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Reaction of Imidazoline-2-Selone with Acids and Its Use for Selective Coordination of Platinum Ions on Silica Surface

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For the past decade, *N*-heterocyclic carbenes (NHC) and related new compounds have been one of the actively studied subjects in organometallic chemistry.[1] NHCs can be prepared from imidazolium salt by abstraction of the central proton using suitable bases[2] or from neutral precursors by C−Cl, C−C, C−B and C−N bond cleavage.[3] NHCs are a good electron donor, comparable to conventional phosphine ligands.[4] Various NHC−metal complexes have been prepared in the last two decades.[5] Similar to the preparation of conventional, transition metal−NHC complexes, 1,3-disubstituted imidazoline-2-selones were prepared from imidazolium salts by proton abstraction and successive treatment of selenium powder.[6]

Platinum is a very important metal in chemistry. It exhibits catalytic properties in diverse organic transformations such as hydroformylation, hydrogenation, and oxidation of methane to methanol.[7] Moreover, its use in automobile devices, chemical fuel cells, and electrolysis as electrodes is industrially important.[8] Recently, its consumption has been rapidly increasing because of this increasing use. However, as platinum is one of the most expensive metals with a limited amount, its recovery and reuse will become a very important scientific issue in the near future. Thus, the selective separation of platinum from conventional cheap transition metal mixtures is quite important for its recovery.[9] In this communication, we report the unexpected reaction of 1,3-disubstituted imidazoline-2-selone with acids and the selective coordination of platinum ions in an aqueous mixture of diverse transition metals.

During the reactivity studies of the selone derivatives, we discovered an unexpected chemical reaction between the silica and selone. As shown in Figure 1a, the conventional silica gel (Merck, TLC silica gel 60 F254), which is used for thin layer chromatography, showed an intriguing color change following treatment with 0.20 M selone in methylene chloride. An orange yellow color was displayed on the silica surface, usually within 10 min (Figure 1a).

The vivid color aroused our curiosity regarding the chemical transformation occurring on the silica surface. We speculated that the reaction resulted from the acidic properties of the silica surface because neutral aluminum oxides (Aldrich, Cat. # 19,997−4) did not show any color change following 12-h selone treatment. This speculation

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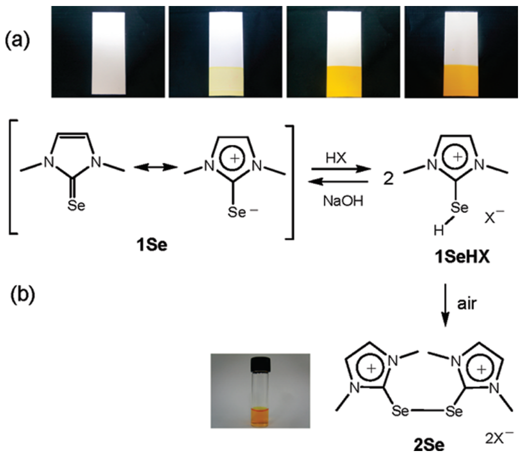

Figure 1. (a) Photographs of the reaction between the TLC plate and **1Se**, before the reaction, and after 10 s and 2 and 10 min (from left to right); (b) the reaction scheme of **1Se** with acid.

was further supported by the following model study. The treatment of 1,3-dimethylimidazoline-2-selone (**1Se,** 0.17 M) with conventional acids such as 1 M hydrochloric acid and acetic acid under air also revealed the same color change from colorless to organge yellow. The colored compound (**2Se**) was isolated from the solution and fully characterized by ^{1}H & ^{13}C nuclear magnetic spectroscopy (NMR), elemental analysis, and signle-crystal X-ray diffraction study.[10] The average C−Se bond length (1.88 Å) in X-ray structure of **2Se** (Figure 2) was much longer than a C−Se double bond (1.74 Å), but shorter than a C−Se single bond (1.94 Å). Its ^{1}H NMR spectrum showed proton peaks at 7.77 (s, 4H), and 3.75 (s, 12H) ppm. In comparison, proton peaks of **1Se** appeared at 6.86 (s, 2H), and 3.72 (s, 6H) ppm.

It has been reported that imidazole-2-selenol undergoes a facile dimerization to form Se−Se bond in presence of air.[11] Also, it has been documented that halogens such as Br_2, I_2, and IBr can be added to selenium atom in selone and the reaction of selone with IBr can induce the dimerization of selone.[12] We suggest that the dimerization of **1Se** resulted from the air oxidation of selenol compound (**1SeHCl**) which was formed by addition of HCl to **1Se**. In this regards, we conducted the reaction of **1Se** with HCl in degassed solution under argon. The bright yellow compound (**1SeHCl**) was isolated and carefully characterized.[10] The elemental analysis of **1SeHCl** confirmed the HCl addition to **1Se**. After treating **1SeHCl** with base, (NaOH), the white selone (**1Se**) were immediately formed with quantitative yield, indicating that the product is a proton-adduct. **1SeHCl** was very sensitive to air and showed a facile spontaneous oxidation to **2Se** even at room temperature under air, which was monitored by ^{1}H NMR spectroscopy. To maintain the peaks of **1SeHCl** in ^{1}H NMR spectrum, a strict inert conditions should be kept. It has been reported that imidazoline selone can exist in zwitterionic form.[11] We suggest that the zwitterionic form can be trapped by the proton of diverse acids. Considering these, the reaction scheme was suggested as in Figure 1b.

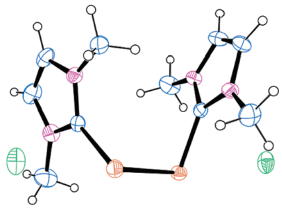

Figure 2. ORTEP drawing (with 30% ellopsoid probability) of **2Se**.

Regardless of the kinds of silica, the reaction of selone was quite general. **1Se** (0.18 g, 1.03 mmol) was dissolved in methylene chloride solution and reacted with mesoporous silica, KIT-6 (0.5 g), for 1 day. KIT-6 (surface area; 668 m^2/g, pore volume 0.81 mL/g, average pore size 7.1 nm) was prepared via the literature method.[13] The color of silica was changed from white to reddish yellow, indicating that the silica surface was functionalized by the reaction of selones. (Figure 3) The resultant silica was washed with methylene chloride five times and dried under a vacuum. To investigate the colored chemical species, we dissolved silica by treatment of HF solution for an hour and the NaCl solution was then added to the reaction mixture. After evoporating water, the colored compound was extracted with methanol. The proton peaks at 7.75 (4H, s) and 3.80 (12H, s) ppm in its ^{1}H NMR spectrum were nearly consistent with those of **2Se**.

Next, we studied the reactivity of surface-functionalized silica (0.23 mmol Se per gram of silica) to diverse small molecules or transition metal ions in water. The generation of the diselenide moiety by the reaction of silica with selones was considered to indicate the good interaction of the functionalized silica with the noble metal ions. We chose the platinum ions among the noble metals because of the recent demand for selective separation of platinum from transition metal mixtures. The selone-functionalized silica successfully underwent selective interaction with platinum ions. Supposing the recovery case of platinum ion from

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(10) **1Se** (0.30 g, 1.7 mmol) was dissolved in the methylene chloride (5 mL) solution to form a colorless solution. This solution was treated with the 1 M HCl (5 mL) solution for 12 h under air. The aqueous solution gradually turned orange-yellow. The aqueous layer was separated carefully. Water and HCl were completely removed under a vacuum to form an orange-colored powder. **2Se**: ^{1}H NMR (300 MHz, D_2O), δ 7.77 (s, 4H), 3.75 (s, 12H) ppm. ^{13}C NMR (75 MHz, D_2O) δ 134.1, 126.6, 37.6 ppm. Elemental anal. Calcd for $C_{10}H_{16}N_4Se_2Cl_2$: C, 28.52; H, 3.83; N, 13.31. Observed: C, 28.69; H, 3.95; N, 13.35. Crystallographic information for **2Se**: CCDC # 724223, monoclinic, space group $P2_1$, $a = 7.805(1)$, $b = 11.080(1)$, $c = 9.119(1)$ Å, $\beta = 106.01(1)°$, $V = 785.41(6)$ Å^3, $Z = 2$, $R_{int} = 0.0197$, $R_1 = 0.0201$, $wR_2 = 0.0410$ ($I > 2\sigma(I)$). For synthesis of **1SeHCl**, the above procedure was conducted in degassed solvent under argon. **1SeHCl**: ^{1}H NMR (300 MHz, D_2O), δ 7.26 (s, 2H), 3.62 (s, 6H) ppm. Elemental anal. Calcd for $C_5H_9N_2SeCl$: C, 28.39; H, 4.29; N, 13.24. Observed: C, 28.10; H, 4.27; N, 12.74.

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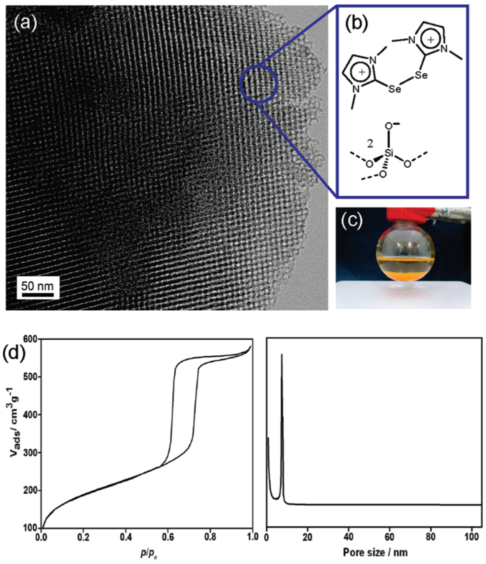

Figure 3. (a) Typical TEM image, (b) the suggested chemical structure, (c) photograph of the functionalized KIT-6 by 1,3-dimethylimidazoline-2-selone, and (d) nitrogen-BET characterization of surface area and pore size distribution.

automobile or electric device wastes (mixture of conventional cheap transition metals), we prepared the model solution containing Cr^{3+} (98 ppm), Mn^{2+}(104 ppm), Fe^{3+}(101 ppm), Co^{2+} (124 ppm), Ni^{2+} (99 ppm), Cu^{2+} (99 ppm), Cd^{2+} (107 ppm), Zn^{2+} (116 ppm), Pb^{2+} (102 ppm) and Pt^{2+} (103 ppm) by dissolving the diverse metal chlorides. We treated the model solution (33 mL) with 0.30 g of the selone-functionalized KIT-6 for 4 h at room temperature. The solution was directly analyzed via inductively coupled plasma atomic emission spectroscopy (ICP-AES). The results are shown in Figure 4. There was no significant change in other metals. However, 96 ppm of the platinum ion was retrieved from the mixture solution with nearly perfect selectivity.[14] According to the kinetic studies, the coordination of platinum ions was completed within the first 10 min.

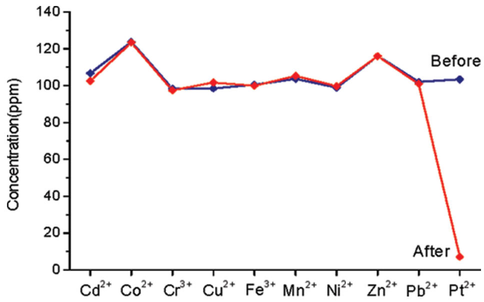

Figure 4. Selective coordination of Pt ions with the functionalized KIT-6 by 1,3-dimethylimidazoline-2-selone (**1Se**). The original solution (before) contained Cd^{2+} (107 ppm), Co^{2+} (124 ppm), Cr^{3+} (98 ppm), Cu^{2+} (99 ppm), Fe^{3+} (101 ppm), Mn^{2+} (104 ppm), Ni^{2+} (99 ppm), Zn^{2+} (116 ppm), Pb^{2+} (102 ppm), and Pt^{2+} (103 ppm). The remaining solution contained Cd^{2+} (104 ppm), Co^{2+} (123 ppm), Cr^{3+} (97 ppm), Cu^{2+} (100 ppm), Fe^{3+} (100 ppm), Mn^{2+} (105 ppm), Ni^{2+} (99 ppm), Zn^{2+} (116 ppm), Pb^{2+} (101 ppm), and Pt^{2+} (7.1 ppm). The concentration values are averages of three measurements.

To understand the origin of the selectivity, we reacted the model compound, **2Se**, with platinum ion in water, leading to the rapid formation of reddish precipitates. The resultant compound was insoluble in water. The ^{1}H NMR spectrum of these precipitates showed peaks at 7.75 (s, 2H) and 3.89 (s, 6H) ppm. Elemental analysis confirmed that the stoichimetric ratio of **2Se** to $PtCl_2$ is 1:1.[15] Single-crystal X-ray analysis showed that the reaction of **2Se** with $PtCl_2$ resulted in Se−Se bond cleavage to form $(C_5H_8Se)_2PtCl_4$. (see the Supporting Information)

In sharp contrast, the other transition metal ions used for the adsorption test did not show a good reactivity with **2Se**. Thus, the selectivity was attributed to the unique reactivity of platinum toward softer selenium in the functionalized silica.

In conclusion, an efficient system for the selective recovery of platinum ions from conventional cheap transition metal mixtures was developed. The selone showed a good reactivity toward the conventional acids. Mesoporous silica functionalized by reaction with selone showed excellent selectivity to platinum ions among various transition metal ions. This selectively was attributed to unique reactivity of platinum ion with the acid-activated selone. We believe that this discovery can be applied not only to the development of selective, platinum ion adsorbents[16] but also to the preparation of platinum-grafted heterogeneous catalysts.

Acknowledgment. This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD, Basic Research Promotion Fund, KRF-2007-313-C00376) and WCU (World Class University) program through the Korea Science and Engineering Foundation funded by the Ministry of Education, Science and Technology (R31-2008-000-10029-0). Dr. H. J. Kim thanks for the Hydrogen Energy R&D Center, a 21st century Frontier R&D Program.

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Supporting Information Available: X-ray structure files of **2Se** and **2Se**-Pt complex (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) It is quite noteworthy that the selone-modified silica showed an excellent selectivity for platinum ions against lead ions. However, in the presence of Hg^{2+} (119 ppm), the selone-modified mesoporous silica did not show a good interaction with platinum ions, which means that these mercury ions should be removed in advance to interact with platinum ions. (a) Abe, S.; Hanamoto, T.; Egawa, Y. *PCT Int. Appl.* **2008**, 20. (b) Sato, K.; Shibuya, H. *PCT Int. Appl.* **2008**, 43. (c) Park, K. H.; Choi, J.; Chun, J.; Kim, H. J.; Son, S. U. *Chem. Commun.* **2008**, 1659.

(15) Preparation of the **2Se**-Pt complex: An aqueous K_2PtCl_4 solution (0.10 g, 0.24 mmol in 3 mL water) was prepared. To this solution was added aqueous **2Se** (2 equiv. to platinum in 2 mL water) solution. Immediately, red precipitates formed that were retrieved by centrifugation. The precipitates were washed with water more than five times and dried under a vacuum. ^{1}H NMR (300 MHz, DMSO-d^6) δ 7.75 (s, 2H), 3.89 (s, 6H) ppm. Elemental anal. Calcd for $C_{10}H_{16}N_4Se_2PtCl_4$: C, 17.48; H, 2.35; N, 8.15. Observed: C, 17.42; H, 2.38; N, 7.90. Crystallographic information: CCDC# 734000, orthorhombic, space group $Pna2_1$, $a = 10.824(3)$, $b = 7.631(1)$, $c = 12.438(2)$ Å, $V = 1787(1)$ Å^3, $Z = 4$, $R_{int} = 0.0440$, $R_1 = 0.0406$, $wR_2 = 0.0782$ ($I > 2\sigma(I)$).

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