

Syntheses of Materials. 1,2-bis(diphenylarseno)ethylene (**23**) and cis-1,2-bis(diphenylphosphino)ethane (**24**), were purchased from either Aldrich or Alfa and recrystallized 3× from butanol before use. 4,4'-diphenyl-2,2'-bipyridine (**21**) and Bathophenanthroline (**22**) were purchased from GFS Chemicals. **21** was ~ 50% pure and was purified by repeated washings and recrystallization from DMF to yield 2.3 g out of 15 g purchased. The following chemicals were used as received. 2,2'-Bipyridine (**26**) was purchased from either Alfa or Aldrich. Hydrogen peroxide 35% in water, acetyl bromide, tert-butyl lithium in hexane and 1.6 M butyl lithium in hexane were purchased from Aldrich. Potassium hexachloroosmate, fuming sulfuric acid, 30% SO₃, and fuming 90% nitric acid were purchased from Alfa.

cis-1,2-vinylenebis(diphenylarsine) (**25**) (Fig. 3): The procedure used was a modification of a previous method resulting in an improved yield of product.³² Diphenylarsine (Organometalics, 25.00 g, 108.6 mmol) was used as received and added to 400 mL of freshly dried (sodium/benzophenone) THF. The solution was stirred under nitrogen and cooled to -78 °C using an acetone/dry ice bath. To this solution was added n-butyl lithium (1.6 M in hexane, 1.05 eq, 114.1 mmol). The solution was allowed to stir for 1 h. The acetone bath was then removed and *cis*-dichloroethylene (TCI-America, 10.66 g, 110.0 mmol) was added. The solution was allowed to slowly warm to 18.5 °C and react overnight. Water was added and the THF was removed by rotary evaporation under vacuum at 40 °C. The water was removed by filtration and the solid material was washed with large amounts of de-ionized water. The sample was dried under vacuum and then recrystallized three times from butanol. Yield: 23.97 g (91%). ¹H NMR (DMSO): 7.63 (s,

2H), 7.35 (20H). Elemental anal. calc.: C, 64.48%; H, 4.58%. found: C, 64.10%; H, 4.28%.

4,4'-dibromo-2, 2'-bipyridine (Fig. 4): The procedure used was an adaptation and combination of the methods reported by Haginiwa³³ and Chase³⁴.

4,4'-di(biphenyl)-2, 2'-bipyridine (**15**): 4,4'-dibromo-2,2'-bipyridine (2.000 g, 6.37 mmol), and biphenyl-4-boronic acid neopentyl glycol ester (4.238 g, 15.92 mmol) were dissolved into 80 mL DMF (Aldrich). The solution was stirred for 1 h under nitrogen and tetrakis(triphenylphosphine) Pd(0) (0.191 mmol) was added. The solution was heated to 60 °C and 10 mL deoxygenated saturated potassium carbonate aqueous solution was added drop wise over a period of 5 min. The solution was then warmed to 85-95 °C. The coupling was allowed to proceed under these conditions for 24 h. The solution was warmed to 115 °C and the reaction was allowed to proceed for an additional 5 h. The solution was cooled to room temperature and poured into 500 mL of 0.25 M KOH solution. The precipitate was collected by vacuum filtration and washed with water, allowed to dry, and then washed with methylene chloride. The methylene chloride layer was a dark brown while the precipitate was a light gray which gave a mass of 461. The gray powder was suspended into 250 mL of xylene (Fisher Scientific) and refluxed for 10 minutes and filtered. Small colorless crystals (150 mg) of 4,4'-bis(*p*-biphenyl)-2,2'-bipyridine formed in the mother liquid. This process was repeated 10 times to yield 1.5 g of material (51%, remainder is the mono-substituted material, which was soluble in organic solvents such as methylene chloride). 4,4'-bis(*p*-biphenyl)-2,2'-bipyridine was very insoluble in organic solvents at room temperature. ¹H NMR (DCCl₃) as a Ru(II)(Heptafluorobutyrate)₂, (Ru(II) (HFB)₂)complex: 9.08 (d, 6H), 7.97 (m, 18H), 7.80

(m, 18H), 7.61 (m, 12H), 7.45 (m, 18 H). Mass spectrometry (m/z): 461.6. Elemental analysis calculated: C, 88.67; H, 5.25; N, 6.08, found C, 89.06; H, 5.32; N, 6.21.

4,4'-bis(diphenylether)-2,2'-bipyridine(**16**) was made following the same procedure as **15**: Yield 0.95 g (30.4%). ¹H NMR (DMSO): 8.750 (d, 2H), 8.631 (m, 4H), 7.904 (m, 4H), 7.800 (m, 4H), 7.459 (t, 2H), 7.147 (m, 8H). Mass spectroscopy (m/z): 493.2. Elemental analysis calculated: C, 82.91; H, 4.91; N, 5.69, found: C, 83.09; H, 4.99; N, 5.77.

4,7-Bis-(p-methoxyphenyl)-1,10-phenanthroline (**17**) and *4,7-Bis-(p-bromophenyl)-1,10-phenanthroline*(**18**): These compounds have been reported previously.¹⁷ Our results essentially matched theirs. They report **18** as a tan solid, we recrystallized 3X from DMF to produce a colorless crystalline solid.

The following phenanthroline derivatives were synthesized from **18**

4,7-Bis-(4'-phenoxy-biphenyl-4-yl)-1,10-phenanthroline (**19**) was made following the same procedure as **15**. Elemental analysis: calculated: C, 86.20; H, 4.82; N, 4.19; found: C, 86.32; H, 4.98; N, 4.28. ¹H NMR (DMSO): 9.20 (d 2H), 8.88-7.65 (m 18H), 7.45 (t 4 H), 7.25-7.06 (m 8H). Recrystallized from benzene to give a colorless crystalline solid.

4,7-Bis-(4-naphthalen-2-yl-phenyl)-1,10-phenanthroline (**20**) was made following the same procedure as **15**. Elemental analysis, calculated: C, 90.38; H, 4.83; N, 4.79; found: C, 90.45; H, 4.86; N, 4.81. ¹H NMR (DCCl₂): 9.29 (d 2H), 8.14 (s 2H), 8.03-7.75 (m 14 H), 7.72-7.63 (m 6H), 7.57-7.46 (m 4H). Recrystallized from DMF to give colorless crystalline solid.

Os(II) bis(4,4'-diphenyl-2,2'-bipyridine) Dichloride (Fig. 5): The procedure used was a modification of a previous report.¹⁹ Potassium hexachloroosmate, (1 g, 2.078 mmol), and

21, (1.40 g, 4.54 mmol), were suspended in DMF (25 mL), purged with nitrogen for 1 h, and refluxed under a nitrogen atmosphere for 3 h. The solution was cooled to 18.5 °C and filtered. Much of the product, a mixture of $[\text{Os}(\mathbf{21})_2\text{Cl}_2]$ and $[\text{Os}(\mathbf{21})_2\text{Cl}_2]^+$ precipitated out as it was only partially soluble in DMF (0.8 g of Os product per 60 mL DMF). Extractions were filtered through a fine frit and performed repeatedly until the filtrate, KCl, was only a light brown color.

2 g of sodium dithionite (Alfa) was added and dissolved in 400 mL cooled de-ionized water (0-3 °C). The DMF solution of the Os compound was added drop wise to the sodium dithionite solution. Instantly a dark purple precipitate of Os(II) bis(4,4'-diphenyl-2,2'-bipyridine) dichloride formed and was collected using vacuum filtration and washed repeatedly with water. This was done repeatedly with each extraction. Yield: 92%. The bathophenanthroline complex had increased solubility and allowed the use of a silica flash column with methylene chloride mobile phase for purification.

[Os(II) bis(4,4'-diphenyl-2,2'-bipyridine) 1,2-bis(diphenylarseno)ethane]²⁺ (**1**) (Fig. 6) : Osmium bis(**21**) dichloride (0.5 g, 0.570 mmol) and **23** (0.291 g, 0.600 mmol) were added to 10 mL of a mixture of 2-(2-ethoxyethoxy)ethanol and glycerol (75:25 by volume). The solution was purged with nitrogen for 1 h and then the solution was refluxed for 1.5 h. After cooling, the solution was added to water and the appropriate counter ion, as the sodium salt of HFB, triflate (Tf), tosylate (Ts), or chloride was added. The precipitate was collected by filtration, washed with water and dried under vacuum at 40 °C. The dried precipitate was dissolved in methylene chloride (20 mL per g of complex) and precipitated with hexane. This was repeated three times to get a bright red product. Yield: 90%. Mass spectrometry (m/z): 647.1. Isotope Pattern: 645.1, 645.6,

646.1, 646.6, 647.1, 647.6, and 648.1. Fragmentation peak at $m/2z = 478.1$ ($m/2z - 308 - 28$), which corresponds to the fragmentation of a bpy ligand and the ethane bridge on the arsine. Elemental analysis, calculated: (HFB counter ions). C, 54.49; H, 3.28; N, 3.26, found C, 54.65; H, 3.36; N, 3.30.

$[Os(II) (4,4'\text{-diphenyl-2,2'\text{-bipyridine}})_2 \text{ cis-1,2-bis(diphenylphosphino)ethylene}]^{2+}$ (HFB)₂ (**2**) (Fig 6): was made following the same procedure as **1** yielding an orange product. Yield: 85%. Mass spectrometry ($m/2z$): 602.7. Isotope pattern $m/2z$: 599.7, 600.2, 600.7, 601.2, 601.7, 602.2, 602.7, 603.2. Elemental analysis, calculated: C, 57.49%; H, 3.34%; N, 3.44%. Found: C, 58.00; H, 3.41; N, 3.33.

$[Os(II) (4,4'\text{-diphenyl-2,2'\text{-bipyridine}})_2 \text{ cis-1,2-vinylenebis(diphenylarsine)}]^{2+}$ (Tf)₂ (**3**) (Fig 6): was made following the same procedure as **1** yielding a red product. Yield: 94%. Mass spectrometry ($m/2z$): 646.1. Isotope pattern ($m/2z$): 643.6, 644.1, 644.6, 645.1, 645.6, 646.1, 646.6, 647.1. Elemental analysis, calculated: C, 54.41%; H, 3.42%; N, 3.52%. Found C, 54.51; H, 3.48; N, 3.36.

$[Os(II) (4,4'\text{-bis(p-diphenylether)-2,2'\text{-bipyridine}})_2 \text{ cis-1,2-vinylenebis(diphenylarsine)}]^{2+}$ (Tf)₂ (**4**) (Fig 6): was made following the same procedure as **1** yielding a red product. Yield: 90% Mass spectrometry ($m/2z$): 830.2. Isotope Pattern for 830.2 peak: 828.2, 828.7, 829.2 829.7, 830.2, 830.7, 831.2. Elemental analysis, calculated: C, 58.89; H, 3.60; N, 2.86, found C, 59.01; H, 3.59; N, 2.88.

$[Os(II) (4,4'\text{-bis(p-biphenyl)-2,2'\text{-bipyridine}})_2 \text{ 1,2-bis(diphenylarseno)ethane}]^{2+}$ (HFB)₂ (**5**) (Fig 6): was made following the same procedure as **1** yielding a brick red product. Yield: 90% Mass spectrometry ($m/2z$): 646.1. Isotope pattern ($m/2z$): 643.6, 644.1,

644.6, 645.1, 645.6, 646.1, 646.6, 647.1. Elemental analysis, calculated: C, 60.54; H, 3.59; N, 2.77, found C; 59.92; H, 3.34; N, 2.70.

$[Os(II) (4,4'\text{-bis}(p\text{-biphenyl})\text{-}2,2'\text{-bipyridine})_2 \text{ cis-}1,2\text{-vinylenebis}(\text{diphenylarsine})]^{2+} (\text{Tf})_2$ (**6**) (Fig 6): was made following the same procedure as **1** a red product. Yield: 89% Mass spectrometry (m/2z): 798.2. Isotope pattern (m/2z): 795.7, 796.2, 796.7, 797.2, 797.7, 798.2, 798.7, and 799.2. Elemental analysis, calculated: C, 60.88; H, 3.73; N, 2.96, found: C, 61.01, H, 4.02; N, 2.85

$[Os(II) (\text{bathophenanthroline})_2 \text{ cis-}1,2\text{-bis}(\text{diphenylphosphino})\text{ethylene}]^{2+} (\text{Tf})_2$ (**7**) (Fig. 6): was made following the same procedure as **1** yielding a yellow-orange product. Yield: 92%. Mass spectrometry (m/2z): 626.2. Isotope pattern (m/2z): 623.7, 624.2, 624.7, 625.2, 625.7, 626.2, 626.7, 627.2, and 627.7, no fragmentation. Elemental analysis, calculated: C, 58.91%; H, 3.51%; N, 3.62%. Found C, 58.78; H, 3.52; N, 3.66.

$[Os(II) (\text{bathophenanthroline})_2 \text{ cis-}1,2\text{-vinylenebis}(\text{diphenylarsine})]^{2+} (\text{Ts})_2$ (**8**) (Fig 6): was made following the same procedure as **1** yielding a red-orange product. Yield: 90%. Mass spectrometry (m/2z): 670.1. Isotope pattern (m/2z): 667.6, 668.1, 668.6, 669.1, 669.6, 670.1, 670.6, 671.1, no fragmentation. Elemental analysis: calculated: C, 55.75%; H, 3.32%; N, 3.42%. Found C, 56.05; H, 3.34; N, 3.44.

$[Osmium(II) (4,7\text{-Bis-}(p\text{-methoxyphenyl})\text{-}1,10\text{-phenanthroline})_2 1,2\text{-bis}(\text{diphenylarseno})\text{ethane}]^{2+} (\text{Ts})_2$ (**9**) (Fig 6): was made following the same procedure as **1** yielding a brick red product. Yield: 89%. Mass spectrometry m/2z = 731.2. Isotope pattern: 728.7, 729.2, 729.7, 730.2, 730.7, 731.2, 731.7, 732.2, and 732.7. Fragment at m/2z – 7.5 for loss of a methyl group. Elemental analysis calc. C, 61.26; H, 4.36; N, 3.11; found C, 61.36; H, 4.41; N, 3.05.

[Osmium(II) (4,7-Bis-(*p*-methoxyphenyl)-1,10-phenanthroline)₂ cis-1,2-bis(diphenylphosphino)ethylene]²⁺(Ts)₂ (**10**) (Fig 6): was made following the same procedure as **1** yielding a yellow-orange product. Yield: 95%. Mass Spectrometry m/2z = 686.2. Isotope pattern: 683.7, 684.2, 684.7, 685.2, 685.7, 686.2, 686.2, 687.2, and 687.7. Fragment at m/2z – 7.5 for the fragmentation of a methyl group. Elemental analysis calc. C, 64.47; H, 4.47; N, 3.27; found C, 64.57; H, 4.65; N, 3.25.

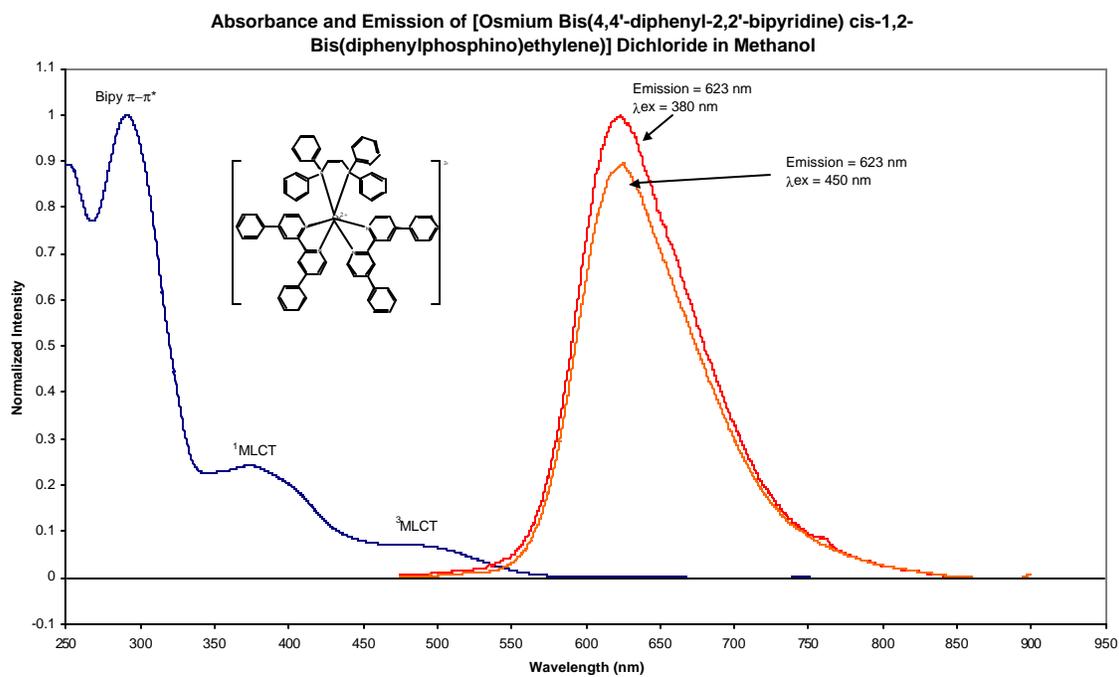
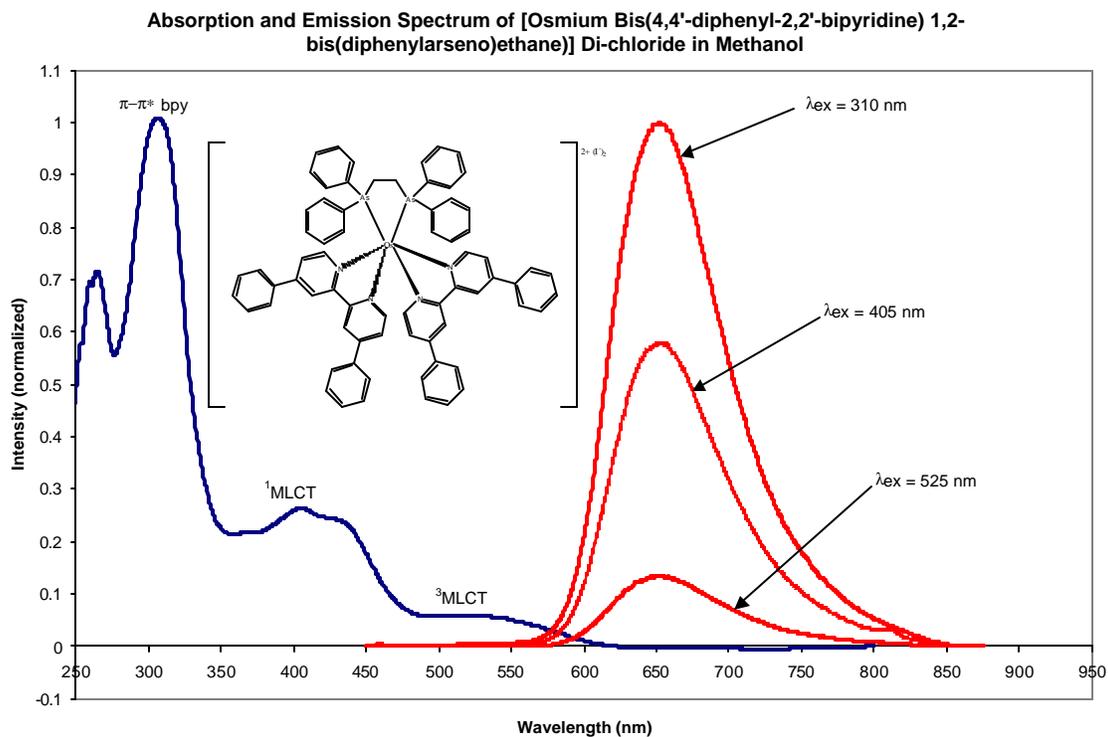
[Osmium(II) (4,7-Bis-(*p*-methoxyphenyl)-1,10-phenanthroline)₂ cis-1,2-vinylenebis(diphenylarsine)]²⁺ (Ts)₂(**11**) (Fig 6): was made following the same procedure as **1** yielding a red product. Yield: 92% Mass Spectrometry m/2z: 730.1. Isotope Pattern: 727.6, 728.1, 728.6, 729.1, 729.6, 730.1, 730.6, 731.1, and 731.6. Fragment appears at m/2z – 7.5 for loss of a methyl group. Elemental analysis calc.: C, 61.33; H, 4.25; N, 3.11; found: C, 61.64; H, 4.33, N, 3.12.

[Osmium(II) (4,7-Bis-(*p*-bromophenyl)-1,10-phenanthroline)₂ cis-1,2-vinylenebis(diphenylarsine)]²⁺(Ts)₂ (**12**) (Fig 6): was made following the same procedure as **1** yielding a dark red product. Yield: 89% Mass spectrometry m/2z = 827.9, isotope pattern 824.4, 824.9, 825.4, 825.9, 826.4, 826.9, 827.4, 827.9, 828.4, 828.9, 829.4, 829.9. Elemental analysis: calculated: C, 51.76; H, 3.31; N, 2.87, Found: C, 52.01; H, 3.38; N, 2.88.

[Osmium(II) (4,7-Bis-(4'-phenoxy-biphenyl-4-yl)-1,10-phenanthroline)₂ cis-1,2-vinylenebis(diphenylarsine)]²⁺(Ts)₂ (**13**) (Fig 6): was made following the same procedure as **1** yielding a red product. Yield: 93% Mass Spectrometry m/2z =1006.1, isotope pattern 1004.2, 1004.7, 1005.2, 1005.7, 1006.2, 1006.7, 1007.2, 1007.7. Elemental analysis, calculated: C, 69.38; H, 4.28; N, 2.38; Found: C, 69.07; H, 4.36; N, 2.44.

[Osmium(II) (4,7-Bis-(4-naphthalen-2-yl-phenyl)-1,10-phenanthroline)₂ cis-1,2-vinylenebis(diphenylarsine)]²⁺(Ts)₂ (**14**) (Fig 6): was made following the same procedure as **1** yielding a red product. Yield: 88% Mass Spectrometry m/z = 922.7, isotope

pattern 920.2, 920.7, 921.2, 921.7, 922.2, 922.7, 923.2, 923.7. Elemental analysis, calculated: C, 70.25; H, 4.33; N, 2.56, Found: C, 70.56; H, 4.32; N, 2.48.



Absorption and Emission of [Osmium (4,4'-di(diphenylether)-2,2'-bipyridine)₂ cis-1,2-vinylenebis(diphenylarsine)] Tosylate₂ in Methylene Chloride

