Aerobic Oxidation of Benzene to Biphenyl Using a Pd(II)/ Molybdovanadophosphoric Acid Catalytic System

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Dedicated to Roger A. Sheldon on the occasion of his 60th birthday.

Abstract: The oxidative coupling reaction of benzene to biphenyl was examined by the use of a $Pd(OAc)_2$/molybdovanadophosphoric acid/O_2 system under mild conditions. $Pd(OAc)_2$ combined with two different types of molybdovanadophosphoric acids exhibited the highest catalytic activity for the biphenyl synthesis. The best turn-over number (TON) of $Pd(OAc)_2$ and the yield of biphenyl reached 109 and 14.3% based on the benzene used, respectively. The rate-determining step of the coupling was found to be the reoxidation step of the reduced molybdovanadophosphoric acid by molecular oxygen.

Keywords: aerobic oxidation; C-C coupling; heteropoly acid; molecular oxygen; palladium

Introduction

The preparation of biphenyl compounds by aryl-aryl coupling is very important not only in organic synthesis but also in industrial chemistry, since biphenyl derivatives are widely used as monomers of various polymers and liquid crystal materials.[1] Although the Ullmann reaction[2] and Suzuki coupling[3] are well-known methods for preparing biphenyls through aryl-aryl coupling, these reactions leading to undesirable by-products like copper iodide or boric salts are not satisfy from the environmental and atom-economical viewpoint. Hence, the development of biphenyl synthesis by the direct coupling of aryl compounds like benzene is an important challenge in organic synthesis. One candidate for an ideal biphenyl synthesis is oxidative coupling of benzene using a palladium catalyst.[4] There have been several reports on the synthesis of biphenyl from benzene by coupling using stoichiometric amounts of $PdCl_2$ and NaOAc,[5] $Pd(OAc)_2$ and perchloric acid,[6] and an olefin complex of $PdCl_2$ and $AgNO_3$[7] in acetic acid. However, the number of studies reported on the biphenyl synthesis through a catalytic process is so far limited,[8] and the turn-over number of Pd(II) in these biphenyl syntheses is still at unsatisfactory levels despite the fact that the reactions are carried out under higher pressures of dioxygen. Recently, benzene has been converted into biphenyl in high selectivity by a $Pd(OAc)_2$/$MoO_2(acac)_2$/O_2 system in acetic acid,[9] but the yield of biphenyl is low (~7%). $PdCl_2$ combined with Zr(IV)/Mn(II)/Co(II) in the presence of 1.1 equiv. of AcONa under air (10.2 atm) in acetic acid has been reported to lead to biphenyl in high yield (*ca.* 84%); however, the turn-over numbers of the $PdCl_2$ are still low (~12).[10] It is known that Pd(II)/heteropoly acid systems are also used for the oxidative coupling of aromatic compounds.[11] For the oxidative acetoxylation of benzene to phenyl acetate accompanying the formation of biphenyl, the Pd(II)/HPMoV system is employed as the catalyst.[11a, b] The Pd(II)/heteropoly acid/PPh_3 system is also reported to catalyze the oxidative coupling of methyl benzoate at 195 °C under an air flow.[11c] In earlier papers, we reported that Pd(II)/molybdovanadophosphate (NPMoV) in the presence or absence of hydroquinone (HQ) is an efficient catalytic system for acetoxylation, acetalization, and Wacker-type oxidation of alkenic compounds.[12] In the course of our study to extend the oxidation using Pd(II) combined with two different molybdovanadophosphate systems, we found that biphenyl can be obtained from benzene in a satisfactory yield by the $Pd(OAc)_2$ catalyst combined with molybdovanadophosphoric acid (HPMoV) under atmospheric dioxygen.

Results and Discussion

In the first place, we examined the oxidative coupling of benzene to biphenyl using $Pd(OAc)_2$ combined with various heteropoly acids (HPA) which serve as the reoxidation catalyst of the reduced Pd(0) to Pd(II) under O_2 (Scheme 1 and Table 1).

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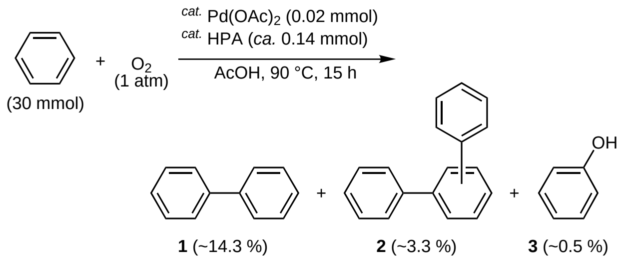
Table 1. Effect of HPA on oxidative coupling of benzene to biphenyl.[a]

Run	HPA	TON/Yield [%][b]			
		1	**2**	**3**	Total
1	none	1/0.1	0/0	0/0	1/0.1
2	$H_3PMo_{12}O_{40} \cdot n\ H_2O$	31/4.2	2/0.2	0/0	33/4.4
3	$H_4PMo_{11}V_1O_{40} \cdot n\ H_2O$	83/10.9	21/2.1	4/0.3	108/13.2
4	$H_5PMo_{10}V_2O_{40} \cdot n\ H_2O$	55/7.1	8/0.8	2/0.2	65/8.0
5	$H_6PMo_9V_3O_{40} \cdot n\ H_2O$	36/4.7	4/0.4	1/0.1	41/5.2
6	$H_7PMo_8V_4O_{40} \cdot n\ H_2O$	37/5.0	3/0.3	1/0.1	42/5.4
7	NPMoV[c]	0/0	0/0	0/0	0/0
8	$H_3PMo_{11}W_1O_{40} \cdot n\ H_2O$	11/1.4	0/0	0/0	11/1.4
9	$H_3PMo_{10}W_2O_{40} \cdot n\ H_2O$	21/2.8	0/0	0/0	21/2.8
10	$H_3PMo_9W_3O_{40} \cdot n\ H_2O$	6/0.9	0/0	0/0	6/0.9
11	$H_3PMo_7W_5O_{40} \cdot n\ H_2O$	4/0.6	0/0	0/0	4/0.6
12	$H_3PMo_3W_9O_{40} \cdot n\ H_2O$	1/0.1	0/0	0/0	1/0.1
13	$H_3PMo_2W_{10}O_{40} \cdot n\ H_2O$	1/0.1	0/0	0/0	1/0.1
14	$H_5PW_{10}V_2O_{40} \cdot n\ H_2O$	7/0.9	0/0	0/0	7/0.9
15	$H_3PW_{12}O_{40} \cdot n\ H_2O$	1/0.1	0/0	0/0	1/0.1

[a] Reaction conditions: $Pd(OAc)_2$ (0.02 mmol), HPA (*ca.* 0.14 mmol, calculated as n = 30), benzene (30 mmol) and in AcOH (10 mL) were placed in a round-bottom flask (30 mL) equipped with a balloon filled with O_2. The reaction mixture was allowed to react under stirring at 90 °C for 15 h.

[b] Turn-over number (TON) and yield were based on $Pd(OAc)_2$ catalyst and benzene, respectively.

[c] The average composition of the NPMoV is shown as $(NH_4)_5H_6PMo_4V_{7.8}O_{40} \cdot n\ H_2O$.[12]



Scheme 1.

A typical reaction was carried out as follows. A solution of $Pd(OAc)_2$ (0.02 mmol), $H_4PMo_{11}V_1O_{40} \cdot n\ H_2O$ ($HPMo_{11}V_1$) (323 mg, *ca.* 0.14 mmol)[13] and benzene (30 mmol) in AcOH (10 mL) was placed in a round-bottom flask (30 mL) equipped with a balloon filled with O_2, and the mixture was allowed to react under stirring at 90 °C for 15 h. The reaction gave biphenyl (**1**) as a main product, and a mixture of *o*-, *m*-, and *p*-terphenyls (**2**) along with a small amount of phenol (**3**). In this reaction, the formation of phenyl acetate was found to be negligible, although the reactions in the presence of NaOAc are reported to give considerable amounts of phenyl acetate.[10,11a, b]

In the absence of HPA, the coupling by $Pd(OAc)_2$ proceeded stoichiometrically to form **1** in an amount comparable to that of the $Pd(OAc)_2$ used (Run 1). The catalytic potential of the $Pd(OAc)_2$ combined with various HPMoV was considerably affected by the vanadium content in the HPMoV catalysts (Runs 2 to 6 and Figure 1). When $H_4PMo_{11}V_1O_{40} \cdot n\ H_2O$ ($HPMo_{11}V_1$) was employed as the reoxidation catalyst, **1**, **2**, and **3** were obtained in 10.9%, 2.1%, and 0.3% yields, respectively, based on the benzene used, and the total TON of $Pd(OAc)_2$ reached 108. This TON was very high compared with that of the coupling reactions reported previously.[9,10] Although the $Pd(OAc)_2$/NPMoV system was an efficient catalytic system for the oxidation of some alkenes,[12] the present reaction was not promoted at all by the $Pd(OAc)_2$/NPMoV catalyst (Run 7). Molybdotungstophosphoric acids (HPMoW) and tungstovanadophosphoric acids (HPWV) were found to be less efficient than HPMoV, but the combined catalytic systems of $Pd(OAc)_2$ with HPMoW and HPWV led to **1** in low yields without formation of **2** and **3** (Runs 8 to 15). In these reactions, the ratio of *o*-, *m*-, and *p*-terphenyls (**2**) was approximately 4:6:5 in every run.

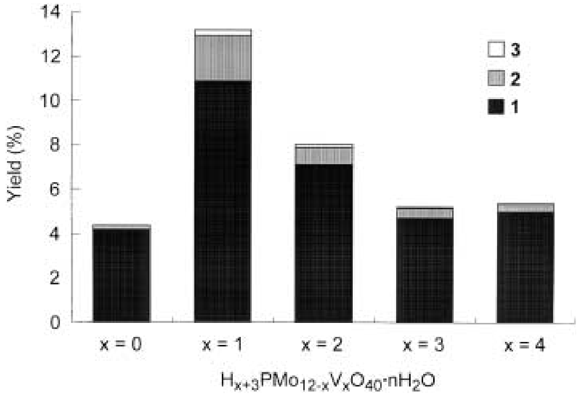


Figure 1. Effect of HPMoV on the $Pd(OAc)_2$-catalyzed coupling of benzene.

Table 2. Oxidative coupling of benzene to biphenyl under various conditions.[a]

Run	Parameter	TON/ Yield [%][b]			
		1	**2**	**3**	Total
	Pd-species (mmol)				
1	$Pd(OAc)_2$ (0.02)	83/10.9	21/2.1	4/0.3	108/13.2
2	$PdCl_2$ (0.02)	16/2.2	1/0.1	1/0.1	18/2.3
3	none	0/0	0/0	0/0	0/0
4	$Pd(OAc)_2$ (0.04)	32/8.6	5/1.1	2/0.2	39/9.9
	$HPMo_{11}V_1$ (mg/mmol)				
5	461/*ca.* 0.20	85/11.3	22/2.2	4/0.3	111/13.8
6	184/*ca.* 0.08	72/9.6	14/1.4	3/0.2	90/11.3
7	92/*ca.* 0.04	49/6.4	8/0.8	3/0.2	60/7.4
8	46/*ca.* 0. 02	33/4.5	3/0.3	2/0.2	39/4.9
9[c]	46/*ca.* 0.02	56/7.5	8/0.8	4/0.3	68/8.5
	AcOH (mL)				
10	5	18/2.5	1/0.1	1/> 0.1	20/2.6
11	15	57/7.5	9/0.9	5/0.3	71/8.6
	Temperature (°C)				
12	70	23/3.1	1/0.1	1/0.1	25/3.3
13	80	54/7.2	6/0.6	2/0.2	62/8.0
14	100	27/3.5	1/0.1	1/0.1	29/3.7
	air (atm)				
15	1	15/1.9	1/0.1	1/0.1	16/2.0
16	10	64/8.3	7/0.7	4/0.3	75/9.3
17	20	67/8.9	11/1.1	2/0.2	81/10.2
	Benzene (mmol)				
18	10	22/8.9	2/0.6	2/0.4	26/9.9
19	20	51/10.0	13/1.9	3/0.3	66/12.2
20	40	96/9.1	19/1.3	5/0.2	119/10.7
21	45	13/1.2	> 1/> 0.1	1/> 0.1	14/1.2
22	50	10/0.8	> 1/> 0.1	0/0	10/0.8

[a, b] The same as Table 1.

[c] 55 h.

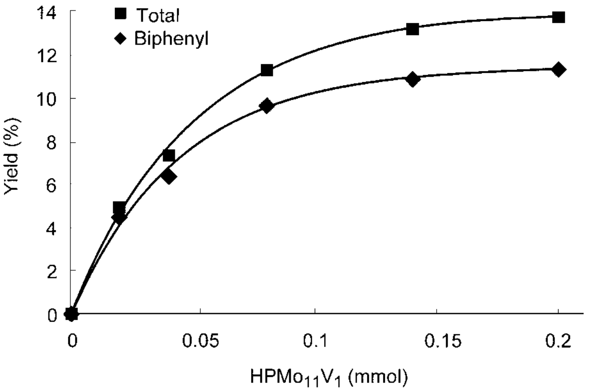


Figure 2. Effect of the amount of $HPMo_{11}V_1$ on the $Pd(OAc)_2$-catalyzed coupling of benzene.

Table 2 shows the aerobic oxidation of benzene to **1** by the Pd(II)/$HPMo_{11}V_1$ system under various reaction conditions.

The catalytic activity of $PdCl_2$ was lower than that of $Pd(OAc)_2$ (Run 2). Needless to say, no reaction took place by $HPMo_{11}V_1$ alone without Pd(II) (Run 3). Although the amount of the $Pd(OAc)_2$ used was doubled, the TON of the Pd(II) and the yield of **1** were not improved (Run 4). In contrast, the TON and yields depended markedly on the amount of $HPMo_{11}V_1$ added to the $Pd(OAc)_2$ (Runs 5 to 8 and Figure 2). The reaction using *ca.* 0.2 mmol of $HPMo_{11}V_1$ gave almost the same results as that using *ca.* 0.14 mmol of $HPMo_{11}V_1$ (Run 1 and Run 5). However, when the amount of $HPMo_{11}V_1$ added to the $Pd(OAc)_2$ was reduced, the TON and yields were gradually decreased with the reduction of the amount of $HPMo_{11}V_1$ (Runs 6 to 8). In these reactions, it is interesting to note that the color of the starting solution is orange, and then turns dark green until the termination of the reaction. This color change may be attributed to the formation of a low-valent V species like V^{4+} by the reduction of the V^{5+} ion in HPMoV. If the regeneration of V^{5+} from the reduced V^{4+} rapidly takes place, the reaction solution may be exhibit an orange color based on the V^{5+} ion rather than the greenish color based on the V^{4+} ion. When the reaction was prolonged for 55 h, the total yield of products increased from 4.9% to 8.5% (Run 9). These results suggest that the reoxidation of V(IV) to V(V) by

Table 3. Oxidative coupling of benzene to biphenyl by combination of two HPMoV's.[a]

Run	$H_{x+3}PMo_{12-x}V_xO_{40} \cdot n\ H_2O$		AverageV content	TON/Yield [%][b]			
	x/(mg)	x/(mg)		**1**	**2**	**3**	Total
1	0/247	1/81	0.25	101/13.5	33/3.3	7/0.5	141/17.3
2	0/164	1/161	0.5	109/14.3	34/3.4	7/0.5	151/18.2
3	0/82	1/242	0.75	96/12.5	24/2.4	5/0.4	125/15.2
4	0/247	2/80	0.5	88/11.7	22/2.2	6/0.4	116/14.3
5	0/164	2/161	1	71/9.5	17/1.7	3/0.2	92/11.4
6	0/82	2/242	1.5	45/6.1	5/0.5	2/0.1	52/6.7
7	0/164	3/156	1.5	43/5.8	8/0.8	3/0.2	54/6.7
8	1/161	2/161	1.5	78/10.2	19/1.8	4/0.2	101/12.3
9[c]	0/164	1/161	0.5	169/11.1	32/1.6	10/0.3	213/13.0

[a] Reaction conditions: A solution of $Pd(OAc)_2$ (0.02 mmol), $H_{x+3}PMo_{12-x}V_xO_{40} \cdot n\ H_2O$ (total *ca.* 0.14 mmol, calculated as n = 30) and benzene (30 mmol) in AcOH (10 mL) was allowed to react under 1 atm of O_2 at 90° C for 15 h.

[b] The same as Table 1.

[c] Benzene (60 mmol) in AcOH (20 mL) was reacted for 27 h.

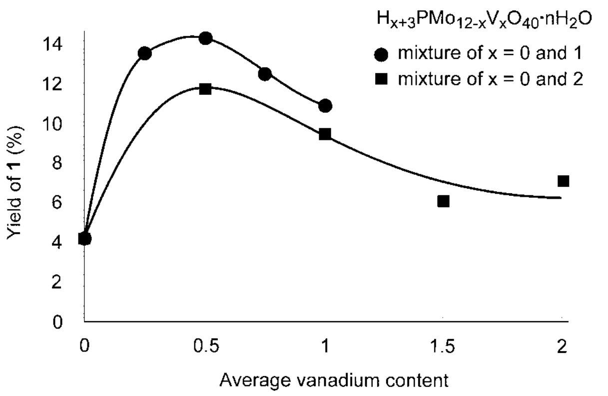


Figure 3. Effect of the average vanadium content in combined HPMoV.

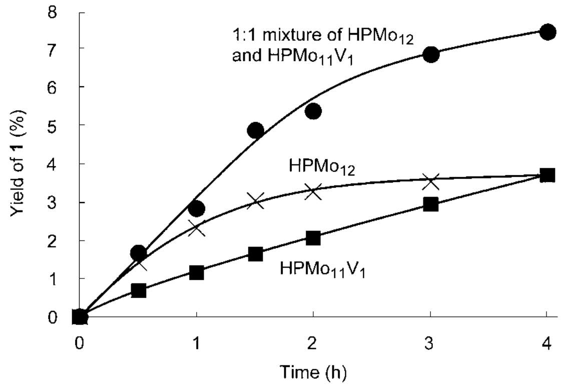


Figure 4. Time dependence curves using $HPMo_{12}$, $HPMo_{11}V_1$, and a 1:1 mixture of $HPMo_{12}$ and $HPMo_{11}V_1$ as a reoxidation catalyst.

O_2 in the reaction solution proceeds more slowly than that of Pd(0) to Pd(II) by HPMoV. Owing to the complexity of the present catalytic system, it is rather difficult to predict clearly the reaction pathway, but it seems likely that the reoxidation step of the reduced HPMoV by O_2 is the slowest step in the present reaction. When the reaction was carried out in 10 mL of AcOH, the best results were obtained (Runs 1, 10, and 11). The reaction at higher temperature over 90 °C resulted in a decrease of **1** (Runs 12 to 14). From reactions under varying pressures of air (1 ~ 20 atm), the coupling was found to proceed smoothly under 10 atm of air (Runs 1, 16, and 17). The present oxidation was markedly affected by the amount of benzene loaded (Runs 18 to 22). The product yields increased with increasing quantity of the benzene up to 40 mmol, but the yields drastically decreased when 45 mmol of the benzene was loaded. It was found that the color of the reaction solution using excess benzene (>45 mmol) varied readily from orange to dark blue, and that the reaction stopped at this stage. This color change suggests that the V^{5+} ion in the HPMoV may be sharply reduced to a low-valent V species like V^{4+} and V^{3+} when excess benzene is present in the reaction system, and reoxidation of the extensively reduced V species in the HPMoV with O_2 to the original oxidation state of the HPMoV becomes difficult. As a result, the reoxidation of Pd(0) to Pd(II) by the HPMoV would be difficult, and the reaction may be terminated at this stage.

The $Pd(OAc)_2$-catalyzed coupling reaction of benzene was examined under the influence of two different types of HPMoV differing in V and Mo contents like $HPMo_{12}$, $HPMo_{11}V_1$, $HPMo_{10}V_2$, and $HPMo_9V_3$ (Table 3). It was found that the catalytic activity of $Pd(OAc)_2$ was considerably affected by the combination of two HPMoV's. $Pd(OAc)_2$ combined with an approximately 1:1 mixture of $HPMo_{11}V_1$ and $HPMo_{12}$ gave the best yield of **1** (14.3%) and the highest TON (151) of $Pd(OAc)_2$ (Run 2). Among the reactions examined by several combinations of different HPMoV catalysts, a molybdovanadophosphate obtained by a 1:1 mixture of the $HPMo_{11}V_1$ and the $HPMo_{12}$ showed the highest activity. The HPMoV derived from a 1:2 mixture of $HPMo_{11}V_1$ and $HPMo_{12}$

also indicated relatively high catalytic activity (Figure 3). The TON of $Pd(OAc)_2$ decreased with increasing of the average V content in HPMoV derived from two HPMoV's. The reaction of benzene (60 mmol) in AcOH (20 mL) by this catalytic system produced **1** in 11.1% yield and the total TON of $Pd(OAc)_2$ was found to reach 213 (Run 9).

In order to obtain further information on the effect of the combination of two HPMoV's in the $Pd(OAc)_2$-catalyzed coupling of benzene, time-dependencies of **1** by the combination of $Pd(OAc)_2$ with $HPMo_{12}$, $HPMo_{11}V_1$, and a 1:1 mixture of $HPMo_{11}V_1$ and $HPMo_{12}$ were followed by GC (Figure 4). In the reaction using $HPMo_{12}$, **1** was formed in 3.0% yield within 1.5 h, but the Pd catalyst was rapidly deactivated. On the other hand, the reaction using $Pd(OAc)_2$ combined with $HPMo_{11}V_1$ progressed slowly to form **1** in lower yield (1.6%) after 1.5 h, but the catalytic activity was maintained for a long time to give **1** in 11% yield after 15 h (Table 1, Run 3). These results suggest that the reoxidation of Pd(0) to Pd(II) is rapidly promoted by the $HPMo_{12}$ rather than the $HPMo_{11}V_1$, but the reoxidation of the reduced Mo species in the $HPMo_{12}$ with O_2 to the original oxidation state of the $HPMo_{12}$ is difficult. When a 1:1 mixture of $HPMo_{11}V_1$ and $HPMo_{12}$ was employed as the reoxidation catalyst, coupling of benzene to **1** proceeded smoothly to give the latter in 14.3% yield at 15 h (Table 3, Run 2). In the $Pd(OAc)_2$-catalyzed reaction of benzene using a 1:1 mixture of $HPMo_{11}V_1$ and $HPMo_{12}$, ^{31}P NMR monitoring of the reaction solution was examined (Figure 5). Before the reaction at 50 °C, two ^{31}P NMR peaks corresponding to $HPMo_{11}V_1$ and $HPMo_{12}$ were observed at $\delta = -1.61$ and -2.26, respectively [Figure 5 (a)]. When the reaction temperature was raised from 50 °C to 90 °C, the ^{31}P NMR spectrum changed to show one broad peak at $\delta = -1.98$ and the peak corresponding to the $HPMo_{11}V_1$ disappeared [Figure 5 (b)]. After 3 h, the peak at $\delta = -1.98$ was slightly shifted to upfield [Figure 5 (c)]. After cooling of the reaction solution at 50 °C, the ^{31}P NMR spectrum showed a signal at $\delta = -2.17$ but two peaks based on the $HPMo_{11}V_1$ and $HPMo_{12}$ were not regenerated [Figure 5 (d)]. At this time, the color of the solution was dark green and **1** was obtained in 3.9% yield. A similar ^{31}P NMR monitoring of the 1:1 mixture of $HPMo_{11}V_1$ and $HPMo_{12}$ while removing the benzene from the reaction solution showed two ^{31}P peaks corresponding to $HPMo_{11}V_1$ and $HPMo_{12}$ even at 90 °C. Although it is difficult to explain the disappearance of the ^{31}P peak based on the $HPMo_{11}V_1$ after the reaction, the $HPMo_{11}V_1$ may be changed to a complex mixture of several reduction states during the reaction. As a result, these ^{31}P signals are difficult to be observed. The details of the synergistic effect of two different types of HPMoV are not clear at this stage, but the redox potential of the HPMoV seems to be very important to prompt the Pd(II)-catalyzed coupling reaction.

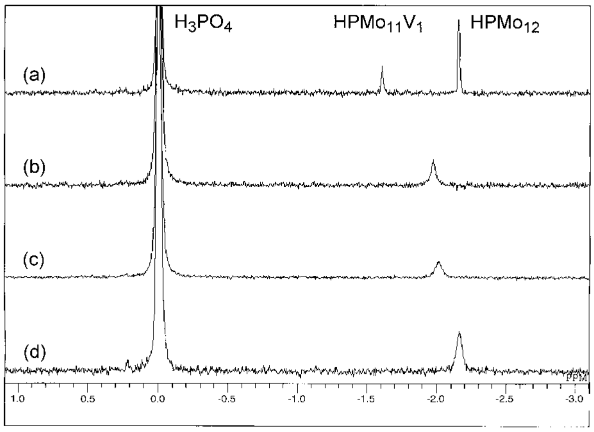
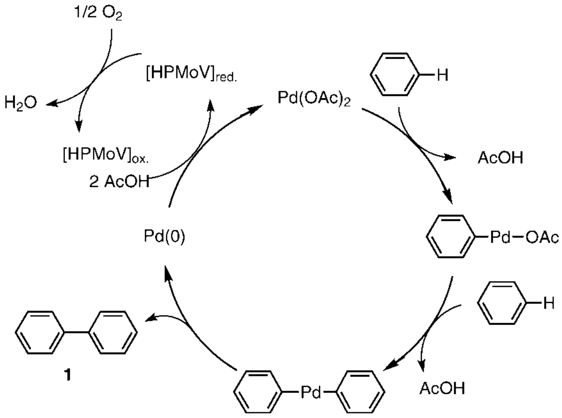


Figure 5. ^{31}P NMR spectra of a mixture of $HPMo_{11}V_1$ and $HPMo_{12}$ in acetic acid in the presence of $Pd(OAc)_2$ and benzene in several conditions; (a) reaction mixture at 50 °C, (b) after raising the temperature to 90 °C, (c) after 3 h at 90 °C, (d) dropped back to 50 °C.

Conclusion

It is thought that the present coupling proceeds via a similar reaction mechanism involving the electrophilic attack of a Pd(II) species to benzene proposed by Lyons (Scheme 2),[11a] and the formed phenylpalladium(II) acetate reacts with benzene followed by reductive elimination to give **1** and Pd(0). The reduced Pd(0) is reoxidized to Pd(II) by the $HPMoV/O_2$ system.

In conclusion, a new reoxidation catalytic system, consisting of two different types of HPMoV, of the reduced Pd(0) was developed. Thus, the oxidative coupling of benzene to biphenyl **1** with O_2 (1 atm) can be efficiently achieved by $Pd(OAc)_2$ using a 1:1 mixture of $HPMo_{11}V_1$ and $HPMo_{12}$ as the reoxidation catalyst. Further investigation to extend the present catalytic system for the oxidative coupling of various aromatic compounds is in progress.



Scheme 2.

Experimental Section

General

All solvents and reagents were purchased from commercial sources and used without further purification unless otherwise noted. All heteropoly acids were obtained from Nippon Inorganic Colour & Chemical Co., Ltd., except for $HPMo_{12}$ (from Wako). Analytical TLC was performed on Merck TLC Plastic sheets F_{254} silica gel 60, using UV light and I_2. NMR spectra were recorded on JEOL JNM-EX-270. ^1H and ^{13}C NMR were measured at 270 and 67.5 MHz, respectively, in $CDCl_3$ with Me_4Si as the internal standard. ^{31}P NMR was measured at 109.25 MHz in AcOH with 85%-H_3PO_4 in sealed capillary as the external standard. The chemical shifts were reported on the δ scale with resonances upfield of H_3PO_4 ($\delta = 0$) as negative. Infrared spectra (IR) were measured on a Perkin Elmer 1600 using the NaCl plate or KBr method. GLC analyses were performed on Shimadzu GC-17A equipped with a flame ionization detector using a 25 m (0.22 mm i.d., 0.25 μm film thickness) ID-BP1 SGE fused silica capillary column. Mass spectra were determined on Perkin Elmer Q-Mass 910 at an ionizing voltage of 70 eV.

Typical Procedure for the Oxidative Coupling of Benzene to Biphenyl (1)

A solution of $Pd(OAc)_2$ (0.02 mmol), $H_4PMo_{11}V_1O_{40} \cdot n\ H_2O$ ($HPMo_{11}V_1$) (323 mg, *ca.* 0.14 mmol) and benzene (30 mmol) in AcOH (10 mL) was placed in a round-bottom flask (30 mL) equipped with a balloon filled with O_2, and the mixture was allowed to react under stirring at 90 °C for 15 h. The reaction gave biphenyl (**1**), a mixture of *o*-, *m*-, and *p*-terphenyls (**2**), and phenol (**3**) in 10.9%, 2.1%, and 0.3% yields, respectively, with total turn-over number of 108 based on $Pd(OAc)_2$ used. All yields were determined by GLC analyses using undecane as internal standard. The products were commercially available and identified through comparison of the isolated product with an authentic sample.

Acknowledgements

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References and Notes

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[13] Molecular weight of $HPMo_{11}V_1$ was estimated as $H_4PMo_{11}V_1O_{40} \cdot 30\ H_2O$.