

ELECTRONIC SUPPLEMENTARY INFORMATION

Cyclometalated $[\text{Os}(\text{C}\sim\text{N})_x(\text{N}\sim\text{N})_{3-x}]^{m+}$ Mimetics of Tris(2,2'-bipyridine)osmium(II): Covering a 2 V Potential Range by Known ($x = 0, 1$) and New ($x = 2, 3$) Species ($\text{C}\sim\text{N} = o\text{-2-phenylpyridinato}$)

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Experimental Details

Materials. All solvents were dried and distilled under nitrogen prior to use. 2-Phenylpyridine, potassium hexafluorophosphate, 2,2'-bipyridine and 1,3-cyclohexadiene were purchased from Sigma Aldrich Chemicals and used as received. Sodium hexachloroosmate(IV) was purchased from Strem Chemicals and converted into $[\text{OsCl}(\mu\text{-Cl})(\eta^6\text{-C}_6\text{H}_6)]_2$ as described elsewhere.¹ The organomercury derivative of 2-phenylpyridine $[\text{Hg}(\text{C}\sim\text{N})_2]$ was prepared as reported.² The complex $[\text{Os}^{\text{II}}\text{Cl}(\text{C}\sim\text{N})(\eta^6\text{-C}_6\text{H}_6)]$ (**2**) was prepared as described.³

Methods. All experiments were performed under dry argon or nitrogen using the Schlenk technique. All NMR spectra were recorded on a JEOL GX300 (¹H at 300.53 MHz) spectrometer in CDCl₃. Chemical shifts (δ) are in ppm and referenced to the residual solvent peaks. Coupling constants (J) are in Hz. Mass spectra (FAB⁺) were obtained using a JEOL JMS-SX102A instrument with *m*-nitrobenzyl alcohol as a matrix. IR spectra were recorded on a Bruker-Alpha ATR apparatus. Elemental analyses were carried using an Exeter Analytical CE-440 instrument analyzer. Electrochemical measurements were performed on a PC-interfaced potentiostat-galvanostat AUTOLAB PGSTAT 12. A three-electrode setup was used with a BAS working glassy carbon electrode, Ag/AgCl reference electrode, and auxiliary Pt electrode. Before each measurement, the working electrode was polished with a diamond paste and rinsed with

acetone and distilled water. Diffusion coefficients for the **1a-d** were calculated using the Randles-Ševcik equation $i = (2.69 \times 10^5) n^{3/2} S D^{1/2} \nu^{1/2} C$ (i is the peak current, n is the electron stoichiometry, D is the diffusion coefficient, S is the electrode surface, ν is the scan rate, and C is the concentration).

EPR measurements were made at 6.7 K using liquid helium in quartz tubes with a Jeol JES-TE300 spectrometer operating at X band frequency (9.4 GHz) at a 100 KHz field modulation with a cylindrical cavity (TE011 mode). The external measurement of the static magnetic field was made with a precision gaussmeter Jeol ES-FC5. Variable temperature experiments were performed from room temperature (292.3 K) to 6.7 K in solid state. Double integration and peak height measurements were used to quantify EPR spectra and for Figure 1S.⁴

Synthesis of 1c. A mixture of **2** (20 mg, 0.043 mmol), Hg(C~N)₂ (11 mg, 0.022 mmol), 2,2'-bipyridine (7 mg, 0.045 mmol) and KPF₆ (16 mg, 0.087 mmol) in 15 mL ethanol was stirred for 48 h at 30 °C. The solvent was evaporated under vacuum and the residue was dissolved in 5 mL of dichloromethane. The solution was brought on a short alumina column under nitrogen. The product was first eluted by dichloromethane and then by a 9:1 (v/v) dichloromethane-acetonitrile mixture. A brown dark band was collected and concentrated. Crystallization by slow diffusion of CH₂Cl₂/diethyl ether gave black crystals which were washed with diethyl ether and dried under vacuum. Yield: 17 mg, 49%. IR-ATR: 832 (PF₆). EM-FAB⁺: 654(20%) [(M+H)-PF₆]⁺, 500(6%) [(M+H)-(phpy + PF₆)]⁺. Anal. Calcd. for C₃₂H₂₄N₄OsPF₆·0.5CH₂Cl₂: C, 46.35; H, 2.99; N, 6.65. Found: C, 46.86; H, 3.03; N, 6.84. EPR (1 mM solution in MeCN): $g_{||} = 2.0245$, $g_{\perp} = 2.5388$.

Synthesis of 1d. To a solution of **2** (20 mg, 0.043 mmol) in 15 mL methanol, Hg(C~N)₂ (55 mg, 0.109 mmol) was added and the mixture was stirred for 24 h at room temperature. The solvent was removed under vacuum and a red residue was dissolved in 5 mL of dichloromethane. The solution was brought on a short alumina column under nitrogen and was first eluted with dichloromethane and then with a 9:1 (v/v) dichloromethane-acetonitrile mixture. A red fraction was collected and concentrated to about 1 mL. Pentane was added to precipitate a red powder which was dried under vacuum for 5 h. Crystallization from CH₂Cl₂/pentane (slow diffusion) gave dark red crystals, which were washed with pentane and dried under vacuum. Yield: 30 mg, 96%. ¹H NMR(CDCl₃): 8.68 (d, 3H, ³J = 4.7), 7.97 (d, 6H, ³J = 7.4), 7.73 (d, 6H, ³J = 7.9), 7.48-7.39 (m, 6H), 7.52-7.20 (m, 3H). ¹³C NMR(CDCl₃): 168.09, 160.50, 148.63, 146.52, 139.36, 136.88, 128.61, 127.60, 127.16, 121.85, 121.29. EM-FAB⁺: 654(30%) [(M+H)]⁺, 575(<5%) [(M+H)-(C₅H₄N)]⁺, 500(24%) [(M+H)-phpy]⁺. Anal. Calcd. for C₃₃H₂₄N₃Os·CH₂Cl₂: C, 55.35; H, 3.55; N, 5.70. Found: C, 55.79; H, 4.12; N, 5.76. EPR (1 mM solution in MeCN): $g_{||} = 2.5275$, $g_{\perp} = 2.0822$.

Details of X-ray Structural Studies (Table 1S). Suitable crystals were grown from CH₂Cl₂/diethyl ether for **1c** and from a CH₂Cl₂/diethyl ether/pentane mixture for **1d**, and were mounted on glass fibers. In all cases, the X-ray intensity data were measured at 298 K on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube (0.71073 Å). The detector was placed at a distance of 4.837 cm from the crystals in all cases. A total of 1800 frames were collected with a scan width of 0.3 in ω and an exposure time of 10 s/frame. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm.⁵ The integration of the data was done using a tetragonal unit cell for **1d** and orthorhombic for **1c** to yield a total of 54674 and 46381 reflections, respectively, to a maximum 2θ angle of 50.00, of which 4590 [R(int) = 0.0679] for **1d** and 5422 [R(int) = 0.0725] for **1c** were independent. Analysis of the data showed in all cases negligible decay during data collections. The structures were solved by the Patterson method using SHELXS-97.⁶ The remaining atoms were located via a few cycles of least squares refinements and difference Fourier maps using the space group P-42₁c with Z = 8 for **1d** and Pbc_a with Z = 8 for **1c**. Hydrogen atoms were input at calculated positions and allowed to ride on the atoms to which they are attached. Thermal parameters were refined for hydrogen atoms on the phenyl groups using a U_{eq} = 1.2 Å² to precedent atom in all cases. For all complexes, the final cycle of refinement was carried out on all non-zero data using SHELXTL and anisotropic thermal parameters for all non-hydrogen atoms. The disordered PF₆ anion of **1c** was modeled in two major contributors and refined anisotropically. The C-Os distances are slightly shorter than N-Os distances, the final refinement led to determine that C19 atom is *trans* to N1 atom and C31 atom is *trans* to N7 atom of phenylpyridinato ligands and bipyridine ligand respectively. In the case of **1d**, the refinement of C-Os and N-Os distances allowed determine that C-Os are shorter than N-Os distances, and each C atom bonded to Os atom is *trans* to each N atom bonded to Os atom.

Table 1S. Crystallographic data for **1d** and **1c**.

	1d	1c
empirical formula	C ₃₃ H ₂₄ N ₃ Os	C ₃₂ H ₂₄ F ₆ N ₄ OsP
formula weight	652.75	799.72
temperature (K)	298(2)	298(2)
wavelength (Å)	0.71073	0.71073
crystal system	tetragonal	orthorhombic
space group	P-42 ₁ c	Pbca
unit cell dimensions (in Å and °)	<i>a</i> =23.4566(10), <i>α</i> =90 <i>b</i> =23.4566(10), <i>β</i> =90 <i>c</i> =9.1255(8), <i>γ</i> =90	<i>a</i> =11.0431(9), <i>α</i> =90 <i>b</i> =15.8867(13), <i>β</i> =90 <i>c</i> =33.671(3), <i>γ</i> =90
volume (Å ³)	5021.0(5)	5907.2(8)
Z	8	8
density (mg/m ³ , calculated)	1.727	1.798
absorption coeff. (mm ⁻¹)	5.107	4.439
F(000)	2552	3112
crystal size (mm)	0.25×0.14×0.12	0.32×0.30×0.04
<i>θ</i> range for data collection (°)	1.74 to 25.35	2.21 to 25.35
index ranges	-28 ≤ <i>h</i> ≤ 28 -28 ≤ <i>k</i> ≤ 28 -10 ≤ <i>l</i> ≤ 10	-13 ≤ <i>h</i> ≤ 13 -19 ≤ <i>k</i> ≤ 19 -40 ≤ <i>l</i> ≤ 40
reflections collected	54674	46381
independent reflection	4590[R(int)=0.0679]	5422[R(int)=0.0725]
absorption correction	empirical	semi-emp. from equiv.
refinement method	full-matrix least-squares on F ²	full-matrix least-squares on F ²
data/restraints/parameters	4590/0/334	5422/411/452
absolute structure parameter	-0.017(7)	
goodness-of-fit on F ²	0.919	1.00
final R indices [<i>I</i> >2σ(<i>I</i>)]	R1=0.0242, wR2=0.0421	R1=0.0432, wR2=0.1050
R indices (all data)	R1=0.0296, wR2=0.0431	R1=0.0736, wR2=0.1215
largest diff. peak and hole (eÅ ⁻³)	0.735 and -0.364	1.187 and -0.482

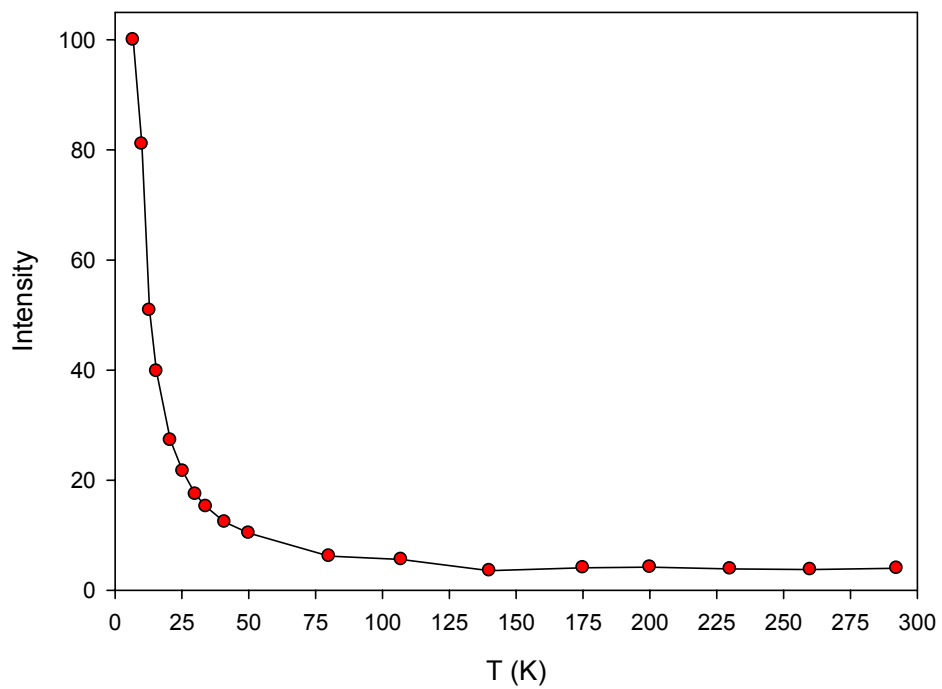


Figure 1S. Temperature dependence of intensities for the EPR components of complex **1d**.

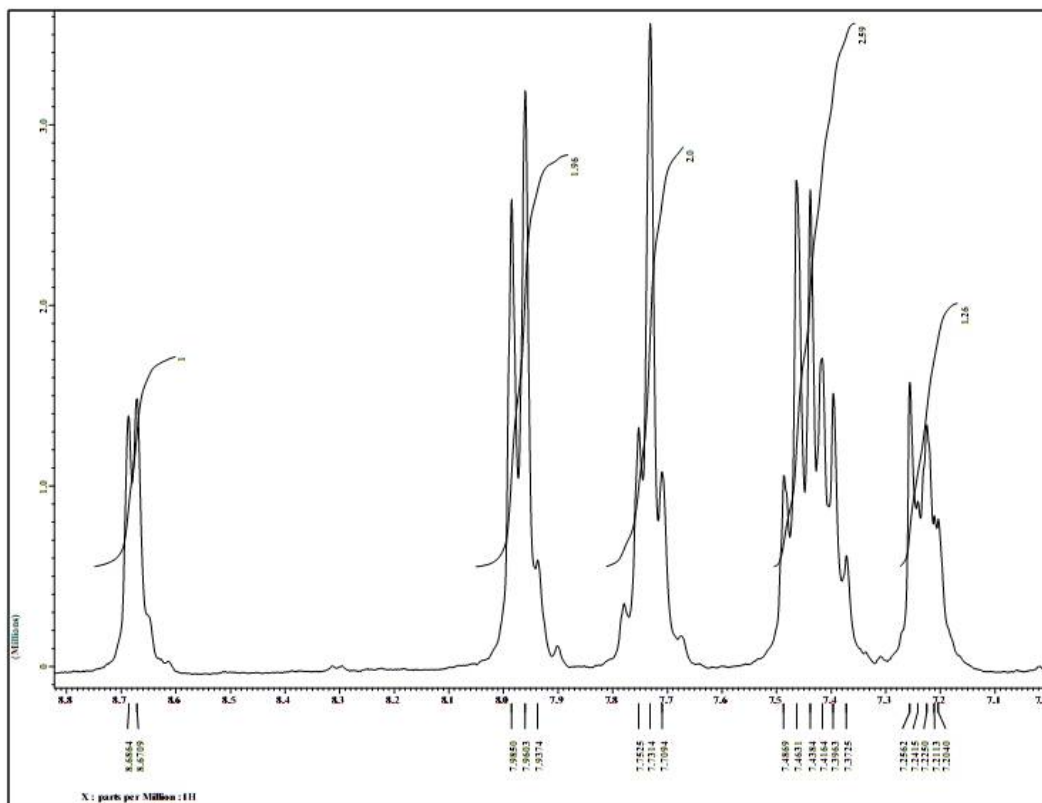


Figure 2S. ^1H NMR spectrum (CDCl_3) of complex **1d**.

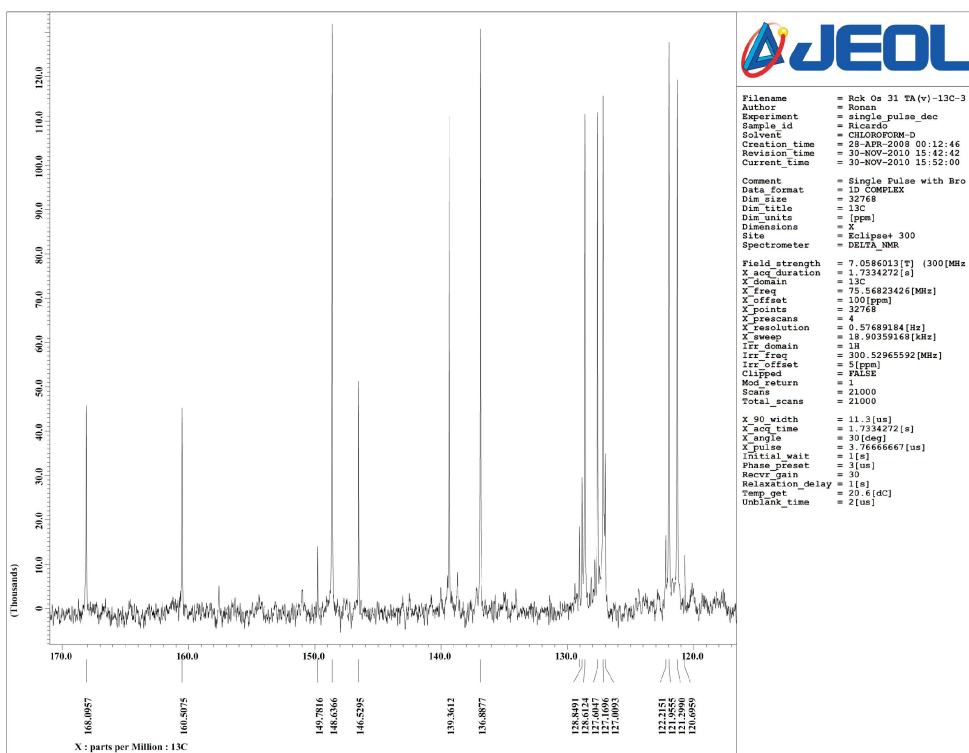


Figure 3S. ^{13}C NMR spectrum (CDCl_3) of complex **1d**.

[Os(phpy)₃], solid, 6.7 K

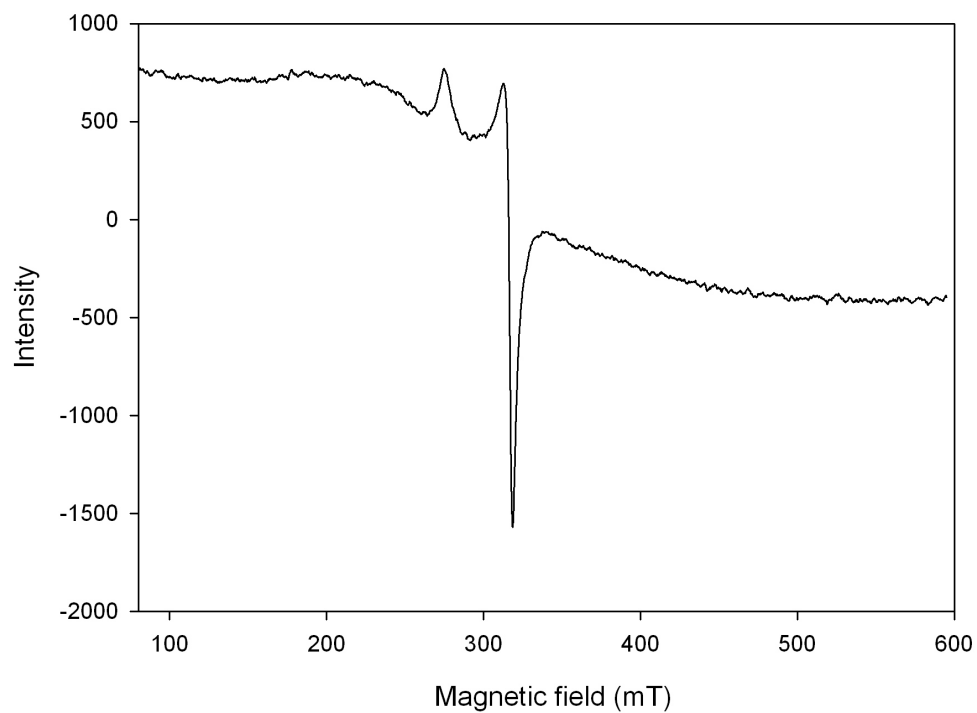


Figure 4S. EPR spectrum (solid state, 6.7 K) of complex **1d**.

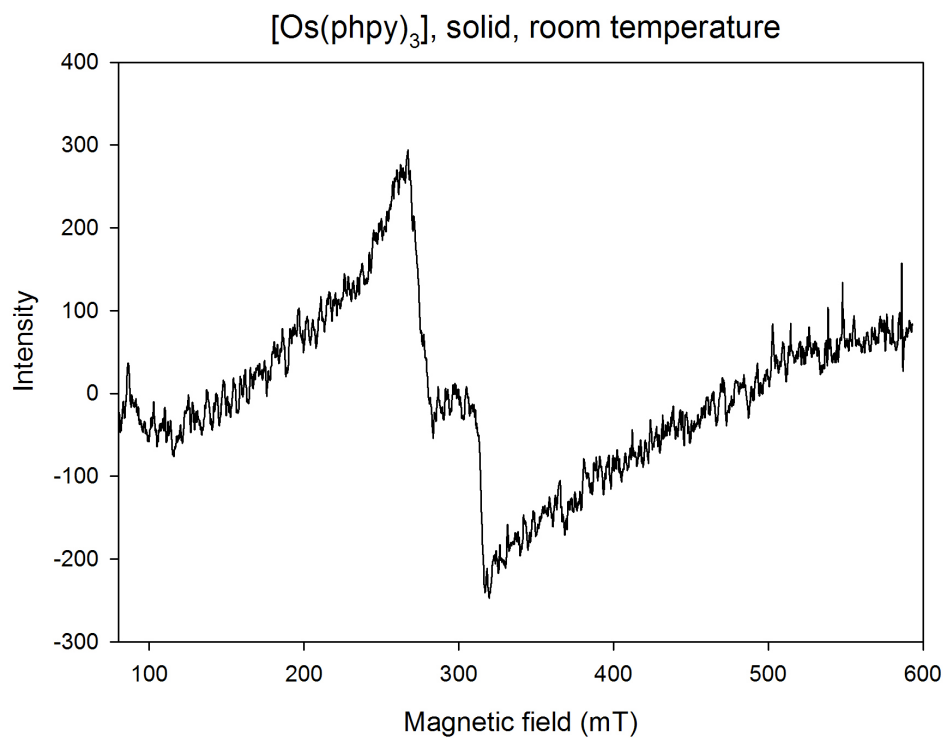


Figure 4S. EPR spectrum (solid state, 292.3K) of complex **1d**.

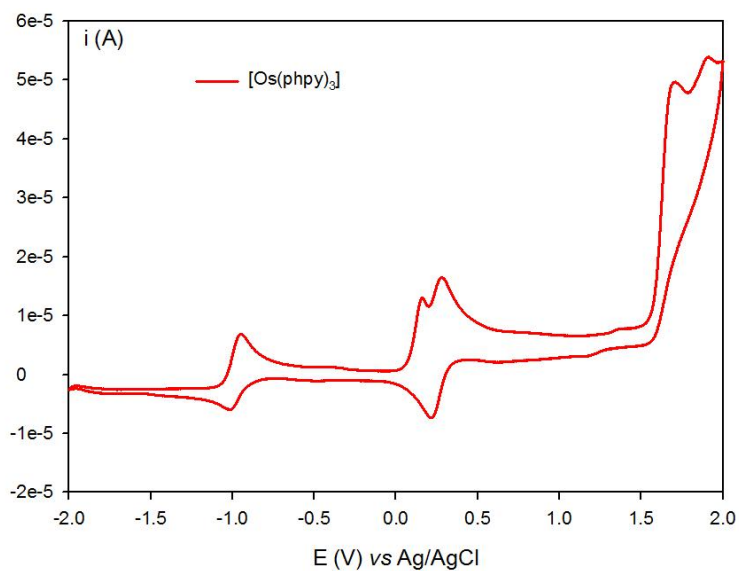


Figure 5S. CV for **1d** in NCMe, [Os] = 1 mM, (*n*-Bu)₄NPF₆ 0.1 M, scan rate 0.1 Vs⁻¹

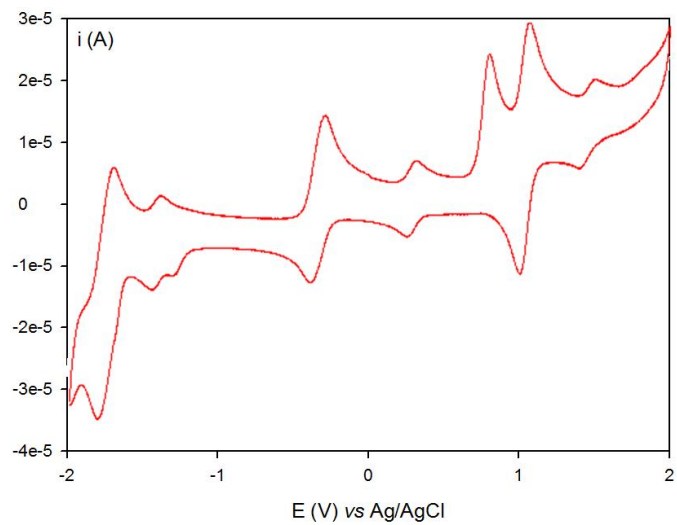


Figure 6S. CV of **1c** in NCMe, [Os] = 1 mM, (*n*-Bu)₄NPF₆ 0.1 M, scan rate 0.1 Vs⁻¹

References

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