

Palladium-catalyzed Aerobic Oxidation Reaction of 1-Heptanol in Water using Water-soluble *N*-Heterocyclic Carbene Ligands

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Received November 5, 2014, Accepted November 19, 2014, Published online January 19, 2015

Keywords: Palladium, *N*-Heterocyclic carbene, Water-soluble, Alcohol oxidation, 1-Heptanol

Recent interest in the concept of “green chemistry” has led many researchers to study and develop catalytic reactions under aqueous conditions.¹ The use of a water-soluble catalyst is required to carry out catalytic reactions in water effectively.² We have reported a methodology to form tetrasubstituted ammonium salts from tertiary amines by a Ni nanoparticle-catalyzed C–Cl bond activation³ and found recently that *N*-heterocyclic carbenes (NHCs) bearing a quaternary ammonium moiety, which acts as a solubilizing agent in water, could be easily prepared by the method. Herein, we wish to communicate our preliminary results on the syntheses of 1,3-dialkylimidazolium compounds containing a quaternary ammonium moiety and a catalytic oxidation reaction of alcohols to acids by their water-soluble NHC–palladium catalysts in water.

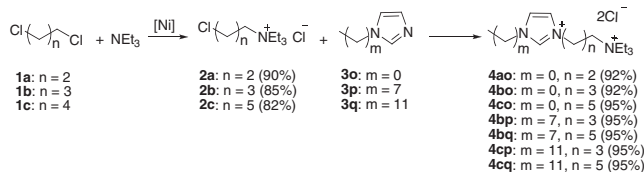
Water-soluble 1,3-dialkylimidazolium compounds⁴ (**4**) containing a quaternary ammonium moiety were prepared from α,ω -dichloroalkanes (**1**) in excellent yields (Scheme 1). The Ni nanoparticle-catalyzed coupling reaction of **1** and triethylamine gave the corresponding quaternary ammonium salts **2** in high yields. Substitution reactions between the chloroalkylated quaternary ammonium salts (**2**) and 1-alkyl-1*H*-imidazoles (**3**) afforded the desired imidazolium compounds (**4**) in excellent yields. All compounds were oily except **4ao**. Structure of **4ao** was confirmed by a single crystal X-ray spectroscopy (see the Supporting Information).

Formation of NHC–palladium complexes from the imidazolium **4** and palladium (II) acetate in water was proved by a ¹³C-NMR study (Figure 1). Figure 1 shows the spectra of a dialkylimidazolium (**4ao**) (a), after a base treatment to

generate the *N*-heterocyclic carbene (b), and the NHC–palladium complex (c). The chemical shift value of the C-2 position of the imidazolium salt, the carbene carbon atom of the NHC, and the carbene carbon atom with Pd complex were observed at 136.3, 225.4, and 167.4 ppm, respectively. The upfield shift of the carbene carbon indicated an NHC–palladium complex was generated *in situ*.⁵

Palladium-catalyzed aerobic oxidation reaction of 1-heptanol to 1-heptanoic acid using water-soluble NHC ligands from **4** in water was investigated as shown in Table 1. The mixture of **4**, a base, and Pd(OAc)₂ in water became homogeneous within 30 min. The catalytic reaction was highly dependent on the reaction conditions, including reaction temperature, base, and NHC ligands. A reaction with ligand **4co** and K₂CO₃ at 100 °C gave the best result (entry 6). Without a base, no reaction was observed because palladium did not form a compound with **4ao** (entry 1). The optimized reaction temperature was found to be 100 °C; when the reaction temperature was elevated to 120 °C, the color of the reaction mixture was rapidly darkened and the yield was dropped dramatically, presumably due to decomposition of the catalysts (entry 2).

At 80 °C, the reaction did not proceed at all only to recover the reactant (entry 3). Ligands derived from **4bp**, **4bq**, **4cp**, and **4cq** gave inferior results to ligands from **4bo** and **4co** under the similar reaction conditions (entries 5–10). At present stage, the reason is not clear but we suppose that the long alkyl chain, especially for **4** having an octyl ($m = 7$) or a dodecyl ($m = 11$) group, might obstruct the interaction between the catalyst and the substrate. Actually, it was found in reactions with **4cp** and **4cq** that the obscure borderline between an aqueous and an organic layer led to a difficulty in separation, eventually giving only poor isolated yields. In conclusion, we have demonstrated that a design of water-soluble imidazolium salts (**4**) allowed the formation of water-soluble palladium complexes that could be used as a catalyst in the oxidation of 1-heptanol to 1-heptanoic acid in high yields in water. We are currently designing new imidazolium salts and acquiring a deeper understanding of the roles of imidazolium salts, including vesicle formation under the reaction conditions.⁶



Scheme 1. Preparation of 1,3-dialkylimidazolium compounds (**4**) containing a quaternary ammonium moiety.

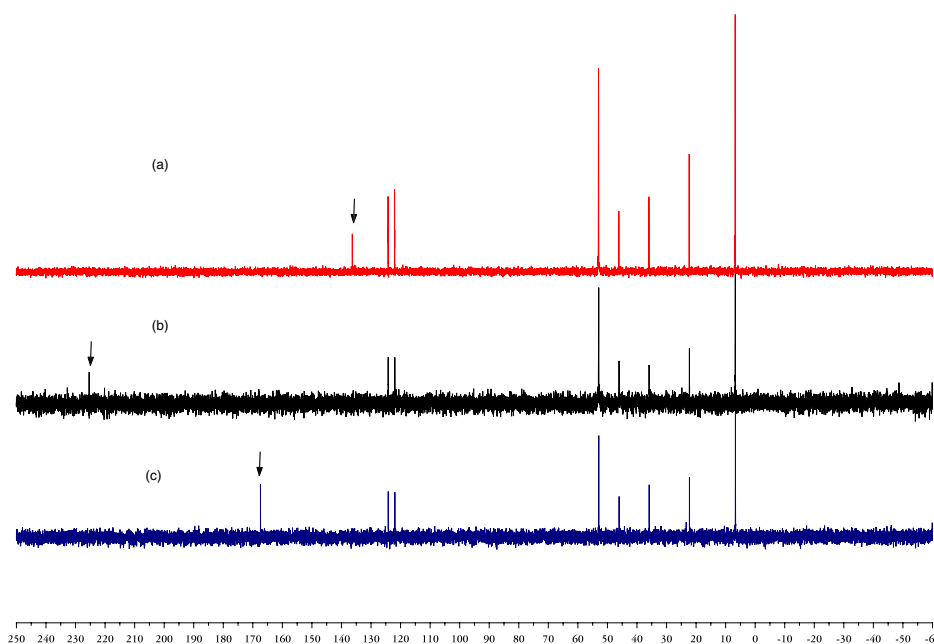


Figure 1. ^{13}C NMR of **4ao** after 10 min stirring (a), **4ao** and K_2CO_3 after 10 min stirring (b), and the solution (b) and $\text{Pd}(\text{OAc})_2$ after 10 min stirring (c) in D_2O (red arrows indicate the C-2 position of an imidazolium salt).

Table 1. Pd-catalyzed oxidation of 1-heptanol using water-soluble NHC ligands from **4** in water.^a

Entry	Ligand	Base (mol %)	Temp (°C)	H_2O (mL)	Yield (%) ^b
1	4ao	—	100	5	Trace
2	4ao	K_2CO_3 (50)	120	5	Trace
3	4ao	K_2CO_3 (50)	80	5	Trace
4	4ao	K_2CO_3 (50)	100	5	54 (54)
5	4bo	K_2CO_3 (50)	100	5	81 (77)
6	4co	K_2CO_3 (50)	100	5	90 (90)
7	4bp	K_2CO_3 (30)	100	8	67 (54)
8	4bq	K_2CO_3 (30)	100	8	59 (51)
9	4cp	K_2CO_3 (30)	100	8	68 (35)
10	4cq	K_2CO_3 (30)	100	8	64 (41)

^a 1.0 mmol scale. The initial ratio of 1-heptanol/Pd/ligand was 1.0/0.050/0.10.

^b ^1H -NMR yields (isolated yields).

Acknowledgments. This work was supported by the National Research Foundation of Korea (NRF) (2007-0093864, 2014-011165, and 2012R1A6A1029029). B.S.C. thanks the Brain Korea 21 fellowship.

Supporting Information. Experimental details, characterization of new compounds, crystal structure, and spectroscopic data are available in the online version of this article.

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