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Electrochemical Generation of Cationic Pd Catalysts and Application to Pd/TEMPO Double-Mediatory Electrooxidative Wacker-Type Reactions

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Cationic palladium complexes with weakly coordinating anions have received much attention as catalysts. Over the past decade, many kinds of cationic palladium-catalyzed reactions have been reported.[1] The most common methods for preparing cationic palladium PdL_mR_n (L = ligands; R = anion, e.g., BF_4^-, PF_6^-, and ClO_4^-) are (i) the reaction of a palladium halide complex with metalated anion counter MR (M = Na^+, Ag^+) and (ii) the reaction of Pd sponge and nitrosonium salt (NOR).

$$\text{(i) } PdL_mX_n \xrightarrow[-n\text{MX}]{n\text{MR}} PdL_mR_n$$

$$\text{(ii) } Pd \xrightarrow[-n\text{NO}]{\text{mL}, n\text{NOR}} PdL_mR_n$$

We have been interested in electrooxidative molecular transformations[2] and, during the course of our study, we extended our research to the oxidative formation of metal complexes. In our preliminary study, we found that palladium acetate was readily electrooxidized at the anode to give cationic palladium species. We sought to improve the electrooxidation reaction to develop a method for the synthesis of cationic palladium and to use the resulting cationic palladium as a catalyst. The potential advantages of the electrooxidative generation system of cationic palladium catalysts are that (i) air and moisture sensitive active catalysts can be generated in situ from stable precursors and (ii) the system can be easily integrated into electrooxidative reactions. We report here the electrooxidative synthesis of cationic palladium complexes $[Pd(CH_3CN)_4][R]_2$ (R = BF_4^-, PF_6^-, and ClO_4^-) and their application to Wacker-type electrooxidation.[3]

First, we attempted the electrooxidation of $Pd(OAc)_2$ in an undivided cell, but palladium metal was deposited on the cathode and the desired metal complex was not obtained. To avoid the reduction of Pd^{2+}, we next conducted the electrooxidation in a divided cell (Table 1). Passage of 3 F/mol of electricity through a CH_3CN solution of $Pd(OAc)_2$ in the presence of tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) gave $[Pd(CH_3CN)_4][BF_4]_2$ (**1a**) in 58% yield (entry 1).[4] In this system, the counteranion would come from the electrolyte. With Bu_4NPF_6, $[Pd(CH_3CN)_4][PF_6]_2$ (**1b**) was formed in 82% yield (entry 2). Bu_4NClO_4 could also be used in the system as an electrolyte to give $[Pd(CH_3CN)_4][ClO_4]_2$ **1c** (64%, entry 3).

It is likely that the reaction proceeded via a Kolbe-type reaction.[5] A plausible mechanism is illustrated in Scheme 1. First, the acetate anion of $Pd(OAc)_2$ would be oxidized on the anode to Pd^{2+} and two molar amounts of acetoxy radical (•OAc). Subsequent decarboxylation would generate carbon dioxide and methyl radical, which would immediately dimerize to give ethane. The remaining cationic Pd^{2+} species, probably stabilized by the coordination of CH_3CN, might react with the anion part of the electrolyte to generate the corresponding cationic palladium species.

Table 1. Electrooxidative Synthesis of Cationic Palladium Catalysts

$$Pd(OAc)_2 \xrightarrow[\substack{CH_3CN\text{, room temp.} \\ \text{divided cell, (Pt)-(Pt)} \\ \text{10 mA, 3 F/mol}}]{\text{electrolyte (0.2 M)}} \text{Pd complex}$$

entry	electrolyte	product	yield (%)[a]
1	Bu_4NBF_4	$[Pd(CH_3CN)_4][BF_4]_2$ (**1a**)	58
2	Bu_4NPF_6	$[Pd(CH_3CN)_4][PF_6]_2$ (**1b**)	82 (58)[b]
3	Bu_4NClO_4	$[Pd(CH_3CN)_4][ClO_4]_2$ (**1c**)	64

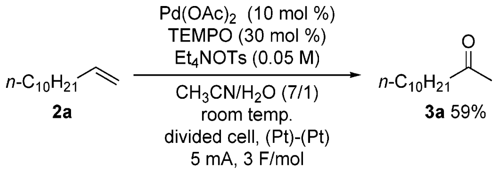
[a] Isolated yield. [b] A total of 2 F/mol of electricity was passed.

Scheme 1. Plausible Mechanism for the Generation of Cationic Palladium Complex **1**

$$Pd(OAc)_2 \xrightarrow{-2e} Pd^{2+} + 2\ {}^{\bullet}OAc$$

$$\xrightarrow[Bu_4NX,\ CH_3CN]{-2CO_2,\ -C_2H_6} \underset{\mathbf{1}}{[Pd(CH_3CN)_4][X]_2}$$

Scheme 2. *N*-Oxyl/Pd Double-Mediatory Electrooxidation of **2a**



To demonstrate the practical utility of this system, the electrooxidative generation system was integrated into an electrooxidative Wacker-type reaction (Scheme 2). Passage of 3 F/mol of electricity through a CH_3CN/H_2O (7/1) solution of 1-dodecene **2a** (0.5 mmol), $Pd(OAc)_2$ (10 mol %), and TEMPO (30 mol %) in the presence of Et_4NOTs (0.05 M) as a supporting electrolyte formed **3a** in 59% yield. The addition of TEMPO was essential for the reaction: without TEMPO, only a trace amount of **3a** was obtained. Noteworthy is that other isomerized ketones were not obtained in the reactions.[6] Using $Pd(TFA)_2$ instead of $Pd(OAc)_2$, the yield of **3a** decreased to 20%. The presence of a phosphine ligand drastically suppressed the reaction. With $PdCl_2(PPh)_2$, only a trace amount of the oxidized product **3a** was obtained, and most of **2a** was recovered. Among the palladium sources that have been examined so far, $Pd(OAc)_2$ gave the best result, suggesting that Kolbe-type decomposition of acetate anion promoted efficient formation of the active palladium species.[7] We assumed that TEMPO might be required for the effective oxidation of Pd(0) to Pd^{2+}.[8]

We next optimized the electrolyte for the electrochemical Wacker-type oxidation (Table 2). As expected, the efficiency of the Wacker-type reaction was highly affected by the electrolyte. With Et_4NBF_4, Et_4NPF_6, or Et_4NClO_4, ketone **3a** was obtained in respective yields of 69%, 66%, and 77%. With Et_4NNTf_2, the yield of the ketone decreased to 48% (entry 4). With Et_4NOAc, the

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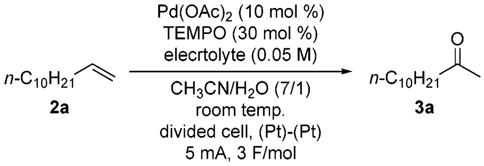
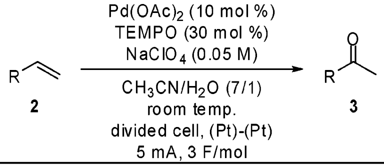
Table 2. *N*-Oxyl/Pd Double-Mediatory Electrooxidation of **2a** Using Various Supporting Electrolytes

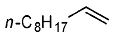
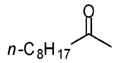
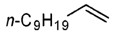
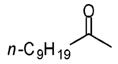
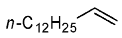
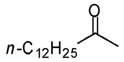
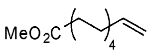
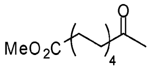
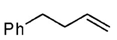
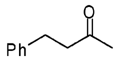
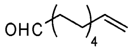
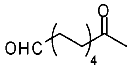
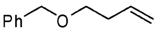
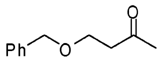


entry	electrolyte	conversion (%)	yield (%)[a]
1	Et_4NBF_4	92	69
2	Et_4NPF_6	95	66
3	Et_4NClO_4	100	77
4	Et_4NNTf_2	85	48
5	Et_4NOAc	19	4
6	$LiClO_4$	100	83
7	$NaClO_4$	100	82
8	$KClO_4$	100	80

[a] Isolated yield.

Table 3. *N*-Oxyl/Pd Double-Mediatory Electrooxidation of Various Olefins



entry	2		product 3		yield[a]
1		**2b**		**3b**	80%
2		**2c**		**3c**	84%
3		**2d**		**3d**	91%
4		**2e**		**3e**	83%
5		**2f**		**3f**	71%
6		**2g**		**3g**	75%
7		**2h**		**3h**	63%

[a] Isolated yield.

Wacker-type reaction did not proceed smoothly, and 81% of starting material **2a** was recovered (entry 5). On the basis of these results, ClO_4^- was determined to be the most effective anion moiety for the reaction. Next, we investigated the effect of the cationic part of the electrolyte. The cationic part did not have as great influence as the anionic moiety. With $LiClO_4$ or $NaClO_4$ as the electrolyte, the yield of **3a** increased slightly to 83% or 82%, respectively (entries 6 and 7).

Finally, we carried out the Wacker-type oxidation using other olefins in a similar electrooxidation system (Table 3). Higher molecular weight terminal alkenes, which are hardly oxidizable substrates for the Wacker reaction because of their low solubility in polar solvents, could be used, and the corresponding ketones were obtained in moderate to high yields (entries 1−3). Especially, the reaction using 1-tetradecene (**2d**) gave tetradecan-2-one (**3d**) in 91% yield (entry 3). We next examined the tolerance of functional groups under these conditions, and found that a variety of functional groups could endure the reaction conditions. For instance, the reaction of substrates bearing ester or phenyl groups gave the corresponding ketones in moderate to good yields (entries 4 and 5). Notably, a formyl group was not oxidized under these conditions. The oxidation of undec-10-enal (**2g**) formed 10-oxoundecanal (**3g**) in 75% yield (entry 6).

In summary, we have developed an electrochemical method for generating cationic palladium complexes $[Pd(CH_3CN)_4][X]_2$, and then used them for the in situ generation of the reagent for accomplishing the electrooxidative Wacker-type reaction. Further investigation of this strategy is in progress in our laboratory.

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Supporting Information Available: Experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) Torii and co-workers reported that the isomerized ketones were obtained as by-products from higher molecular weight alkenes in the electrooxidative Wacker-type reactions using $(p\text{-Br-}C_6H_4)_3N$ or hydroquinone as a mediator.[3b]

(7) Hayashi and Uozumi reported the high efficiency of cationic Pd, catalysts in a Wacker-type reaction, see: Uozumi, Y.; Kato, K.; Hayashi, T. *J. Org. Chem.* **1998**, *63*, 5071.

(8) In the presence of triphenylamine and Bu_4NX, the electrooxidation of $Pd(OAc)_2$ gave cationic Pd complex $[Pd(CH_3CN)_4][X]_2$. On the other hand, when $Pd(OAc)_2$ was electrooxidized in the presence of TEMPO, the Pd complex bearing TEMPO was also obtained. The complex also might work as an active catalyst for the Wacker-type reaction. While the exact structure has not been clear yet, elemental analyses suggested that the complex might be $[Pd(CH_3CN)_4(tempo)][X]$. The identification of the exact structure is undertaken.

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