Supporting Information

Manuscript: Electronic effects in oxo-transfer reactions catalysed by Salan molybdenum(VI) *cis*-dioxo complexes

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Synthesis of Ligands and Complexes

N,N'-dimethyl-*N,N'*-*bis*[(5-chloro-2-hydroxyphenyl)methylene]-1,2-diaminoethane (H_2L^{Cl}). This compound was prepared in an analogous manner to that described above for H_2L^{Br}, except 4-chlorophenol (2.92 g, 22.7 mmol) was used in place of 4-bromophenol to yield a white powder (2.36 g, 56 %). ^{1}H NMR (400MHz, $CDCl_3$, 298K): 10.66 (br s, 2H, ArOH), 7.15 (dd, 2H, $^3J_{HH}$ = 8.7, $^4J_{HH}$ = 2.5, ArH), 6.96 (d, 2H, $^4J_{HH}$ = 2.5, ArH), 6.79 (d, 2H, $^3J_{HH}$ = 8.7, ArH), 3.79 (s, 4H, NCH_2Ar), 2.67 (s, 4H, $N(CH_2CH_2)N$), 2.31 (s, 6H, NCH_3). ^{13}C NMR (400MHz, $CDCl_3$, 298K): 156.42, 128.79, 128.24, 123.71, 122.96, 117.58 (ArC), 61.34, 53.89 (CH_2), 41.66 (CH_3). MS (ESI): *m/z* = 369, $[M+H]^+$. *Elemental analysis for $C_{18}H_{22}Cl_2N_2O_2$ (F.W. 369.3):* C, 58.54; H, 6.00; N, 7.59%. Found C, 58.62; H, 6.06; N, 7.52 %.

N,N'-dimethyl-*N,N'*-*bis*[(5-iodo-2-hydroxyphenyl)methylene]-1,2-diaminoethane (H_2L^I). This compound was prepared in an analogous manner to that described above for H_2L^{Br}, except 4-iodophenol (4.99 g, 22.7 mmol) was used in place of 4-bromophenol to yield a white powder (2.13 g, 34 %). ^{1}H NMR (400MHz, $CDCl_3$, 298K): 9.91 (br s, 2H, ArOH), 7.46 (dd, 2H, $^3J_{HH}$ = 8.5, $^4J_{HH}$ = 2.1, ArH), 7.27 (d, 2H, $^4J_{HH}$ = 2.1, ArH), 6.64 (d, 2H, $^3J_{HH}$ = 8.5, ArH), 3.66 (s, 4H, NCH_2Ar), 2.66 (s, 4H, $N(CH_2CH_2)N$), 2.29 (s, 6H, NCH_3). ^{13}C NMR (400MHz, $CDCl_3$, 298K): 157.73, 137.73, 136.95, 124.15, 118.73, 80.59 (ArC), 61.08, 53.86 (CH_2), 41.65 (CH_3). MS (ESI): *m/z* = 553, $[M+H]^+$. *Elemental* *analysis for $C_{18}H_{22}I_2N_2O_2$ (F.W. 552.19):* C, 39.15; H, 4.02; N, 5.07%. Found C, 39.10; H, 4.03; N, 5.00 %.

N,N'-dimethyl-*N,N'-bis*[(5-methoxy-2-hydroxyphenyl)methylene]-1,2-diaminoethane (H_2L^{OMe}). This compound was prepared in an analogous manner to that described above for H_2L^{Br}, except 4-methoxyphenol (2.82 g, 22.7 mmol) was used in place of 4-bromophenol to yield a white powder (3.12g, 76 %). ^{1}H NMR (400MHz, $CDCl_3$, 298K): 10.22 (br s, 2H, ArOH), 6.82-6.73 (m, 4H, ArH), 6.56 (d, 2H, $^4J_{HH}$ = 2.8, ArH), 3.76 (s, 6H, $ArOCH_3$), 3.67 (s, 4H, NCH_2Ar), 2.67 (s, 4H, $N(CH_2CH_2)N$), 2.30 (s, 6H, NCH_3). ^{13}C NMR (400MHz, $CDCl_3$, 298K): 152.52, 151.50, 122.30, 116.61, 114.45, 113.70 (ArC), 61.84, 54.12 (CH_2), 55.74, 41.66 (CH_3). MS (ESI): *m/z* = 361, $[M+H]^+$. *Elemental analysis for $C_{20}H_{28}N_2O_4$ (F.W. 360.5):* C, 66.64; H, 7.83; N, 7.77%. Found C, 66.62; H, 7.80; N, 7.63 %.

N,N'-dimethyl-*N,N'-bis*[(5-fluoro-2-hydroxyphenyl)methylene]-1,2-diaminoethane (H_2L^F). This compound was prepared in an analogous manner to that described above for H_2L^{Br}, except 4-fluorophenol (2.54 g, 11.3 mmol) was used in place of 4-bromophenol to yield a white powder (534 mg, 14 %). ^{1}H NMR (400MHz, $CDCl_3$, 298K): 10.35 (br s, 2H, ArOH), 6.88 (td, 2H, $^3J_{HF}$ = 8.6, $^3J_{HH}$ = 8.6, $^4J_{HH}$ = 3.0, ArH), 6.78 (dd, 2H, $^3J_{HF}$ = 8.6, $^4J_{HH}$ = 4.7, ArH), 6.70 (dd, 2H, $^3J_{HH}$ = 8.6, $^4J_{HF}$ = 3.0, ArH) 3.67 (s, 4H, $ArCH_2N$), 2.67 (s, 4H, $N(CH_2CH_2)N$), 2.30 (s, 6H, NCH_3). ^{13}C NMR (400MHz, $CDCl_3$, 298K): 156.01 (d, $^1J_{CF}$ = 236.3), 153.66, 122.40 (d, $^3J_{CF}$ = 6.8), 116.89 (d, $^3J_{CF}$ = 7.3), 115.14 (d, $^2J_{CF}$ = 17.3), 114.91 (d, $^2J_{CF}$ = 17.9) (ArC), 61.44, 53.96 (CH_2), 41.68 (CH_3). ^{19}F NMR (400MHz, $CDCl_3$, 298K): –125.59 (ArF). MS (ESI): *m/z* = 373, $[M+H]^+$. *Elemental analysis for $C_{18}H_{22}F_2N_2O_2$ (F.W. 336.4):* C, 64.27; H, 6.59; N, 8.33%. Found C, 64.35; H, 6.52; N, 8.49 %.

[MoO_2L^{Me}]. This compound was prepared in an analogous manner to that described for [MoO_2L^H], except H_2L^{Me} (329 mg, 1.0 mmol) was used in place of H_2L^H to yield an orange powder (326 mg, 71 %). ^{1}H NMR (400MHz, $CDCl_3$, 298K): 7.03 (dd, 2H, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 1.4, ArH), 6.84 (d, 2H, $^4J_{HH}$ = 1.4, ArH), 6.76 (d, 2H, $^3J_{HH}$ = 8.1, ArH), 5.06 (d, 2H, $^2J_{HH}$ = 14.3, $ArCH_2N$), 3.53 (d, 2H, $^2J_{HH}$ = 14.3, $ArCH_2N$), 3.07 (d, 2H, $^2J_{HH}$ = 9.5, ($N(CH_2CH_2)N$)), 2.71 (s, 6H, NCH_3), 2.29 (s, 6H, $ArCH_3$), 2.11 (d, 2H, $^2J_{HH}$ = 9.5, ($N(CH_2CH_2)N$)). ^{13}C NMR (400MHz, $CDCl_3$, 298K): 157.49, 130.10, 130.06, 129.85, 121.79, 118.39 (ArC), 64.86, 51.98 (CH_2), 48.11, 20.54 (CH_3). MS (ESI): *m/z* = 457, $[M+H]^+$. *Elemental analysis* *for $C_{20}H_{26}N_2O_4Mo$ (F.W. 454.4):* C, 52.87; H, 5.77; N, 6.17%. Found C, 53.00; H, 5.88; N, 6.24 %.

$[\mathrm{MoO_2L^{Br}}]$. This compound was prepared in an analogous manner to that described above for $[\mathrm{MoO_2L^{H}}]$, except $\mathrm{H_2L^{Br}}$ (458 mg, 1.0 mmol) dissolved in 20 mL of dichloromethane was used in place of $\mathrm{H_2L^{H}}$ dissolved in acetonitrile to yield an orange powder (334 mg, 57 %). ^{1}H NMR (400MHz, d_6-DMSO, 298K): 7.41-7.35 (m, 4H, ArH), 6.74-6.69 (m, 2H, ArH), 4.64 (d, 2H, $^2J_{HH}$ = 14.8, $ArCH_2N$), 3.84 (d, 2H, $^2J_{HH}$ = 14.8, $ArCH_2N$), 2.76 (d, 2H, $^2J_{HH}$ = 9.9, $(N(CH_2CH_2)N)$), 2.57 (s, 6H, NCH_3), 2.34 (d, 2H, $^2J_{HH}$ = 9.9, $(N(CH_2CH_2)N)$). ^{13}C NMR (500MHz, d_6-DMSO, 298K): 158.65, 132.23, 131.65, 125.33, 120.06, 111.62 (ArC), 62.37, 51.75 (CH_2), 47.53 (CH_3). MS (ESI): *m/z* = 587, $[M+H]^+$. *Elemental analysis for $C_{18}H_{20}Br_2N_2O_4Mo$ (F.W. 584.1):* C, 37.01; H, 3.45; N, 4.80%. Found C, 37.09; H, 3.50; N, 4.84 %.

$[\mathrm{MoO_2L^{I}}]$. This compound was prepared in an analogous manner to that described above for $[\mathrm{MoO_2L^{H}}]$, except $\mathrm{H_2L^{I}}$ (552 mg, 1.0 mmol) dissolved in 20 mL of dichloromethane was used in place of $\mathrm{H_2L^{H}}$ dissolved in acetonitrile to yield an orange powder (369 mg, 54 %). ^{1}H NMR (400MHz, d_6-DMSO, 298K): 7.59-7.47 (m, 4H, ArH), 6.58 (d, 2H, $^3J_{HH}$ = 8.2, ArH), 4.63 (d, 2H, $^2J_{HH}$ = 14.7, $ArCH_2N$), 3.81 (d, 2H, $^2J_{HH}$ = 14.7, $ArCH_2N$), 2.76 (d, 2H, $^2J_{HH}$ = 9.8, $(N(CH_2CH_2)N)$), 2.57 (s, 6H, NCH_3), 2.33 (d, 2H, $^2J_{HH}$ = 9.8, $(N(CH_2CH_2)N)$). ^{13}C NMR (400MHz, $CDCl_3$, 298K): 159.70, 138.51, 138.00, 126.32, 120.95, 83.58 (ArC), 62.69, 52.18 (CH_2), 48.00 (CH_3). MS (ESI): *m/z* = 681, $[M+H]^+$. *Elemental analysis for $C_{18}H_{20}I_2N_2O_4Mo$ (F.W. 678.1):* C, 31.88; H, 2.97; N, 4.13%. Found C, 31.79; H, 2.90; N, 4.07 %.

$[\mathrm{MoO_2L^{NO_2}}]$. This compound was prepared in an analogous manner to that described above for $[\mathrm{MoO_2L^{H}}]$, except $\mathrm{H_2L^{NO_2}}$ (390 mg, 1.0 mmol) dissolved in 20 mL of dichloromethane was used in place of $\mathrm{H_2L^{H}}$ dissolved in acetonitrile to yield an orange powder (223 mg, 43 %). ^{1}H NMR (400MHz, d_6-DMSO, 298K): 8.30-8.10 (m, 4H, ArH), 6.95(d, 2H, $^3J_{HH}$ = 8.9, ArH), 4.71 (d, 2H, $^2J_{HH}$ = 14.9, $ArCH_2N$), 4.11 (d, 2H, $^2J_{HH}$ = 14.9, $ArCH_2N$), 2.80 (d, 2H, $^2J_{HH}$ = 9.9, $(N(CH_2CH_2)N)$), 2.64 (s, 6H, NCH_3), 2.43 (d, 2H, $^2J_{HH}$ = 9.9, $(N(CH_2CH_2)N)$). ^{13}C NMR (400MHz, d_6-DMSO, 298K): 170.05, 145.62, 131.59, 130.59, 129.08, 124.28 (ArC), 67.38, 57.17 (CH_2), 52.90 (CH_3). MS (ESI): *m/z* = 519, $[M+H]^+$. *Elemental analysis* *for $C_{18}H_{20}N_4O_8Mo$ (F.W. 516.3):* C, 41.87; H, 3.90; N, 10.85%. Found C, 41.90; H, 3.79; N, 10.87 %.

[MoO_2L^{OMe}]. This compound was prepared in an analogous manner to that described above for [MoO_2L^H], except H_2L^{OMe} (361 mg, 1.0 mmol) was used in place of H_2L^H to yield an orange powder (300 mg, 61 %). ^{1}H NMR (400MHz, $CDCl_3$, 298K): 6.82-6.73 (m, 4H, ArH), 6.58-6.54 (m, 2H, ArH), 5.07 (d, 2H, $^2J_{HH}$ = 14.3, $ArCH_2N$), 3.76 (s, 6H, $ArOCH_3$), 3.52 (d, 2H, $^2J_{HH}$ = 14.3, $ArCH_2N$), 3.07 (d, 2H, $^2J_{HH}$ = 9.5, ($N(CH_2CH_2)N$)), 2.69 (s, 6H, NCH_3), 2.13 (d, 2H, $^2J_{HH}$ = 9.5, ($N(CH_2CH_2)N$)). ^{13}C NMR (400MHz, $CDCl_3$, 298K): 153.89, 153.55, 122.69, 119.29, 114.72, 114.34 (ArC), 64.91, 52.01 (CH_2), 55.76, 48.06 (CH_3). MS (ESI): *m/z* = 489, $[M+H]^+$. *Elemental analysis for $C_{20}H_{26}N_2O_6Mo$ (F.W. 486.4):* C, 49.39; H, 5.39; N, 5.76 %. Found C, 49.30; H, 5.31; N, 6.02 %.

[MoO_2L^F]. This compound was prepared in an analogous manner to that described above for [MoO_2L^H], except H_2L^F (200 mg, 0.59 mmol) was used in place of H_2L^H to yield a yellow powder (189 mg, 68 %). ^{1}H NMR (400MHz, $CDCl_3$, 298K): 6.94 (td, 2H, $^3J_{HF}$ = 8.6, $^3J_{HH}$ = 8.6, $^4J_{HH}$ = 3.1, ArH), 6.82 (dd, 2H, $^3J_{HF}$ = 8.6, $^4J_{HH}$ = 4.9, ArH), 6.76 (dd, 2H, $^3J_{HH}$ = 8.6, $^4J_{HF}$ = 3.1, ArH) 5.05 (d, 2H, $^2J_{HH}$ = 14.6, $ArCH_2N$), 3.55 (d, 2H, $^2J_{HH}$ = 14.6, $ArCH_2N$), 3.06 (d, 2H, $^2J_{HH}$ = 9.6, ($N(CH_2CH_2)N$)), 2.72 (s, 6H, NCH_3), 2.19 (d, 2H, $^2J_{HH}$ = 9.6, ($N(CH_2CH_2)N$)). ^{13}C NMR (400MHz, d_6-DMSO, 298K): 156.40 (d, $^1J_{CF}$ = 236.3), 156.23, 124.50 (d, $^3J_{HF}$ = 8.3), 119.47 (d, $^3J_{HF}$ = 8.4), 116.47 (d, $^2J_{HF}$ = 23.9), 115.86 (d, $^2J_{HF}$ = 22.6) (ArC), 63.21, 52.23 (CH_2), 47.99 (CH_3). ^{19}F NMR (400MHz, d_6-DMSO, 298K): -121.29 (ArF). MS (ESI): *m/z* = 465, $[M+H]^+$. *Elemental analysis for $C_{18}H_{20}F_2MoN_2O_2$ (F.W. 462.3):* C, 46.76; H, 4.36; N, 6.06%. Found C, 46.69; H, 4.44; N, 5.97 %.

[$MoO_2(H_2L^H)$]. This compound was prepared in an analogous manner to that described above for [MoO_2L^H], except H_4L^H (272 mg, 1.0 mmol) was used in place of H_2L^H to yield an orange powder (259 mg, 66 %). ^{1}H NMR (400MHz, d_6-DMSO, 298K): 7.23-7.05 (m, 4H, ArH), 6.82 (t, 2H, $^3J_{HH}$ = 8.0, ArH), 6.72 (d, 2H, $^3J_{HH}$ = 8.0, ArH), 5.25 (br s, 2H, NH), 4.79 (d, 2H, $^2J_{HH}$ = 14.5, $ArCH_2N$), 3.89 (d, 2H, $^2J_{HH}$ = 14.5, $ArCH_2N$), 2.74 (d, 2H, $^2J_{HH}$ = 7.8, ($N(CH_2CH_2)N$)), 2.30 (d, 2H, $^2J_{HH}$ = 7.8, ($N(CH_2CH_2)N$)). ^{13}C NMR (400MHz, d_6-DMSO, 298K): 160.32, 130.15, 128.20, 122.49, 120.47, 118.80 (ArC), 53.10, 46.25 (CH_2). MS (EI): *m/z* = 400, $[M+H]^+$. *Elemental analysis for $C_{16}H_{18}N_2O_4Mo$ (F.W. 398.3):* C, 48.00; H, 5.05; N, 7.00 %. Found C, 48.24; H, 4.96; N, 7.03 %.

— X-Ray Crystallography

Fig. S1 The molecular structure of [MoO_2L^{Cl}] (30% probability ellipsoids).

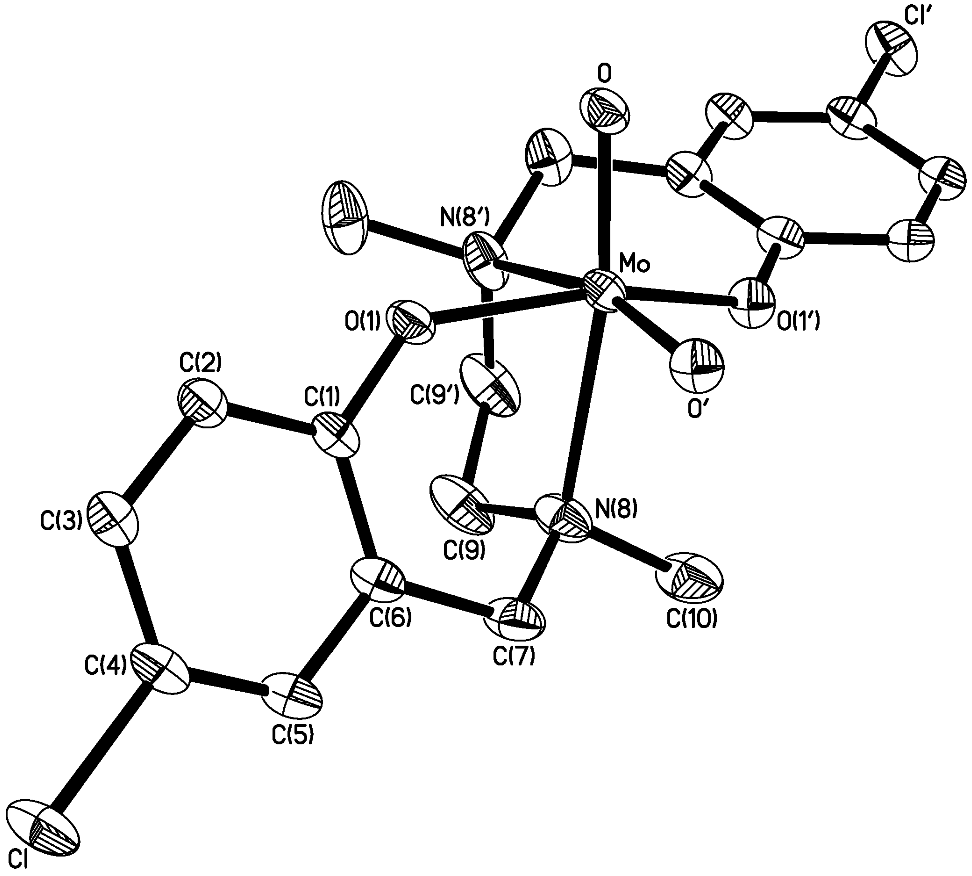
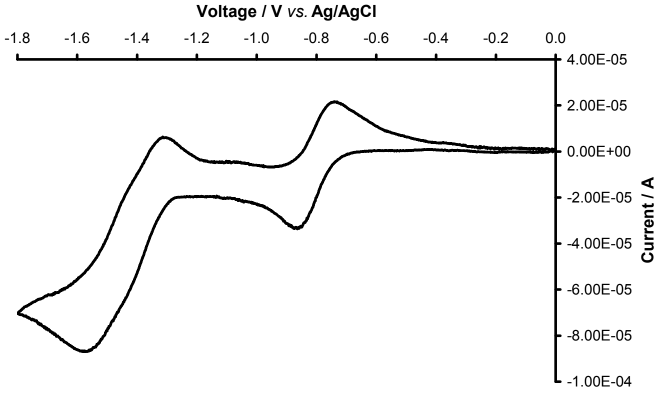


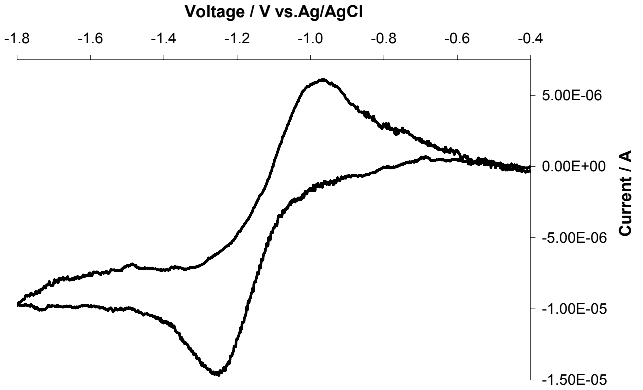
Fig. S1

Cyclovoltametry Studies

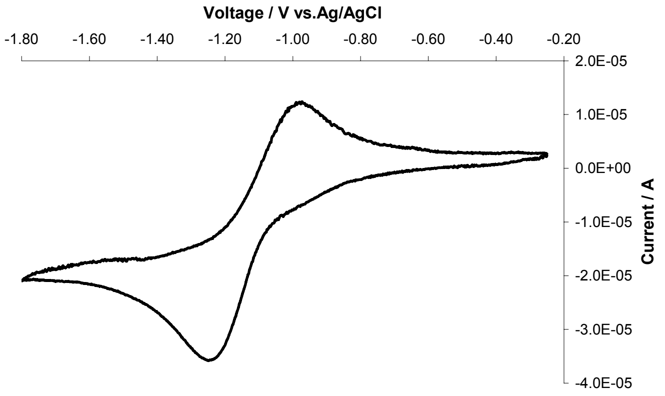
$[MoO_2L^{NO_2}]$



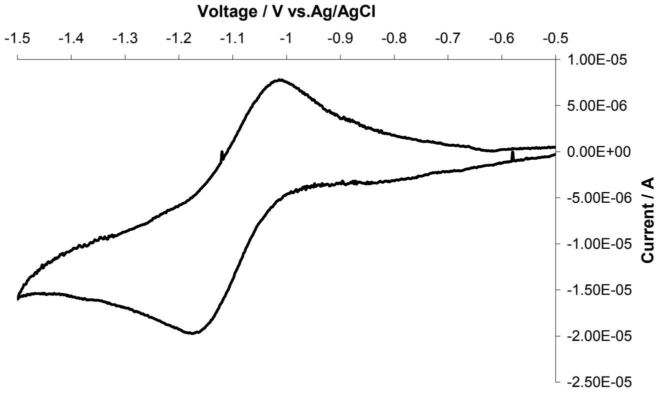
$[MoO_2L^{Cl}]$



$[MoO_2L^{Br}]$



$[MoO_2L^I]$



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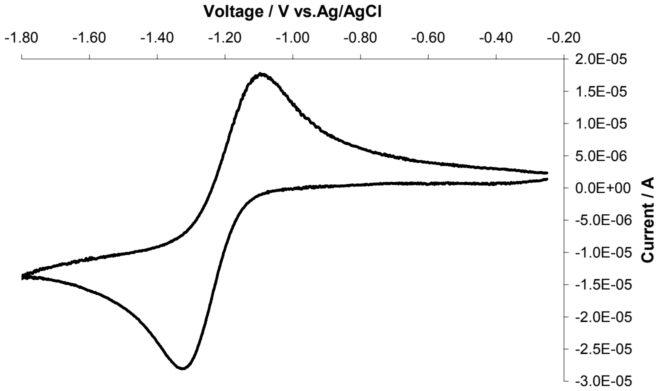

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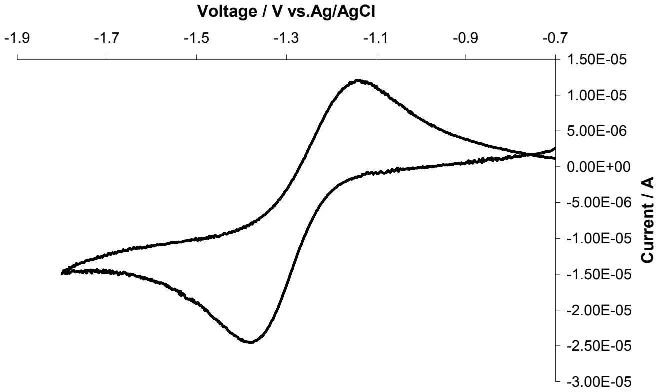
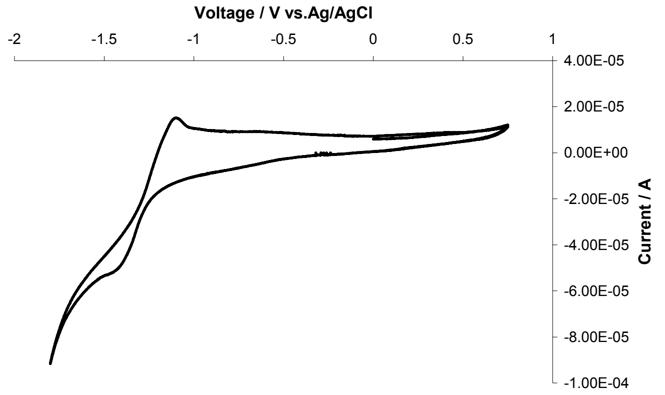


$[MoO_2L^{OMe}]$



$[MoO_2(H_2L^H)]$