Appendix

A. Cut off solvents

Table 42 The solvent for UV-Visible spectrum and the minimum values for measurement

Solvents	λ(nm)
$CHCl_3$	245
CH_2Cl_2	230
DMF	270
DMSO	265
CH_3CN	195

B. Bond distances (Å) and bond angles (°)

Table 43 The bond distances (Å) and bond angles (°) of *trans*-Ru(dmsazpy)$_2$Cl$_2$ complex

Bond distances

Atoms	Distance (Å)
Ru((1))-Cl((1))	2.3805(7)
Ru((1))-Cl((2))	2.3794(7)
Ru((1))-N((1))	2.073(2)
Ru((1))-N((3))	2.015(2)
Ru((1))-N((5))	2.063(3)
Ru((1))-N((7))	2.024(2)
S((1))-C((2))	1.718(3)
S((1))-C((3))	1.723(3)
S((2))-C((13))	1.717(2)
S((2))-C((14))	1.722(3)
N((1))-C((1))	1.371(3)
N((1))-C((3))	1.326(4)
N((2))-N((3))	1.321(3)
N((2))-C((3))	1.357(4)
N((3))-C((4))	1.405(4)
N((4))-C((7))	1.358(4)
N((4))-C((10))	1.456(4)
N((4))-C((11))	1.451(5)
N((5))-C((12))	1.372(3)
N((5))-C((14))	1.324(4)
N((6))-N((7))	1.326(4)

Table 43 (continued)

Atoms	Distance (Å)
N((6))-C((14))	1.356(3)
N((7))-C((15))	1.402(3)
N((8))-C((18))	1.359(4)
N((8))-C((21))	1.456(4)
N((8))-C((22))	1.453(5)
C((1))-C((2))	1.346(4)
C((1))-H((1))	0.949(3)
C((2))-H((2))	0.950(3)
C((4))-C((5))	1.395(4)
C((4))-C((9))	1.401(4)
C((5))-C((6))	1.365(4)
C((5))-H((3))	0.950(3)
C((6))-C((7))	1.413(4)
C((6))-H((4))	0.950(3)
C((7))-C((8))	1.419(4)
C((8))-C((9))	1.371(4)
C((8))-H((5))	0.948(3)
C((9))-H((6))	0.949(3)
C((10))-H((7))	0.950(3)
C((10))-H((8))	0.950(4)
C((10))-H((9))	0.952(3)
C((11))-H((10))	0.950(3)
C((11))-H((11))	0.950(4)
C((11))-H((12))	0.949(4)
C((12))-C((13))	1.344(4)

Table 43 (continued)

Atoms	Distance (Å)
C((12))-H((13))	0.950(2)
C((13))-H((14))	0.950(3)
C((15))-C((16))	1.401(4)
C((15))-C((20))	1.405(4)
C((16))-C((17))	1.365(4)
C((16))-H((15))	0.950(3)
C((17))-C((18))	1.409(4)
C((17))-H((16))	0.950(3)
C((18))-C((19))	1.424(4)
C((19))-C((20))	1.366(4)
C((19))-H((17))	0.950(3)
C((20))-H((18))	0.949(3)
C((21))-H((19))	0.951(3)
C((21))-H((20))	0.950(4)
C((21))-H((21))	0.950(4)
C((22))-H((22))	0.949(3)
C((22))-H((23))	0.950(3)
C((22))-H((24))	0.950(3)
Cl((3))-C((23))	1.709(6)

Table 43 (continued)

Bond angles (^{o})

Atoms	Angles (^{o})
Cl((1))-Ru((1))-Cl((2))	173.17(3)
Cl((1))-Ru((1))-N((1))	86.06(8)
Cl((1))-Ru((1))-N((3))	90.94(7)
Cl((1))-Ru((1))-N((5))	91.07(8)
Cl((1))-Ru((1))-N((7))	91.99(8)
Cl((2))-Ru((1))-N((1))	89.98(8)
Cl((2))-Ru((1))-N((3))	93.54(7)
Cl((2))-Ru((1))-N((5))	84.37(8)
Cl((2))-Ru((1))-N((7))	91.88(8)
N((1))-Ru((1))-N((3))	76.44(9)
N((1))-Ru((1))-N((5))	102.62(9)
N((1))-Ru((1))-N((7))	177.9(1)
N((3))-Ru((1))-N((5))	177.7(1)
N((3))-Ru((1))-N((7))	104.47(9)
N((5))-Ru((1))-N((7))	76.54(9)
C((2))-S((1))-C((3))	89.2(1)
C((13))-S((2))-C((14))	89.1(1)
Ru((1))-N((1))-C((1))	139.7(2)
Ru((1))-N((1))-C((3))	108.8(2)
C((1))-N((1))-C((3))	110.8(2)
N((3))-N((2))-C((3))	109.8(2)
Ru((1))-N((3))-N((2))	118.2(2)
Ru((1))-N((3))-C((4))	129.1(1)
N((2))-N((3))-C((4))	112.7(2)

Table 43 (continued)

Atoms	Angles (^{O})
C((7))-N((4))-C((10))	121.0(2)
C((7))-N((4))-C((11))	121.0(3)
C((10))-N((4))-C((11))	117.8(2)
Ru((1))-N((5))-C((12))	138.3(2)
Ru((1))-N((5))-C((14))	109.4(2)
C((12))-N((5))-C((14))	111.2(2)
N((7))-N((6))-C((14))	109.6(2)
Ru((1))-N((7))-N((6))	118.2(2)
Ru((1))-N((7))-C((15))	129.2(2)
N((6))-N((7))-C((15))	112.6(2)
C((18))-N((8))-C((21))	121.0(3)
C((18))-N((8))-C((22))	121.0(2)
C((21))-N((8))-C((22))	117.6(2)
N((1))-C((1))-C((2))	115.2(3)
N((1))-C((1))-H((1))	122.4(3)
C((2))-C((1))-H((1))	122.4(3)
S((1))-C((2))-C((1))	110.8(2)
S((1))-C((2))-H((2))	124.6(2)
C((1))-C((2))-H((2))	124.7(3)
S((1))-C((3))-N((1))	114.0(2)
S((1))-C((3))-N((2))	122.5(2)
N((1))-C((3))-N((2))	122.9(2)
N((3))-C((4))-C((5))	122.1(2)
N((3))-C((4))-C((9))	119.3(2)
C((5))-C((4))-C((9))	118.6(3)

Table 43 (continued)

Atoms	Angles (^{o})
C((4))-C((5))-C((6))	121.3(2)
C((4))-C((5))-H((3))	119.3(3)
C((6))-C((5))-H((3))	119.4(3)
C((5))-C((6))-C((7))	121.1(2)
C((5))-C((6))-H((4))	119.4(3)
C((7))-C((6))-H((4))	119.4(3)
N((4))-C((7))-C((6))	121.5(2)
N((4))-C((7))-C((8))	121.4(2)
C((6))-C((7))-C((8))	117.1(2)
C((7))-C((8))-C((9))	121.2(2)
C((7))-C((8))-H((5))	119.5(3)
C((9))-C((8))-H((5))	119.4(3)
C((4))-C((9))-C((8))	120.6(2)
C((4))-C((9))-H((6))	119.7(3)
C((8))-C((9))-H((6))	119.6(3)
N((4))-C((10))-H((7))	109.5(3)
N((4))-C((10))-H((8))	109.5(3)
N((4))-C((10))-H((9))	109.5(2)
H((7))-C((10))-H((8))	109.4(3)
H((7))-C((10))-H((9))	109.3(4)
H((8))-C((10))-H((9))	109.6(3)
N((4))-C((11))-H((10))	109.4(3)
N((4))-C((11))-H((11))	109.4(4)
N((4))-C((11))-H((12))	109.6(3)
H((10))-C((11))-H((11))	109.5(3)

Table 43 (continued)

Atoms	Angles (^{o})
H((10))-C((11))-H((12))	109.5(4)
H((11))-C((11))-H((12))	109.5(4)
N((5))-C((12))-C((13))	114.6(2)
N((5))-C((12))-H((13))	122.6(3)
C((13))-C((12))-H((13))	122.8(3)
S((2))-C((13))-C((12))	111.2(2)
S((2))-C((13))-H((14))	124.4(2)
C((12))-C((13))-H((14))	124.4(2)
S((2))-C((14))-N((5))	113.8(2)
S((2))-C((14))-N((6))	122.6(2)
N((5))-C((14))-N((6))	123.2(3)
N((7))-C((15))-C((16))	122.1(2)
N((7))-C((15))-C((20))	119.5(2)
C((16))-C((15))-C((20))	118.5(2)
C((15))-C((16))-C((17))	120.9(2)
C((15))-C((16))-H((15))	119.6(2)
C((17))-C((16))-H((15))	119.6(3)
C((16))-C((17))-C((18))	121.6(2)
C((16))-C((17))-H((16))	119.1(3)
C((18))-C((17))-H((16))	119.3(2)
N((8))-C((18))-C((17))	122.3(2)
N((8))-C((18))-C((19))	120.7(2)
C((17))-C((18))-C((19))	117.0(2)
C((18))-C((19))-C((20))	121.2(2)
C((18))-C((19))-H((17))	119.4(2)

Table 43 (continued)

Atoms	Angles (^{o})
C((20))-C((19))-H((17))	119.4(3)
C((15))-C((20))-C((19))	120.7(2)
C((15))-C((20))-H((18))	119.7(2)
C((19))-C((20))-H((18))	119.6(3)
N((8))-C((21))-H((19))	109.5(3)
N((8))-C((21))-H((20))	109.6(3)
N((8))-C((21))-H((21))	109.4(3)
H((19))-C((21))-H((20))	109.4(3)
H((19))-C((21))-H((21))	109.5(4)
H((20))-C((21))-H((21))	109.5(4)
N((8))-C((22))-H((22))	109.5(3)
N((8))-C((22))-H((23))	109.5(3)
N((8))-C((22))-H((24))	109.5(3)
H((22))-C((22))-H((23))	109.5(4)
H((22))-C((22))-H((24))	109.5(3)
H((23))-C((22))-H((24))	109.4(3)

Table 44 The bond distances (Å) and bond angles (^{o})

of *cis*-Ru(dmsazpy)$_2$Cl$_2$ complex

Bond distances

Atoms	Distance (Å)
Ru((1))-Cl((1))	2.4166(7)
Ru((1))-Cl((2))	2.4025(8)
Ru((1))-N((1))	2.031(3)
Ru((1))-N((3))	2.042(2)
Ru((1))-N((5))	2.041(3)
Ru((1))-N((7))	2.012(2)
S((1))-C((2))	1.713(3)
S((1))-C((3))	1.722(3)
S((2))-C((13))	1.719(3)
S((2))-C((14))	1.725(3)
N((1))-C((1))	1.370(3)
N((1))-C((3))	1.323(4)
N((2))-N((3))	1.314(4)
N((2))-C((3))	1.359(3)
N((3))-C((4))	1.409(3)
N((4))-C((7))	1.362(3)
N((4))-C((10))	1.452(4)
N((4))-C((11))	1.452(4)
N((5))-C((12))	1.371(3)
N((5))-C((14))	1.327(4)

Table 44 (continued)

Atoms	Distance (Å)
N((6))-N((7))	1.324(4)
N((6))-C((14))	1.364(3)
N((7))-C((15))	1.401(3)
N((8))-C((18))	1.367(3)
N((8))-C((21))	1.451(4)
N((8))-C((22))	1.447(4)
C((1))-C((2))	1.353(4)
C((1))-H((1))	0.951(3)
C((2))-H((2))	0.951(3)
C((4))-C((5))	1.410(5)
C((4))-C((9))	1.388(4)
C((5))-C((6))	1.366(4)
C((5))-H((3))	0.951(3)
C((6))-C((7))	1.416(4)
C((6))-H((4))	0.950(3)
C((7))-C((8))	1.406(5)
C((8))-C((9))	1.371(4)
C((8))-H((5))	0.951(3)
C((9))-H((6))	0.950(3)
C((10))-H((7))	0.950(2)
C((10))-H((8))	0.951(3)
C((10))-H((9))	0.950(3)
C((11))-H((10))	0.949(3)
C((11))-H((11))	0.950(3)
C((11))-H((12))	0.950(3)

Table 44 (continued)

Atoms	Distance (Å)
C((12))-C((13))	1.351(4)
C((12))-H((13))	0.950(3)
C((13))-H((14))	0.950(2)
C((15))-C((16))	1.405(4)
C((16))-C((17))	1.371(3)
C((16))-H((15))	0.950(3)
C((17))-C((18))	1.415(4)
C((17))-H((16))	0.951(3)
C((18))-C((19))	1.408(4)
C((19))-C((20))	1.376(3)
C((19))-H((17))	0.950(3)
C((20))-H((18))	0.950(3)
C((21))-H((19))	0.950(3)
C((21))-H((20))	0.950(4)
C((21))-H((21))	0.950(3)
C((22))-H((22))	0.950(3)
C((22))-H((23))	0.950(3)
C((22))-H((24))	0.951(3)

Table 44 (continued)

Bond angles (^{o})

Atoms	Angle (^{o})
Cl((1))-Ru((1))-Cl((2))	92.71(2)
Cl((1))-Ru((1))-N((1))	85.24(6)
Cl((1))-Ru((1))-N((3))	86.92(6)
Cl((1))-Ru((1))-N((5))	91.02(6)
Cl((1))-Ru((1))-N((7))	168.17(7)
Cl((2))-Ru((1))-N((1))	91.09(7)
Cl((2))-Ru((1))-N((3))	167.94(7)
Cl((2))-Ru((1))-N((5))	83.75(6)
Cl((2))-Ru((1))-N((7))	88.51(7)
N((1))-Ru((1))-N((3))	76.86(9)
N((1))-Ru((1))-N((5))	173.49(8)
N((1))-Ru((1))-N((7))	106.52(9)
N((3))-Ru((1))-N((5))	108.31(9)
N((3))-Ru((1))-N((7))	94.33(9)
N((5))-Ru((1))-N((7))	77.41(9)
C((2))-S((1))-C((3))	89.1(1)
C((13))-S((2))-C((14))	88.7(1)
Ru((1))-N((1))-C((1))	135.8(2)
Ru((1))-N((1))-C((3))	111.5(2)
C((1))-N((1))-C((3))	111.6(3)
N((3))-N((2))-C((3))	111.3(2)
Ru((1))-N((3))-N((2))	117.1(2)
Ru((1))-N((3))-C((4))	130.4(2)
N((2))-N((3))-C((4))	112.5(2)

Table 44 (continued)

Atoms	Angle (^{o})
C((7))-N((4))-C((10))	120.1(3)
C((7))-N((4))-C((11))	121.0(3)
C((10))-N((4))-C((11))	118.7(2)
Ru((1))-N((5))-C((12))	135.8(2)
Ru((1))-N((5))-C((14))	110.8(1)
C((12))-N((5))-C((14))	110.9(3)
N((7))-N((6))-C((14))	110.7(2)
Ru((1))-N((7))-N((6))	118.1(1)
Ru((1))-N((7))-C((15))	130.1(2)
N((6))-N((7))-C((15))	111.7(2)
C((18))-N((8))-C((21))	120.0(2)
C((18))-N((8))-C((22))	120.1(2)
C((21))-N((8))-C((22))	119.7(2)
N((1))-C((1))-C((2))	114.1(3)
N((1))-C((1))-H((1))	122.9(3)
C((2))-C((1))-H((1))	123.0(3)
S((1))-C((2))-C((1))	111.4(2)
S((1))-C((2))-H((2))	124.3(3)
C((1))-C((2))-H((2))	124.3(3)
S((1))-C((3))-N((1))	113.8(2)
S((1))-C((3))-N((2))	124.6(3)
N((1))-C((3))-N((2))	121.5(3)
N((3))-C((4))-C((5))	121.9(2)
N((3))-C((4))-C((9))	120.9(3)
C((5))-C((4))-C((9))	117.2(3)

Table 44 (continued)

Atoms	Angle (^{o})
C((4))-C((5))-C((6))	121.6(3)
C((4))-C((5))-H((3))	119.2(3)
C((6))-C((5))-H((3))	119.2(3)
C((5))-C((6))-C((7))	121.0(3)
C((5))-C((6))-H((4))	119.4(3)
C((7))-C((6))-H((4))	119.6(3)
N((4))-C((7))-C((6))	121.3(3)
N((4))-C((7))-C((8))	121.7(3)
C((6))-C((7))-C((8))	117.0(2)
C((7))-C((8))-C((9))	121.2(3)
C((7))-C((8))-H((5))	119.4(3)
C((9))-C((8))-H((5))	119.4(3)
C((4))-C((9))-C((8))	122.0(3)
C((4))-C((9))-H((6))	119.1(3)
C((8))-C((9))-H((6))	119.0(3)
N((4))-C((10))-H((7))	109.5(3)
N((4))-C((10))-H((8))	109.5(3)
N((4))-C((10))-H((9))	109.5(3)
H((7))-C((10))-H((8))	109.4(3)
H((7))-C((10))-H((9))	109.5(3)
H((8))-C((10))-H((9))	109.4(3)
N((4))-C((11))-H((10))	109.5(2)
N((4))-C((11))-H((11))	109.4(3)
N((4))-C((11))-H((12))	109.4(3)
H((10))-C((11))-H((11))	109.5(3)

Table 44 (continued)

Atoms	Angle (°)
H((10))-C((11))-H((12))	109.5(3)
H((11))-C((11))-H((12))	109.5(2)
N((5))-C((12))-C((13))	114.6(3)
N((5))-C((12))-H((13))	122.7(3)
C((13))-C((12))-H((13))	122.7(2)
S((2))-C((13))-C((12))	111.4(2)
S((2))-C((13))-H((14))	124.2(3)
C((12))-C((13))-H((14))	124.3(3)
S((2))-C((14))-N((5))	114.3(2)
S((2))-C((14))-N((6))	124.0(2)
N((5))-C((14))-N((6))	121.6(3)
N((7))-C((15))-C((16))	121.9(2)
N((7))-C((15))-C((20))	120.7(3)
C((16))-C((15))-C((20))	117.4(2)
C((15))-C((16))-C((17))	121.7(2)
C((15))-C((16))-H((15))	119.1(2)
C((17))-C((16))-H((15))	119.2(3)
C((16))-C((17))-C((18))	121.0(3)
C((16))-C((17))-H((16))	119.5(2)
C((18))-C((17))-H((16))	119.5(2)
N((8))-C((18))-C((17))	121.7(3)
N((8))-C((18))-C((19))	121.2(2)
C((17))-C((18))-C((19))	117.1(2)
C((18))-C((19))-C((20))	121.4(2)
C((18))-C((19))-H((17))	119.3(2)

Table 44 (continued)

Atoms	Angle (°)
C((20))-C((19))-H((17))	119.4(3)
C((15))-C((20))-C((19))	121.5(3)
C((15))-C((20))-H((18))	119.3(2)
C((19))-C((20))-H((18))	119.2(2)
N((8))-C((21))-H((19))	109.5(3)
N((8))-C((21))-H((20))	109.4(3)
N((8))-C((21))-H((21))	109.4(3)
H((19))-C((21))-H((20))	109.5(3)
H((19))-C((21))-H((21))	109.5(3)
H((20))-C((21))-H((21))	109.5(4)
N((8))-C((22))-H((22))	109.5(3)
N((8))-C((22))-H((23))	109.5(3)
N((8))-C((22))-H((24))	109.5(2)
H((22))-C((22))-H((23))	109.5(3)
H((22))-C((22))-H((24))	109.5(3)
H((23))-C((22))-H((24))	109.5(3)

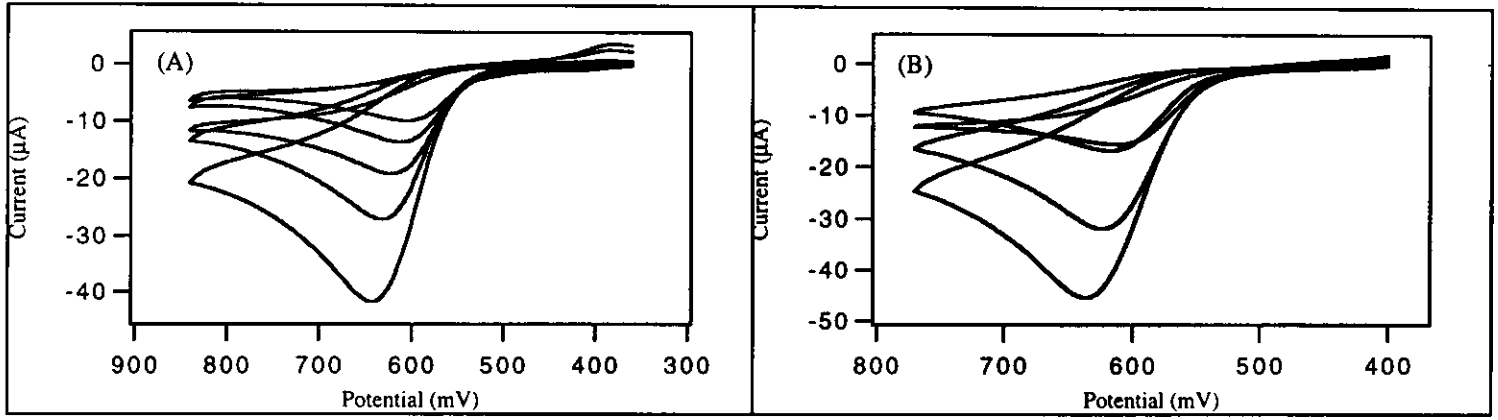


Figure 37 Cyclic voltammograms of ligand group I (A) dmsazpy, (B) desazpy scanned with various scan rates (50-1000 mV/s)

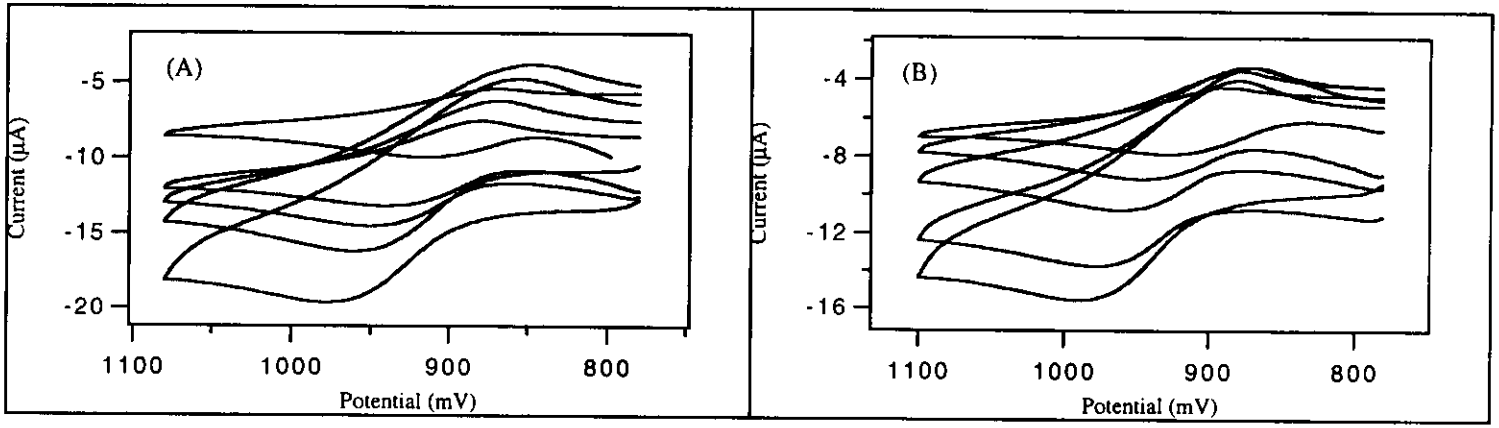


Figure 38 Cyclic voltammograms of ligand group II (A) dmsazpy, (B) desazpy scanned with various scan rates (50-1000 mV/s)

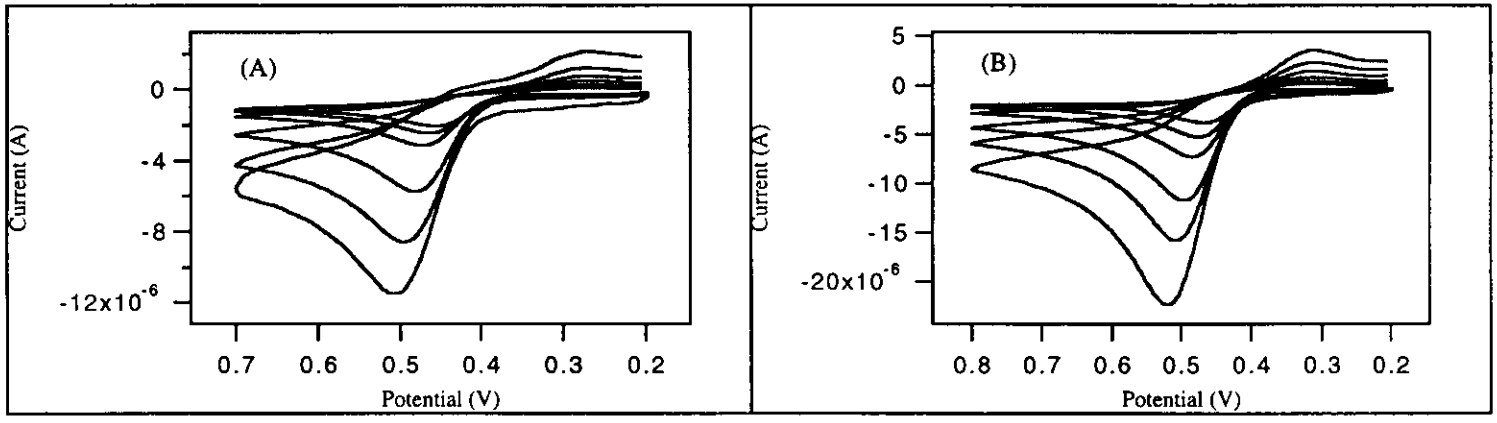
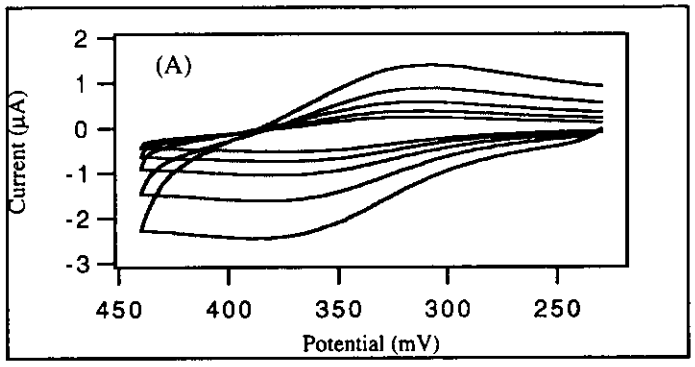
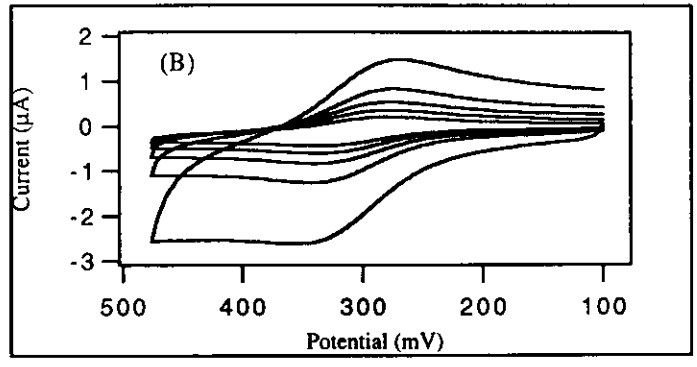


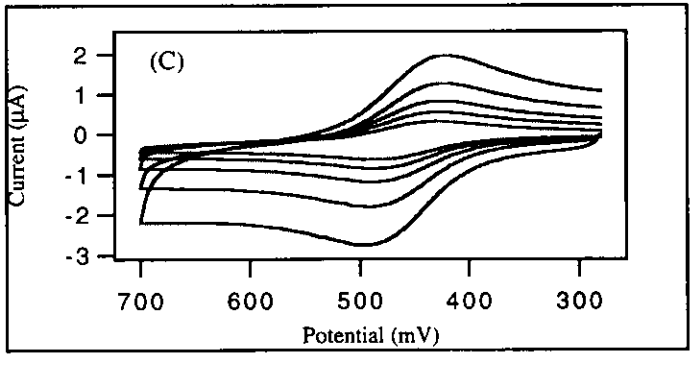
Figure 39 Cyclic voltammograms of (A) *N,N*-dimethylaniline and (B) *N,N*-diethylaniline scanned with various scan rates (50-2000 mV/s)



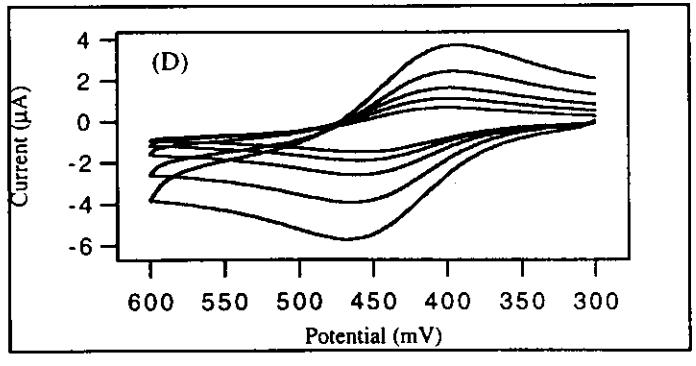
trans-Ru(dmsazpy)$_2$Cl$_2$



trans-Ru(desazpy)$_2$Cl$_2$

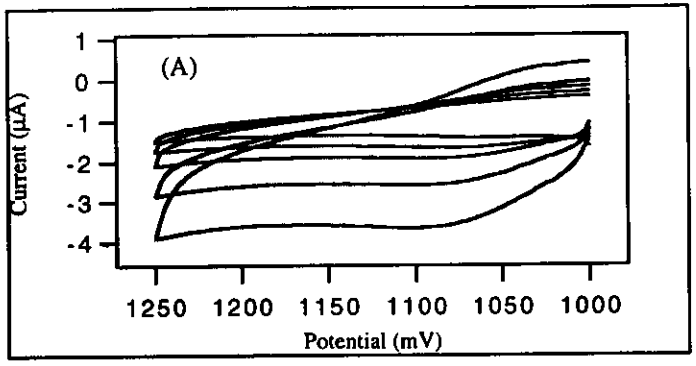


cis-Ru(dmsazpy)$_2$Cl$_2$

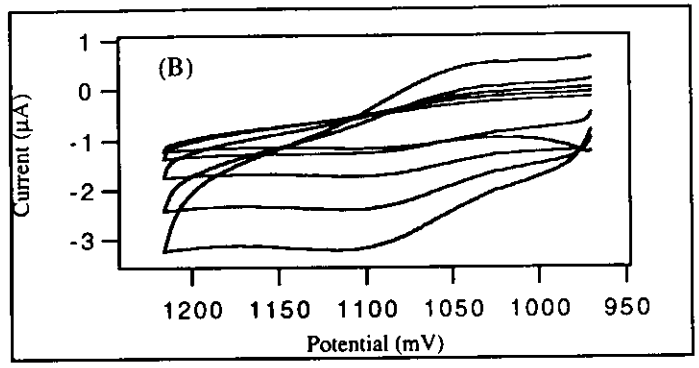


cis-Ru(desazpy)$_2$Cl$_2$

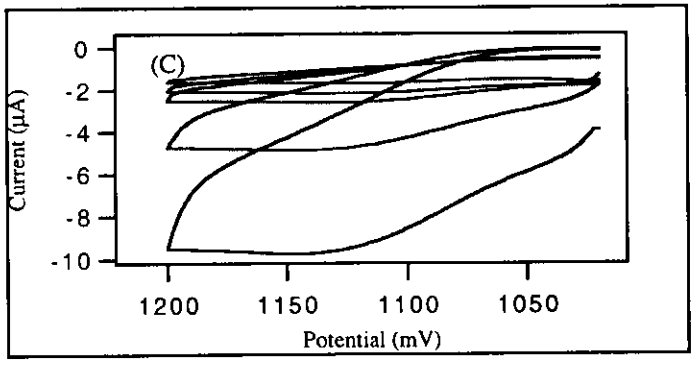
Figure 40 Cyclic voltammograms of couple I in oxidation range of A-D *trans*- and *cis*-Ru(L)$_2$Cl$_2$ (L= dmsazpy and desazpy) by varying scan rates (50-2000 mV)



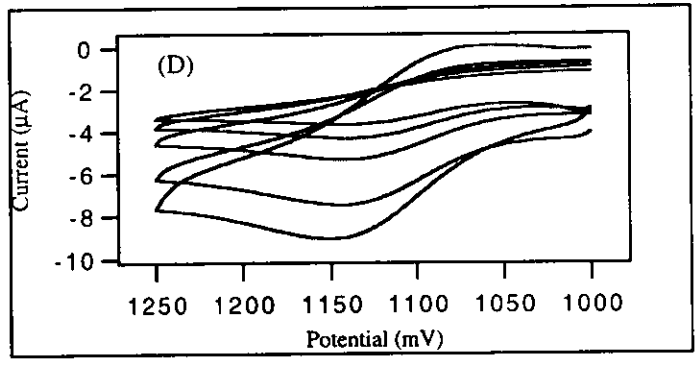
trans-Ru(dmsazpy)$_2$Cl$_2$



trans-Ru(desazpy)$_2$Cl$_2$



cis-Ru(dmsazpy)$_2$Cl$_2$



cis-Ru(desazpy)$_2$Cl$_2$

Figure 41. Cyclic voltammograms of couple II in oxidation range of A-D *trans*- and *cis*-Ru(L)$_2$Cl$_2$ (L = dmsazpy and desazpy) by varying scan rates 50-2000 mV/s)

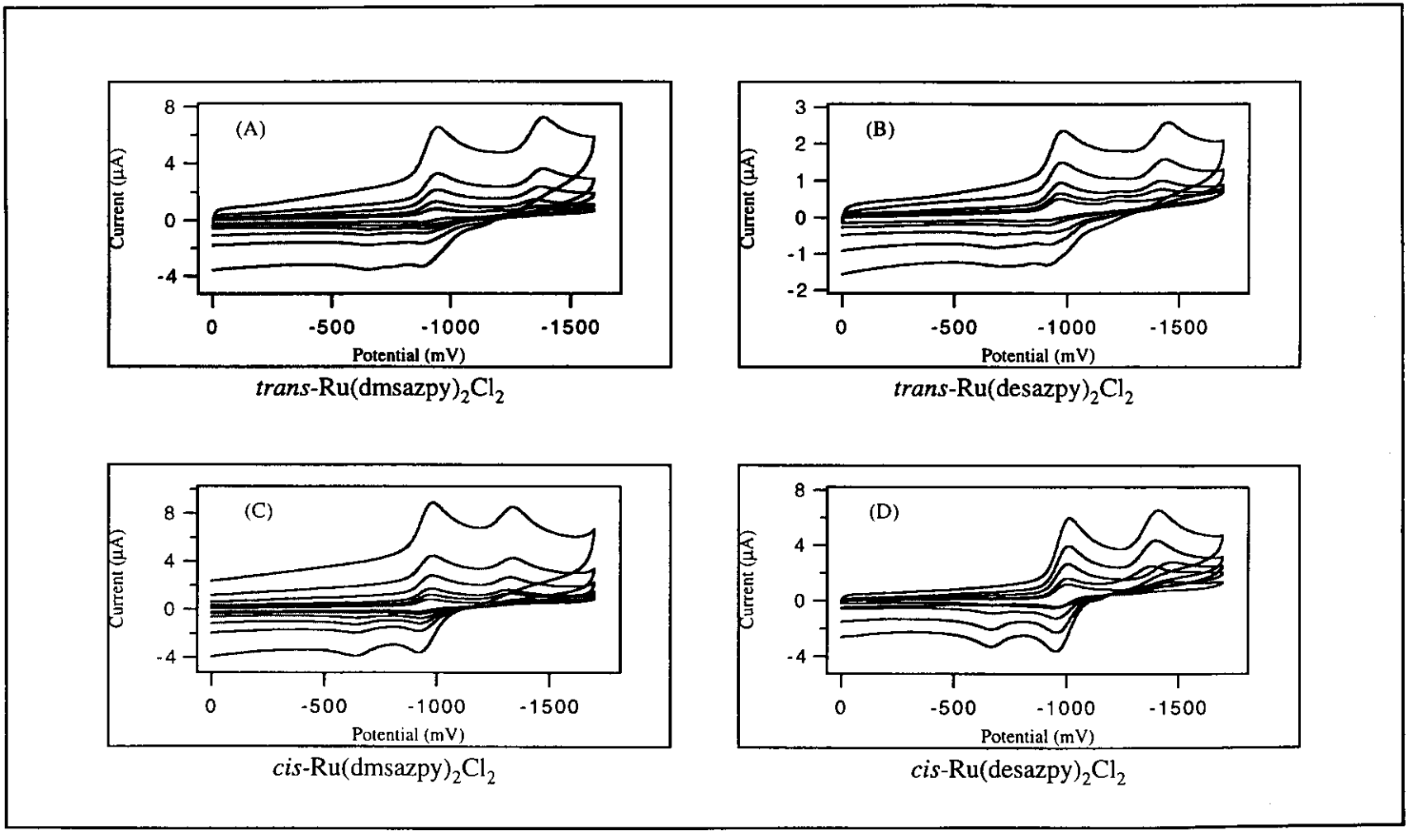


Figure 42 Cyclic voltammograms of reduction range of A-D *trans-* and *cis*-$Ru(L)_2Cl_2$ (L = dmsazpy and desazpy) by varying scan rates (50-2000 mV/s)