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Research paper

Synthesis, characterization and catalytic activity of gold complexes with pyridine-based selone ligands

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ABSTRACT

Three neutral pyridine-based selone compounds, 2,6-bis(1-methylimidazole-2-selone)pyridine (**Bmsp**), 2,6-bis(1-ethylimidazole-2-selone)pyridine (**Besp**) and 2,6-bis(1-isopropylimidazole- 2-selone)pyridine (**Bpsp**) have been synthesized and characterized. Reactions of $HAuCl_4$ with pyridine-based selone ligands result in the formation of the complexes $[Au(L)Cl_2]^+[AuCl_2]^-$ (L = **Bmsp** (**1**); L = **Besp** (**2**) and L = **Bpsp** (**3**)), respectively. All compounds have been characterized by elemental analysis, NMR IR spectra and electrospray ionization mass spectroscopic (ESI-MS). The molecular structure of **2** has been determined by X-ray crystallography. Moreover, the gold complexes are efficiently catalyzed nitroarenes reduction to aromatic amines in the presence of sodium tetrahydroborate reducing agent in water.

1. Introduction

Functionalized anilines are important structural motifs that are found in a variety of agrochemicals, dyes, pharmaceuticals, and pigments and other industrially useful products [1–6]. Therefore, a variety of protocols for synthesizing functionalized anilines have been developed [7–19]. The desirable method for the synthesis of functionalized anilines is the reduction of nitroarenes using transition metal catalysts in the presence of sodium tetrahydroborate ($NaBH_4$) [20]. A number of homogeneous and heterogeneous catalysts have also been reported as viable catalysts for this hydrogenation. Heterogeneous gold catalysts have become an important topic since the 1980s [21], since 2000 homogeneous gold catalysis has become a highly active field [22,23]. Furthermore, occasionally reactions typically catalyzed by homogeneous catalysts have also been reported to be catalyzed by heterogeneous catalysts [24], and occasionally reaction typically catalyzed by heterogeneous catalysts have also been reported to be catalyzed by homogeneous gold(III) complexes [25]. Gold-based catalysts supported by metal oxides (such as TiO_2, Fe_2O_3, Fe_3O_4, SiO_2 and Al_2O_3) [26–32], carbon nanotube [33], polymer [34,35], graphene oxide [36], and gold complexes [37–40] are all good candidate for the hydrogenation of nitroarenes due to their high catalytic activities.

Imidazoline-2-chalcogenone ligands NHC = E (NHC = N-heterocyclic carbene, E = S, Se) are good σ-donors and weak π-acceptors which can be easily modified using appropriate available NHC precursors to attain the desired steric-bulk or electronic properties [41–43]. Reports about transition metal complexes with imidazoline-2-chalcogenone ligands have been reported within past few years [44–49]. And the catalytic activities of these complexes are comparable with the most efficient metal-NHC complexes for organic transformation [50–52]. However, the transition metal complexes with selone ligands are reported rarely due to difficulty in synthesis, handing and malodorous nature of the organoselenium ligands [46]. Continuing our research interests in imidazoline-2-chalcogenone metal complexes for their rich chemistry [53–56], we try to prepare the gold complexes with pyridine-based [57,58] selone ligands and hope to exploit their catalytic applications in hydrogenation of nitroarenes.

Herein, we report the synthesis and characterization of three gold complexes with pyridine-based selone compounds: $[Au(L)Cl_2]^+[AuCl_2]^-$ (L = **Bmsp** (**1**), **Bmsp** = 2,6-bis(1-methylimidazole-2-selone)pyridine; L = **Besp** (**2**), **Besp** = 2,6-bis(1-ethylimidazole-2-selone)pyridine and L = **Bpsp** (**3**), **Bpsp** = 2,6-bis(1-isopropylimidazole-2-selone)pyridine), and further examine their catalytic ability in direct nitroarenes reduction to aromatic amines in the presence of $NaBH_4$ reducing agent in water. Our preliminary results indicate that gold complexes show promising catalytic activities in nitroarenes reduction reaction. The elucidation of solid state structure of the gold complex **2** was also obtained through single crystal X-ray diffraction.

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2. Experimental

2.1. Materials and physical measurements

Commercial reagents were analytical grade and used as received from Aladdin and Energy chemical. All manipulations were carried out under nitrogen using standard schlenk and vacuum-line techniques. All solvents were purified and degassed by standard procedures. The starting materials 2,6-bis(1-methylimidazolium) pyridine dibromide, 2,6-bis(1-ethylimidazolium)pyridine dibromide and 2,6-bis(1-isopropylimidazolium)pyridine dibromide were synthesized according to the procedures described in the literature [55]. All catalytic reactions were monitored by TLC using 0.25 mm silica gel plates with UV indicator (60F-254). ^{1}H and ^{13}C NMR were recorded on a 300 MHz or 500 MHz NMR spectrometer at room temperature. IR spectra were recorded on a Niclolet AVATAR-360IR spectrometer. Element analyses were performed on an Elementar III vario EI Analyzer. Mass spectra were obtained with MicroTof (Bruker Daltonics, Bremen, Germany) spectrometers.

2.2. Synthesis of **Bmsp**

In a 25 mL Schlenk tube were placed with 2,6-bis(1-methylimidazolium)pyridine dibromide (201.5 mg, 0.5 mmol), Se (94.8 mg, 1.2 mmol), K_2CO_3 (165.9 mg, 1.2 mmol) and 6.0 mL methanol as solvent. The mixture was allowed to reflux for 12 h after which the methanol was removed with a rotary evaporator. The remaining solid was shaken with 3 × 10 mL CH_2Cl_2 which was then filtered and rotary evaporated. The product was recrystallized from CH_2Cl_2/MeOH to give white solid. Yield: (258 mg 65%) (based on 2,6-bis(1-methylimidazolium)pyridine dibromide). Anal. Calcd. for $C_{13}H_{13}N_5Se_2$ (397.20): C, 39.10; H, 3.28; N, 17.77. Found: C, 39.15; H, 3.30; N, 17.58. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.90 (d, J = 8 Hz, pyridine, 2H), 8.05 (t, pyridine, 1H), 7.54 (d, J = 3 Hz, imidazole, 2H), 6.92 (d, J = 3 Hz, imidazole, 2H), 4.52 (s, $2CH_3$, 6H). ^{13}C NMR (500 MHz, $CDCl_3$): δ 156.72, 149.40, 140.15, 120.95, 119.18, 118.97, 37.86 ppm. IR (KBr, cm^{-1}): 3358 (w), 3281 (w), 3188 (w), 3165 (w), 3130 (w), 3099 (w), 1666 (w), 1624 (vs), 1571 (m), 1471 (vs), 1448 (s), 1395 (m), 1369 (m), 1290 (m), 1236 (m), 1121 (w), 1074 (w), 985 (w), 874 (w), 797 (m), 671 (w), 555 (w).

2.3. Synthesis of **Besp**

The synthesis procedure was similar to the ligand **Bmsp** to afford the white solid **Besp**, using 2,6-bis(1-ethylimidazolium)pyridine dibromide (217 mg, 0.5 mmol), Se (94.8 mg, 1.2 mmol), K_2CO_3 (165.9 mg, 1.2 mmol). Yield: (213 mg 50%) (based on 2,6-bis(1-ethylimidazolium)pyridine dibromide). Anal. Calcd. for $C_{15}H_{17}N_5Se_2$ (426.98): C, 42.16; H, 4.01; N, 16.40. Found: C, 42.20; H, 4.05; N, 16.36. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.86 (d, J = 8 Hz, pyridine, 2H), 8.12 (t, pyridine, 1H), 7.57 (d, J = 3 Hz, imidazole, 2H), 6.98 (d, J = 3 Hz, imidazole, 2H), 4.26 (m, $2CH_2$ 4H), 1.46 (t, $2CH_3$, 6H). ^{13}C NMR (500 MHz, $CDCl_3$): δ 155.73, 149.39, 139.91, 119.60, 119.35, 119.15, 45.34, 14.60 ppm. IR (KBr, cm^{-1}): 3177 (w), 3140 (w), 3097 (w), 2965 (w), 2864 (w), 1647 (w), 1605 (s), 1576 (m), 1533 (w), 1464 (s), 1408 (s), 1392 (s), 1354 (w), 1303 (m), 1281 (s), 1258 (s), 1223 (s), 1155 (m), 1134 (m), 1115 (m), 1076 (w), 1040 (w), 995 (w), 985 (w), 966 (w), 949 (m), 903 (w), 802 (s), 800 (s), 785 (m), 773 (m), 735 (w),716 (m), 688 (w), 655 (m), 599 (w), 509 (w).

2.4. Synthesis of **Bpsp**

The synthesis procedure was similar to the ligand **Bmsp** to afford the white solid **Bpsp**, using 2,6-bis(isopropyllimidazolium) pyridine dibromide (220.4 mg, 0.5 mmol), Se (94.8 mg, 1.2 mmol), K_2CO_3 (165.9 mg, 1.2 mmol). Yield: (245 mg 55%) (based on 2,6-bis (isopropyllimidazolium)pyridine dibromide). Anal. Calcd. for $C_{17}H_{21}N_5Se_2$ (455.01): C, 44.83; H, 4.65; N, 15.39. Found: C, 44.88; H, 4.62; N, 15.36. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.82 (d, J = 8 Hz, pyridine, 2H), 8.04 (t, pyridine, 1H), 7.58 (d, J = 3 Hz, imidazole, 2H), 7.02 (d, J = 3 Hz, imidazole, 2H), 5.39 (m, 2CH, 2H), 1.45 (d, J = 6 Hz, $4CH_3$, 12H). ^{13}C NMR (500 MHz, $CDCl_3$): δ 155.30, 149.39, 139.72, 119.96, 119.93, 119.79, 119.7, 51.36, 22.28, 22.25 ppm. IR (KBr, cm^{-1}): 3175 (w), 3132 (w), 3094 (w), 2970 (w), 2866 (w), 1666 (w), 1598 (m), 1572 (m), 1456 (s), 1416 (m), 1400 (m), 1385 (w), 1368 (w), 1337 (m), 1327 (w), 1277 (m), 1225 (s), 1153 (w), 1134 (w), 1113 (m), 1047 (w), 1018 (w), 991 (w), 883 (w), 835 (w), 804 (m), 781 (m), 718 (m), 685 (w), 664 (m), 584 (w), 554 (w), 500 (w).

2.5. Synthesis of complex [Au(**Bmsp**)Cl_2][$AuCl_2$] (**1**)

In a 25 mL Schlenk tube were placed with **Bmsp** (59.55 mg, 0.15 mmol), $HAuCl_4$ (132 mg, 0.32 mmol), 5 mL methanol as solvent. The mixture was stirred at room temperature overnight and then the solvent was removed with a rotary evaporator; the resulting solid was washed with methanol and diethyl ether, and then dried in vacuo. The product was recrystallized from MeCN/CH_2Cl_2 to give brown deep-red powder. Yield: (67.5 mg, 45%) (based on **Bmsp** ligand). Anal. Calcd. for $C_{13}H_{13}Au_2Cl_4N_5Se_2$ (932.94): C, 16.74; H, 1.40; N, 7.51. Found: C, 16.77; H, 1.16; N, 7.50. ^{1}H NMR (300 MHz, CD_3OD): δ 8.52 (t, pyridine, 1H), 8.17 (d, J = 2 Hz, pyridine, 2H), 7.95 (d, J = 6 Hz, imidazole, 2H), 7.70 (d, J = 2 Hz, imidazole, 2H), 4.25 (s, 6H). ^{13}C NMR (500 MHz, CD_3OD): δ 148.06, 143.98, 138.89, 125.57, 124.02, 121.55, 38.5. ppm. ESI-MS (positive ions) for [Au(**Bmsp**)]$^{3+}$: m/z 595.9160 (calcd for [Au(**Bmsp**)]$^{3+}$ 595.9167). IR (KBr, cm^{-1}): 3421(w), 2943(w), 1816(w), 1672(m), 1627(s), 1562(m), 1508(w), 1476(s), 1440(m), 1408(w), 1379(w), 1300(w), 1238(m), 1138(w), 986(w), 878(w), 802(w), 734(w), 551(w), 501(w).

2.6. Synthesis of complex [Au(**Besp**)Cl_2][$AuCl_2$] (**2**)

Prepared by the same procedure as described above for **1**, using **Besp** (49.65 mg, 0.15 mmol) and $HAuCl_4$ (132 mg, 0.32 mmol). Yield: (77.3 mg, 50%) (based on **Besp** ligand). Anal. Calc. for $C_{15}H_{17}Au_2Cl_4N_5Se_2$ (961.00): C, 18.75; H, 1.78; N, 7.29. Found: C, 18.72; H, 1.71; N, 7.22. ^{1}H NMR (300 MHz, CD_3OD) δ 8.51 (t, pyridine,1H), 8.20 (d, J = 2 Hz, imidazole, 2H), 8.08 (d, J = 2 Hz, imidazole,2H), 7.97 (d, J = 2 Hz, pyridine, 2H), 4.70–4.72 (m, 4H, CH_2), 1.60 (t, $2CH_3$, 6H). ^{13}C NMR (500 MHz, CD_3OD) δ 148.08, 146.59, 143.99, 124.64, 123.90, 122.09, 47.19, 13.95. ESI-MS (positive ions) for [Au(**Besp**)]$^{3+}$: m/z 623.9461 (calcd for [Au(**Besp**)]$^{3+}$ 623.9480). IR (KBr, cm^{-1}): 3395 (w), 3138 (w), 3070 (w), 2976 (w), 2929 (w), 2868 (w), 1732 (w), 1627 (w), 1597 (w), 1554 (w), 1458 (s), 1431 (m), 1398 (w), 1352 (w), 1301 (w), 1267 (m), 1221 (m), 1134 (w), 1088 (w), 1043 (w), 995 (w), 954 (w), 814 (w), 775 (w), 735 (w), 679 (w), 544 (w), 501 (w).

2.7. Synthesis of complex [Au(**Bpsp**)Cl_2][$AuCl_2$]$^-$ (**3**)

Prepared by the same procedure as described above for **1**, using **Bpsp** (68.0 mg, 0.15 mmol) and $HAuCl_4$ (132 mg, 0.32 mmol). Yield: (87.3 mg, 55%) (based on **Bpsp** ligand). Anal. Calc. for $C_{17}H_{21}Au_2Cl_4N_5Se_2$ (989.05): C, 20.64; H, 2.14; N, 7.08. Found: C, 20.70; H, 2.18; N, 7.15. ^{1}H NMR (300 MHz, CD_3OD) δ 8.53 (t, pyridine, 1H), 8.25 (d, J = 2 Hz, imidazole, 2H), 8.12 (d, J = 2 Hz, imidazole, 2H), 7.99 (d, pyridine, 2H), 5.48 (m, CH, 2H), 1.57 (d, CH_3, 6H), 1.28 (d, CH_3, 6H). ^{13}C NMR (500 MHz, CD_3OD) δ 148.08, 144.47, 137.10, 124.93, 121.99, 121.42, 54.40, 21.64, 21.00. ESI-MS