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Account / Revue

Synthesis and catalytic properties of diphosphinidenecyclobutene-coordinated palladium and platinum complexes

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Abstract

This account describes our recent studies on organopalladium and platinum complexes bearing 1,2-diaryl-3,4-diphosphinidenecyclobutenes (DPCB–Y). The DPCB–Y ligands bear extremely low-lying π* orbitals mainly located around the sp^2-hybridized phosphorus atoms and have a marked tendency to engage in metal to phosphorus π-back-bonding. This property is useful for catalysis, leading to highly efficient organic transformations with hitherto unknown reactivities and selectivities. Detailed catalytic mechanisms are reported for dehydrogenative silylation of ketones and direct conversion of allylic alcohols into *N*- and *C*-allylation products. ***To cite this article: F. Ozawa, M. Yoshifuji, C. R. Chimie 7 (2004)***.

Résumé

Cette revue décrit nos travaux les plus récents sur les complexes organopalladium et organoplatine portant des cyclobutènes 1,2-diaryl-3,4-diphosphinidene (DPCB–Y). Les ligands DPCB–Y ont des orbitales π extrêmement basses, principalement localisées sur l'atome de phosphore sp^2 hybridé et ont une forte tendance à participer à la liaison π phosphore–métal. Cette propriété est utile en catalyse et conduit à des transformations très efficaces, avec des réactivités et des sélectivités jusqu'à présent inconnues. Les mécanismes catalytiques détaillés sont reportés pour la déshydrogénation par silylation des cétones et la conversion directe des alcools allyliques en produits d'allylation N– et C–. ***Pour citer cet article : F. Ozawa, M. Yoshifuji, C. R. Chimie 7 (2004)***.

Keywords: sp^2-Hybridyzed phosphorus; Diphosphinidenecyclobutene; Palladium complex; Platinum complex; Catalysis

Mots clés : Phosphore sp^2 hybride ; Cyclobutène diphosphinidène ; Complexes de palladium ; Complexes de platine ; Catalyse

1. Introduction

It has been well documented that chemical properties of organotransition metal complexes may be finely tuned by supporting ligands both from electronic and steric points of view [1]. In this context, diversity of ligand choice is a highly desirable situation for designing the most appropriate catalysts for individual reactions. From the electronic point of view, ligands are roughly classified into two categories, σ-donors and

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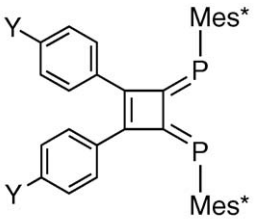
π-acceptors. The former type has a wide variety of selections, including tertiary phosphines, nitrogen bases (e.g., 2,2′-bipyridine, diimines), cyclopentadienyl and its derivatives, and Arduengo-type carbenes (i.e., 1,3-diarylimidazol-2-ylidenes) [2]. On the other hand, the supporting ligands that possess strong π-accepting ability are still limited. Thus, although carbon monoxide and isocyanides are well-known π-acceptors for transition metals, they are frequently reactive toward organometallic species and therefore unfit as efficient ligands.

We recently demonstrated that 1,2-diaryl-3,4-diphosphinidenecyclobutenes bearing sp^2-hybridized phosphorus as coordinating atoms (DPCB–Y, Chart 1) can be used as highly effective π-acceptors for palladium and platinum [3–10]. They are fairly stable in catalytic systems, and form novel organometallic complexes with unique catalytic properties. This account summarizes those results. The related chemistry for other low-coordinated phosphorus compounds has been reviewed [11].

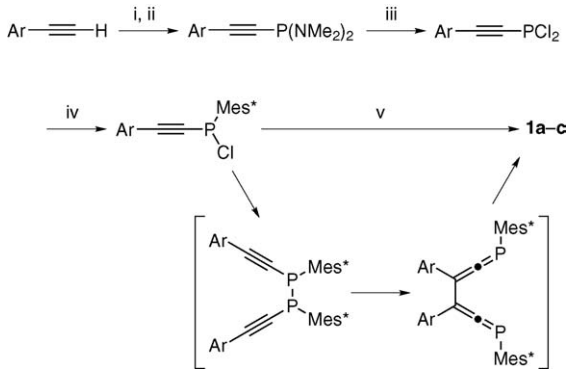


1a: Y = OMe [DPCB-OMe]
1b: Y = H [DPCB]
1c: Y = CF_3 [DPCB-CF_3]
Mes* = 2,4,6-tri-*t*-butylphenyl

2. Preparation and structures of DPCB–Y complexes

2.1. Preparation of DPCB–Y ligands

The synthetic routes to diphosphinidenecyclobutenes have been examined by three groups [12–14]. In the present study, we prepared DPCB–Y ligands by a slightly modified method of Appel's route (Scheme 1) [8,15]. Thus, arylacetylenes were lithiated and allowed to react with $ClP(NMe_2)_2$ [16] in Et_2O at –78 °C (steps *(i)* and *(ii)*). The (arylethynyl)bis-

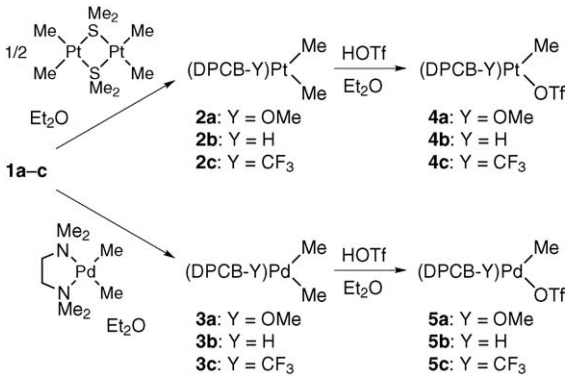


Scheme 1. *(i)* *n*-BuLi/Et_2O/–78 °C, *(ii)* $ClP(NMe_2)_2$/Et_2O/–78 °C, *(iii)* dry-HCl/Et_2O/room temp., *(iv)* Mes*Li/THF/–78 °C, (*v*) Zn/THF/room temp.

(dimethylamino) phosphines thus formed were converted without isolation to dichlorophosphines by the treatment with dry HCl at room temperature (step *(iii)*). Dimethylammonium chloride generated in the systems was removed by filtration after precipitation with pentane, and 2,4,6-tri-*t*-butylphenyl group (Mes*) was introduced in THF using Mes*Li [17] (step *(iv)*). Treatment of the resulting chlorophosphines bearing arylethynyl and Mes* groups with zinc powder at room temperature led to P–P coupling, followed by Cope rearrangement to give bis(phosphaallenyl) intermediates, which are spontaneously converted into **1** in the reaction systems (step *(v)*). The products were isolated by silica-gel column chromatography with hexane elution as bright yellow crystalline solids in 30–50% yields based on arylacetylenes employed. Step *(v)* must be operated in the dark, otherwise *(E,Z)*-isomers of **1** are obtained as major products [14]. This step takes half a day for completion. The reaction progress may be followed by ^{31}P NMR spectroscopy.

2.2. Preparation and structures of DPCB–Y complexes

Dichloro complexes MCl_2(DPCB–Y) (M = Pd, Pt) were prepared by the reactions of $MCl_2(MeCN)_2$ with the ligands in benzene or THF, and the X-ray structure of $PdCl_2$(DPCB) was reported [3]. On the other hand, dimethyl and monomethyl complexes were synthesized as summarized in Scheme 2 [8]. Ligand displacement of $Pt_2Me_4(\mu\text{-}SMe_2)_2$ and $PdMe_2$(tmeda) (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) with DPCB–Y ligands proceeded in Et_2O at room tempera-



Scheme 2.

ture to give reddish orange or orange crystalline solids of dimethyl complexes **2** and **3** in 80–99% yields. The use of Et_2O as solvent was of particular importance for synthesizing the complexes in high yields. Thus, the synthetic reactions proceeded heterogeneously in Et_2O, and this condition was profitable to minimize undesirable side reactions leading to degradation of DPCB–Y ligands. The dimethyl complexes thus prepared reacted smoothly with trifluoromethanesulfonic acid (HOTf) in Et_2O at room temperature to give monomethyl complexes **4** and **5** in over 82% yields after isolation [8,9].

Fig. 1 shows X-ray structures of **2a** and **2b** [4,8]. Both complexes adopt square planar geometry around the platinum. The coordination plane (A) is coplanar to the cyclobutene ring (B), but almost perpendicular to the aryl rings (C and D) on the phosphorus atoms. The most interesting feature is significantly the parallel orientation of the two benzene rings (E and F), which are nearly coplanar with the cyclobutene ring (B). Thus, the dihedral angles between B and E (or F) are 25.2(2) and 25.7(2)° for **2a** and 23.2(1)° for **2b**, respectively, and these values are significantly smaller than that of free DPCB (40.0 and 42.6°) [12]. This fact could be rationalized by assuming the presence of a wide π-conjugated system spread over the molecule including platinum, diphosphinidenecyclobutene ring, and two benzene rings [8]. The effective π-conjugation between platinum and DPCB–Y is caused by back-donation of d_π electrons on platinum to the π* orbitals of the ligand.

The occurrence of strong π-back-donation interaction between platinum and DPCB–Y ligands was also indicated by unusually downfield chemical shifts of the ethylene protons in [PtMe(η^2-ethylene)(DPCB–Y)]OTf complexes (δ 5.02–5.22). On the other hand, DPCB–Y ligands were found to be intermediate σ-donors between diphosphines and diimines [8].

The (π-Allyl)palladium complexes bearing DPCB–Y ligands **(6)** were synthesized in 85–96% yields by the reactions of [Pd(η^3-C_3H_5)(μ-Cl)]$_2$ with DPCB–Y and AgOTf in CH_2Cl_2 at room temperature (Scheme 3) [9]. Fig. 2 shows the X-ray structure of **6b** [5]. The C1–C2 and C2–C3 distances for the allyl ligand (1.376(8) and 1.383(8) Å, respectively) were very similar to those of [Pd(η^3-C_3H_5)(dppf)]OTf (1.372(8) and 1.305(8) Å; dppf = 1,1′-bis(diphenylphosphino)ferrocene). Furthermore, the three Pd–C distances (2.168(5)–2.178(4) Å) were also comparable to those of the dppf complex (2.171(6)–2.187(4) Å).

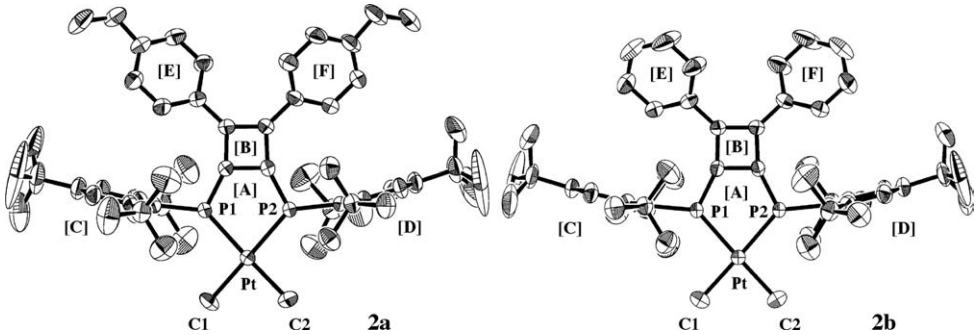
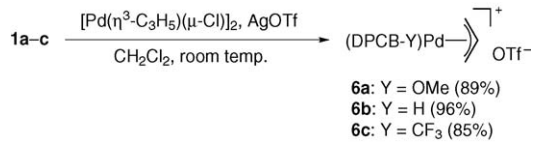


Fig. 1. Molecular structures of **2a** and **2b**. Hydrogen atoms are omitted for simplicity. Selected bond distances (Å) and angles (deg): **(2a)** Pt–P1 = 2.2948(7), Pt–P2 = 2.2878(8), Pt–C1 = 2.089(4), Pt–C2 = 2.074(3), P1–Pt–P2 = 83.33(3), P1-Pt–C1 = 96.2(1), P2–Pt–C2 = 94.5(1), C1–Pt–C2 = 85.9(2); **(2b)** Pt–P1 = Pt–P2 = 2.2909(8), Pt–C1 = Pt–C2 = 2.093(3), P1–Pt–P2 = 82.85(4), P1-Pt–C1 = P2–Pt–C2 = 96.1(1), C1–Pt–C2 = 85.1(2). Dihedral angles between least-square planes (deg): **(2a)** [A]–[B] = 0.8(1), [A]–[C] = 95.71(8), [A]–[D] = 90.93(8), [B]–[E] = 25.2(2), [B]–[F] = 25.7(2); **(2b)** [A]–[B] = 1.4(1), [A]–[C] = [A]–[D] = 92.5(1), [B]–[E] = [B]–[F] = 23.2(1).



Scheme 3.

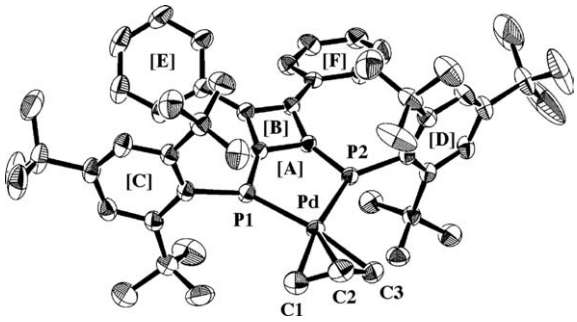


Fig. 2. Molecular structure of **6b**. Triflate anion and hydrogen atoms are omitted for simplicity. Selected bond distances (Å) and angles (deg): Pd–P1 = 2.322(1), Pd–P2 = 2.326(1), Pd–C1 = 2.178(4), Pd–C2 = 2.168(5), Pd–C3 = 2.168(5), C1–C2 = 1.376(8), C2–C3 = 1.383(8), P1–Pd–P2 = 85.50(4), C1–C2–C3 = 119.9(5). Dihedral angles between least-square planes (deg): [A]–[B] = 2.3(1), [A]–[C] = 100.3(1), [A]–[D] = 93.2(1), [B]–[E] = 32.2(2), [B]–[F] = 28.2(2).

Table 1 lists the ^{1}H NMR data for the allyl ligands of **6a–c**, together with the data for dppf and diimine analogues. Although the signals tend to shift to downfield in the order [diimine < dppf < DPCB–OMe **(1a)** < DPCB **(1b)** < DPCB–CF_3 **(1c)**], the variation of the chemical shifts with ligands is rather small. Thus, the (π-allyl)palladium moiety of **6a–c** has a similar structural feature to that of diimine and diphosphine analogues. However, it was found that the DPCB–Y complexes exhibit extremely high reactivity in stoichiometric and catalytic systems (vide infra).

3. Catalytic reactions using DPCB–Y complexes

Reflecting the strong π-accepting ability of DPCB–Y ligands, their palladium and platinum complexes show rather unique chemical properties leading to highly efficient metal-catalysed reactions including Sonogashira coupling of *p*-bromonitrobenzene with trimethylsilylacetylene [3], ethylene-polymerisation [4,18], hydroamination of 1,3-dienes with aniline [5], dehydrogenative silylation of ketones [6], and direct conversion of allylic alcohols into *N*- and *C*-allylation products [7]. The following sections deal with the last two reactions, mainly focusing on their mechanisms.

3.1. Dehydrogenative silylation of ketones

Dialkyl and alkyl-aryl ketones readily react with $HSiMe_2Ph$ at 50 °C in the presence of catalytic amounts of methylplatinum triflate **4b** (3 mol%) and pyridine (3 mol%), affording exclusively silyl enol ethers as dehydrogenative silylation products (Scheme 4) [6]. This reaction may be conducted in toluene or without solvent. The lack of hydrosilylation products (i.e., $R^1CH(OSiMe_2Ph)CH_2R^2$) is of particular interest, because platinum complexes are generally highly efficient for hydrosilylation.

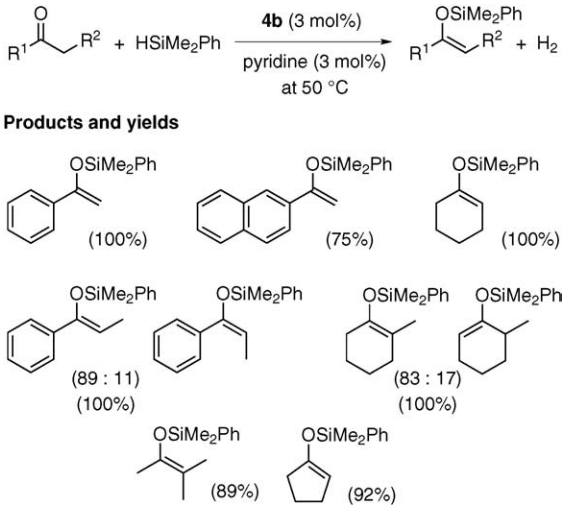
Scheme 5 illustrates our proposed mechanism for the reaction of acetophenone. Initially, **4b** reacts with $HSiMe_2Ph$, pyridine, and residual water in the system to give methane, $PhMe_2SiOSiMe_2Ph$, pyridinium triflate, and hydrido(silyl)platinum **7b** (step *(i)*). This complex is interconverted with a platinum(0) species **A** (step *(ii)*). Oxidative addition of HOTf to **A** forms hydridoplatinum **B**, which is in equilibrium with its dimer **8b** (steps *(iii)* and *(iv)*). Coordination of ketone to **B**, followed by proton-abstraction from **C** by pyridine, gives a platinum enolate **D** and pyridinium triflate (steps *(v)* and *(vi)*). The Pt–O bond in **D** is then cleaved by hydrosilane to afford silyl enol ether as the catalytic reaction product and dihydridoplatinum **E** (step *(vii)*). Finally, reductive elimination of H_2 from **E** regenerates **A** (step *(viii)*).

Several steps in this mechanism could be confirmed by stoichiometric reactions [9]. Thus, **4b** actually

Table 1
^{1}H NMR chemical shifts (δ ppm) for (π-allyl)palladium triflates in $CDCl_3$ at 20 °C

Ligand	*anti*-H	*syn*-H	*central*-H
DPCB–OMe (**1a**)	3.64	4.92	5.86
DPCB (**1b**)	3.73	4.99	5.94
DPCB–CF3 (**1c**)	3.91	5.11	6.06
dppf	3.47	4.00	5.87
diimine[a]	3.53	3.65	5.83

[a] diimine = bis(phenylimino)acenaphthene.

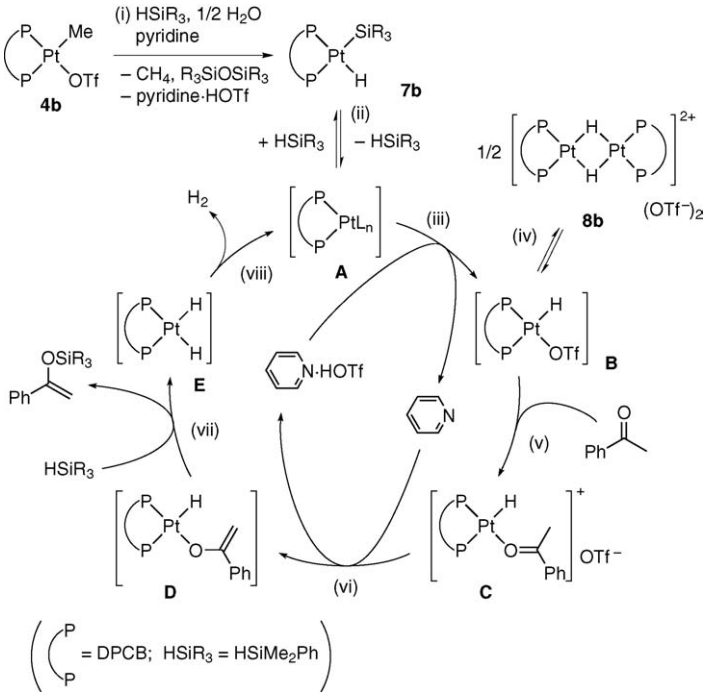


Scheme 4.

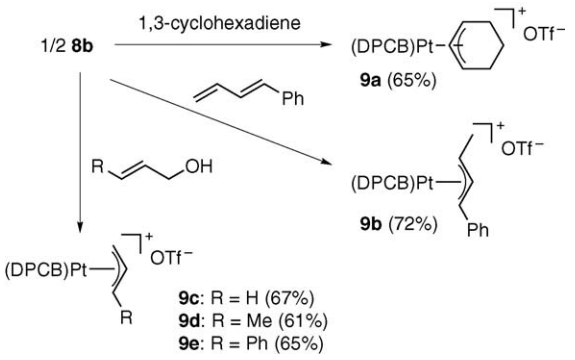
formed **7b** in quantitative yield by the treatment with pyridine (1 equiv) and an excess amount of $HSiMe_2Ph$ (10 equiv) in wet CD_2Cl_2 at room temperature. In this reaction, the formation of methane and $PhMe_2SiOSiMe_2Ph$ was confirmed by ^1H NMR spectroscopy and GLC. On the other hand, in the absence of pyridine and with 1 equiv of $HSiMe_2Ph$, **4b** was converted to **8b** in quantitative yield. Hence, the sequence of the reactions in steps *(i)* to *(iv)* was reproduced. Complexes **7b** and **8b**, independently prepared from $Pt(cod)_2$ (cod = 1,5-cyclooctadiene), efficiently catalysed the dehydrogenative silylation. The reaction of acetophenone with $HSiMe_2Ph$ (1 equiv) in the presence of **7b** (3 mol%) and pyridinium triflate (6 mol%) at 50 °C was complete in 3.5 h to give a quantitative yield of $CH_2{=}C(OSiMe_2Ph)Ph$. Furthermore, the reaction in the presence of **8b** (1.5 mol%) and pyridine (3 mol%) formed the dehydrogenative silylation product, quantitatively, in 3.5 h at 50 °C. These catalytic activities were comparable to that observed for **4b**. Thus, the reaction with **4b** and pyridine (each 3 mol%) took 4.5 h at 50 °C for completion.

3.2. Catalytic conversion of allylic alcohols into N- and C-allylation products

The hydridoplatinum complex **8b** exhibited interesting reactivities toward other organic substrates (Scheme 6) [9]. For example, **8b** reacted with dienes in $ClCH_2CH_2Cl$ at 50 °C to give the corresponding π-allyl complexes **9a** and **9b**. Furthermore, the reactions of **8b** with allylic alcohols formed π-allyl com-



Scheme 5.

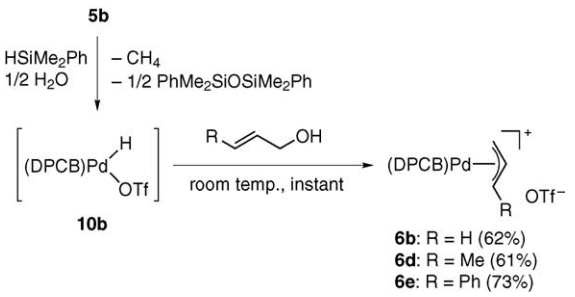


Scheme 6.

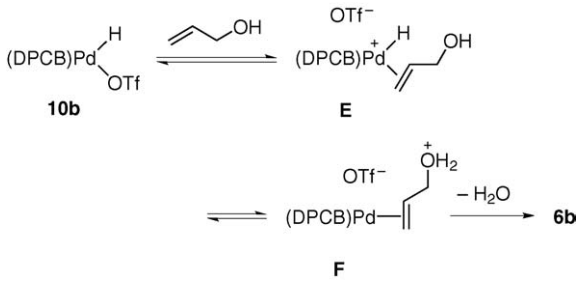
plexes **9c–e**. All reactions proceeded cleanly without side-reactions as confirmed by ^{31}P NMR spectroscopy.

The hydridopalladium triflate **10b**, in situ generated from **5b**, $HSiMe_2Ph$ (1 equiv), and residual water in CH_2Cl_2, showed much higher reactivity than the platinum analogue [9]. The reactions with phenylbutadiene and cyclohexadiene spontaneously formed the corresponding π-allyl complexes. Furthermore, **10b** rapidly caused C–O bond cleavage of allylic alcohols to give π-allyl complexes **6b, 6d**, and **6e** (Scheme 7).

The π-allyl complex formation from 1,3-dienes should be a key elementary process for catalytic hydroamination of these substrates [5]. On the other hand, the direct conversion of allylic alcohols into π-allyl complexes is of great significance, in connection with catalytic allylation of active methylene compounds and amines [19]. Thus, the *N*- and *C*-allylation catalysed by palladium complexes (i.e., the so-called Tsuji–Trost reaction) is a versatile synthetic means of constructing C–N and C–C bonds in organic chemistry. This reaction generally employs allylic esters derived from allylic alcohols as substrates, because (π-allyl)palladium intermediates are usually generated in catalytic systems by oxidative addition of allylic substrates (allyl–OY), and this process involves nucleophilic substitution of the OY groups by Pd(0) species. Owing to the poor leaving ability of the OH group, it is necessary to convert allylic alcohols to esters having OY groups with higher leaving ability. The extremely facile cleavage of the non-activated allyl–OH bonds induced by **10b** is therefore of particular interest and possibly serves as a key elementary process for direct conversion of allylic alcohols into N- and C-allylation products [7]. We proposed the mechanism given in Scheme 8 for the allyl–OH bond cleavage. It was considered that the strong π-accepting ability of DPCB ligand makes **10b** highly acidic to allow the proton transfer from Pd to OH group in intermediate **E**. The resulting **F** undergoes elimination of water to give **6b** [9].

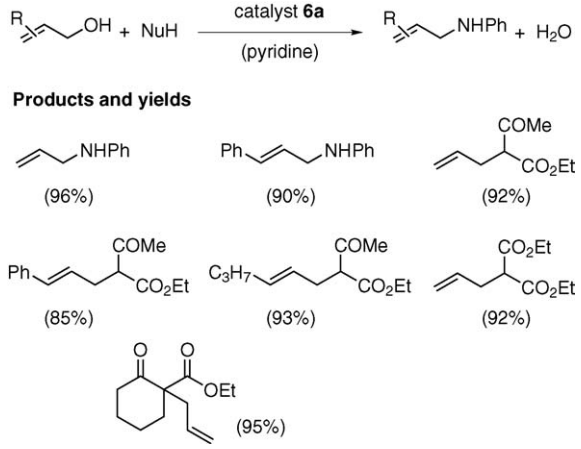


Scheme 7.

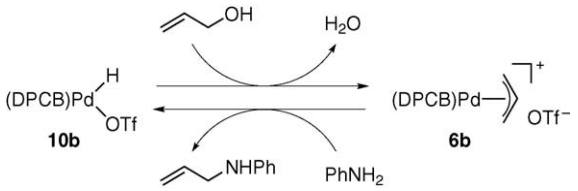


Scheme 8.

Representative examples of the catalytic allylation are given in Scheme 9. *N*-Allylation of aniline proceeded with 0.1 mol% of **6a** at room temperature, whereas *C*-allylation of active methylene compounds was operative with catalytic amounts of **6a** (2 mol%) and pyridine (10 mol%) at 50 °C for several hours. In



Scheme 9.

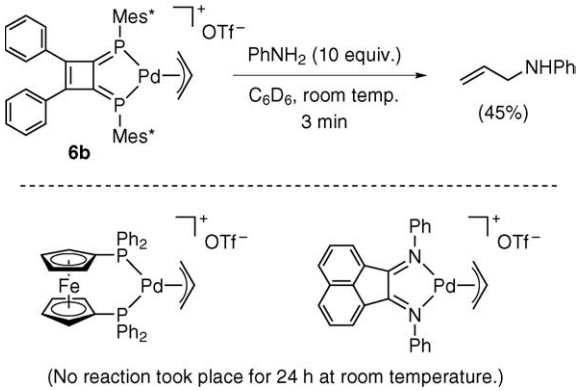


Scheme 10.

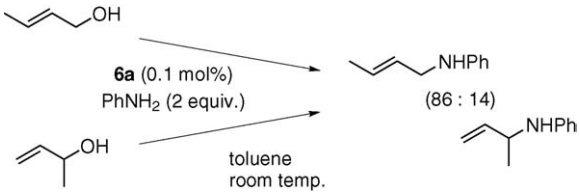
all runs, monoallylation products were obtained in over 85% yields, along with the formation of water as the only co-product. The catalytic activity was significantly affected by the nature of Y on the DPCB–Y ligands (**6a** > **6b** > **6c**).

Scheme 10 shows the catalytic mechanism proposed for the reaction of allyl alcohol with aniline in the presence of **6b**. The C–O bond cleavage promoted by palladium hydride **10b** forms π-allyl complex **6b**, as already confirmed by stoichiometric examinations (Scheme 7). Complex **6b** then reacts with aniline to afford *N*-allylaniline and **10b**. The latter process was confirmed by a stoichiometric experiment using **6b** and aniline. Thus, the reaction proceeded rapidly at room temperature (Scheme 11). In contrast, (π-allyl)palladium triflates bearing dppf and diimine ligands were unreactive under the same reaction conditions [5].

As already discussed with X-ray structural parameters and NMR data, the π-allyl complexes listed in Scheme 11 have very similar structures to each other. Nevertheless, DPCB complex **6b** showed much higher reactivity toward aniline than the dppf and diimine complexes. Accordingly, the highly reactive nature of **6b** must be attributed to the stability of transition state. The reaction of **6b** with aniline very probably proceeds



Scheme 11.

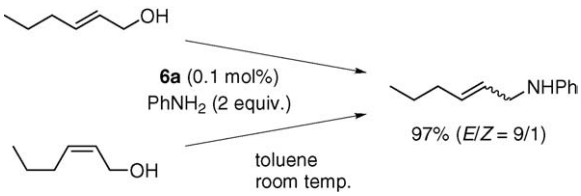


Scheme 12.

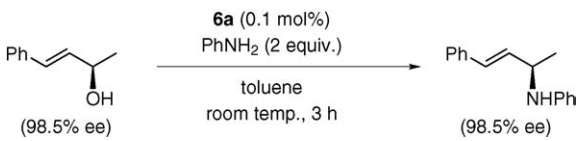
via nucleophilic attack of aniline to the π-allyl ligand from the opposite side of palladium. This process causes increase in the electron density of palladium. The strong π-accepting ability of DPCB will effectively reduce the increasing electron density to stabilize the transition state.

Although the novel C–O bond cleavage process promoted by a hydridopalladium complex is involved, the present catalysis preserved the regio- and stereochemical courses generally observed for palladium-catalysed allylation reactions [7]. Thus, the two regioisomers of butenyl alcohol were converted to *N*-(2-butenyl)aniline and *N*-(1-methyl-2-propenyl)aniline in almost the same regioselectivity (Scheme 12). Similarly, the reactions of the *(E)*- and *(Z)*-isomers of 2-hexenyl alcohol gave a nearly identical distribution of stereoisomers (Scheme 13). These results are consistent with a catalytic mechanism involving rapid interconversion between the *syn*- and *anti*-isomers of π-allyl intermediates.

Furthermore, an optically active alcohol shown in Scheme 14 was converted to the corresponding allylated aniline with retention of the configuration of allylic carbon [7]. This type of stereochemistry has been observed for common allylation systems and attributed to the occurrence of two inversion processes at



Scheme 13.



Scheme 14.

the C–O bond cleavage and the external attack of aniline to the π-allyl intermediate [19].

4. Conclusion

The palladium and platinum complexes bearing DPCB–Y ligands exhibited rather unique structures and reactivities, significantly different from common organometallic complexes having tertiary phosphine and nitrogen-based ligands. The highly reactive nature observed in several catalytic reactions was reasonably rationalized by considering the strong π-accepting property of sp^2-hybridized phosphorus compounds toward transition metals.

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