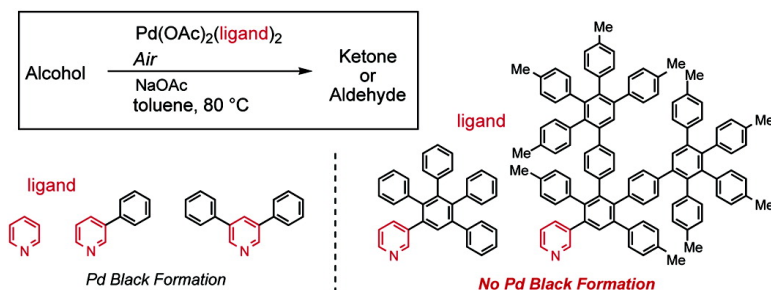


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J. Am. Chem. Soc., **2004**, 126 (21), 6554-6555 • DOI: 10.1021/ja031936l • Publication Date (Web): 07 May 2004

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Homogeneous Palladium Catalyst Suppressing Pd Black Formation in Air Oxidation of Alcohols

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A homogeneous transition metal-catalyzed reaction is one of the most versatile methods for synthesizing useful and necessary molecules. However, there is a persistent problem that metal aggregation and precipitation cause catalyst decomposition and a considerable loss of catalytic activity.¹ In particular, Pd catalysts are known to aggregate easily and form Pd black, although they realize a wide variety of useful reactions in organic synthesis.² To overcome this intrinsic problem of homogeneous Pd catalysis, we explored a new class of Pd catalyst with adopting aerobic oxidation of alcohols as a probe reaction.

Recently, aerobic oxidation of alcohols catalyzed by a homogeneous transition metal complex has received considerable attention as an environmentally benign reaction.³ Among them, Pd catalyst shows a good catalytic activity^{4,5} and asymmetric oxidation also has been realized.⁶ However, if reaction conditions were not fixed properly in these reactions, the Pd black formed very easily.^{3a,4a,d,e,5} There are two keys to successful catalytic reaction without the Pd black formation. One is sufficient oxygen partial pressure (typically 1 atm molecular oxygen,^{4a–e,g,5c,6} rather than air^{4f,5}). The other is low substrate to catalyst molar ratio (S/C: typically 20^{4a,c–f,6a,d,e} or less^{4f,6b}).

Herein we report a new catalyst system that suppresses the Pd black formation even under 1 atm air and with a high S/C (> 1000). None of the homogeneous palladium catalysts reported so far^{4–7} would survive under these reaction conditions. We designed and prepared pyridine derivatives having a 2,3,4,5-tetraphenylphenyl⁸ substituent and its higher dendritic unit at the 3-position (**1** and **2**). The palladium complexes having **1** and **2** as a ligand, namely, Pd(OAc)₂(**1**)₂ and Pd(OAc)₂(**2**)₂, successfully suppress the Pd black formation and achieved the highest TON = 1480 in homogeneous palladium-catalyzed air oxidation of alcohols.^{9,10}

Dendrimers having a 2,3,4,5-tetraphenylphenyl moiety were synthesized by Müllen et al. and utilized as polyphenylene nanomaterials.⁸ We are interested in their spatially spread rigid structure. A series of novel pyridine derivatives bearing the 2,3,4,5-tetraphenylphenyl substituent, **1–6**, were synthesized (Figure 1). Due to its limited solubility of **3**, a methylated analogue (**2**) was prepared. These pyridine ligands **1–5** as well as pyridine (Py), 3-phenylpyridine (3-PhPy), 3,5-diphenylpyridine (3,5-diPhPy), and 2,2'-bipyridine (Bipy) readily reacted with Pd(OAc)₂ in toluene and afforded the Pd(OAc)₂(ligand)₂ complexes quantitatively. The molecular structure of Pd(OAc)₂(**1**)₂ determined by crystallographic analysis is shown in Figure 2.¹¹ It is evident that the 2,3,4,5-tetraphenylphenyl substituent at the 3-position of the pyridine ring spatially spreads out and covers the wide area over the long-range from the Pd center. On the other hand, steric congestion around the Pd coordination sphere is essentially the same as that of corresponding pyridine complex Pd(OAc)₂(Py)₂,¹² implying that the large substituent at the 3-position would not obstruct the metal center.

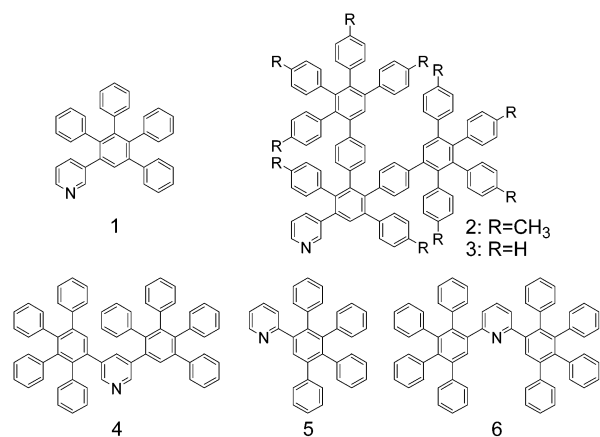


Figure 1. Novel pyridine ligands having 2,3,4,5-tetraphenylphenyl moiety.

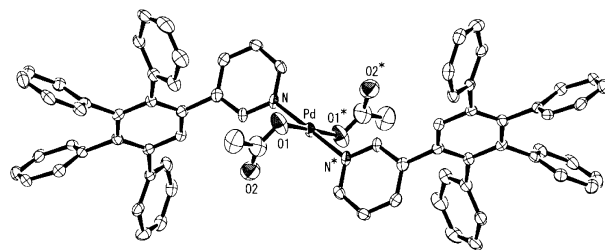


Figure 2. ORTEP drawing of Pd(OAc)₂(**1**)₂ with thermal ellipsoids at 50% probability levels. Hydrogen atoms have been omitted for clarity.

Actually, Pd(OAc)₂(Py)₂ and Pd(OAc)₂(**1**)₂ showed comparable catalytic activity at S/C = 20 in the aerobic oxidation of alcohols.

The Pd(OAc)₂(ligand)₂ was employed as a catalyst in the air oxidation in toluene at 80 °C (Table 1). The molar ratio of the alcohol to Pd(OAc)₂(ligand)₂ was fixed to 1000 (S/C = 1000). As an additive, NaOAc^{4b,5a} (0.1 equiv based on the alcohol) was employed.

Pd(OAc)₂ did not show catalytic activity in the oxidation of 1-phenylethanol (run 1). On the other hand, Pd(OAc)₂(Py)₂ catalyzed the oxidation and afforded acetophenone in 23% yield in 2 h. However, at this moment, the Pd catalyst decomposed completely into Pd black¹³ and the oxidation stopped (run 2). Pd(OAc)₂(3-PhPy)₂ and Pd(OAc)₂(3,5-diPhPy)₂ also resulted in complete Pd black formation within 6 h and afforded acetophenone in 34 and 32% yields, respectively (run 3 and 4). The reaction with Pd(OAc)₂(Bipy)₂ was very sluggish, although no Pd black formed (run 5). In contrast, Pd(OAc)₂(**1**)₂ afforded acetophenone in 87% yield without the Pd black formation (run 6) and the product was isolated in 97% yield after a prolonged reaction time (130 h). The higher dendritic analogue Pd(OAc)₂(**2**)₂ is a more efficient catalyst (run 7), realizing the highest TON = 1480 with S/C = 2000 (run 8). Pd(OAc)₂(**4**)₂ also catalyzed the reaction without the Pd black

Table 1. Effect of Pyridine Ligands on Palladium-Catalyzed Air Oxidation of Alcohols^a

run	alcohol	ligand ^b	time (h)	% yield ^c	Pd black formation ^d
1	1-phenylethanol ^e	none	7	trace	+
			24	trace	+
			24	23	+
2		Py	2	23	+
			24	23	+
3		3-PhPy	6	34	+
			6	32	+
4		3,5-diPhPy	6	32	+
			24	3	–
			72	6	–
5		Bipy	24	3	–
			72	6	–
			72	57	–
6		1	24	57	–
			72	87	–
			72	87	–
7		2	24	78	–
			72	>99 (95)	–
			72	74	–
8 ^f		2	96	74	–
			96	74	–
			96	74	–
9		4	24	44	–
			72	63	–
			96	67	–
10	2-octanol ^g	Py	2	21	+
			5	23	+
11 ^h		Py	2	21	+
			5	23	+
12		3-PhPy	3	21	+
			3	15	+
13		3,5-diPhPy	3	15	+
			3	15	+
14		1	96	69	–
			96	79 (75)	–
15		2	96	79 (75)	–
			96	67	–
16		4	96	67	–
			96	67	–

^a At 80 °C with S/C = 1000 in toluene under air (balloon). ^b Ligand of the Pd(OAc)₂(ligand)₂. ^c Determined by GC. Isolated yields in parentheses. ^d +: Complete Pd black formation. –: No Pd black formation. ^e 1-Phenylethanol (2 mmol), Pd(OAc)₂(ligand)₂ (0.002 mmol), NaOAc (0.2 mmol), and toluene (1 mL). ^f S/C = 2000, Pd(OAc)₂(2)₂ (0.001 mmol). ^g 2-Octanol (2.5 mmol), Pd(OAc)(ligand)₂ (0.0025 mmol), NaOAc (0.25 mmol), and toluene (0.8 mL). ^h With additional pyridine (0.02 mmol).

Table 2. Palladium-Catalyzed Air Oxidation of Various Alcohols^a

run	alcohol	S/C	ligand ^b	time (h)	% yield ^c	Pd black formation	
1	benzyl alcohol	1000	2	48	78 ^d	–	
				1	48	74 ^d	–
				2	23 ^d	+	
2	2-heptanol	1000	2	72	72	–	
				1	72	52	–
				8	27	+	
3	3-octanol ^e	1250	2	96	63	–	
				1	96	65	–
				4	18	+	
4	3,3-dimethyl-2-butanol	1000	1	96	89	–	
				4	32	+	
				4	32	+	
5	1-(4-methylphenyl)ethanol	750	1	44	81	–	
				3	32	+	
				3	32	+	
6	4-isopropylbenzyl alcohol	720	1	45	74 ^d	–	
				1	24 ^d	+	
				1	24 ^d	+	
7	2-hexanol	1000	1	96	72	–	
				2	24	+	
				2	24	+	
8	<i>trans</i> -2-methylcyclohexanol	1300	1	74	65	–	
				3	17	+	
				3	17	+	

^a At 80 °C with Pd(OAc)₂(ligand)₂ (0.002 mmol) and NaOAc (0.1 equiv to the alcohol) in toluene (1 mL) under air (balloon). ^b Ligand of the Pd(OAc)₂(ligand)₂. ^c Determined by GC. ^d Corresponding aldehyde. ^e Toluene (0.8 mL).

formation (run 9). However, the use of Pd(OAc)₂(5)₂ and a mixture of Pd(OAc)₂ and 6 (6/Pd = 2) as the catalyst resulted in trace yields due to the Pd black formation. Thus, the spatially spread moiety at the 3-position, not at the 2-position, effectively suppresses the Pd black formation and maintains the catalytic activity for a long time.¹⁴ Similar suppression was also observed in oxidation of 2-octanol (runs 10–16). Pd(OAc)₂(Py)₂ afforded Pd black within 2 h (run 10). It is noteworthy that even if an excess of pyridine (8 equiv) with respect to Pd(OAc)₂(Py)₂ was added (N/Pd = 10) in this system, Pd black formed within 5 h (run 11).

The marked effects of 1 and 2 over pyridine (Py) as a ligand at a high S/C ratio were also observed in the oxidation of other alcohols under air (Table 2). Pd(OAc)₂(1)₂ and Pd(OAc)₂(2)₂ maintained the catalytic activity to provide the products in high yields, while Pd(OAc)₂(Py)₂ afforded the Pd black within 1–4 h. A similar oxidation of allylic and primary aliphatic alcohols with Pd(OAc)₂(1)₂ and Pd(OAc)₂(Py)₂ resulted in low yields (5–30%). Further studies on prevention of catalyst deactivation are now in progress.

Supporting Information Available: Experimental procedures and spectroscopic data for 1–6 (PDF) and crystallographic data for Pd(OAc)₂(1)₂ (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (13) Pd black formation is affected considerably by the S/C ratio. Maintaining the same concentration of Pd(OAc)₂(Py)₂ as that in run 2 in Table 1 led to observation of complete Pd black formation within 2 h (S/C = 1000, run 2 in Table 1), 3 h (S/C = 700), 5 h (S/C = 400), and 7 h (S/C = 100), but no Pd black formation was observed with S/C = 50.
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JA031936L