C_5H_5 ligand in the apical position and with the four CF_3SO_3-κO ligands forming the basal plane (Figure 3). We believe that the different reactivity of **1** towards AgOAc and AgOTf can be ascribed to the different nature of the two counterions.[27] Whereas the acetate can be regarded as a relatively strongly coordinating anion, which binds to the Ti atom in a bidentate fashion and would afford a covalent ester with the tropylium cation, the triflate anion is a more weakly coordinating anion and therefore capable of forming a thermodynamically favorable tropylium salt. Thereby, the high electrophilicity of the cyclopentadienyl–titanium fragment will require coordination of four triflate ions and consequently result in the formation of the ate-complex **10**.

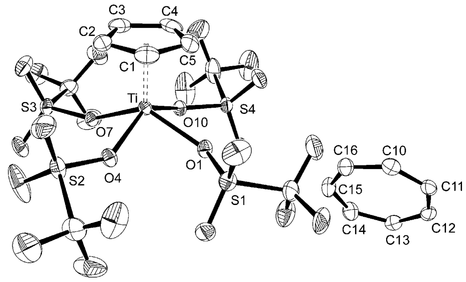


Figure 3. ORTEP drawing of **10** with thermal displacement parameters drawn at 50% probability. Selected bond lengths [Å] and angles [°]: Ti–O1 2.017(2), Ti–O4 2.005(2), Ti–O7 2.001(2), Ti–O10 1.963(2); O1-Ti-O7 138.68(8), O4-Ti-O10 133.34(8).[31]

Considering the stoichiometry of the above redox process (Scheme 3), the reactions between the phosphanes **4** and **5** and Pd(OAc)$_2$ were repeated with an L:Pd ratio of 8:3 (2.67-fold phosphane excess according to a three-electron redox process with 0.67 equiv of L providing two electrons). In fact, the palladium(0) complexes were isolated in significantly higher yields of 70% (**6**) and 78% (**7**); Scheme 2). We were able to confirm that these palladium(0) species are indeed able to serve as (pre-)catalysts for Suzuki–Miyaura coupling of mesityl and 2,4,6-triisopropylphenyl bromide with phenyl boronic acid, and these reactions proceed at a similar rate under the reaction conditions used for $Pd(OAc)_2$ in combination with the phosphanes **4** and **5**.[29] It should be noted, however, that these results do not imply that the isolable L_2Pd^0 complexes **6** and **7** themselves represent the catalytically active species, since the corresponding adducts L_1Pd^0 are usually considered to be the active catalysts for many phosphane/palladium systems, and their formation can be rationalized by an equilibrium between the L_2Pd^0 and L_1Pd^0 species.[2,30] Furthermore, variation of the L:Pd ratio from 2.0 (as shown in Table 1) to 2.67 and 1.67 (see the Supporting Information)[29] did not reveal a clear impact on the catalytic performance, so that, at this stage, we are unable to provide clear evidence for L_2Pd^0 or L_1Pd^0 species operating as the active catalysts.

In conclusion, a new type of phosphane ligand has been introduced, and the cycloheptatrienyl–cyclopentadienyl titanium fragment serves as an integrated reducing agent. The sandwich moiety is able to provide three or four electrons depending on the oxidant. Consequently, palladium(0) species are efficiently formed from $Pd(OAc)_2$ in the presence of the phosphanes **4** and **5**, which results in exceptionally short reaction times observed for biaryl formation by Suzuki–Miyaura cross-coupling. This concept will be further exploited for other palladium-catalyzed C–X coupling reactions, and its applicability towards catalytic processes involving other (more or less) noble metals will be also investigated.

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