

Stereospecific, Unsymmetrical Photosubstitution in a Ligand-Bridged Dimer

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Oligomeric metal complexes are of fundamental interest in studies of electron and energy transfer, as well as of potential use as components in nanodevices.¹ We have concentrated our efforts on preparing linear oligomers with well-defined geometries that exhibit anisotropic properties. For example, in the recent syntheses of $[\text{Re}(\text{CO})_3(\text{bpy})(\mu\text{-dppene})\text{Re}(\text{CO})_2(\text{bpy})(\mu_2\text{-dppene})\text{Re}(\text{CO})_3(\text{bpy})]^{3+}$ and $[\text{Re}(\text{CO})_3(\text{bpy})(\mu\text{-dppene})\text{Re}(\text{CO})_2(\text{bpy})(\text{dppene})]^{2+}$ (where bpy is 2,2'-bipyridine and dppene is (*E*)-1,2-bis(diphenylphosphino)ethylene), *cis,trans*- $[\text{Re}(\text{bpy})(\text{CO})_2(\text{dppene})_2]^{2+}$ is formed thermally by utilizing trans-disubstitution of *fac*- $\text{Re}(\text{bpy})(\text{CO})_3\text{OTf}$ with dppene followed by symmetrical or unsymmetrical capping with *fac*- $\text{Re}(\text{CO})_3(\text{bpy})^+$ units, respectively.² These examples are the first that couple trans-substitution chemistry with bridging ligands for the preparation of highly luminescent linear oligomers, although other trans-substitution strategies have been exploited where chromophoric monomer units are potential synthons for extended structures.^{3–7} Here, we present a preparative route to linear oligomeric Re(I) polypyridine complexes as a result of a *single, stereospecific* photosubstitution of a CO ligand trans to a bridging ligand in a symmetric dimeric precursor.

During luminescence studies of the dimer $[\text{Re}(\text{CO})_3(\text{bpy})(\mu\text{-dppene})\text{Re}(\text{CO})_3(\text{bpy})]^{2+}$ (**1**) we observed that an accurate emission yield ($\Phi_{\text{em}} = 0.35 \pm 0.06$ in CH_2Cl_2 at 20 °C) could be calculated only by taking into account the extreme photosensitivity of the complex. Subsequent steady state photolysis in CH_3CN yielded a single product, $[\text{Re}(\text{CO})_3(\text{bpy})(\mu_2\text{-dppene})\text{Re}(\text{CO})_2(\text{bpy})\text{CH}_3\text{CN}]^{2+}$ (**2**), consistent with photolytic substitution of a single carbonyl (see Scheme 1).⁸

Characterization of complex **2** was achieved by a combination of elemental analysis, ³¹P NMR and IR spectroscopies, and electrospray ionization mass spectrometry (ESI-MS) (see Table 1). The quantum yield of photosubstitution for the reaction, Φ_{CO} , was determined to be 0.27 (N_2 , CH_3CN solution at 20 °C).⁹ Pre-

parative photolysis of **1** also was used to introduce anionic ligands into the coordination sphere (e.g., Cl^- , OTf^- ; complexes **3** and **4**, respectively) as shown in Scheme 1.¹⁰ While compounds **2** and **3** form by irradiating the symmetric dimer **1** in the presence of a large excess of coordinating ligand (i.e., CH_3CN and Cl^- , respectively), it is interesting to note that compound **4** is prepared in high yield by irradiating the OTf^- salt of **1** in a noncoordinating solvent (CH_2Cl_2 , $\Phi_{\text{CO}} = 0.33$). Photosubstitution of the counterion is similar to that found for $[\text{Re}(\text{CO})_4(\text{N-N})]\text{OTf}$ which undergoes efficient substitution of the OTf^- upon the loss of an axial carbonyl.¹¹ Monomers of the form *fac*- $[\text{Re}(\text{CO})_3(\text{bpy})(\text{PR}_3)]^+$ also exhibit CO photosubstitution.^{12,13}

The photosubstitution products of complex **1** shown in Scheme 1 were targeted because they all possess a thermally labile ligand and, therefore, can be used as synthetic intermediates for higher order, more complex, trans-bridging oligomeric structures. For example, reaction of **2** with triphenylphosphine (PPh_3) leads to thermal substitution of CH_3CN by PPh_3 forming $[\text{Re}(\text{CO})_3(\text{bpy})(\mu_2\text{-dppene})\text{Re}(\text{CO})_2(\text{bpy})(\text{PPh}_3)]^{2+}$ (**5**).¹⁴ As shown in Table 1, the ³¹P NMR spectrum consists of five resonances for the three distinct types of phosphorus nuclei. This is a result of trans coupling of the phosphines, indicating that PPh_3 is introduced in a position trans to the dppene. Bridging diphosphine ligands such as *t*-dppene and 1,4-bis(diphenylphosphino)benzene (dppb) were reacted in a similar manner (complexes **6** and **7**, respectively; see Scheme 1),¹⁴ forming dimers that contain a “dangling ligand” capable of bridging to another metal center for the generation of longer linear oligomers. Complex **6** has been prepared previously

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(7) Masood, M. A.; Sullivan, B. P.; Hodgson, D. J. *Inorg. Chem.* **1994**, *33*, 4611.

(8) Preparation of $[\text{Re}(\text{CO})_3(\text{bpy})(\mu\text{-dppene})\text{Re}(\text{CO})_2(\text{bpy})(\text{CH}_3\text{CN})]^{2+}$ (OSO_2CF_3)₂ (complex **2**): Compound **1** (0.065 g, 4.2×10^{-5} mol) was dissolved in 200 mL of CH_3CN . The solution was then irradiated with sunlight for 2 h. The solvent was removed by rotary evaporation, and the product was reprecipitated from CH_2Cl_2 by addition of ether, collected by suction filtration, and rinsed several times with ether. The orange powder was then purified by column chromatography on acidic alumina (3:1 acetone, CH_3CN) (79% yield after purification). Anal. Calcd: C, 42.3; H, 2.65; N, 4.49. Found: C, 42.35; H, 2.72; N, 4.45. ESI-MS (**2**): $m/z = 1410.7$ (calcd $m/z = 1411.4$ [**2** - OTf^+]).

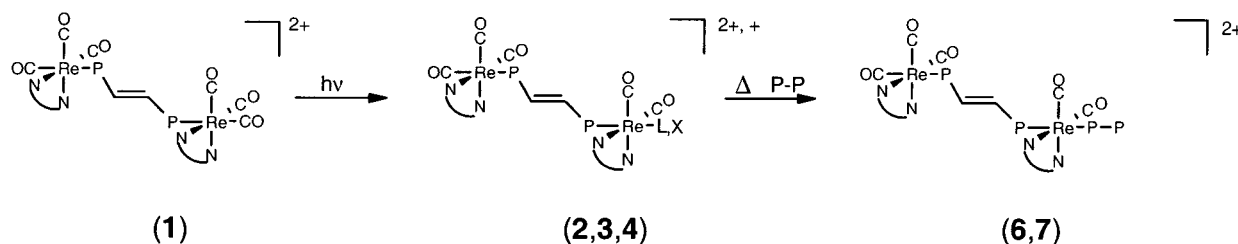
(9) Complex **1** (3.5×10^{-5} M) was irradiated at a 90° angle with 336 nm light using a Hg lamp with equipped with a monochromator. The sample was degassed and sealed under a N_2 atmosphere in a quartz emission cuvette. Absorption spectra were recorded every 60 s until ca. 99% completion. $\text{Ru}(\text{bpy})_3\text{Cl}_2$ in degassed CH_2Cl_2 was used for actinometry with a known Φ_{ph} of 0.1 (Caspar, J. V. Dissertation, North Carolina Chapel Hill, 1982). The rates of the reactions were determined by fitting the kinetic data using Spectfit 2.1 software.

(10) Preparation of $[\text{Re}(\text{CO})_3(\text{bpy})(\mu\text{-t-dppene})\text{Re}(\text{CO})_2(\text{bpy})(\text{X})^+ (\text{OSO}_2\text{CF}_3)^-$ (where X is Cl^- or OTf^- , complexes **3** and **4**, respectively): Compound **1** (0.065 g, 4.2×10^{-5} mol) was dissolved in 200 mL of MeOH with a 10-fold molar excess of tetrabutylammonium chloride (TBACl) and purged with N_2 for 25 min. The solution was irradiated with sunlight for 2 h. Solvents were removed by rotary evaporation, and the product was reprecipitated from CH_2Cl_2 by addition to a stirred solution of ether. Product was collected by suction filtration and washed several times with ether. Compound **3** was purified by column chromatography on acidic alumina (2:1 acetone, CH_3CN) (86% yield). Anal. Calcd: C, 44.43; H, 2.72; N, 3.99. Found: C, 44.05; H, 2.84; N, 4.02. ESI-MS (**3**): $m/z = 1256.8$ (calcd m/z 1256.7, [**3** - OTf^+]). Compound **4** was prepared in a similar manner in neat CH_2Cl_2 . Compound **4** could not be purified by column chromatography because of the extreme lability of the OTf^- ligand (88% crude yield). Anal. Calcd: C, 41.90; H, 2.52; N, 3.69. Found: C, 40.97; H, 2.72; N, 3.70. ESI-MS (**4**): $m/z = 1370.2$ (calcd $m/z = 1370.3$, [**4** - OTf^+]).

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(13) Helms, J. B.; Sullivan, B. P. Work in progress.

Scheme 1. Photochemical and Thermal Preparation of Unsymmetrical Dimers^a

^a L is CH₃CN, and X is OTf⁻ or Cl⁻, and P-P is a bridging diphosphine ligand. See text for detailed steps.

Table 1. Spectral and Photophysical Data for the Complexes^{a,b}

no.	complex	³¹ P NMR shifts (ppm) ^c	IR freq (cm ⁻¹) ^d	E _{op} (nm) ^e	E _{em} (nm) ^f
1	[Re(CO) ₃ (bpy)(μ-dppene)Re(CO) ₃ (bpy)] ²⁺	+14.9	2043, 1960, 1928	346 (3.92)	524
2	[Re(CO) ₃ (bpy)(μ-dppene)Re(CO) ₂ (bpy)CH ₃ CN] ²⁺	+27.1, +14.3	2041, 1957, 1942, 1927, 1868	380 (3.71)	682
3	[Re(CO) ₃ (bpy)(μ-dppene)Re(CO) ₂ (bpy)Cl] ⁺	+28.4, +14.3	2040, 1955, 1925, 1850	450 (3.56)	g
4	[Re(CO) ₃ (bpy)(μ-dppene)Re(CO) ₂ (bpy)OTf] ⁺	+25.91, +15.58	2041, 1957, 1932, 1863	420 (3.63)	696
5	[Re(CO) ₃ (bpy)(μ-dppene)Re(CO) ₂ (bpy)PPh ₃] ²⁺	+25.1, +24.1, +18.8, +17.8, +14.3	2041, 1957, 1939, 1925, 1868	410 (3.57)	617
6 ^h	[Re(CO) ₃ (bpy)(μ-dppene)Re(CO) ₂ (bpy)η ¹ -dppene] ²⁺	+18.7, +17.8, +16.5, +15.5, +13.4, -5.0	2042, 1957, 1942, 1926, 1870	426 (3.53)	623
7	[Re(CO) ₃ (bpy)(μ-dppene)Re(CO) ₂ (bpy)dppb] ²⁺	+25.0, +24.0, +18.8, +17.8, +14.3, -4.0	2042, 1958, 1941, 1926, 1870	410 (3.49)	618

^a All complexes are triflate salts. ^b Abbreviations: dppene is (*E*)-1,2-bis(diphenylphosphino)ethylene, dppb is 1,4-bis(diphenylphosphino)benzene, bpy is 2,2'-bipyridine, and OTf is trifluoromethylsulfonate. ^c In CD₃CN with 85% phosphoric acid external standard except **3** obtained in acetone-*d*₆ and **4** obtained in CDCl₃. ^d In MeCl₂. ^e E_{op} is the absorption spectrum maximum for the lowest energy MLCT excited state (appears as an undefined shoulder, log ε is reported). ^f E_{em} is emission spectrum maximum corresponding to the lowest energy MLCT excited state. Corrected emission data recorded on an SLM model 8000C spectrofluorimeter. ^g Emission was not observed for complex **3** in solution. ^h Spectral data for **6** from Woessner, S. A. Ph.D. Dissertation, University of Wyoming, 2000.

by refluxing **1** with excess *t*-dppene in chlorobenzene.² Here we present an alternative synthetic route using mild conditions that leads explicitly to **6**. Complex **7** demonstrates our ability to introduce a variety of bridging ligands during stepwise synthesis thereby allowing auxiliary tuning of the electronic properties as well as providing a means of distinguishing between individual molecular components of the oligomer via ³¹P NMR spectroscopy.

Multiple photosubstitution is common in polycarbonyl complexes since replacement of a carbonyl with the incoming ligand usually lowers the ligand field resulting in red-shifted product absorption, and therefore some degree of secondary photolysis.¹⁵ Without an intervening physical variable (e.g., insolubility of the photoproduct), it is our experience that these reactions are preparatively inconvenient. Consequently, the observation that only one carbonyl is lost from the symmetric dimer (**1**) which is composed of identical ends containing the *fac*-Re(CO)₃(bpy) unit is notable. Lack of secondary photolysis is consistent with spectral data that suggests that rapid and efficient energy transfer from the tricarbonyl excited state to the newly formed dicarbonyl Re(I) occurs in the products. Emission studies reveal that excitation into the tricarbonyl-localized MLCT manifold in complex **2** (336 nm where 60% of photons are absorbed by the

tricarbonyl unit) leads to emission from only the low-energy MLCT excited state localized on the dicarbonyl unit. This behavior is analogous to that of a recently prepared trimer, where rapid energy transfer resulted in emission from the dicarbonyl Re(I) excited state following excitation of the tricarbonyl ends.²

The transient IR spectrum of **6** is also consistent with rapid energy transfer from the tricarbonyl to the dicarbonyl Re(I) unit.¹⁶ For example, the bleach of the ground state after 337 nm irradiation is followed by the appearance of a new set of excited state dicarbonyl modes. Thus, on the time scale of the experiment (~150 ns), the excited state exists solely on the dicarbonyl end of the dimer. Furthermore, the position of the excited state carbonyl modes is essentially identical to that of the monomer *cis,trans*-[Re(bpy)(CO)₂(dppene)₂]²⁺, indicating that there is little or no mixing between the Re centers.

Stereospecific, unsymmetrical photosubstitution in dimers serves as an important synthetic tool because the *trans* labilizing effect of the phosphine ligand in the ground state¹⁷ is preserved in the excited state. The ultimate success of the preparative photochemistry, however, can be traced directly to the rapid energy transfer in the product, which inhibits further photosubstitution.

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(14) Preparation of [Re(CO)₃(bpy)(μ-*t*-dppene)Re(CO)₂(bpy)(PR₃)₂]²⁺ (OSO₂CF₃)₂ (where PR₃ is PPh₃, dppb, and *t*-dppene; complexes **5**, **6**, and **7**, respectively): The PR₃ dimer can be made from either the acetonitrile dimer (**2**) or the triflate dimer (**4**) and reacting with a 3-fold excess of PR₃ in a 3:1 EtOH/water solution and heating at reflux under a nitrogen atmosphere for 12 h. In each case the solvents were removed by rotary evaporation and the product reprecipitated from CH₂Cl₂ by addition of ether. The yellow precipitate was then collected by suction filtration and rinsed several times with ether to remove excess PR₃. Anal. Calcd (**5**): C, 47.86; H, 2.99; N, 3.14. Found: C, 47.32; H, 2.99; N, 3.16. ESI-MS (**5**): *m/z* = 1632.5 (calcd *m/z* = 1632.6, [5 - OTf]⁺). Anal. Calcd (**7**): C, 50.71; H, 3.18; N, 2.85. Found: C, 50.21; H, 3.25; N, 2.88. ESI-MS (**7**): *m/z* = 1816.8 (calcd *m/z* = 1816.9 [7 - OTf]⁺).

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