

Supporting information

Cyclometallation *via* Carbon–Fluorine Bond Activation induced by Silver Particles

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1. Experimental details

1.1 Instrumentation

^1H and ^{19}F spectra were recorded on Bruker Avance 300, Avance III 400 or DRX300 NMR spectrometers. ^1H (400.11 MHz) were referenced internally to tetramethylsilane ($\delta = 0$) using the residual protio solvent resonance. ^{19}F (376.48 or 282.40 MHz) were referenced externally to trichlorofluoromethane ($\delta = 0$). Electrospray mass spectra were recorded on a Waters Micromass LCT Premier or a Bruker Daltonics micrOTOF mass spectrometer. Elemental analysis was performed by ASEP, The School of Chemistry and Chemical Engineering, Queen's University Belfast. Scanning electron microscopy was performed using an Hitachi S-4700 scanning electron microscope. EDS analysis was performed using a Thermo-Noran System 6 Energy dispersive X-ray spectrometer.

1.2 Materials

$[\text{Cp}^*\text{IrCl}]_2^+$ and $\mathbf{1}^2$ were prepared as previously described. Silver(I) oxide was obtained from Sigma Aldrich (reagentPlus[®], 99%, product no. 221163).

1.3 Synthesis and reactions

Preparation of $\mathbf{2}$: The preparation was performed under dinitrogen and in the absence of light. Silver(I) oxide (0.066 g, 0.284 mmol) was added to 1-(pentafluorobenzyl)-3-methylimidazolium bromide (0.064 g, 0.187 mmol) in dichloromethane (30 cm³). The mixture was stirred at room temperature for 1½ hours, and pentamethylcyclopentadienyl iridium dichloride dimer (0.076 g, 0.095 mmol) was then added. The mixture was stirred for a further 4 hours. The solution was filtered through celite twice and the filtrate was concentrated to about 5 cm³. Pentane was added slowly with swirling until it began to turn turbid. Crystals were obtained on cooling. The crystals were filtered off, washed with hexane and dried *in vacuo*. Yield: 0.091 g (79%). ^1H NMR (400.11 MHz, CDCl_3): δ_{H} 7.01 (d, $^3J_{\text{HH}} = 2$ Hz, 1H, $\text{C}_3\text{H}_2\text{N}_2$), 6.96 (d, $^3J_{\text{HH}} = 2$ Hz, 1H, $\text{C}_3\text{H}_2\text{N}_2$), 5.30 (s, CH_2Cl_2), 5.21 (d, $^2J_{\text{HH}} = 14.5$ Hz, 1H, CH_2), 4.49 (d, $^2J_{\text{HH}} = 14.5$ Hz, 1H, CH_2), 3.91 (s, 3H, NCH_3), 1.74 (s, 15H, Cp^*). ^{19}F NMR (376.48 MHz, CDCl_3): δ_{F} -114.0 (dd, $J_{\text{FF}} = 29, 14$ Hz, 1F), -147.7 (dd, $J_{\text{FF}} = 21, 14$ Hz, 1F), -158.4 (dd, $J_{\text{FF}} = 29, 20$ Hz, 1F), -165.3 (dd, $J_{\text{FF}} = 21, 20$ Hz, 1F). ESI-MS: calcd for $\text{C}_{21}\text{H}_{22}\text{F}_4\text{IrN}_2$, 571.1421; found $[\text{M} - \text{Cl}]^+$, 571.1368. Anal. Calcd for $\text{C}_{21}\text{H}_{22}\text{ClF}_4\text{IrN}_2 \cdot 1\frac{1}{2}\text{CH}_2\text{Cl}_2$: C, 38.72; H, 3.60; N, 4.01. Found: C, 38.85; H, 3.70; N, 3.80%.

Subsequent preparations of $\mathbf{2}$ were performed in air, and without excluding light.

Identification of silver fluoride and silver chloride as by-products: Following the synthesis of a sample of $\mathbf{2}$ using the procedure above, D_2O (ca. 2 cm³), in which silver(I) fluoride is soluble, was added to the solid residue. The ^{19}F NMR spectrum of the aqueous extract displayed a resonance at $\delta -122.2$ consistent with the fluoride anion in water ($\delta -119$).³ Addition of a few drops of conc. hydrochloric acid produced a white precipitate, which dissolved on addition of dilute aqueous ammonia, consistent with the presence of Ag^+ .⁴ The observations are consistent with the presence of silver(I) fluoride in the residue. The remaining residue was washed with distilled water. Dilute (2 M) aqueous ammonia (ca. 20 cm³), in which both silver(I) chloride and silver(I) oxide are soluble, was added to the residue, which dissolved fully. Addition of a few drops of conc. nitric acid produced a white precipitate, consistent with the presence of both Ag^+ and Cl^- in the solution.⁴ The observations are

consistent with the presence of silver(I) chloride in the residue. [CARE: While no adverse incidents occurred during these experiments, dissolution of silver(I) oxide in aqueous ammonia can lead to the formation of explosive and shock sensitive silver nitride (fulminating silver). Dilute (2 M) aqueous ammonia was used, and the samples were treated with acid immediately after each experiment had been completed to prevent the formation of the nitride.]

Confirmation of the identity of commercial silver(I) oxide: Addition of dilute aqueous ammonia to commercial silver(I) oxide led to rapid and complete dissolution, consistent with silver(I) oxide. Addition of dilute aqueous hydrochloric acid gave a white precipitate.⁴

The effect of stirring silver(I) oxide in dichloromethane: A sample of silver(I) oxide (*ca.* 0.2 g) was stirred, by means of a Teflon coated magnetic flea on a magnetic stirrer, in dichloromethane (*ca.* 10 cm³) for 2 hours. The black solid was filtered off and left in air until dry. Dilute aqueous ammonia (*ca.* 2 cm³) was added to a *ca.* 0.02 g sample and the mixture shaken repeatedly for *ca.* 5 minutes. The majority of the black solid remained undissolved, consistent with elemental silver. The solution was decanted, and a few drops of nitric acid added. No precipitate was observed, indicating the absence of silver chloride in the stirred sample.⁴ Addition of dilute aqueous hydrochloric acid resulted in the precipitation of a white solid, indicating that some silver(I) oxide was also present in the stirred sample.

The effect of grinding silver(I) oxide: A sample of silver(I) oxide (*ca.* 0.2 g) was ground manually using a pestle and mortar for 15 mins. Dilute aqueous ammonia (*ca.* 2 cm³) was added to a *ca.* 0.02 g sample and the mixture shaken repeatedly for *ca.* 5 minutes. *Ca.* 0.01 g of black solid remained undissolved, consistent with elemental silver.

The effect of stirring silver(I) oxide without solvent: A sample of silver(I) oxide (*ca.* 0.2 g) was stirred, by means of a Teflon coated magnetic flea on a magnetic stirrer for 2 hours. Dilute aqueous ammonia (*ca.* 2 cm³) was added to a *ca.* 0.02 g sample and the mixture shaken repeatedly for *ca.* 5 minutes. A substantial amount (*ca.* 90%) of the black solid remained undissolved, consistent with elemental silver. The solution was decanted, and a few drops of hydrochloric acid added. A white precipitate was observed, indicating the presence of Ag⁺ in solution.⁹ Dilute aqueous nitric acid was added to the remainder, which dissolved. The observations are consistent with a *ca.* 9:1 mixture of elemental silver and silver oxide.

1.4 Single crystal X-ray diffraction

Single yellow, blade-shaped crystals of **2** were obtained by recrystallization from dichloromethane and pentane. A suitable crystal (0.700 × 0.360 × 0.040 mm³) was selected and mounted on MITIGEN holder in oil on a Rigaku R-Axis SPIDER IP diffractometer. The crystal was kept at *T* = 120(2) K during data collection. Using WinGX⁵ and Olex⁶, the structure was solved with the Superflip⁷ structure solution program, using the Charge Flipping solution method. The model was refined with version 2014/7 of ShelXL⁸ using Least Squares minimization. Crystal data: C₂₂H₂₄Cl₃F₄IrN₂, *M_r* = 690.98, monoclinic, *P*₂₁/n (No. 14), *a* = 11.1891(8) Å, *b* = 15.6168(11) Å, *c* = 14.3860(10) Å, β = 109.252(2)°, *V* = 2373.2(3) Å³, *T* = 120(2) K, *Z* = 4, *Z'* = 1, μ(MoK_α) = 6.008, 32257 reflections measured, 5430 unique (*R*_{int} = 0.1617) which were used in all calculations. The final *wR*₂ was 0.1059 (all data) and *R*₁ was 0.0503 (*I* > 2σ(*I*)).

The CIF file has been deposited with the Cambridge Structural Database (CCDC reference number 1500912) and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax (+44) 1223-336-033; or

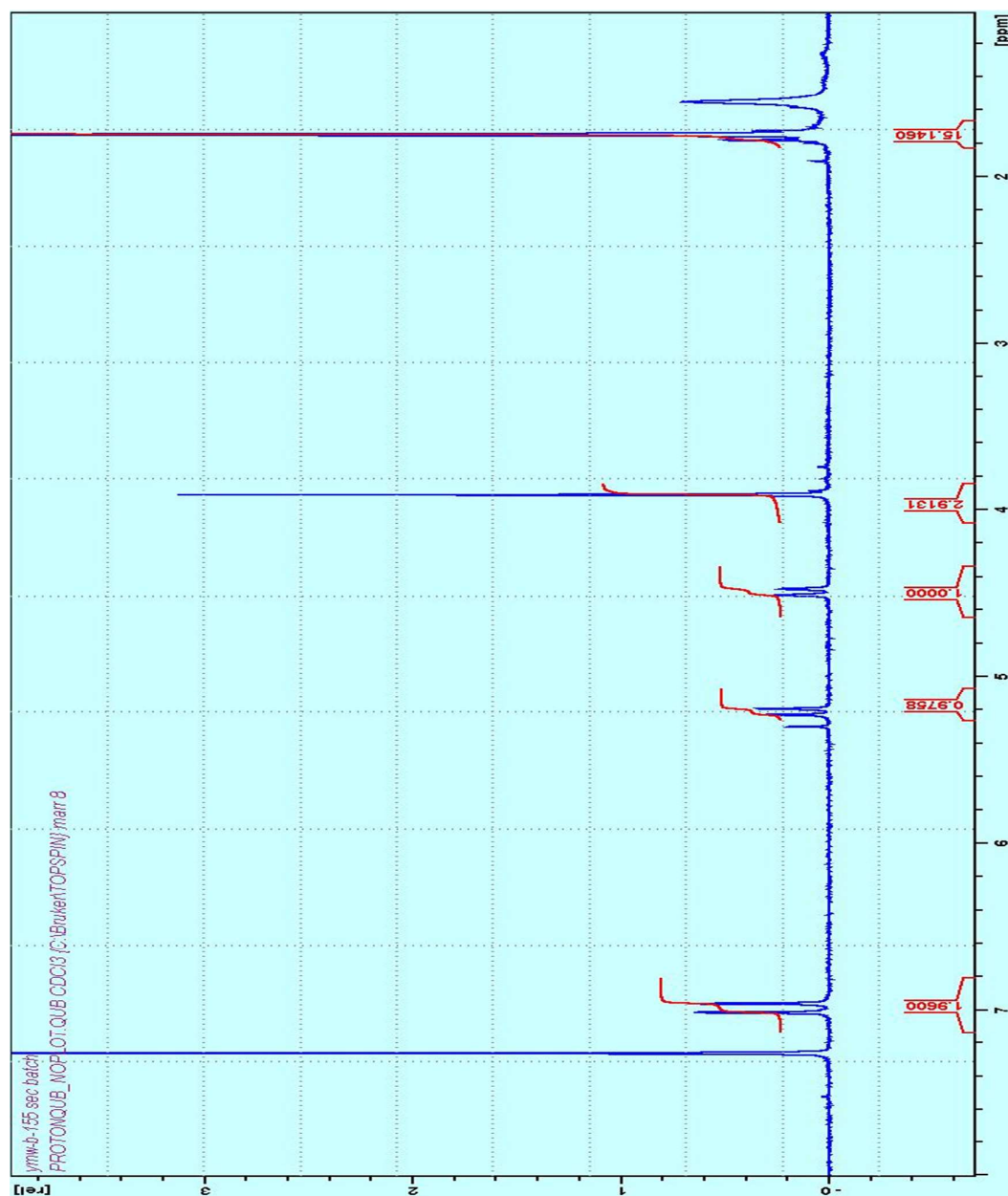
deposit@ccdc.cam.ac.uk).

1.5 References

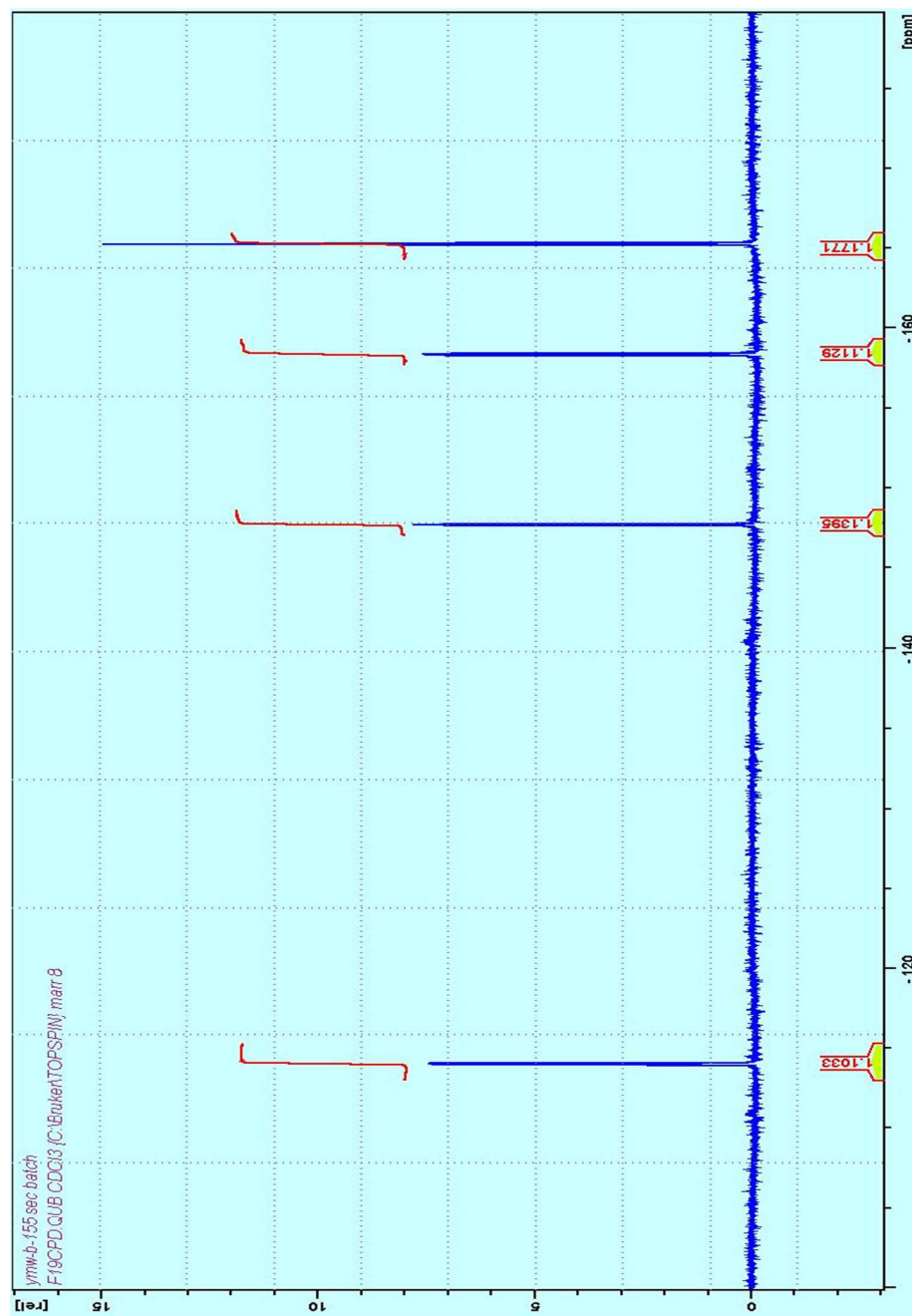
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2. Figures

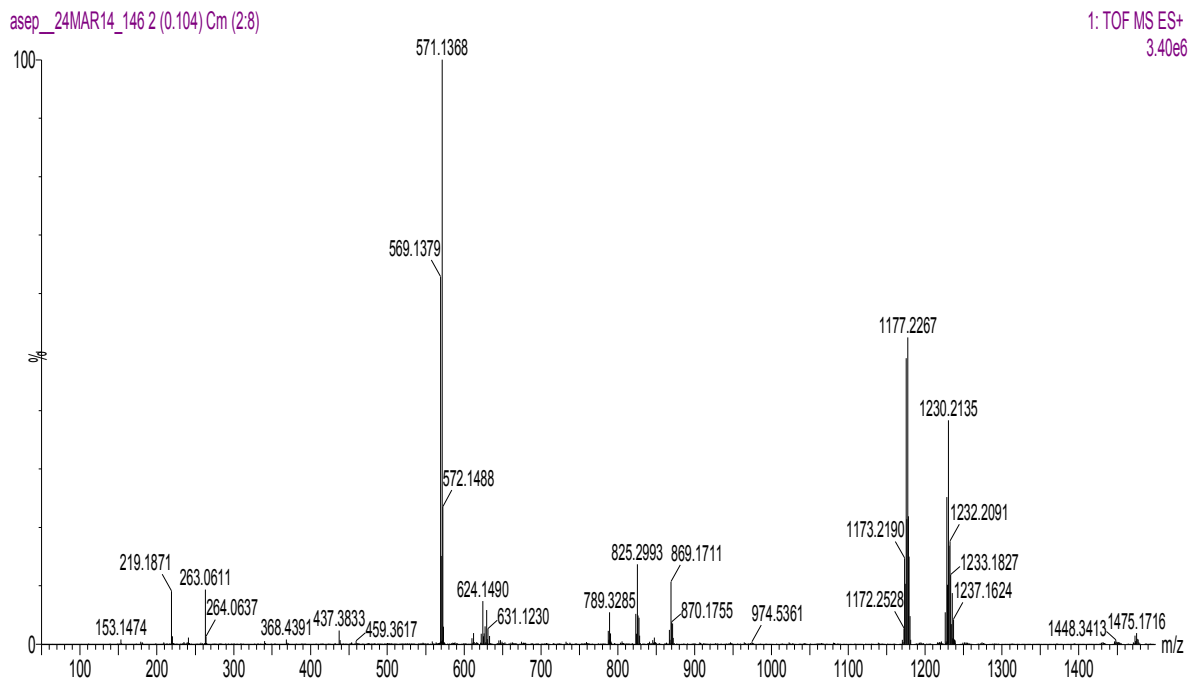
2.1 Figure S1. ^1H NMR spectrum of **2**



2.2 Figure S2. ^{19}F NMR spectrum of **2**



2.3 Figure S3. Electrospray mass spectrum of **2**



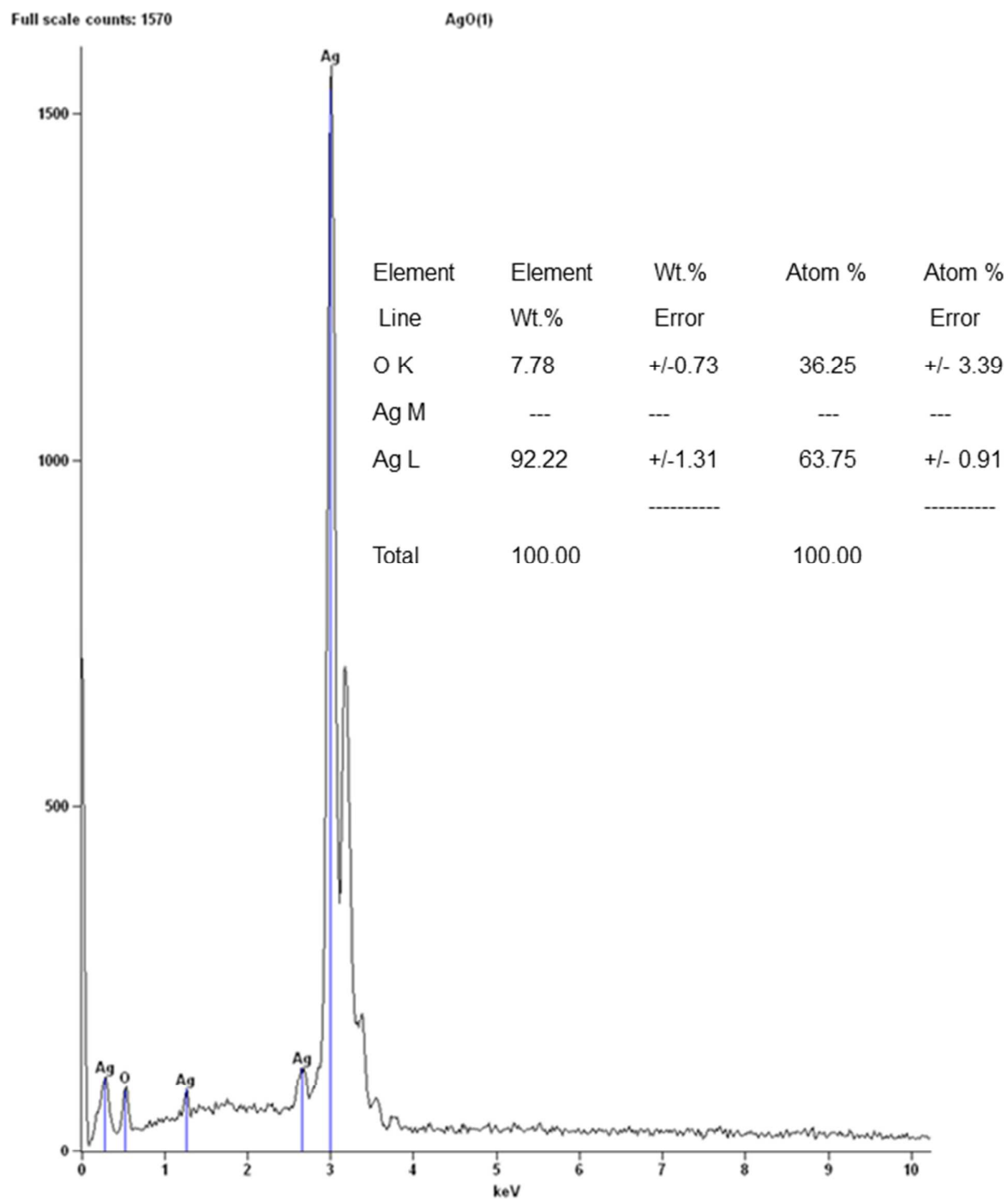
Calcd for $C_{21}H_{22}F_4IrN_2$, 571 $[M - Cl]^+$.

Calcd for $C_{21}H_{26}F_4IrN_3Cl$, 624 $[M + NH_4]^+$.

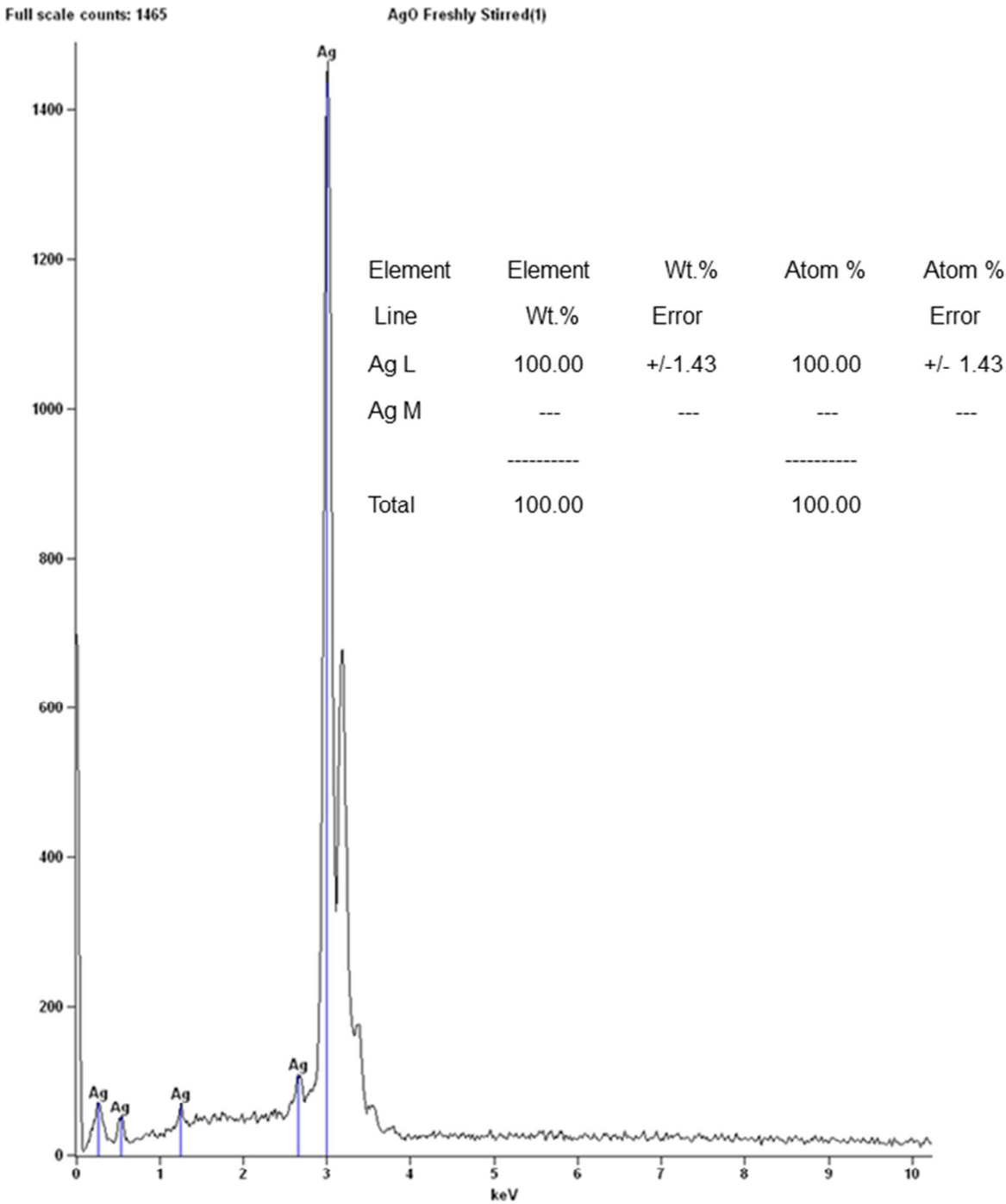
Calcd for $C_{42}H_{44}F_8Ir_2N_4Cl$, 1177 $[2M - Cl]^+$.

Calcd for $C_{42}H_{48}F_8Ir_2N_5Cl_2$, 1230 $[2M + NH_4]^+$.

2.4 Figure S4. Energy dispersive X-ray spectrum of commercial silver(I) oxide



2.5 **Figure S5.** Energy dispersive X-ray spectrum of commercial silver(I) oxide after stirring in dichloromethane for 2 hours.



2.6 Figure S6. Silver on the thread of a bottle of silver(I) oxide.

