Available online at www.sciencedirect.com

SCIENCE DIRECT

Journal of Organometallic Chemistry 664 (2002) 59–65

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Highly selective synthesis of biphenyl by the $Pd(OAc)_2/HPA/O_2/AcOH$ catalyst system

Makoto Okamoto, Midori Watanabe, Teizo Yamaji *

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 6-10-1, Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

Received 4 July 2002; received in revised form 6 September 2002; accepted 12 September 2002

Abstract

A new catalytic system, $Pd(OAc)_2/H_3PMo_{12}O_{40}/O_2/AcOH-H_2O$ (2:1), has been found to give biphenyl by the oxidative dimerization of benzene with 100% selectivity and 19% yield under the conditions of 130 °C, 10 atm and 4 h. $PdHPMo_{12}O_{40}$ itself was also found to act as a catalyst to give 95% of selectivity of biphenyl with a lower yield. A plausible mechanism of this system is also discussed.

Keywords: Biphenyl; Oxidative dimerization; Benzene; $Pd(OAc)_2$; $H_3PMo_{12}O_{40}$

1. Introduction

Biphenyl is an important industrial material used as a heat transfer agent, an antimildew agent or a raw material of synthetic resins [1,2]. It is presently manufactured in a vapor phase dehydrogenative dimerization of benzene [2]. However, a low temperature liquid phase synthesis of biphenyl from benzene is also interesting both scientifically and industrially. The Pd-catalyzed dimerization of benzene in a liquid phase has been studied extensively [3–6] However, there are few reports on the selectivity of biphenyl synthesis in the presence of O_2 and acetic acid except that we reported recently [7].

Kozhevnikov and coworkers reported that the selectivity of biphenyl in $PdSO_4$-catalyzed dimerization of benzene using a Keggin type HPA, $H_5PMo_{10}V_2O_{40}$ as a cocatalyst by oxygen in $AcOH-H_2O$ (80:20) with sulfuric acid to the system. It was 73% on the basis of absorbed oxygen at 84 °C [8]. As seen from these data it seemed to be difficult to increase the selectivity for biphenyl because of the preferential hydroxylation of benzene at a high temperature.

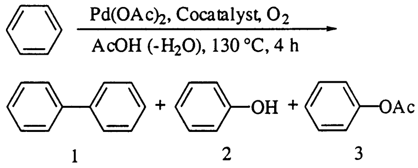
We have reported that biphenyl can be synthesized with a high selectivity (88%) by the Pd-catalyzed dimerization of benzene in the presence of $MoO_2(acac)_2$ as a cocatalyst and O_2 in acetic acid [7].

In continuing study, we have recently investigated the effect of HPAs of Keggin type containing molybdenum such as $H_4SiW_{12-n}Mo_n$, $H_{15-n}PV_{12-n}Mo_nO_{40}$, and $H_3PW_{12-n}Mo_nO_{40}$ as a cocatalyst in the $Pd(OAc)_2$-catalyzed dimerization of benzene in the presence of O_2 and acetic acid (Eq. (1)) and found that HPAs of Keggin type containing molybdenum act as an excellent cocatalyst to obtain biphenyl from benzene in the $Pd(OAc)_2/HPA/O_2/AcOH$ catalyst system. One of main purposes of this research is to develop a process to be applied industrially with no by-products. It is also our target in the future to recycle the catalyst which has the same anion ligand in a catalyst with a solvent. Here we report the details.

---

* Corresponding author. Tel./fax: +81-92-6424374
E-mail address: yamaji@cstf.kyushu-u.ac.jp (T. Yamaji).

0022-328X/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0022-328X(02)01901-0



(1)

2. Results and discussion

2.1. Efficiency of oxidative dimerization of benzene with various heteropolyacid cocatalysts

Table 1 shows representative results of various HPA cocatalysts. The reaction without a HPA as a cocatalyst gives a mixture of 1, 2, and 3 (entry 1). We have carried out the reaction using $H_3PW_{12-n}Mo_nO_{40}$ as a HPA. From this table, the addition of a HPA as a cocatalyst retarded the formation of phenol dramatically. $H_3PMo_{12}O_{40}$ exhibited the best result of 94% (entry 8). $H_3PW_2Mo_{10}O_{40}$ was the second best (entry 7). The substitution of P with Si in $H_3PMo_{12}O_{40}$ did not change much the selectivity of biphenyl (entry 11). However, the use of $H_4SiW_6Mo_6O_{40}$ and $H_7PV_4Mo_8O_{40}$ exhibited inferior results (entries 9 and 10) as compared with the corresponding $H_3PW_{12-n}Mo_nO_{40}$.

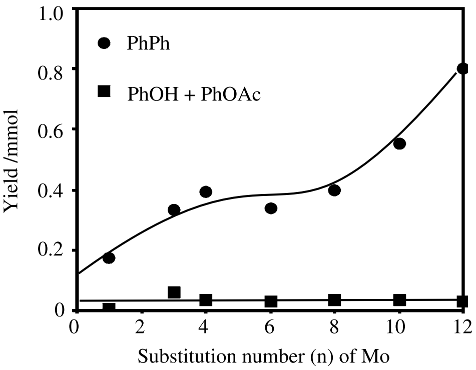


Fig. 1. Effect of composition of $H_3PW_{12-n}Mo_nO_{40}$. Conditions: volume of autoclave (100 cm^3), $Pd(OAc)_2$ (0.13 mmol), HPA (Mo/Pd = 0.5), AcOH (3.0 g), benzene (38 mmol), O_2 (10 kg cm^{-2}), 130 °C, 4 h.

To elucidate the effect on the substitution number of molybdenum atom in $H_3PW_{12-n}Mo_nO_{40}$, the relationship of the yield of the products against the substitution number of molybdenum atom in $H_3PW_{12-n}Mo_nO_{40}$ was examined (Fig. 1). As shown in Fig. 1, the yield of biphenyl increased with increasing the substitution number of molybdenum atom in $H_3PW_{12-n}Mo_nO_{40}$. The HPA fully substituted by molybdenum atom ($H_3PMo_{12}O_{40}$) gave the best result. The selectivity of phenols stayed low, almost constant through the increase of molybdenum ratio.

Table 1
Effect of HPAs [a]

Entry	HPA	Product (mmol) [b]			1/(1+2+3) (%)
		1	2	3	
1	None	0.47	0.44	0.03	50
2	$H_3PW_{11}Mo_1O_{40}$	0.17	0.00	0.00	100
3	$H_3PW_9Mo_3O_{40}$	0.34	0.06	0.01	83
4	$H_3PW_8Mo_4O_{40}$	0.39	0.04	0.01	89
5	$H_3PW_6Mo_6O_{40}$	0.34	0.03	0.01	89
6	$H_3PW_4Mo_8O_{40}$	0.40	0.03	0.01	91
7	$H_3PW_2Mo_{10}O_{40}$	0.55	0.03	0.01	93
8	$H_3PMo_{12}O_{40}$	0.80	0.03	0.02	94
9	$H_4SiW_6Mo_6O_{40}$	0.42	0.11	0.02	76
10	$H_7PV_4Mo_8O_{40}$	0.79	0.29	0.02	72
11	$H_4SiMo_{12}O_{40}$	0.71	0.04	0.02	92

[a] Conditions: volume of autoclave (100 cm^3), $Pd(OAc)_2$ (0.13 mmol), HPA (Mo/Pd = 0.5), AcOH (3.0 g), benzene (38 mmol), O_2 (10 kg cm^{-2}), 130 °C, 4 h.

2.2. Effect of substitution of acidic protons of a heteropolyacid by a Pd^{2+} or a tetrabutylammonium cation

In order to compare the results with proton type HPAs, we investigated the reactions using HPAs substituted by a Pd^{2+} or tetramethylammonium cations.

Table 2 summarizes the results of the effect of replacing the acidic protons in a HPA by a Pd^{2+} or tetrabutylammonium (TBA) cations. As can be seen from the table $PdHPMo_{12}O_{40}$ gave the same result with the corresponding $H_3PMo_{12}O_{40}$ (entry 8). The change of P to Si in $PdHPMo_{12}O_{40}$ type HPA afforded almost the same result (entry 5). The decrease of Mo/Pd ratio in the system to 0.25 increased the selectivity to 95% (entry 4).

Table 2
Effect of HPAs [a]

Entry	HPA	Product (mmol) [b]			1/(1+2+3) (%)
		1	2	3	
1	None	0.47	0.44	0.03	50
2	$PdHPW_6Mo_6O_{40}$	0.41	0.10	0.01	79
3	$PdH_2SiW_6Mo_6O_{40}$	0.39	0.05	0.01	87
4	$PdH_2SiMo_{12}O_{40}$ [c]	0.86	0.04	0.01	95
5	$PdH_2SiMo_{12}O_{40}$	0.88	0.06	0.01	93
6	$PdH_2SiMo_{12}O_{40}$ [d]	0.52	0.05	0.01	90
7	$PdH_2SiMo_{12}O_{40}$ [e]	0.67	0.06	0.01	91
8	$PdHPMo_{12}O_{40}$	0.82	0.03	0.02	94
9	$PdHPMo_{12}O_{40}$ [f]	0.19	0.01	0.00	95
10	$(TBA)_3PW_6Mo_6O_{40}$	0.40	0.17	0.02	68

[a] Conditions: volume of autoclave (100 cm^3), $Pd(OAc)_2$ (0.13 mmol), HPA (Mo/Pd = 0.5), AcOH (3.0 g), benzene (38 mmol), O_2 (10 kg cm^{-2}), 130 °C, 4 h.

[b] Determined by GC.

[c] Mo/Pd = 0.25.

[d] Mo/Pd = 0.75.

[e] Mo/Pd = 1.0.

However, the same replacement of P to Si gave a better selectivity in $PdH_2SiW_6Mo_6O_{40}$ (entry 3).

The increase of Mo/Pd ratio to 0.05–0.1 decreased biphenyl productivity and selectivity (entries 6 and 7).

The change of all protons by TBA cations in $H_3PW_6Mo_6O_{40}$ also decreased the selectivity (entry 10).

The most striking result is that $PdHPMo_{12}O_{40}$ itself acted as a catalyst to give 95% selectivity of biphenyl with a lower yield of biphenyl (entry 9). The productivity ratio of entries 9/entry 8 for biphenyl is 0.23. On the contrary Pd usage ratio of entries 9/entry 8 is 0.1. This means that the complex of the type of $PdHPMo_{12}O_{40}$ can produce as much as 2.3-fold of biphenyl in the case of entry 9. This suggests that when a proton type HPA cocatalyst is added to the Pd catalyst it may form a kind of Pd–HPA complex to act as an active catalyst to facilitate the production of biphenyl.

2.3. *Effect of composition of $H_3PW_{12-n}Mo_nO_{40}$ against TONs of Pd*

It is interesting to see the effect of composition of heteropolyacid on the productivity of Pd. Fig. 2 shows such results. One can see that the TON ratio in the presence of $H_3PW_{12-n}Mo_nO_{40}$ and in the absence of it increases with the increase of n from 1 to 4 and stays constant until 6, then increases again to 12. However, the ratio does not exceed 1 in the case of these types of heteropolyacids up to n 10. This means that selectivity increase depresses the productivity of biphenyl in case of a HPA of these types indicating the difference of type of catalytic mode with or without HPA in the reaction. $H_3PMo_{12}O_{40}$ acted very effectively.

2.4. *Effect of weight ratio of H_2O against AcOH in a solvent*

We found that a complex formation of Pd with a HPA might accelerate the reaction. By this information we tried to add H_2O to the solvent to increase the solubility of a HPA in the solvent. The results are shown in Table 3. Best yield of biphenyl was obtained in a solvent with AcOH/H_2O ratio of 2. Entries 2 and 3 also showed these effects giving higher yields than the case of no water in the solvent. When H_2O only was used as a solvent, no biphenyl was formed.

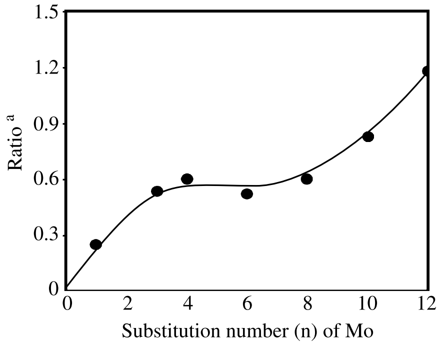


Fig. 2. Effect of composition of $H_3PW_{12-n}Mo_nO_{40}$. Conditions: volume of autoclave (100 ml), $Pd(OAc)_2$ (0.13 mmol), $H_3PW_{12-n}Mo_nO_{40}$ (Mo/Pd = 0.5), PhH (38 mmol), AcOH (3.0 g), O_2 (10 atm), 130 °C, 4 h. [a] TON with a HPA/TON without a HPA.

Table 3
Effect of the weight ratio of H_2O against AcOH solvent [a]

Entry	AcOH (g)	H_2O (g)	Product (mmol) [b]			1/(1+2+3) (%)
			1	2	3	
1	3	0	0.80	0.03	0.02	94
2	2	1	2.42	0.08	0.07	94
3	1	2	1.40	0.01	0.02	98
4	0	3	0.00	0.00	0.00	–

[a] Conditions: volume of autoclave (100 ml), $Pd(OAc)_2$ (0.13 mmol), $H_3PMo_{12}O_{40}$ (5.5 mmol), PhH (38 mmol), AcOH, H_2O, O_2 (10 atm), 130 °C, 4 h.

2.5. *Effect of the amount of $H_3PMo_{12}O_{40}$ in AcOH–H_2O solvent*

By adding more HPA in a more soluble solvent, the productivity of biphenyl may increase. We changed the amount of HPA added to the solvent of AcOH–H_2O (weight ratio 2:1). These results are shown in Table 4. When 0.06 mmol amount of HPA is added to the system it gave all biphenyl and no phenols at all (entry 2). It is a very surprising fact. When the amount was increased up to 0.28 mmol the selectivity stayed 100% and the yield also stayed almost constant. However, the yield decreased after that. It may be due to the formation of an undesired active complex. Fig. 3 shows the yield of biphenyl versus the amount of the HPA. From this figure one can see that around 0.2 mmol of HPA is appropriate for this reaction.

Table 4
Effect of the amount of $H_3PMo_{12}O_{40}$ in AcOH–H_2O solvent [a]

Entry	$H_3PMo_{12}O_{40}$ (mmol)	Product (mmol) [b]			1/(1+2+3) (%)
		1	2	3	
1	0.01	0.80	0.03	0.02	94
2	0.06	3.13	0.00	0.00	100
3	0.17	3.63	0.01	0.00	100
4	0.28	3.46	0.01	0.00	100
5	0.56	1.78	0.02	0.00	99

[a] Conditions: volume of autoclave (100 cm^3), $Pd(OAc)_2$ (0.13 mmol), $H_3PMo_{12}O_{40}$, PhH (38 mmol), AcOH (2.0 g), H_2O (1.0 g), O_2 (10 kg cm^{-2}), 130 °C, 4 h.

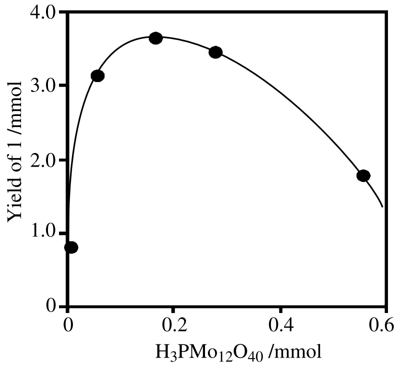


Fig. 3. Effect of the amount of $H_3PMo_{12}O_{40}$. [a] Conditions: volume of autoclave (100 cm^3), $Pd(OAc)_2$ (0.13 mmol), $H_3PMo_{12}O_{40}$, PhH (38 mmol), AcOH (2.0 g), H_2O (1.0 g), O_2 (10 kg cm^{-2}), 130 °C, 4 h. [b] Determined by GC.

2.6. Effect of radical scavengers

In order to investigate the reaction mechanism we did the experiments using radical scavengers in this reaction system. Table 5 gives the results. Entry 2 supports that the formation of phenol is explained by a radical mechanism. Entry 3 also supports the radical process. The polyol scavenger did not give a clear-cut result because of its partial decomposition in the reaction system (entry 4). Other scavengers (entries 5–7) decomposed completely at this temperature and inhibited this reaction. It is under investigation why the reaction was stopped by the decomposition of these scavengers.

2.7. ^{31}P-NMR spectra of $H_3PMo_{12}O_{40}$, $PdHPMo_{12}O_{40}$ and the reaction mixture

Fig. 4 shows the ^{31}P-NMR spectra of HPA ($H_3PMo_{12}O_{40}$), $PdHPMo_{12}O_{40}$ and the reaction mixture at room temperature in d-water. They show two types of peaks, one at around -3.4–-3.6 ppm and the other around -1.31 to -1.32 ppm in the former two complexes. The first peak is responsible for PMo_{12} species and the second is for PMo_9 species. The reaction

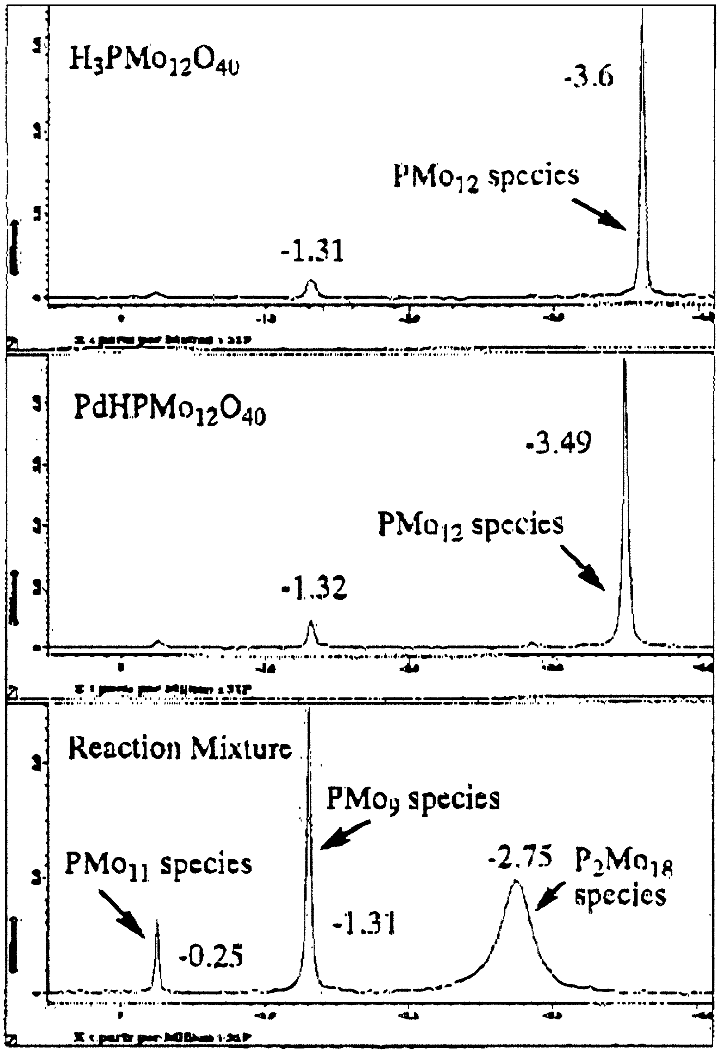
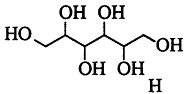
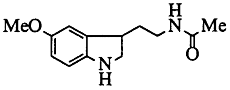
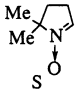
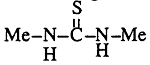


Fig. 4. ^{31}P-NMR spectra of active species in the reaction (ppm from down field from 85% H_3PO_4).

Table 5
Effect of radical scavengers [a]

Entry	Radical scavenger	Product (mmol)[b]			1/(1+2+3) %
		1	2	3	
1	None	0.47	0.44	0.03	50
2	DMSO	1.29	0.11	0.03	90
3	^{t}BuOH	0.44	0.37	0.03	52
4		0.67	0.78	0.05	45
5		trace	0.03	trace	-
6		0.03	0.04	trace	-
7	 $Me{-}\underset{H}{N}{-}\overset{S}{\overset{\Vert}{C}}{-}\underset{H}{N}{-}Me$	0.01	0.04	trace	-

[a] Conditions: volume of autoclave (100 cm^3), $Pd(OAc)_2$ (0.13 mmol), radical scavenger (1.0 mmol), PhH (38 mmol), AcOH (3.0 g), O_2 (10 kg cm^{-2}), 130 °C, 4 h.

[b] Determined by GC.

mixture showed three peaks at −2.75, −1.31 (main peak), and −0.25 ppm. These three peaks are responsible for P_2Mo_{18}, PMo_9 and PMo_{11}, respectively. The striking fact is that the peak for PMo_{12} species is not found in the reaction mixture showing that PMo_{12} species does not exist in the reaction system.

By the facts obtained above we estimated the active species of the reaction in the following way [9]. $PMo_{12}O_{40}^{3-}$ species reacts with water to give $PMo_9O_{31}(H_2O)^{3-}$ species losing $3MoO_3$. $PMo_9O_{31}(H_2O)^{3-}$ undergoes deprotonation or protonation to give a variety of PMo_9O_{31} species in Fig. 5. This $PMo_9O_{31}(H_2O)^{3-}$ species gives a $P_2Mo_{18}O_{62}^{6-}$ species at a low temperature like room temperature. However, this species is not observed at high temperature like 130 °C. The $PMo_{12}O_{40}^{3-}$ species also forms $PMo_{11}O_{39}^{7-}$ species. Considering all these possibilities we estimated the active species of this reaction are a variety of PMo_9O_{31} ones forming the equilibrium depending on the reaction conditions as given in Fig. 5.

2.8. Possible mechanism and catalytic image of an active catalyst

The attainment of high selectivity of biphenyl by a HPA containing Mo is estimated in the following way as depicted by Fu and Ono [10]. The OH radical from HOOH formed [4] reacts with OH radical of Mo-polyanion of a HPA to form H_2O and oxomolybdenum species (Mo=O) which then reacts with AcOH to give Mo–OH and AcO^-. This catalytic cycle is completed as shown in Fig. 6.

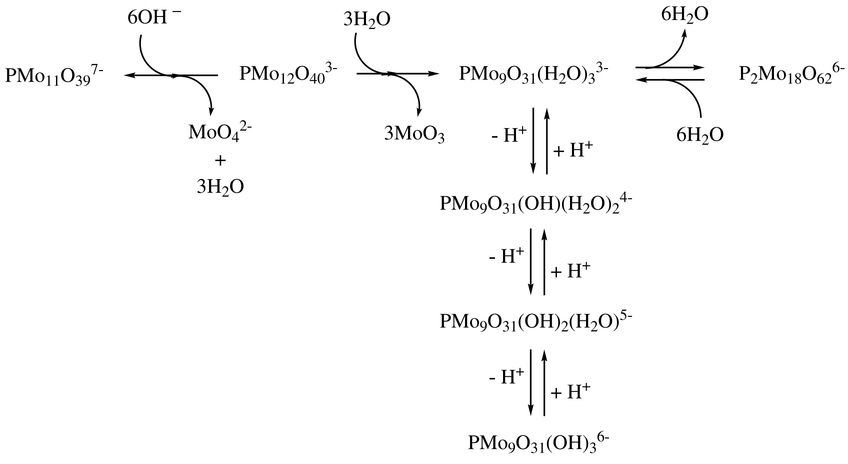


Fig. 5. The variation of a HPA structure.

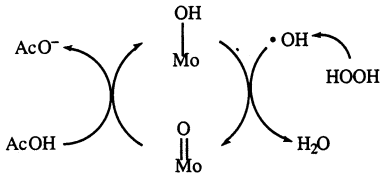


Fig. 6. Scavenging hydroxy species by Mo(OH) species of a HPA.

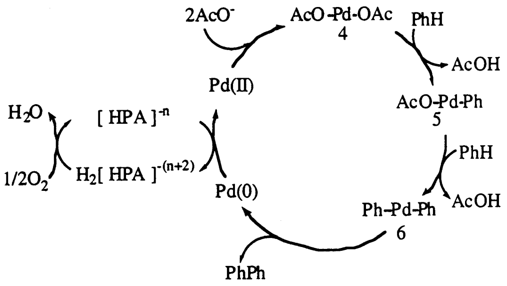


Fig. 7. Possible mechanism.

By considering the facts given and above discussion we would like to postulate the following possible mechanism and catalytic image of our biphenyl synthesis reaction in Figs. 7 and 8.

The main point in the possible reaction mechanism is that Pd(0) is reoxidized by the help of a HPA polyanion through the formation of the complex shown in Fig. 8 affording Mo–O–Pd bonding to facilitate the production of Pd^{2+} from Pd(0) and attains a high selectivity of biphenyl by the formation of Mo–OH bond in a HPA polyanion to react with a OH radical from HOOH formed. The increase of properly composed Mo atom in a HPA may increase the chance of an active catalyst to decompose OH radical to give a high selectivity of biphenyl.

This Mo atom increase also might give more chances to form a Pd–O–Mo bonding to facilitate a formation of Pd(II) from Pd(0) by oxygen molecule.

Therefore, the most productivity and the selectivity 100% of biphenyl by $Pd(OAc)_2$ may be attained by $H_3PMo_{12}O_{40}$ cocatalyst which has properly composed Mo atoms for this reaction. The oxidation through Pd–O–Mo bonding may be stable but not so fast as a direct oxidation of Pd(0) by molecular oxygen.

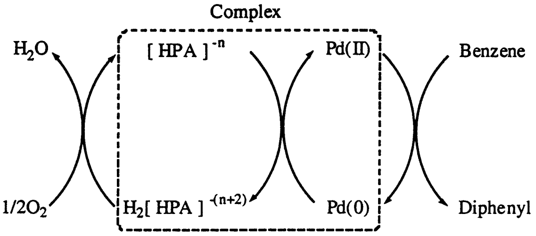


Fig. 8. Possible mechanistic roles of $Pd(OAc)_2$ and HPA in the oxidative dimerization of benzene to biphenyl.

Kozhernikov and coworkers [8] used a low temperature like 84 °C. We used a temperature like 130 °C. The activity difference of a complex at different temperatures might have caused the difference of the best cocatalyst. These are now under investigation.

3. Conclusion

It was found that biphenyl could be synthesized with 100% selectivity by Pd-catalyzed dimerization of benzene in the presence of $H_3PMo_{12}O_{40}$ as a cocatalyst and O_2 in $AcOH/H_2O$ solvent at 130 °C.

It was also found that $PdHPMo_{12}O_{40}$ itself can act as a catalyst to give 95% selectivity with a lower yield of biphenyl.

4. Experimental

Pd salts of HPA were gifted generously from Teijin Ltd. All other reagents were obtained commercially and used as received.

A typical reaction was carried out as follows: in a 100-cm^3 stainless steel autoclave equipped with a magnetic stirrer bar, a pressure gauge and a thermocouple were charged C_6H_6 (38 mmol), AcOH (3 g), 0.13 mmol of $Pd(AcO)_2$ and a HPA (Mo/Pd = 0.5) and then oxygen was introduced to the pressure of 10 atm after flashing two times. The mixture was heated at 130 °C with stirring for 4 h. After the reaction the products were analyzed by gas chromatography. The analyses were performed on a Shimazu GC-14B system with a SUPELCO WAX capillary column of 60 m × 0.32 mm × 0.5 mm using naphthalene as an internal standard under the conditions of injection and detector temperatures (100–200 °C, 2 min^{-1}) and He (220 kPa).

^{31}P-NMR spectra were recorded on a JEOL ECP-400 (162 MHz) spectrometer using D_2O as a solvent at 25 °C; chemical shifts were expressed in parts per million downfield from 85% H_3PO_4.

Acknowledgements

This work was supported by Research Institute of Innovative Technology for the Earth (RITE 12C31). Heteropolyacids were generously gifted by Nippon Inorganic Color and Chemical Co., Ltd.

References

[1] I.S. Popushoi, E.D. Kogan, E.P. Styngach, M.S. Yamko, O.M. Radul, A.I. Reinbold, Izu. Akad. Nauk. Mold. SSR, Ser. Biol. Khim. Nauk. 1 (1987) 69.

[2] A. Standen, Kirk-Othmer Encyclopedia of Chemical Technology, vol. 7, 2nd ed., Interscience Publishers, New York, 1972, p. 191.

[3] H. Itatani, H. Yoshimoto, Chem. Ind. (1971) 674.

[4] R. Van Helden, G. Verberg, Rec. Trav. Chim. Pays-bas 84 (1965) 1263.

[5] (a) Y. Ichikawa, T. Yamaji, Japanese Patent 10303, 1975;
(b) Y. Ichikawa, T. Yamaji, Chem. Abstr. 83 (1975) 147271m.

[6] Y. Fujiwara, I. Moritani, K. Ikegami, R. Tanaka, S. Teranishi, Bull. Chem. Soc. Jpn. 43 (1970) 863.

[7] M. Okamoto, T. Yamaji, Chem. Lett. (2001) 212.

[8] G.U. Mennenga, A.I. Rudenkov, K.I. Matveev, I.V. Kozhevnikov, React. Kinet. Catal. Lett. 5 (1976) 401.

[9] The Chemical Society of Japan, Jikken Kagaku Koza, 4th ed., No. 17, Maruzen Co. Ltd., Japan, 1991, p. 462.

[10] Z. Fu, Y. Ono, J. Mol. Catal. A: Chem. 118 (1997) 293.