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Homoleptic ruthenium(III) chalcogenolates: a single precursor to metal chalcogenide nanoparticles catalyst[†]

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Eight homoleptic metal(III) arylchalcogenolate polymers $[M(EPh-p-X)_3]_n$ (M = Ru, Cr, and Mo) were characterized by PXRD. Structural solution of $[Ru(SPh-p-tBu)_3]_n$ 1 was achieved by Rietveld refinement of the PXRD data. Pyrolysis of $[Ru(SePh)_3]_n$ 4 produced nanostructured RuSe₂, which selectively catalyzed the reduction of nitro compounds in the presence of other functionalities.

Functional self-assembled coordination polymers (SACPs) have potential diverse applications such as new materials for gas storage,¹ advanced electronics,² and as new catalysts for organic synthesis.³ Homoleptic metal chalcogenolates are a class of functional SACPs with attractive optoelectronic properties and intriguing structures arising from the metal ions and chalcogenide atoms organized in one-dimensional and two-dimensional structures.⁴ The utilization of pre-organized networks of metal ions and chalcogenide atoms for the metamorphosis from organometallic polymers into metal chalcogenide nanoparticles has been demonstrated.⁵ Semiconducting transition metal chalcogenide nanoparticles have continued to receive considerable interest because of their potential applications in photovoltaic devices,6 field-effect transistors,⁷ fuel cells,⁸ and catalysis.⁹ In this work, five homoleptic ruthenium arylchalcogenolate polymers $[Ru(EPh-p-X)_3]_n$ (E = S, X = tBu 1, iPr 2, OMe 3; E = Se, X = H 4, tBu 5, two homoleptic chromium arylthiolate polymers $[Cr(SPh-p-X)_3]_n$ (X = H 6, tBu 7), and $[Mo(SPh-p-tBu)_3]_n$ 8 were prepared and characterized by powder X-ray diffraction (PXRD). Pyrolysis of 4 gave nanocrystalline ruthenium diselenide (nano-RuSe2) as revealed from the transmission electron microscopy (TEM) image as well as PXRD data. The nano-RuSe2 was demonstrated to be an efficient catalyst for chemoselective reduction of organic nitro compounds in the presence of other functionalities.

Polymers **1–3**, **6–8** were prepared in 70–90% yields by heating $Ru_3(CO)_{12}$, $Cr(CO)_6$ or $Mo(CO)_6$ with the corresponding

para-substituted thiophenols at 195 °C under Ar for 12 h.¹⁰ Alternatively, 1 can be prepared by heating a mixture of Ru(acac)₃ and 4-tert-butylthiophenol at 195 °C under Ar for 12 h. The latter method was preferred as the product was free from polymeric metal carbonyl [Ru(SR)₂(CO)₂]_n contamination.¹¹ We conceive that $[Ru(SR)_2(CO)_2]_n$ was formed at a lower temperature and subsequently dissolved in the reaction mixture to undergo further reaction with excess para-substituted thiophenol to form the homoleptic polymer $[Ru(SR)_3]_n$. Attempts to synthesize homoleptic polymers with other substituted arylthiophenols were not successful,‡ and only the reactions of 4-tert-butylthiophenol, 4-isopropylthiophenol and 4-methoxythiophenol with Ru₃(CO)₁₂ afforded polycrystalline solids 1-3. Presumably, the arylthiols bearing tert-butyl, isopropyl or methoxy substituent can enhance the solubility of $[Ru(SR)_2(CO)_2]_n$ in the reaction mixture, subsequent reactions of which with para-substituted thiophenols gave the polymers 1-3. Polymers 4 and 5 were prepared by refluxing Ru(acac)₃ with PhSeH or *p*-tBu-PhSeH in an aqueous alcoholic medium under Ar for 12 h.‡ The solids obtained are air-stable and powder X-ray diffraction (PXRD) experiments revealed that 1-8 are isostructural to each other (Fig. S2 in ESI).

Structural solution of 1 (CCDC 823139) was obtained by Rietveld refinement from the PXRD data.¹² 1 crystallized in hexagonal $P6_3/m$ with a = b = 17.403(1) Å, c = 5.417(8) Å. Fig. 1 shows the perspective view of 1 along the *b*-axis. 1 consists of a 1-D chain of ruthenium atoms with each adopting a face-sharing octahedral geometry with a Ru-Ru and a Ru-S distance of 2.709 Å and 2.209 Å respectively and a Ru–S–Ru angle of 75.63°. The Ru-Ru distance in 1 is comparable to the Ru-Ru distance of 2.87 Å in $[Ru(SPh)_3]_n$ reported by Strähle.¹⁰ A TEM image revealed that a solid sample of 1 contained phase-pure irregular nanoparticles. Subsequent selected area electron diffraction (SAED) study on individual nanocrystals of 1 revealed a d spacing of 15.26 Å, which is consistent with the PXRD data. Indexing of the PXRD patterns of polymers 2, 3, 6, 7, and 8 revealed a hexagonal space group with a = 16.18 Å, 14.22 Å, 12.96 Å, 17.04 Å, and 17.57 Å respectively. The lengths of a-axis for 1, 7, and 8 are similar (17.04–17.57 Å) as the cell dimension is predominantly determined by the size of ligand (-SPh-p-tBu). The order of the lengths of *a*-axis (1 > 2 > 3 > 6) is consistent with the size of the *para* substituent on the phenyl ring (tBu > iPr > OMe > H).

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Fig. 1 (a) Perspective drawing of the chains structure of 1 viewed along the *b* direction. Hydrogen atoms have been omitted for clarity. (b) TEM and (c) SAED image of polycrystalline 1. The scale bars represent 200 nm and 0.5 nm^{-1} respectively.

Polymers 1–8 were subjected to thermogravimetric analysis (TGA) and all of them showed similar decomposition temperature at around 300–350 °C. The residual products were found to be RuS₂ (1, 2 and 3), RuSe₂ (4 and 5), CrS₂ (6 and 7), and MoS₂ (8) based on the calculations from weight percentage. The low decomposition temperature of these metal chalcogenolate polymers indicates that they are apposite to be single-source precursors for metal chalcogenides. The structural integrity of both 1 and 7 was evaluated by variable-temperature (VT) PXRD and the patterns of 1 measured at temperatures from 30–440 °C are depicted in Fig. 2 (Fig. S3 in ESI for VT-PXRD of 7). At 300 °C, the characteristic peaks of 1 and 7 disappeared completely but no diffraction peaks from the resultant MS₂



Fig. 2 VT-PXRD patterns of 1 at 30 °C to 440 °C.

(M = Ru, Cr) were observed up to 440 °C, indicating that the as-formed MS₂ were amorphous.

The PXRD patterns of the pyrolysis product of 4 at different temperatures under vacuum (0.02 mmHg) for 4 h are depicted in Fig. 3. No distinctive peaks were observed when 4 was pyrolyzed at 200 °C, indicating the polymer skeleton was destroyed. When the temperature of pyrolysis was increased to 450 °C, new diffraction peaks could be observed. The as-formed solid residue was identified by matching its diffraction pattern with authentic crystal data of RuSe₂¹³ and by using energy dispersive X-ray spectroscopy (EDS). TEM images and SAED of the solid residue revealed that they were crystalline nanoparticles with diameters in the range of 3-15 nm. We envisaged that the resultant nano-RuSe₂ could be a useful catalyst¹⁴ if it is supported on an inert matrix such as graphite. A composite of nano-RuSe₂ deposited on graphite was achieved by pyrolyzing a physical mixture of polymer 4 and graphite under vacuum. PXRD confirmed that the nano-RuSe₂ was formed on the surface of graphite without disturbing the crystallinity.

The catalytic property of *nano*-RuSe₂ was demonstrated by the reduction of nitro-containing aromatic compounds using aqueous hydrazine as reductant (Scheme 1). Reduction of **9a** with hydrazine monohydrate in the presence of 1 mol%



Fig. 3 (a) PXRD patterns of pyrolysis residue from 4 at 200–450 °C under vacuum (0.02 mmHg) for 4 h. Simulated PXRD pattern from RuSe₂ coordination data from ref. 13 is presented at the topmost. Dotted lines show the two theta positions which match with the simulated pattern. Diffraction originating from graphite is indicated by *. (b) TEM and (c) SAED of the *nano*-RuSe₂-deposited graphite. The scale bars represent 5 nm and 5 nm⁻¹ respectively.



Scheme 1 (i) 10 equiv. $NH_2NH_2 \cdot H_2O$, 1 mol% *nano*-RuSe₂, ethanol reflux. Reaction time is indicated for each substrate. Conversion yields are reported based on ¹H-NMR determination. Isolated yields in parentheses were obtained by column chromatography.

nano-RuSe₂ in refluxing ethanol gave 10a in quantitative yield within 24 h. Replacing the hydroxymethyl group with an electron-donating group such as n-propyl group (9b) or hydroxyl group (9c) resulted in a drop of substrate conversion (38% and 20% respectively) as monitored by ¹H-NMR. Bromoaryl compounds are readily de-brominated in catalytic reduction but in our catalytic system, 9d was reduced into 10d in 100% conversion and was isolated in 64% yield together with N-arylation product. In contrast, reduction of 9d using mild reducing agent NaBH₄ and using heterogeneous Pd(0)/C as catalyst was reported to give aniline.¹⁵ O-Benzyl is a common protecting group for alcohols and phenols. Avoiding the removal of this protecting group is difficult if the nitrocontaining substrate is reduced by using heterogeneous Pd catalyst such as 10% Pd(0)/C or Pd(0)EnCat[™] 30NP nanoparticulate.¹⁶ Reduction of 9e with nano-RuSe₂ catalyst showed 42% substrate conversion with the product 10e obtained in 40% isolated yield. We also examined the reduction of dinitro aromatics like 9f as controlling the reduction of one nitro group in dinitro compounds was difficult.¹⁸ The mono reduced compound 10f was achieved with a 100% substrate conversion and a 70% isolated yield. Electron-deficient substrate 9g with a nitrile group ortho to the nitro group was reduced under high pressure (50 psi) with heterogeneous Pd(0) catalyst.¹⁷ By using nano-RuSe₂ catalyst, 10g was obtained in 100% isolated yield within 25 h. Chemoselectivity was also observed in the case of 9h as only the nitro group ortho to the phenolic OH was reduced and the nitro group para to the OH group remained intact. Noteworthily, 9h could be reduced into 1,3-diaminophenol without any selectivity by formic acid in the presence of 10% Pd(0)/C.¹⁹

SACPs 1–8 were prepared and characterized with PXRD, TEM, SAED, and EDS. The polymers are isostructural to each other. Nanocrystalline *nano*-RuSe₂ was obtained by heating polymer 4 under vacuum. Catalytic performance of the *nano*- $RuSe_2$ towards reduction of nitro-containing aromatics was found to be efficient (quantitative isolated yield for **10a** and **10f**) and chemoselective.

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Notes and references

‡ Reactions of Ru₃(CO)₁₂ with 2-methylthiophenol, 3-methylthiophenol, 4-methylthiophenol, 4-ethylthiophenol, 3,4-dimethylthiophenol, 2,4,6-trimethylthiophenol, and dodecahexanethiol did not produce polycrystalline homoleptic polymeric solid. Representative experimental: [Ru(SePh)3], 4. Diphenyl diselenide (0.156 g, 0.5 mmol) was added to a solution of NaOH (0.03 g, 0.75 mmol) in water (10 mL), and a solution of NaBH₄ (0.0285 g, 0.75 mmol) in methanol (10 mL) was added. The yellow suspension was heated until a clear solution was obtained. After cooling to room temperature, the solution was adjusted to pH \approx 5-6 by dropwise addition of concentrated hydrochloric acid (12 M). Ru(acac)₃ (0.133 g, 0.33 mmol) was added and the reaction mixture was refluxed for 12 h. The insoluble dark green precipitate was filtered and washed with methanol $(3 \times 10 \text{ mL})$ and diethyl ether (10 mL). The resultant dark green solid was placed in a vacuum oven (5 mmHg, 40 °C) for 12 h. Yields: 85% (0.16 g). Elemental analysis calcd (%): C 37.96, H 2.64; found: C 37.22, H 2.65.

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