

Electronic Supplementary Information

Homoleptic Ruthenium(III) Chalcogenolates: A Single Precursor to Metal Chalcogenide Nanoparticles Catalyst

Sharon Lai-Fung Chan,^a Kam-Hung Low,^a Gary Kwok-Ming So^a Stephen Sin-Yin Chui,^a and Chi-Ming Che^{*a}

^a Department of Chemistry, State Key Laboratory on Synthetic Chemistry, and Institute of Molecular Functional Materials, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, China. Fax: 852 2857 1586; Tel: 852 2859 2154; E-mail: cmche@hku.hk

General

Scanning electron microscopic (SEM) image was recorded by LEO 1530 scanning electron microscope. Transmission electron microscopic (TEM) image and selected area electron diffraction (SAED) pattern were recorded by FEI Philips Tecnai 20 transmission electron microscope. Elemental analyses were performed at MEDAC LTD in the United Kingdom or at the Chinese Academy of Sciences, Beijing. The IR spectra were recorded on a Nicolet Nexus 670 Fourier-transform infrared spectrophotometer. Thermogravimetric data were obtained using a Perkin-Elmer Thermal Analyzer TGA-7 under a stream of flowing N₂. NMR spectra were recorded on a Bruker DPX-300 spectrometer (chemical shifts reported in ppm using TMS as internal reference). Mass spectra were obtained on a Thermo Scientific DFS High Resolution Magnetic Sector MS instrument by using the electron-impact ionization technique (40 eV). Thiophenol, 4-*tert*-butylthiophenol, 4-isopropylthiophenol, and 4-methoxythiophenol were purchased from Fluorochem Ltd. Ru₃(CO)₁₂, Cr(CO)₆, and Mo(CO)₆ were purchased from Strem Chemical, Inc. Diphenyl diselenide, selenium (> 99.99%), 4-*tert*-butylphenylmagnesium

bromide solution (2.0 M in diethyl ether), 4-nitrobenzyl alcohol, 1-bromo-4-nitrobenzene, 4-Nitrophenol, 4-methyl-2-nitrobenzotrile, 1,4-dinitrobenzene, and 2,4-dinitrophenol were purchased from Sigma-Aldrich Co. 1-Nitro-4-*n*-propylbenzene was purchased from Alfa Aesar Ltd. Hydrazine hydrate solution (80%) was purchased from Riedel-de Haën. 1-Nitro-4-(phenylmethoxy)benzene was prepared by literature procedure.^[S1]

General synthetic procedure for polymer 1 – 3 and 6 – 8:

A mixture of metal carbonyl (0.191 g, 0.3 mmol for Ru₃(CO)₁₂; 0.200 g, 0.9 mmol for Cr(CO)₆; 0.238 g, 0.9 mmol for Mo(CO)₆) and thiophenol or *para*-substituted thiophenol (2 mL) was heated at 250 °C under argon for 12 hours. After cooled down to room temperature, the precipitate formed was filtered in air and washed with chloroform (3 × 5 mL) and diethyl ether (3 × 5 mL).

[Ru(SPh-*p*-*t*Bu)₃]_n (1). Obtained as a dark green solid from Ru₃(CO)₁₂ and 4-*tert*-butylthiophenol. Yield: 75%. Elemental analyses for C₃₀H₃₉S₃Ru, Calcd.: (%) C, 60.4; H, 6.54; S, 16.1. Found: (%) C, 59.9; H, 6.51; S, 16.4. IR (KBr/cm⁻¹): ν_{C-H}: 3058 (w), 2960 (s), 2902 (m), 2867 (m), 1590 (w), 1486 (m), 1460 (m), 1392(m), 1361 (m), 1268 (m), 1201 (w), 1116 (m), 1011 (m), 819 (s) and 551 (s).

[Ru(SPh-*p*-*i*Pr)₃]_n (2). Obtained as a dark green solid from Ru₃(CO)₁₂ and 4-*iso*-propylthiophenol (2 mL). Yield: 70%. Elemental analyses for C₂₇H₃₃S₃Ru, Calcd.: (%) C, 58.5; H, 5.95; S, 17.3. Found: (%) C, 58.1; H, 5.9; S, 17.0. IR (KBr/cm⁻¹): ν_{C-H}: 3009 (w), 2960 (s), 2868 (w), 1635 (m), 1483 (w), 1384 (M), 1050 (m), 1013 (m), 819 (m), 545 (m).

[Ru(SPh-*p*-OMe)₃]_n (3). Obtained as a dark green solid from Ru₃(CO)₁₂ and 4-methoxythiophenol (2 mL). Yield: 73%. Elemental analyses for C₂₇H₃₃S₃Ru, Calcd.: (%) C, 45.5; H, 3.97; Found: (%) C, 45.1; H, 3.94. IR (KBr/cm⁻¹): ν_{C-H}: 2998 (w), 2937 (w), 2832 (w), 1588 (s), 1569 (m), 1490 (s), 1463 (m), 1439 (m), 1287 (m), 1247 (m), 1172 (m), 1105 (w), 1027 (m), 818 (m), 796 (w) and 517 (m).

[Cr(SPh)₃]_n (6). Obtained as a yellowish brown solid from Cr(CO)₆ and thiophenol. Yield: 85%. Elemental analyses for C₁₆H₁₅S₃Cr, Calcd.: (%) C, 57.0; H, 4.0; S, 25.3. Found: (%) C, 56.8; H, 4.1; S, 25.0. IR(KBr/cm⁻¹): ν_{C-H}: 3053 (w), 1643 (m), 1578 (m), 1476 9 (m), 1436 (m), 1023 (m), 733 (s), 684 (s).

[Cr(SPh-*p*-*t*Bu)₃]_n (7). Obtained as a pale brown solid from Cr(CO)₆ and 4-*tert*-butylthiophenol. Yield: 90%. Elemental analyses for C₃₀H₃₉S₃Cr, Calcd.: (%) C, 65.8; H, 7.1; S, 17.6. Found: (%) C, 65.3; H, 7.2; S, 17.5. IR (KBr/cm⁻¹): ν_{C-H}: 2963 (s), 2903 (m), 2867 (m), 1637 (m), 1498 (m), 1486 (m).

[Mo(SPh-*p*-*t*Bu)₃]_n (8). Obtained as a brick red solid from Mo(CO)₆ and 4-*tert*-butylthiophenol. It was found to be unstable upon exposure to air. Yield: 82%. Elemental analyses for C₃₀H₃₉S₃Mo, Calcd.: (%) C, 65.8; H, 7.1. Found: (%) C, 65.3; H, 7.2. IR (KBr/cm⁻¹): ν_{C-H}: 2961 (s), 2903 (m), 2867 (m), 1634 (m), 1467 (m), 1362 (m), 1116 (m), 1011 (m), 819 (s), 551 (m).

Synthesis of bis(4-*tert*-butylphenyl) diselenide. It was prepared by a modified literature procedure.^[s2] In a 250 mL two-neck round-bottom flask, ground selenium powder (0.395 g, 5.0 mmol) was suspended in 50 mL dried THF under a nitrogen atmosphere and the setup was cooled to 0 °C by an ice-water bath. 4-*tert*-butylphenylmagnesium bromide solution (2.0 M in diethyl ether, 5.0 mL) was added to the reaction flask at 0 °C and the ice-water bath was removed after the addition. The reaction mixture was stirred at room temperature for 16 h and all solid selenium disappeared. Iodine (2.54 g, 10.0 mmol) was added to the mixture at room temperature and stirred for additional 3 h. Saturated aqueous ammonium chloride solution (10 mL) and water (50 mL) were added to the reaction mixture. The reaction mixture was extracted with diethyl ether (3 × 10 mL) and the organic layers were combined and washed with brine (30 mL) and dried (MgSO₄). The organic solvents were removed by rotary evaporator and the solid residue was recrystallized with hexane. The titled compound was obtained as light yellow solid (1.17 g, 55%). ¹H-NMR (300 MHz, CDCl₃): δ = 1.31 (s, 18H), 7.25 – 7.58 (m, 8H); EIMS: *m/z* 426.0 [*M*⁺].

Synthesis of [Ru(SePh-*p*-*t*Bu)₃]_n (5). Prepared from bis(4-*tert*-butylphenyl) diselenide and ruthenium acetylacetonate as described for **4**. Yield: 82%. Elemental analyses for C₃₀H₃₉Se₃Ru, Calcd.: (%) C, 48.8; H, 5.3. Found: (%) C, 48.3; H, 5.6.

Structural determination using powder XRD data.

Sample Preparation and Data Collection: Solid samples of **1–8** was freshly prepared, dried and mechanically ground into fine powder samples. For each sample, the fine powder was side-loaded onto a glass holder to form a flat surface (*ca.* 14 mm (diameter) × 0.5 mm (depth)). Step-scanned powder diffraction data were independently collected using Bruker D8 Advance θ/θ diffractometer with parallel X-ray radiation ($\lambda_{\text{CuK}\alpha} = 1.5406\text{\AA}$, rated as 1.6 kW) via a Göbel mirror. After a preliminary data collection, the mounted sample was unpacked and reloaded onto the same holder to minimize the systematic errors from particle statistics and preferred orientation of the solid samples. Data collection parameters were: 2θ range = 3–60°, step size = 0.02°, scan speed = 10 second/step. A replicated dataset of each sample was obtained, indicating that sample damage by X-ray irradiation was negligible. The phase purity of the solid sample was checked by ICDD (International Center for Diffraction Data, PDF-2 Release 2004) database matching search and all samples were free of known crystalline impurities.

Structure Solution: Preliminary lattice parameters of **1** were obtained by indexing the first 12-15 resolved diffraction peaks. Using the indexing program DICVOL04,^[s3] a hexagonal unit cell was indexed [$a = b = 17.427(7)\text{\AA}$, $c = 5.432(6)\text{\AA}$, $M(12) = 32.2$, $F(12) = 42.2$ (0.0158, 18)]. Indexing the four additional peaks at higher angles ($>30^\circ$ (2θ)) led to doubling of c -axis length with a lower figure of merit. The first four successive diffraction maxima could be indexed as [100], [110], [200] and [210] reflections with a characteristic ratio as $q:\sqrt{3}q:2q:\sqrt{7}q$ ($q = 1/d$). All the initial lattice parameters of **1** were refined by the Pawley fit algorithm.^[s4] Background coefficients, zero-point and profile shape variables were refined together to attain improved profile fitting with reliability indicators R_{wp} , R_{p} and $\chi^2 < 10$. Space group assignment was performed by a trial-and-error approach, in which the expected systematic absences of extracted intensities were examined. The space group P6₃/m (No. 176) for **1** was chosen because (a) all

observed peaks were indexed and matched with the calculated Bragg positions and (b) high occurrence (325 times for $P6_3/m$, 149 times for $P6_3$, 53 times for $P6_3/mc$, 49 times for $P6_3/mmc$) out of 250,000 crystal structures appeared in the Cambridge Structural Database (CSD 2005 release). According to the unit cell volume, 13 non-hydrogen atoms were needed for each asymmetric unit (formula mass unit $Z \sim 6$). Based on the $[\text{Ru}(\text{L})_3]$ formulation, only 1/6 of the Ru atom and half of a ligand molecule were required in such a way that the former was on the special position at $(0,0,1/2)$ for the S_6 axis and the ligand laid on the crystallographic mirror plane with half occupancy. A starting model of the 4-*tert*-butylthiophenol ligand was built using the program ISIS DRAW version 2.14 and was later converted to sets of fractional coordinates which were written in a Z-matrix file format by the program Babel (<http://www.eyeopen.com/babel/>) or OPENBABEL (<http://openbabel.sourceforge.net>). The following restrained bond distances (Å) were used: Ru–S 2.250, C(sp²)–S 1.78, C(sp³)–C(sp³) 1.54, C(sp³)–C(sp²) 1.43, C(sp²)–C(sp²) 1.39, C(sp² or sp³)–H 0.96. The restrained bond angle (°) for C(sp²)-C(sp²)-C(sp²)/C(sp²)-C(sp²)-S and C(sp²)-C(sp³)-C(sp³) were 120 and 109.5 respectively. The carbon atoms of the phenyl rings in **1** were constrained into a regular hexagon. All aromatic hydrogen atoms were added to their parent carbon atoms according to an idealized geometry. Calculation of the structure solution of **1** were initiated by a global optimization of experimental diffraction profiles using a simulated annealing algorithm implemented in the program DASH.^[s5] More than 1000 trial structures were calculated using default parameters and fixing the Ru atom at the special position $(0,0,1/2)$. The three positional parameters and four orientation angles of the 4-*tert*-butylthiophenol were varied. When the calculated χ^2 was reduced to a minimal level (5–10 times of the original profile χ^2 value), the structure solutions were examined in the context of bond distances and bond angles as well as the graphical fit between the calculated and experimental diffractographs. Occasionally, the initial position of S atom was readily located and the rest of the structure model was progressively completed by adding the remaining light atoms (C, H) afterwards.

Structural refinement: Prior to any structural refinement, the chemically sensible structure solution was manually adjusted so as to remove those unrealistic close non-bonded contacts by applying the appropriate sets of atom-atom distance restraints (minimum non-bonded distances of 2.0 Å and 2.6 Å for H···H and H···C respectively). For instance, when those bad contacts

disappeared, the corresponding weighing factors of those distance restraints were reduced accordingly or the restraints were removed. The model adjustment process was repeated many times until there were no overlapped atoms or unrealistic bad contacts for non-bonded atoms. Subsequent Rietveld profile refinement by the full matrix least squares was carried out by GSAS/EXPGUI suite programs.^[s6] Scattering factors, corrected for real and imaginary anomalous dispersion terms were taken from the internal library of GSAS. Overall scale factor and the coefficients of the linear interpolation background function were refined. Profile shape parameters (Pseudo-Voigt function),^[s7] instrumental parameters (S/L) and (H/L), sample displacement (shft), Gaussian peak width (GW) and the Lorentzian peak broadening factor due to the microstrain effect of crystallites (LY) were sequentially refined. When the refinement of all these non-structural parameters became converged with a negligible (shift/esd)² value, the model-biased profile refinement was switched in which the unit cell parameters, atomic coordinates, background, peak profile parameters were refined together to give the final $R_p = 0.0645$, $R_{wp} = 0.0910$, $R_{exp} = 0.0452$ and $R_B = 0.0857$. Graphical plot of the final refinement cycle is shown in Figure S1.

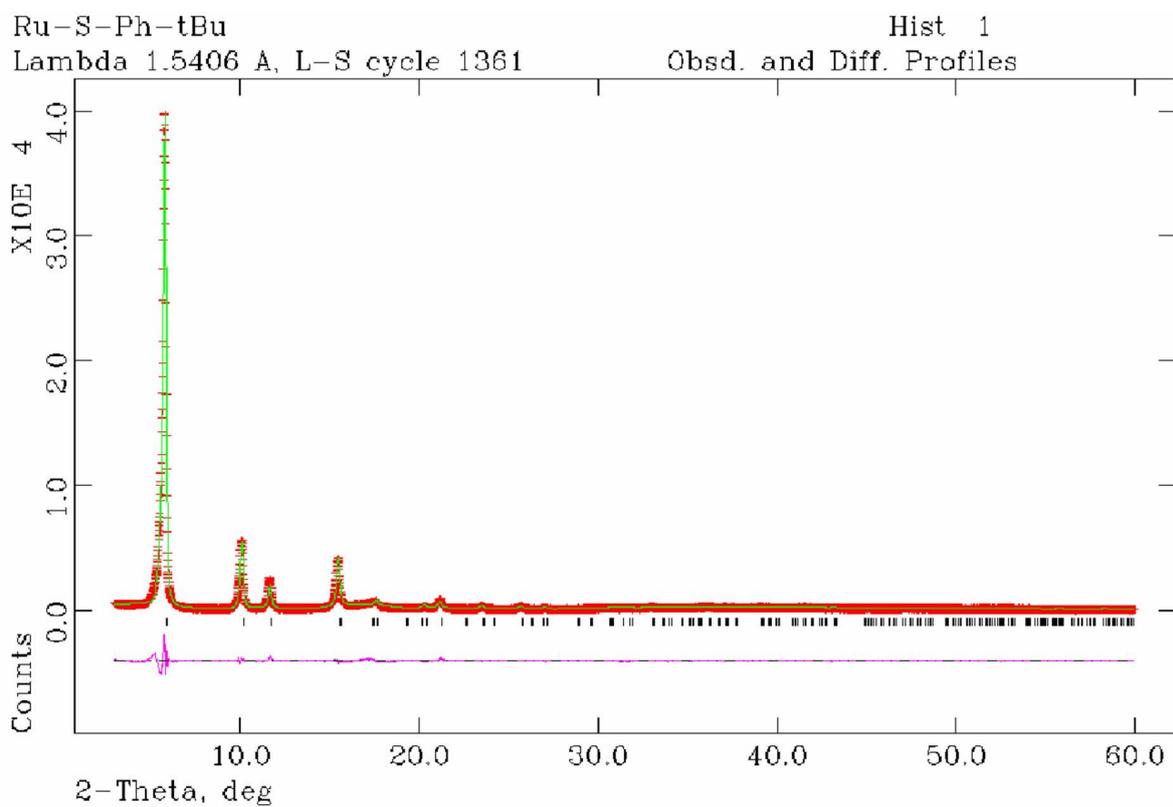


Figure S1. Graphical plot of the final Rietveld refinement cycle for **1** (Red crossed signs = observed data points, green line = calculated profile, vertical ticks = Bragg peak positions). Difference plot (magenta) between the experimental and calculated powder diffraction profiles is shown at the bottom of the plot.

Crystal system	Hexagonal
Space group	P6 ₃ /m
a [Å]	17.403 (1)
b [Å]	17.401 (1)
c [Å]	5.417 (8)
α [°]	90
β [°]	90
γ [°]	120
V [Å ³]	1420.7(23)
Z	2
M _r	596.89
ρ calcd [gcm ⁻³]	1.395
2 θ range	3–60
Data points, $y_{i,o}$	5701
Reflections, N _{obs}	332
Variables, N _{var}	93
Restraints	60
R _p [a]	0.0645
R _{wp} [a]	0.0910
R _{wp} (expected) [a]	0.0452
R _B [b]	0.0857
Goodness of fit	2.06
Max. [shift/esd] ² (mean)	0.69 (0.02)

Table S1. Results of structural refinements for **1**.

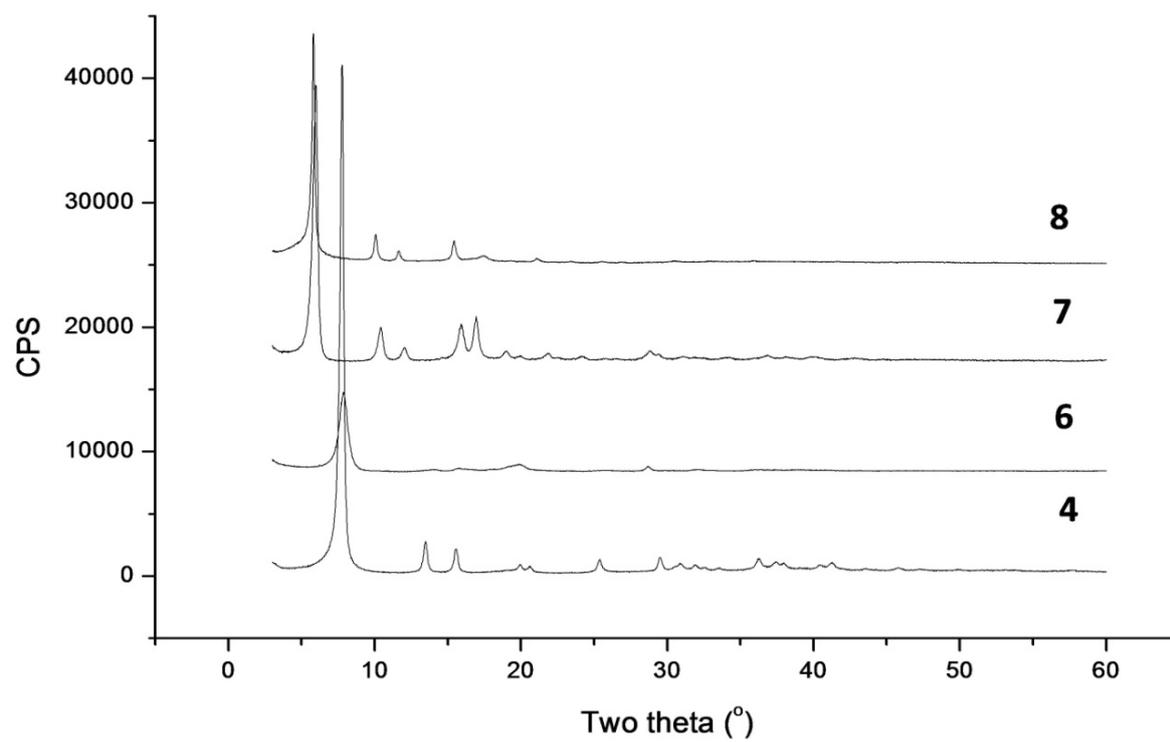


Figure S2a. PXR D patterns of SACPs **4**, and **6 – 8**.

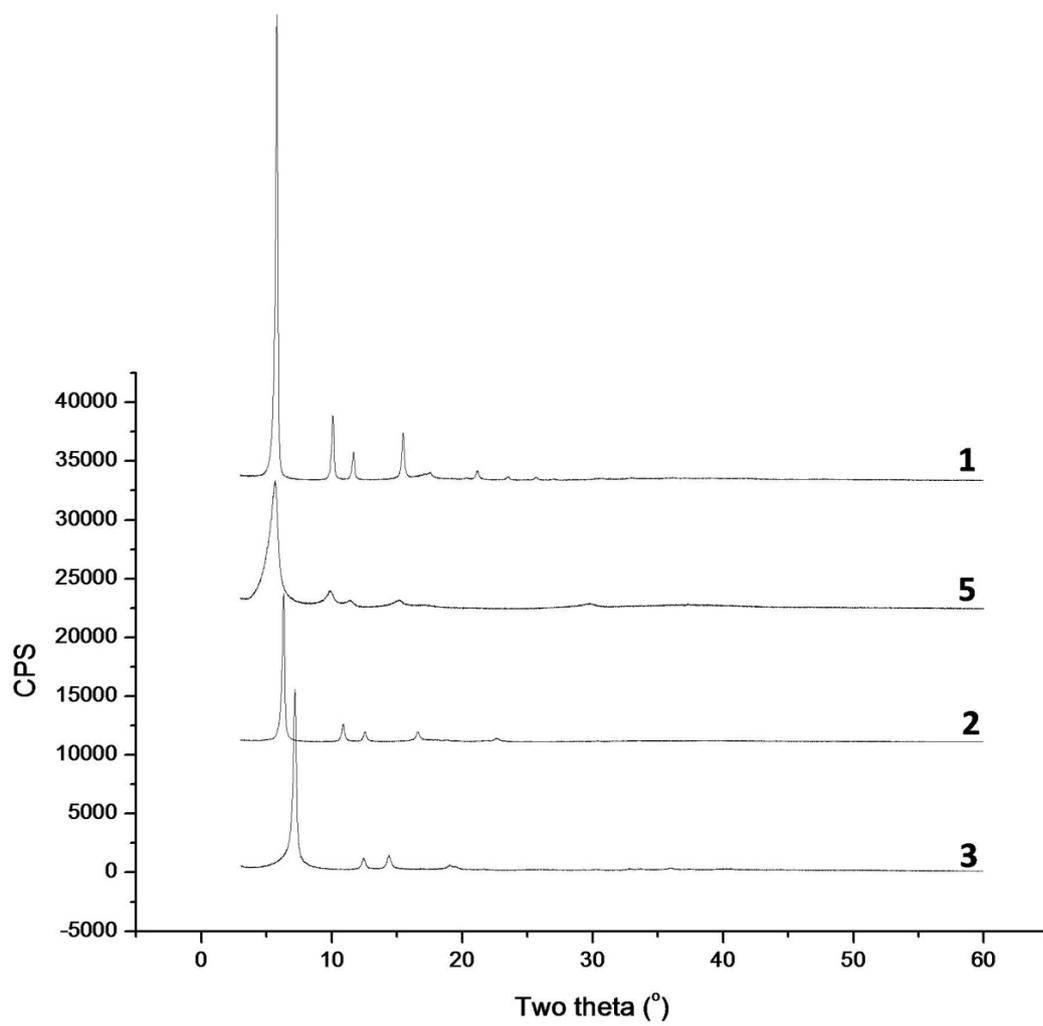


Figure S2b. PXRD patterns of SACPs 1 – 3, and 5.

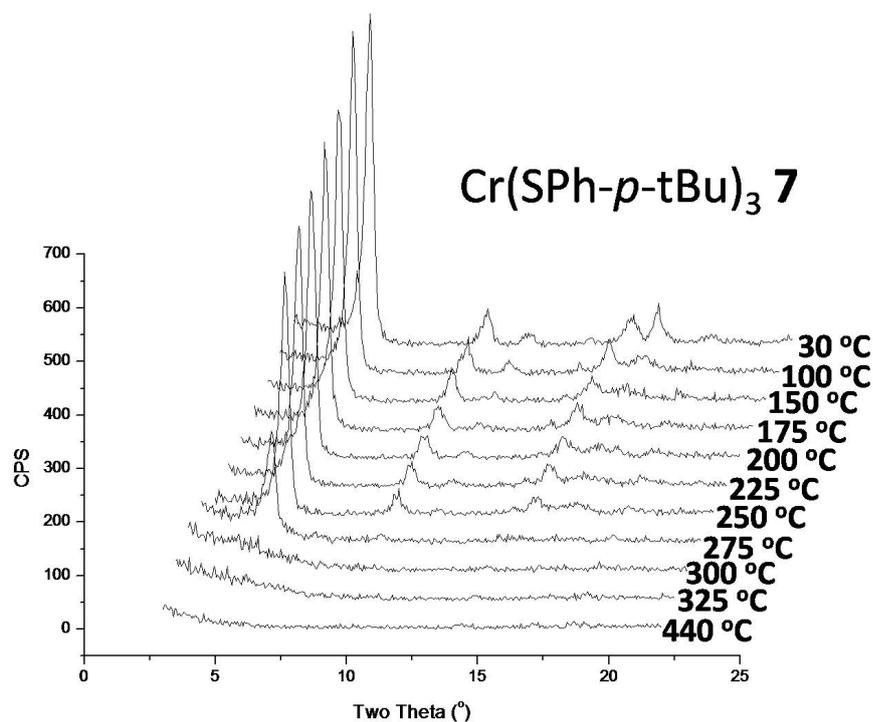


Figure S3. VT-PXRD patterns of 7.

Synthesis of *nano*-RuSe₂ from 1. SACP 1 (30 mg, 0.05 mmol) was added into a Schlenk tube. The Schlenk tube was pump filled with nitrogen gas, argon gas or evacuated by a vacuum pump respectively for 1 hour and then closed. The Schlenk tube containing the sample was placed into a pre-heated furnace and pyrolysed under inert atmosphere or vacuum at desired temperature as mentioned for 4 hours. The solid residue was collected when the Schlenk tube was cooled to room temperature. The product was characterized by PXRD, TEM, SAED, and EDS.

Catalytic reduction of substituted nitroaromatic compounds with *nano*-RuSe₂. Substituted nitroaromatic compound (2.0 mmol) and *nano*-RuSe₂ (5 mg, 0.02 mmol) were added into a 50 mL round-bottom flask. Ethanol (absolute, 25 mL) was added to dissolve the substituted nitroaromatic compound completely. Hydrazine hydrate solution (80%, 0.8 mL, 20 mmol) was

added. The reaction mixture was refluxed at 78 °C. The reaction progress was monitored by TLC and substrate conversion was determined by ¹H-NMR. The corresponding aniline product was isolated from the reaction mixture by flash column chromatography (SiO₂) using hexane/ethyl acetate mixtures of different ratios as eluents. The pure product was characterized by ¹H-NMR and compared with literature data.

Reference

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