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Highly Active Pd(0) Catalyst from $Pd(OAc)_2$–Bu_3P Combination in Untapped 1:1 Ratio: Preparation, Reactivity, and ^{31}P–NMR

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Low ligated Pd(0), Reduction of Pd(II), $^{31}P\{^1H\}$-NMR, β-elimination, Cyclic conjugated dienes

***Abstract:** Reaction of $Pd(OAc)_2$ with Bu_3P (1:1) in benzene or THF afforded extraordinarily active zerovalent palladium species as a pale yellow solution, the nature of which has been discussed on the basis of the significant difference in catalytic reactivity and $^{31}P\{^1H\}$–NMR features between such a catalyst and one prepared from $Pd_2(dba)_3$ and excess Bu_3P.*

Diverse applicability of Pd(0)–phosphine complexes to catalytic organic synthesis has certainly led to richer comprehension of this rapidly growing organotransition-metal chemistry. We usually employ commercially available Pd(0) catalyst such as $Pd(Ph_3P)_4$ or $Pd_2(dba)_3$ together with phosphines for this end, while, however, there have as yet been poorly understood the number of the ligand on the palladium atom with regard to actively operating catalyst or the coordination equilibrium between dba (dibenzylideneacetone), a strongly coordinating bidentate ligand, and phosphines. One of other prevailing procedures to generate Pd(0) catalyst is the reduction of Pd(II) salts such as $Pd(OAc)_2$ or $PdCl_2$ with reducing agents such as phosphines, olefins, CO, alcohols, or metal hydrides, leaving behind Pd(0) catalyst *in situ*. Recent reports by Amatore and Jutand,[1a] or Ozawa and Hayashi[1b] on the reduction of $Pd(OAc)_2$ with triarylphosphines have shed light on this important field.

This situation has also provided impetus for our studies on development of truly active Pd(0) catalyst and it turned out that the reaction of $Pd(OAc)_2$ with *one–mole equivalent* of tributylphosphine (Bu_3P) in THF, benzene, or even hexane at room temperature led to the achievement of such an objective, which is the subject of this paper. The preparation of this catalyst is simple and straightforward. To the suspension of $Pd(OAc)_2$[2] in benzene or THF (partially dissolved brown mixture) was added an equimolar amount of Bu_3P[3] under argon atmosphere and the $Pd(OAc)_2$ quickly dissolved to effect a pale yellow, clear solution (**CatA**). This solution was used in this study to exhibit high catalytic activity with excellent selectivity, the reason responsible for which is also discussed on the basis of the comparison of both $^{31}P\{^1H\}$–NMR features and reactivity in elimination of polycyclic allylic carbonates (**1** — **4**) for **CatA**, together with **CatA2** [$Pd(OAc)_2$:Bu_3P=1:2], **CatA3** [$Pd(OAc)_2$:Bu_3P=1:3], and **CatA4** [$Pd(OAc)_2$:Bu_3P=1:4], and the catalyst prepared from $Pd_2(dba)_3$ and Bu_3P in 1:4 ratio (**CatB**).

Preliminary studies on $^{31}P\{^1H\}$–NMR of the catalysts have been done employing a solution of these catalysts in THF–C_6D_6 (1:1) under argon atmosphere and the results are illustrated in Fig. 1. **CatA** (C–1) exhibited three major signals at 9.27, 22.0, and 23.9 ppm with an integral ratio 4:1:6 and no resonance due to free Bu_3P (A in Fig. 1) or tributylphosphine oxide (Bu_3PO) (B in Fig. 1). Because no assignment of any signal except for both free Bu_3P and Bu_3PO was possible at present, we cannot propose any structural correlation with the signals in C–1. Increasing the amount of Bu_3P (**CatA2**, **CatA3**, and **CatA4**), the spectra (C–1) dramatically changed to give spectra C–2, C–3, and C–4 which were basically the same within the range of Bu_3P content of these three catalysts. There have observed, however, still no free, sharp Bu_3P signal in these spectra, and Bu_3PO signal, though weak, was detected as an only identifiable peak at around 43 ppm. In marked contrast to these, the **CatB** NMR (D–2 in Fig. 1) definitely showed the presence of an enhanced, free Bu_3P signal, which clearly means that the dba ligands are unable to be displaced with Bu_3P at 20°C and, therefore, this catalyst must be fully ligated. Although the rationalization of **CatA** should not be without the characterization of the three signals mentioned above (C–1 in Fig. 1) and the fate of the acetoxy ligands of $Pd(OAc)_2$, what is important at present is the recognition as follows: **CatA** should be totally different from **CatA2**—**CatA4** and/or **CatB**, and would bear not trivalent but oxidized phosphorous ligands of other class, though not elucidated, and can facilely accommodate olefinic double bonds of substrates to form π-allyl complexes leading to σ-palladium intermediates amenable to a β-elimination process. This would be responsible for the observed (*vide infra*) high catalytic activity of **CatA**. Thus, we should explain the difference, if any, between **CatA** and **CatB** on those bases mentioned above.

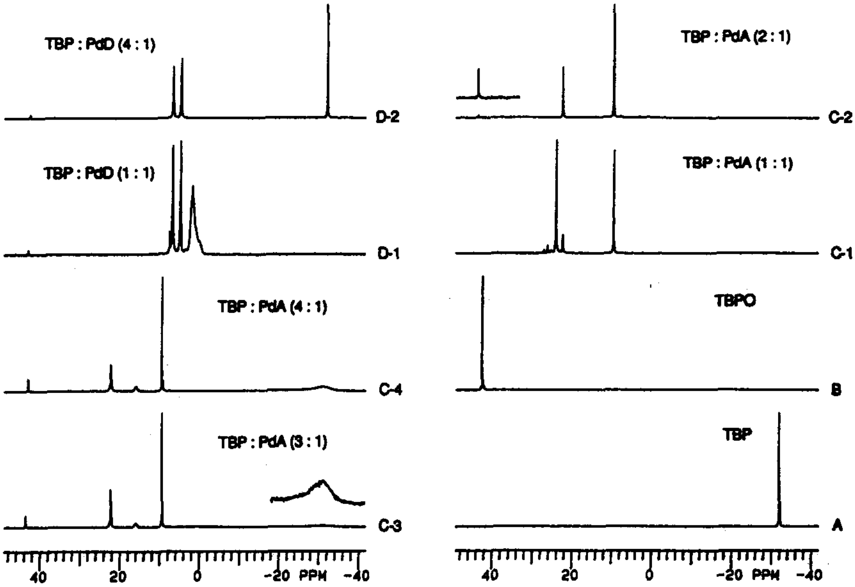


Figure 1. $^{31}P\{^1H\}$–NMR spectra of various palladium–Bu_3P complexes recorded on a Varian–VXR200S instrument (202 MHz) with H_3PO_4 as an external standard at 20 °C: TBP = Bu_3P; TBPO = Bu_3PO; PdA = $Pd(OAc)_2$; PdD = $Pd_2(dba)_3$.

In a previous report[4] we have delineated that **CatA** delightfully promoted the conversion of α-oriented allylic carbonates (**1** and **3**) to homoannular conjugated dienes (HOD: **5** and **7**) or their β-isomers (**2** and **4**) to heteroannular conjugated dienes (HED: **6** and **8**), respectively, under mild conditions with high selectivity and clear-cut trend depending on the stereochemistry of carbonate-bearing centers. In Table 1 are listed the results for **CatB**, **CatA2**, and **CatA4** together with, for comparison, the previous results[4] for **CatA**. The plausible mechanism is outlined in Scheme I involving every possible pathway. One striking feature is that **CatB** required much higher temperature (*refluxing in dioxane*) (entries 11–15) to effect the reaction likewise in sharp contrast to the case of **CatA** (*room temperature*) (entries 1–7). In addition, **CatB** exhibited unpredictable regiochemical dependency upon not only the stereochemistry of the carbonate groups but also types of the protecting groups (R in **1** or **2**) or molecular structures themselves. In particular, the selective formations of HED **8** from **3** (entry 12) and HOD **5b** from **2b** (entry 14) by **CatB** seem puzzling because the regiochemical outcomes were reversed to the cases for **CatA** (entries 3 and 6).

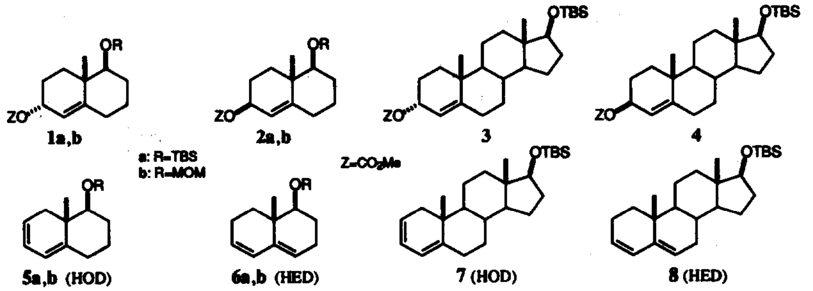


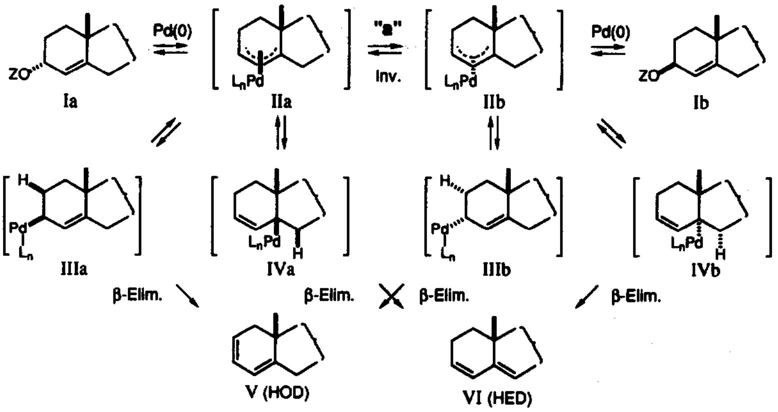
Table 1. Results of Pd(0)–catalyzed elimination of cyclic carbonates 1—4.

Entry	Sub (stereo)[a]	Pd (mol%)[b]	Solvent	Temp	Time/h	Yield/%[c]	HOD[d]	:	HED[e]
1	**1a** (α)	**CatA** (10)	PhH	rt	6	94	90 (**5a**)		10 (**6a**)
2	**1b** (α)				6	95	92 (**5b**)		8 (**6b**)
3	**3** (α)		THF	rt	3	93	93 (**7**)		7 (**8**)
4	**3** (α)				1[f]	21[g]	>99 (**7**)		<1 (**8**)
5	**2a** (β)		PhH	rt	4	90	<1 (**5a**)		>99 (**6a**)
6	**2b** (β)				4	93	<1 (**5b**)		>99 (**6b**)
7	**4** (β)		THF	rt	3	99	<1 (**7**)		>99 (**8**)
8	**1a** (α)	**CatA2** (10)	THF	refl	2	88	77 (**5a**)		23 (**6a**)
9	**1a** (α)	**CatA4** (10)	THF	refl	4	90	68 (**5a**)		32 (**6a**)
10	**1a** (α)	**CatB** (10)	dioxane	refl	3.5	78	95 (**5a**)		5 (**6a**)
11[h]	**1b** (α)				12	95	93 (**5b**)		7 (**6b**)
12	**3** (α)				2.5	93	21 (**7**)		79 (**8**)
13	**2a** (β)				7	93	15 (**5a**)		85 (**6a**)
14[h]	**2b** (β)				12	95	90 (**5b**)		10 (**6b**)
15	**4** (β)				5	95	8 (**7**)		92 (**8**)

(a) Stereochemistry of the carbonate groups. (b) **CatA**, **CatA2**, and **CatA4** from Pd(OAc)$_2$: Bu$_3$P=1:1, 1:2, and 1:4, respectively; **CatB** from Pd$_2$(dba)$_3$:Bu$_3$P=1:4. (c) For chromatographically pure product. (d) HOD=homoannular conjugated diene. (e) HED=heteroannular conjugated diene. (f) Interrupted at 20% conversion. (g) Substrate (79%) recovered. (h) Taken from ref. 5.

These impressive outcomes would be rationalized by invoking the critical difference between **CatA** and **CatB** cited above. Such difference would be correlated for **CatA** or **CatB** with large or small rate of the formation of π-allyl complexes (IIa and IIb) and the β-elimination of σ-palladium intermediates (IIIa, IIIb, IVa, and IVb), respectively. For instance, the predominant formation of **8** from **3** for **CatB** may be explained by taking into account the intervention of path "a" (Scheme I)[5] which may become significant enough to compete with the β-elimination steps (IIIa V and IVa VI) because of their sluggishness: IIIa- and/or IVa-type intermediates could reverse their initial stereochemistry leading predominantly to a IVb-type intermediate, the immediate precursor of **8** because otherwise **8** from **3** must involve a IVa-type intermediate which seems highly unlikely for steric reasons.[6] In fact, evidence pointed to the presence of the route "a" has been obtained. Firstly, at the early stage of the reaction of 3 with **CatA**, no 8 was detected at all (entry 4), which was actually formed in 6.5% yield at 100% conversion (entry 3) because a relative increase in concentration ratio [IIa]/[**CatA**], which necessarily emerges as the reaction progresses, would result in a relative increase in the probability of path "**a**". A second line of evidence for the route "**a**" has been derived from the observation that high-Bu_3P content (more ligated) catalysts such as **CatA2** or **CatA4** displayed very low HOD–HED selectivities (entries 8 and 9) in the reaction of **1a**.

Scheme I.



We have demonstrated that **CatA** is surely zerovalent palladium species and its synthetic potential seems enormous in the light of both previous[4,7] and present documentations. It should be noted that the success of catalytic reactions heavily hinges on the rational design of the catalyst itself as demonstrated and the desired type of Pd(0) complexes coordinated by definite numbers of ligand could hopefully be prepared *in situ* by adding a definite amount of the desired ligand after treatment of $Pd(OAc)_2$ with the equimolar amount of Bu_3P. The real nature of **CatA** would be unveiled as an outgrowth of our involvement in investigations on mechanism of the reduction of $Pd(OAc)_2$ with the equimolar amount of Bu_3P, which is currently our major concern.

Acknowledgment: We thank to the SC–NMR Laboratory of Okayama University for ^{31}P–NMR experiments.

References and notes:

(1) (a) Amatore, C.; Jutand, A.; M'Barki, M. A. *Organometallics*, **1992**, *11*, 3009. (b) Ozawa, F.; Kubo, A.; Hayashi T. *Chem. Lett.* **1992**, 2177.
(2) Commercially available $Pd(OAc)_2$ was treated with boiling benzene and the mixture, while hot, was filtered. The hot filtrate was concentrated to dryness to give purified $Pd(OAc)_2$.
(3) The purity of Bu_3P is also crucial. We used a product purchased from Aldrich in "sure-sealed" bottle.
(4) Mandai, T.; Matsumoto, T.; Nakano, Y.; Teramoto, H.; Kawada, M.; Tsuji, J. *Tetrahedron Lett.* **1992**, *33*, 2549.
(5) Takahashi, T.; Nakagawa, N.; Minoshima, T.; Yamada, H.; Tsuji, J. *Tetrahedron Lett.* **1990**, *30*, 4333.
(6) Stability order for σ-palladium intermediates in bicyclo[4.4.0]-system (R = TBS, Pd–L_n= PdOMe) estimated by MM2: IVb (11.5 kcal/mol) < IIIb (12.9 kcal/mol) < IIIa (13.5 kcal/mol) < IVa (17.7 kcal/mol).
(7) (a) Mandai, T.; Matsumoto, T.; Kawada, M.; Tsuji, J. *J. Org. Chem.* **1992**, *57*, 1326; (b) Mandai, T.; Matsumoto, T.; Kawada, M.; Tsuji, J. *J. Org. Chem.* **1992**, *57*, 6090.

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