Tetrahedron Letters 52 (2011) 1512–1514

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Fluorescent sensing system for palladium(II) based on the Heck reaction

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ARTICLE INFO

Article history:
Received 3 December 2010
Revised 20 January 2011
Accepted 26 January 2011
Available online 1 February 2011

ABSTRACT

In this paper, we report a fluorescent sensing system based on the palladium-catalyzed Heck reaction between *N*-methyl vinylpyridinium and 4-bromo-*N*,*N*′-dimethylaniline. Generation of a new fluorophore as a product enhances fluorescence and permits selective detection of palladium(II) among other metal species.

Palladium metal is widely used in the fields of environmental and material sciences;[1,2] for example, it is frequently used in catalytic converters, dental crowns, fuel cells, and so on.[3] Moreover, it plays an important role in synthetic chemistry as a catalyst. In several carbon–carbon bond-forming reactions such as Heck, Suzuki, and Sonogashira coupling reactions, palladium compounds play pivotal roles in accelerating the reaction rate.[4] Organic synthesis that uses palladium as the catalyst is widely applied in the production of medicinal substances. However, palladium metal species may be left over even after rigorous purification; they can harm the human body.[5] Similar to its previously mentioned drawbacks in medicinal applications, it can cause harm to the human body when employed in dental applications or used as a catalyst in controlling automobile emissions.

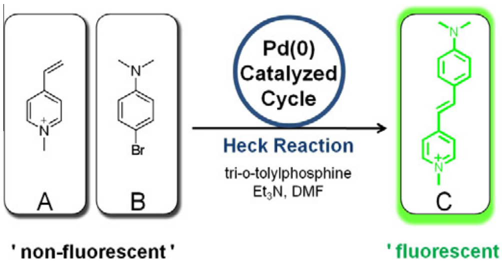
Even very low doses of palladium can trigger allergic reactions in susceptible individuals. Palladium salts may cause eye and skin irritation. Moreover, continued exposure to palladium species can induce more serious symptoms such as inhibition of enzyme reactions, coordination to the thymine moiety in DNA, and accumulation in body organs.[6] Therefore, it is important to develop efficient tools to detect palladium species.

Currently, spectroscopic methods such as plasma emission spectroscopy, atomic absorption spectroscopy, X-ray fluorescence, and ICP-MS are commonly used techniques for quantifying palladium with high sensitivity. These methods, however, require expensive instruments and trained operators.[7] Therefore, continual researches have been conducted for the effective detection of palladium species. For example, Koide and co-workers developed high-performance fluorescent sensors for palladium detection based on a fluorescein derivative. Especially, Koide co-workers have designed excellent fluorescent sensors for palladium detection based on a fluorescein derivative. The sensors exhibit bright green fluorescence with high sensitivity and good selectivity upon the addition of palladium.[8] However, Koide's system has a disadvantage in that it detects platinum in addition to palladium and requires reducing agents for palladium(II). Several fluorescent probes that can overcome these problems have been developed.[9]

Herein, we report a fluorescence sensing system that can selectively detect palladium among other metals through the palladium-catalyzed Heck reaction. The Heck reaction is a typical palladium-catalyzed carbon–carbon bond-forming reaction between an unsaturated halide and an alkene. Scheme 1 shows our main strategy. The sensing system is composed of two simple molecules; *N*-methylvinylpyridinium unit (A) and 4-bromo- *N*,*N*′-dimethylaniline (B). Although both A and B do not exhibit fluorescence originally, after the addition of palladium, the two are connected through a vinyl group to generate a fluorophore C. Therefore, the system is able to detect the presence of both Pd(0) and Pd(II) because Pd(II) can be reduced to Pd(0) by reducing agents.[8a]

Compound B is commercially available, and *N*-methyl vinylpyridinium iodide (A) was synthesized by the methylation of 4-vinylpyridine using excess iodomethane and K_2CO_3 (Scheme 2).

We first examined the fluorescent emission spectra of the reaction mixture before and after the Heck reaction between A and B using palladium(II) species, a reducing agent (tri-*o*-tolylphosphine, $C_{21}H_{21}P$), and triethylamime (TEA).[10,11] When using palladium



Scheme 1. Fluorescent sensing protocol of palladium species. Compound C is generated via a Heck reaction between *N*-methyl-vinylpyridinium (A) and 4-bromo-*N*,*N*′-dimethylaniline (B).

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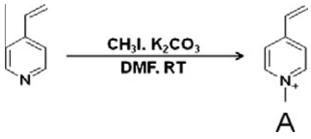
doi:10.1016/j.tetlet.2011.01.118



Scheme 2. Synthesis of A.

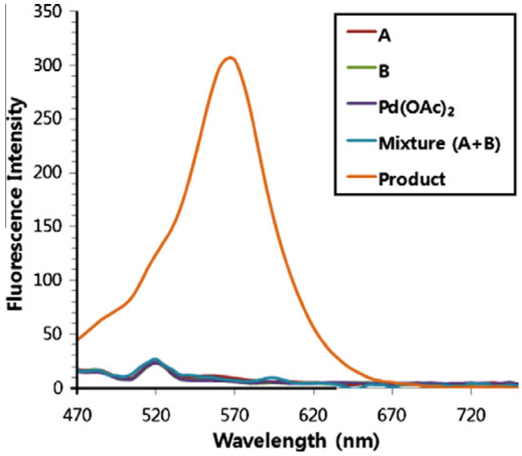


Figure 1. Typical emission spectra (λ_{ex} = 450 nm) of the sensing system ([A] = [B] = 100 μM in DMF, 2 equiv TEA, 0.5 equiv $Pd(OAc)_2$, 0.5 equiv tri-*o*-tolylphosphine). The reaction proceeded at 65 °C for 3 h.

acetate ($Pd(OAc)_2$), after the reaction proceeded for 3 h at 65 °C, a 40-fold increase was observed in the fluorescence emission intensity at λ_{max} of 565 nm (Fig. 1). This result indicates that C was generated through the Heck reaction between A and B. C shows its maximum emission intensity at 565 nm.[12] The presence of C was further detected by GC/MS (see Supplementary data).

This sensing system was found to be highly selective for palladium. Figure 2 shows the fluorescence intensity of the reaction mixture toward various metal acetates and other metal species, which are known as catalytic metal species. We used 10–15 equiv of metal species other than palladium (20–30 times the concentration of Pd); however, the reaction mixture containing these metal ions showed a slight increase in the fluorescence intensity. The fluorescence intensity of the reaction mixture using 0.5 equiv of palladium was 5- to 38-fold larger than that using other metal species. Specifically, platinum, whose physical and chemical properties are similar to those of palladium, hardly induced any fluorescence change.

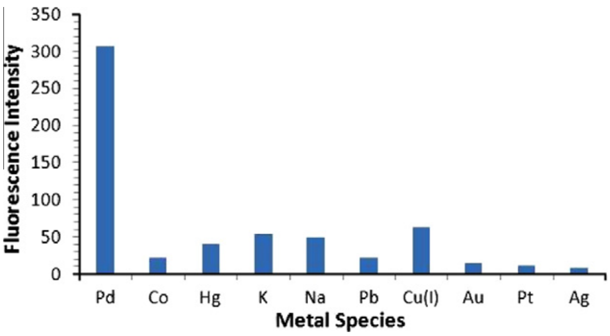


Figure 2. Fluorescence intensity upon addition of Pd (0.5 equiv), metal acetates ($Co(OAc)_2{\cdot}4H_2O$, $Hg(OAc)_2$, KOAc, NaOAc, and $Pb(OAc)_2$, each 10 equiv, 1 mM in DMF) and transition metal species (Cu_2O, AuI, $PtCl_2$, and $AgNO_3$, each 15 equiv, 1.5 mM in DMF) at 565 nm.

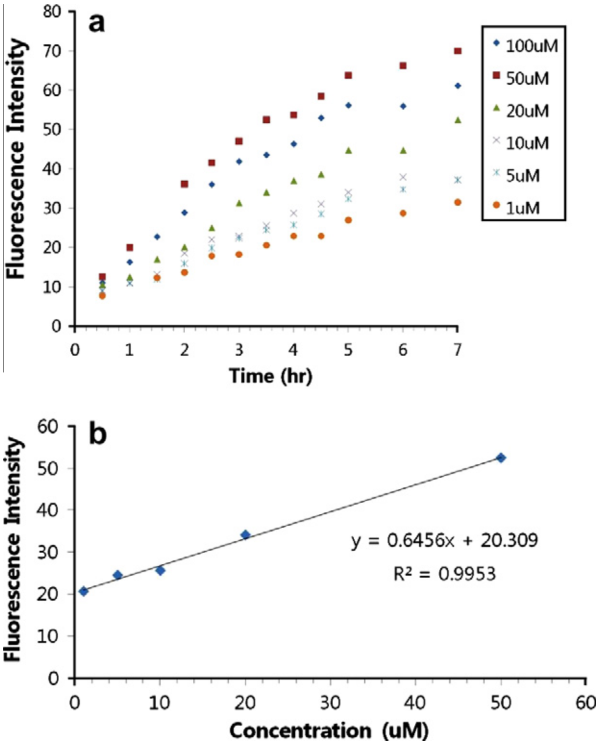


Figure 3. (a) Reaction rate analysis at room temperature. Spectra shown above are for 100 μM of A and B in DMF with palladium catalyst concentrations of 1, 5, 10, 20, 50, and 100 μM (0.01, 0.05, 0.1, 0.2, 0.5, and 1 equiv) in DMF. The fluorescence was monitored at 30-min intervals and collected at 565 nm. (b) Fluorescence intensity of samples with various concentrations after 3.5 h. The fluorescence intensity data show a linear correlation with the concentration of palladium in the range of 1 μM (0.01 equiv) to 50 μM (0.5 equiv) in DMF, which enabled the calculation of the detection limit.

Next, we measured the time-dependent fluorescence change at various concentrations of palladium at room temperature (Fig. 3a). The maximum fluorescence intensity increased steadily and was dependent on the concentration of palladium. The highest emission intensity was observed in the case of 0.5 equiv (50 μM) of palladium.

Linear dependence of the reaction rate on the palladium concentration was observed at room temperature, from which the detection limit (signal to noise ratio of 3) of the sensing system was determined to be 5.45 μM after 3.5 h (Fig. 3b).

Recently, Ahn and co-workers emphasized the importance of direct and convenient detection of palladium(II) ions without reducing agents.[9a] Concurring with this view, we tested whether the sensing system is able to detect palladium(II) with or without a ligand (tri-*o*-tolylphosphine). A similar fluorescence enhancement was observed (Fig. 4) in both cases, and the molecule C could be confirmed by GC/MS (Supplementary data). The proposed mechanism for the ligand-free Heck reaction with palladium acetate is also described in Supplementary data.[13]

In summary, we have developed a palladium(II) sensing system with two simple molecules: *N*-methyl vinylpyridinium (A) and 4-bromo-*N*,*N*′-dimethylaniline (B). Although both A and B do not exhibit any fluorescence originally, they produce a fluorophore through the Heck reaction. Although the reaction system is accelerated on heating, it can detect palladium(II) even at room temperature. The developed fluorescent sensing system is highly selective for palladium(II) among other metal species and is able to detect palladium(II) with or without the presence of any ligand.

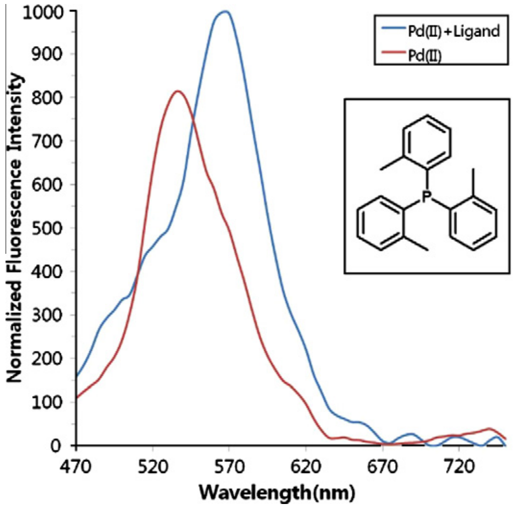


Figure 4. Fluorescence emission of the sensing system with or without reducing agents. Palladium(II) was introduced in the form of $Pd(OAc)_2$ at 65 °C for 3 h. The maximum fluorescence intensity was observed at 535 nm without a ligand and at 565 nm with a ligand. Inset: structure of ligand, tri-*o*-tolylphosphine.

Acknowledgments

This work was supported by the NRF grant funded by the MEST (Grant No. 2009-0080734) and. S.Y.Y thanks the Ministry of Education for the BK fellowship. H.-W.R is the recipient of POSCO TJ Park Postdoctoral Fellowship.

Supplementary data

Supplementary data (NMR, GC/MS spectra and fluorescence data (PDF)) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.01.118.

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